"CASE STUDIES IN
THE DETERMINATION OF
THE ORIGINAL SURFACE LIMITS OF
THE FERROUS ARMOUR OF
THE ORDER OF ST JOHN,
PALACE ARMOURY, MALTA"

by

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ABSTRACT

Ferrous heritage artefacts either from a burial environment, or in an indoor museum, can be either totally or partly masked by (or even comprised of) corrosion product (CP) layers. Some CP layers reduce surface legibility and corrosion resistance, and possibly contain altered traces of original surfaces. The correct amount of corrosion product cleaning required for all artefact materials and environments is not yet a *fait accompli…* As Bertholon suggests, "…we must question our attitudes about the cleaning of other archaeological or museum objects"[1]. The way the corrosion products evolve on mid-late Early Modern Period wrought iron and low-carbon steel in an atmospheric environment, and any capability of retaining the *limit of the original surface* (or *limitos* after Bertholon[2]), is the topic of this dissertation. This experimental research diagnostically determined the presence of the limitos in atmospherically corroded steel to indicate an appropriate level of CP removal during conservation treatments of historical wrought ferrous artefacts. Specific attention and adaptation of the findings was made to a historically accessible and atmospherically exposed collection: the partly corroded 16th-17th century northern Italian-style wrought iron and low-carbon steel munition armour of the Order of St John, Palace Armoury (PA), Malta.

International conservation philosophy and practice towards munition armour with corrosion products was examined via a literature review and a questionnaire issued for this research and returned by twenty-four armour conservator-restorers representing twenty-one organisations based in Europe and North America.

Non-invasive and non-destructive study of the Palace Armoury's largely undecorated munition armour collection, and its environment, enabled the deduction of the specific corrosion processes, and the formation of resulting corrosion product morphologies. The information gained from *authentic armour* was used to corrode

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[1] Bertholon, 2001c, p. 11.

[2] Bertholon, R. (2000). La limite de la surface d'origine des objets métalliques archéologiques: Caractérisation, localisation et approche des méchanismes de conservation. U.F.R. d'Art et d'Archéologie. Paris, Université Paris 1 Sorbonne-Panthéon.

quantities of *armour analogues* (contemporary artefact simulation material) in the laboratory. Destructively studying the resulting corrosion product morphologies determined that *markers* were present above (e.g. applied particles, protective coating) and corresponding with (e.g. surface marks) the limitos. The limitos on these ferrous surfaces was typified by certain vertically displaced CP morphologies and coherency depended on their formation process and extent of underlying corrosion. *Filiform corrosion* morphologies always exhibited *evidence* of the previous metal surface (i.e. topographical *micro-grooves*) in the raised filaments of its corrosion products. However, *local to general corrosion* morphologies demonstrated that the limitos was only *evidenced* with these micro-grooves if the corrosion was during its earliest corrosion phase: as corrosion in the subsurface pit continued, any initially apparent original micro-grooves in the surface became more displaced and were eventually totally deformed and fragmented beyond recognition. Despite not being directly identifiable by the former micro-grooves, justification for the retention of these deformed limitos materials was made by *association* with other material properties they shared with the evidenced micro-groove CPs. The presence of micro-grooves on both of these limitos corrosion product structures, i.e. *filiform corrosion* and early *local to general corrosion* morphologies, was substantiated with the PA's munition armour, which had recently had its protective coating removed. It was asserted that the limitos (with its definition adapted to the historical context for this selection of munition armour) was influenced not only by the extent of corrosion, but also by interventions from custodians of the collection while in active service or on static gallery display.

The Palace Armoury employee, presently responsible for corrosion product removal procedures on armour, performed current Armoury techniques on the authentic munition armour and on the armour analogues. Documentation of these surfaces demonstrated these techniques did not respect any of the limitos CP surfaces determined by this research to be present in corrosion products. The PA's approach *aims* to remove all CPs above the level of the adjacent uncorroded metal surfaces and also the CPs inside the corrosion pits; despite this being practically fully unachievable due to the inaccessible pit depth and concerns about damaging the adjacent metal. The presence of partly corroded surfaces in conjunction, with the PA's non-localised and unmagnified CP removal techniques, means that abrading/polishing is simultaneously depleting adjacent metal surfaces on munition armour surfaces. Using simple physical techniques available in common conservation laboratories, corrosion product removal (to the level determined by this research to respect the limitos) was performed by the author on the armour analogues. The approach, necessarily under binocular microscope magnification, was time-consuming and the result was a surface dominated by corrosion products, which are not usually retained on armour; either in Malta or internationally.

Discussion with the two Palace Armoury curators exemplified the general subjectivity of attitudes towards corrosion products and the supposed appropriate surface finishes for ferrous munition armour. Instability and aesthetic issues imparted by corrosion products were the main points of discourse; in agreement with international munition armour conservation philosophy and practice. To reach reasoned conclusions on the subjective aspects of some conservation-restoration approaches it was recommended conservators and curators further discuss the objectives of an artefact CP removal treatment and inform museum staff and the wider public of the broad rationales. Before future decisions are made regarding this research's newly proposed conservative level of corrosion product removal from munition armour, a reappraisal of the PA's fundamental environment and preventive conservation practices was recommended: a holistic perspective of the Palace Armoury's material-environment system would benefit the conservation of the limitos corrosion products, and also the metal of the munition armour of the Order of St John.

DEDICATION

To Elwyn, Neville, Hamish, Keith, Anne-Claire, Badidou, Claire, Dana, Duncan, Keiran, Marianne & Vanessa for imparting their endless inspiration, support and inquiring minds; for without, the following personal undertaking would have been wholly unachievable.

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The twenty-four unnamed armour conservator-restorer respondents (including their curator & conservation scientist colleagues) to the international questionnaire on ferrous munition armour corrosion products.

AUTHOR'S DECLARATION

I, the undersigned, declare that this work has been done entirely by myself under the supervision of Dr Christian Degrigny with appropriate referencing to sources utilised. This dissertation has never been presented to any other educational institution, nor published through any other means prior to this presentation.

James B. Crawford

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PREFACE

This Master of Conservation applied research dissertation is complementary to the 3.5-year (2004-2008) European Commission 6th Framework Programme research project Promet (Protection of metals)[3]: a multidisciplinary consortium that investigated advanced analysis techniques and applied anti-corrosion materials for protecting indoor metallic cultural heritage against corrosion in the Mediterranean environment.

One of Promet's Maltese partners, Heritage Malta, selected the large metal armour collection and environment of the Palace Armoury for its investigations. The collection's military history as functional tools of warfare and static museum trophies has involved cycles of periodic neglect followed by undocumented enthusiastic restoration interventions; intrinsically evidenced by the artefacts themselves.

The development and testing of barrier coatings and corrosion inhibitors new to cultural heritage conservation was one of the main objectives of Promet. Unlike industrial applications, heritage conservation practitioners do not have the flexibility of creating a surface to suit the needs of a corrosion protection material. Rather, the protection material must be principally designed around the surface properties of the artefact.

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[3] For further information refer to www.promet.org.gr

1 INTRODUCTION

The development of conservation strategies based more on scientific evidence, and less on empirical and subjective practices, is a prime objective for contemporary conservation of tangible cultural heritage. The recognition of metal corrosion products (CPs) as providing a resource of an artefact's surface features, albeit modified by corrosion processes, has grown in acceptance in the heritage conservation domain. Since surface information (e.g. manufacture marks, evidence of use & maintenance) and artefact shape can be found in metal corrosion products conservation ethics require consideration of preservation of these materials.

Corrosion of historic ferrous plate body armour is an international conservation problem. The conversion of metal into corrosion products is clearly detrimental to the metal, but questions remain around an appropriate level of corrosion product removal. To date, approaches to armour CPs appear to remain empirical. This research dissertation explores the past and present conservation strategies applied to CPs on a collection of ferrous armour on open-display in an indoor environment. The applied research aims to determine the possible presence of the *limit of the original surface* (*limitos*) in corrosion products on mid-late Early Modern Period wrought ferrous plate munition armour. It follows a diagnostic, non-subjective approach to determine if the limitos within CP strata coming from its last metallic state might be identifiable and practically conservable during a treatment intervention.

Chapter 2 presents the historical, scientific, and conservation background to the problem as sourced from the literature and personal communications. The mid 16th-mid 17th century northern Italian-style munition armour of the Order of the Knights of St John, housed at the Palace Armoury (PA), Malta, was used as a corrosion case study and their history is described in detail in that chapter. The wider context of current international armour conservation-restoration philosophy and practice and recently developing approaches to archaeological metal conservation-restoration are also presented; the latter comprises a summary explanation of Bertholon's work on the original surface limits of archaeological metals.

Chapter 3 provides the framework and rationale supporting the practical experimental methods of the research and includes details on the employed materials and techniques of investigation. As an innovative means of advancing the research question, the fabrication of contemporary experimental metal samples, which were purposefully made with *corresponding* and *superior limitos markers*, is described there.

Chapter 4 presents the results and results' interpretation from the various experimental research phases performed at the Palace Armoury and in the laboratory on authentic mid 16th-mid 17th century munition armour, and their contemporary analogues. The gradual determination of the limitos on these materials is realised in this chapter.

Chapter 5 discusses the validity of the methodology and results, and the wider implications for historic armour conservation and their corrosion products. Collaboration with the two Palace Armoury curators provides conservation-related discussion stemming from curatorial perspectives about the munition armour's surface stability, significance and aesthetics.

Chapter 6 concludes the research by summarising the major findings and relates their consequences to: conservators practically approaching the corrosion products on the Palace Armoury's wall-displayed munition armour, and also to curators who must consider their role in the corrosion process-corrosion product removal cycle and the historical significance of these armour's surfaces.

Chapter 7 and Chapter 8 respectively outline wider recommendations for the Palace Armoury's holistic environmental management and future research avenues for the determination of the limitos on more heavily corroded wrought ferrous metals in atmospheric environments and with other material-environments.

2 HISTORICAL, SCIENTIFIC & CONSERVATION CONTEXT

This opening chapter provides the background to the subsequent experimental research by: detailing the long and varied historical development and management of the munition armour now at the Palace Armoury; outlining concepts and examples of ferrous corrosion in indoor environments; and summarising important developments in the conservation of modified original surfaces in the corrosion products of metal archaeological artefacts. Philosophy and practice of contemporary armour conservation-restoration is presented via a literature review and via the presentation of trends recorded by a current international questionnaire on ferrous munition armour and their CPs. Complementary reference to the PA and its munition armour is made throughout with information obtained from recent material and environmental science studies.

2.1 THE ORDER OF ST JOHN & MALTA, THE PALACE ARMOURY MUNITION ARMOUR COLLECTION: FABRICATION, HISTORY & ENVIRONMENT

This subsection summarises the numerous major historic events and policies, distant and more recent, which have brought a specific and large part of the Palace Armoury collection to its present day environment and conservation condition.

October 26, 1530 marked the arrival in Malta of the itinerant Christian Hospitaller Knights of the Order of St John of Jerusalem, heralding in a new époque of Maltese history[4]. Previously, the defeated Knights and their loyal Rhodian followers, then led by Grand Master Philippe Villiers de L'Isle Adam, were evicted

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[4] For the historical development of the Order of the Knights of St John of Jerusalem from charitable monks (late 11th century) serving Christian pilgrims in the Holy Land of Levant during the Holy Crusades, to assailants against the Muslim faith (mid 12th-early 13th century onwards) and to a corsairing Mediterranean naval power (post late 13th century) based in Cyprus, Rhodes and Malta, the reader is referred to: Mizzi, J. (1970) A Bibliography of the Order of St. John of Jerusalem (1925-1969). Malta, Council of Europe; and Mallia-Milanes, V. (ed.) (1993) Hospitaller Malta 1530-1798: Studies in Early Modern Malta and the Order of St John of Jerusalem. Malta, Mireva Publications

from Rhodes by Suleiman the Magnificent and his Ottoman Turks[5]. Finally after seven years of negotiations with Charles V, King of Spain and Holy Roman Emperor, an agreement was reached that allowed the Order to settle in the Maltese Islands[6]. The proximity to the so-called *infidel* (in Levant and northern Africa, Figure 2-1) made Malta suitable for the Order to continue waging their religious war on Islam, while also offering relative isolation and autonomy from other various adverse affairs in continental Europe[7].

Figure 2-1 The Islamic world circa AD 1500 (below broad green line) and Malta on the Christendom frontier[8]

Inevitably, the Order's continuing regional presence, forming a frontier between seemingly irreconcilable faiths, made the organisation and distribution of a large military capacity for the Order a life or death necessity. The Palace Armoury building and its contained movable heritage forms a significant part of the tangible history of the Order's military organisation in Malta[9]. The present collection of arms and armour housed at the Armoury of the Grand Masters' Palace, Valletta, Malta (Figure 2-2) is testimony to its erratic history. Ever since the collection's intermittent commissioning and acquisition, it has always remained in the custodianship of the governing administration of the day and subsequently witnessed fluctuations in its

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[5] Mallia-Milanes, 1993, pp. 2, 5
[6] Ibid., pp. 2-3
[7] Ibid., pp. 2-3, 7-8
[8] Brice, 1981, http://ccat.sas.upenn.edu/~rs143/map6.jpg – accessed 03/02/2007
[9] Magro Conti, 2007, pers. comm.

interest and consequent welfare[10]. The last decade of the PA has been subject to high visitor attendance[11], while more recently, scientific investigations have followed, including those relevant to this research dissertation.

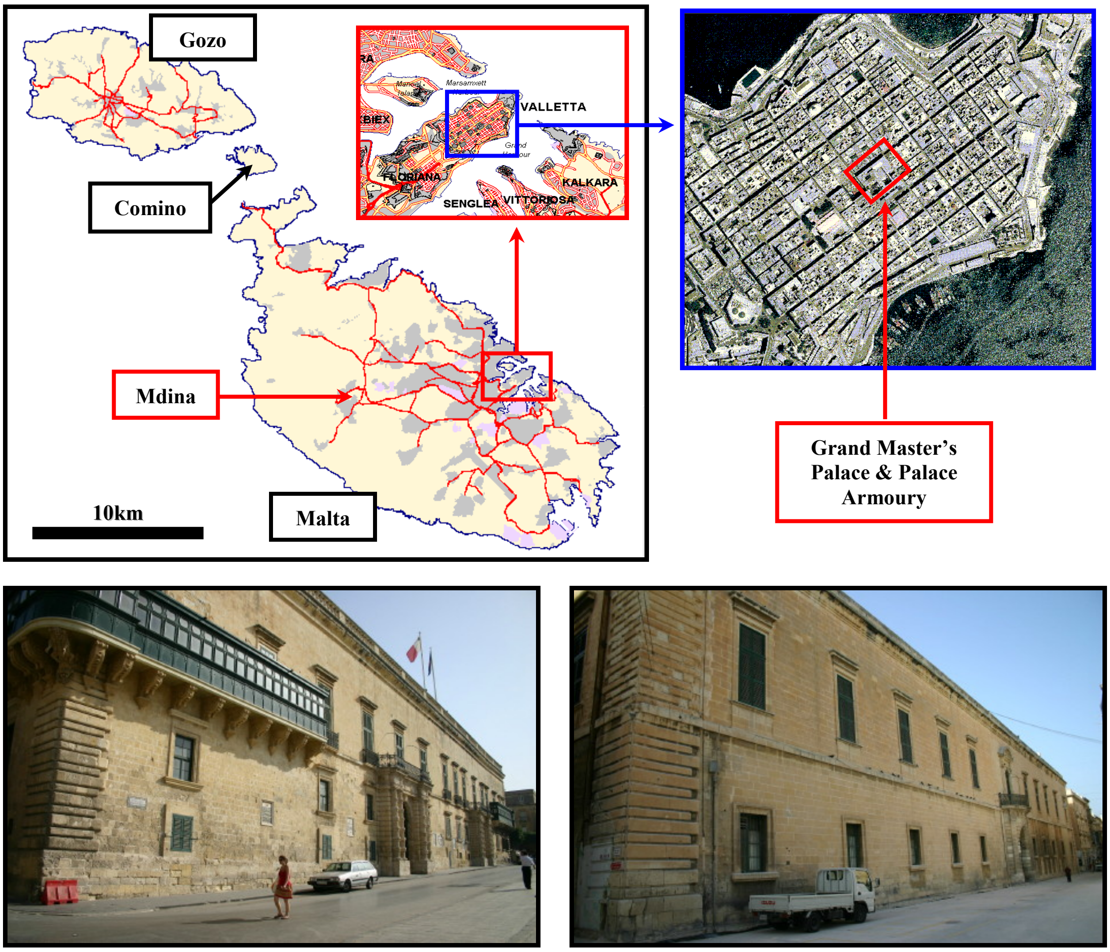

Figure 2-2 Upper left: Context map of the Maltese Islands with the cities of Valletta, Vittoriosa & Mdina[12] Upper right: Context aerial view of the Palace Armoury in Valletta[13] Lower left: Exterior of Grand Masters' Palace, Republic Street[14] Lower right: Exterior of Grand Masters' Palace Armoury, Merchants Street[15]

The development and provenance of the arsenal housed at the Palace Armoury can be traced to before Grand Master Alof de Wignacourt who installed it within the Grand Masters' Palace in 1604[16]. The armoury's transferral from opposite the Palace in Piazza San Giorgio was one of Wignacourt's military reforms undertaken when a perceived threat from the Turks had arisen, and when greater

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[10] Ibid.

[11] Over 100 000 persons per annum (Argyropoulos, in press, Chapter 5, p. 17)

[12] MEPA, 2006, http://www.mepa.org.mt/Planning/index.htm?MapServer.htm&1 – accessed 12/08/2006

[13] Ibid.

[14] Crawford, 2005-2007, pers. photog. permission courtesy of E. Magro Conti

[15] Ibid.

[16] Spiteri, 2003, pp. 69, 75

regulation of firearm proliferation was demonstrated by a series of decrees made by the Order from the mid to late 16th century[17]. An engraving (Figure 2-3) depicts the Grandmasters' Palace at a time when the upper floors of the future Palace Armoury were not yet constructed[18] and the *Publicca Armeria*, as it was referred to, was still located in Piazza San Giorgio[19].

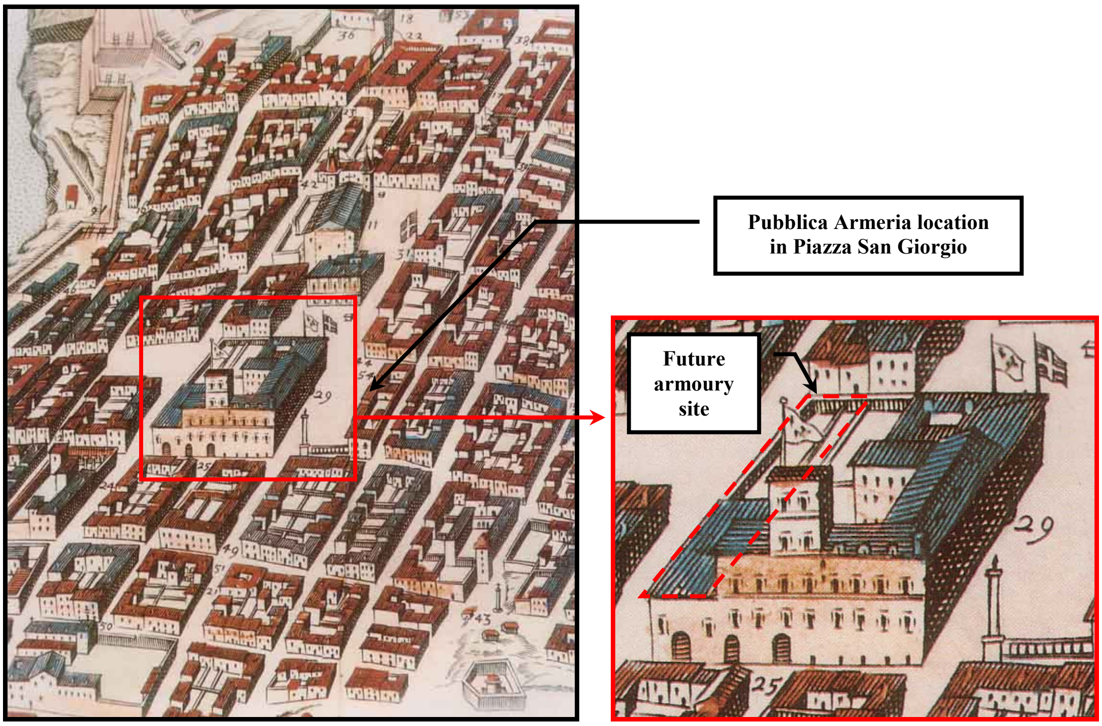

Figure 2-3 Detail from an engraving of Valletta Francesco Villamena published in 1602 in Giacomo Bosio's History of the Order of St John[20]. It is possible that the content of the map dates even earlier since it is said the map was a copy of an earlier map dating to 1582[21]

Some of the artefacts in the collection date from before the Great Siege of Malta (1565), and some were brought with the Order to Malta[22]. The collection currently under custodianship of the Palace Armoury is vast and varied. Not only does it comprise the arms and armour currently housed on the ground floor of the Grand Masters' Palace of the Order of St John, but it also includes items found in the Grand Masters' Palace State Room corridors, various government ministerial buildings, former auberges of the Knights, and other sites around Malta and Gozo[23]. The heterogeneity and wide distribution (with varying environments) of such a collection makes its accurate description, conservation assessment and historical

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[17] Spiteri, 2003, pp. 72-73, 127
[18] Bonello, 2001, p. 28,
[19] Spiteri, 2003, p. 12
[20] Ganado, 2001, p. 16
[21] Spiteri, 2006, p. 71
[22] Spiteri, 2003, p. 17
[23] Magro Conti, 2007, pers. comm.

development impossible for a single research framework of this size. To focus on one research question, armour of one typology (i.e. shape, features etc.) currently housed in the Palace Armoury and attributable to the Order of St John is considered here.

2.1.1 ARMOUR TYPOLOGY, DATING & PROVENANCE

The specific group of artefacts in this study are plate munition armour. They are of a *Pisan* typology believed to date to the mid 16th-mid 17th centuries and provenance from northern Italy[24, 25] (Figure 2-4). The armour consists of *half-armour*, not full suits (*harnesses*) with full leg and foot protection. This group of armour is hereafter often simply referred to as *munition armour*.

Figure 2-4 Assembly of 16th-17th century northern Italian-style munition half-armour and helmets of the *peaked morion* type at the Palace Armoury[26]

The exact workshops or suppliers are unknown, as hallmark stamps are generally not found and subsequent historical research has been minimal[27, 28]. Unmarked armour is typical of lesser quality Italian steel armour even more so after the debut of the 16th century[29]. However, it is likely that the workshops could have

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[24] Ibid.

[25] It is clarified that a northern Italian typology is probably Italian, but not certainly, since it is possible that a northern Italian style could have been copied and produced outside northern Italy (Stroud, 2006-2007, pers. comm. & Williams, 2003, p. 61).

[26] Crawford, 2005-2007, pers. photog. permission courtesy of E. Magro Conti

[27] Magro Conti, 2007, pers. comm.

[28] Only a fraction of one percent of the archives of the Order of St John has been consulted and has identified the armour workshop of one armour suit (Magro Conti, 2007, pers. comm.).

[29] Williams, 2003, pp. 67, 203-204

been located in Milan and Brescia, two towns that were arms and armour production centres of northern Italy's Lombardy region[30]. Brescia is reputed to have made more mass-produced armour and less high quality ones[31]. By the early 15th century, Milan is cited as being involved in armour mass-production as evidenced by the city's fulfilment of an order of 6 000 armour (including 2 000 infantry armour) in several days[32]. Such earlier mass-production would have later been suitable for the numerous munition armour of the 16th-17th centuries found today at the Palace Armoury. An eminent metallurgist of historic arms and armour, Dr Alan Williams, points out that the Lombardy region was still capable of such production until times contemporary to the munition armour in this study, "Milan and Brescia continued to make mass-produced armour of modest price until well into the 17th century"[33].

These munition armour were maintained by the Order, but were worn by the permanent troops (mercenaries from all over Europe) of the Knights of the Order of St John and are importantly to be differentiated from the types worn by the Knights and the Grand Masters in ceremony, the latter two types bearing increasingly decorated surfaces (Figure 2-5)[34].

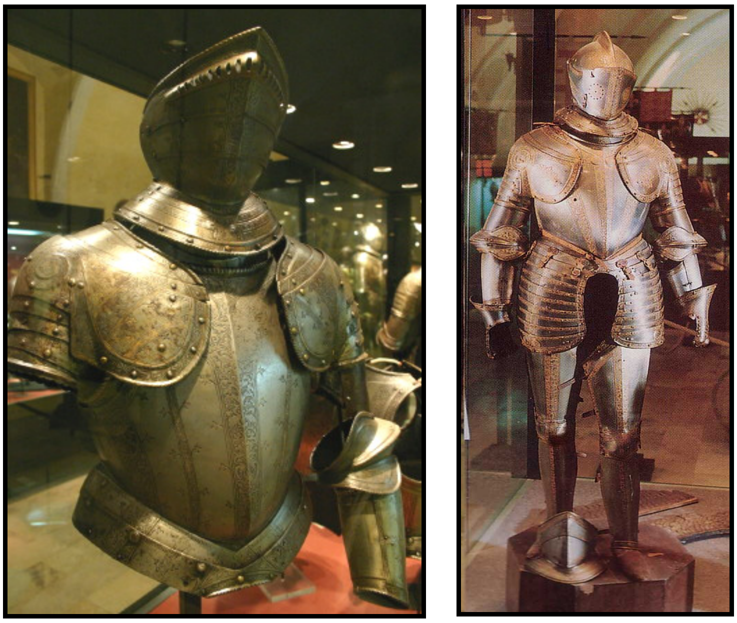

Figure 2-5 Left: Northern Italian-style etched Knight's Armour (circa 1570-1580)[35] Right: Northern Italian Pisan style gilt parade armour of Grand Master Verdelin (circa 1580)[36]

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[30] Ibid., pp. 56-58
[31] Ibid., p. 57
[32] Ibid.
[33] Ibid., p. 211
[34] Stroud, 2006-2007, pers. comm.
[35] Crawford, 2005-2007, pers. photog. permission courtesy of E. Magro Conti

The munition armour currently comprise the majority of the armour in the Palace Armoury collection and are displayed predominantly on the walls of the two Arms and Armour Halls, in the Palace corridors and are also stored in the reserves[37]. The following subsections outline the fabrication of these armour and trace the development of the armour's history, their cleaning[38] interventions and the ambient environment, which these armour are likely to have experienced.

2.1.2 MUNITION ARMOUR FABRICATION: MATERIALS & TECHNIQUES

Broadly, the munition armour at the Palace Armoury are made predominantly from multiple forged *ferrous*[39] (iron (Fe), or steel) metal plates (*lames*) of varying dimensions. The following subsection outlines the possible processes involved in producing these major components of the armour. Significantly, the munition armour at the PA were fabricated during a period when northern Italian munition armour production standards had regressed: poorer quality and non-hardened ferrous metals were more common[40].

2.1.2.1 Metal extraction & processing

Biringuccio, a Siennese metallurgist and armament maker of the 16th century, attests to the abundance of iron ores of various kinds in Italian regions, including Brescia, during the 16th century[41]: a potentially convenient local resource for Lombard armour production. The specific processes of ferrous ore smelting[42], and any conducted fining[43], to produce the metal for the many individual plates comprising the Palace Armoury munition armour are unknown. Extractive metallurgy cannot be fully determined merely from metallographic studies[44] and the

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[36] Spiteri, 2001, pp. 134-135

[37] Magro Conti, 2007, pers. comm.

[38] For purposes of brevity, "cleaning" will often be used to refer to "corrosion product removal" and is not to be confused with cleaning surfaces of foreign deposited particles. Cleaning away of these corrosion products can therefore be partial or complete.

[39] For purposes of convenience and brevity, when discussing iron and iron-based metals like alloys such as carbon steels, they will often be grouped as being *ferrous*. In the cases where information is specific to either iron or steel, these specific terms will be applied. This is not to be confused with the ferrous ion (Fe^{2+}) when discussing the iron cation or with corrosion products/mineral species based on this cation – clarification will be made in the instances where the 2+ valence state cation is intended.

[40] Williams, 2003, p. 203

[41] Biringuccio, 1990, p. 61

[42] 2.1.2.1.1 Direct process: bloomery furnace, 2.1.2.1.2 Indirect process: blast furnace & finery, & 2.1.2.1.3 Blast furnace-direct process

[43] 2.1.2.1.2 Indirect process: blast furnace & finery & 2.1.2.1.4 Cofusion-indirect process

[44] Dillmann et al., 2002, p. 327

collection has barely been studied in terms of *slag*[45] composition[46, 47]. Nonetheless, since both iron and steel (mostly of the low-carbon type)[48] are known to be present in the munition armour and they are typologically dated to the mid-late Early Modern Period[49], these metals were likely to have been produced via a certain number of processes. The most commonly cited ferrous smelting processes active during the mid-late Early Modern Period are either the *direct* or *indirect processes*.

The direct process (otherwise known as the bloomery process), is the much older of these two processes in Europe and was first established in and disseminated from the Caucasus and the Fertile Crescent during the second millennium BC[50]. Two to three thousand years later, in the 12th century, the development of the European indirect process began.

Of note, there appears from the literature to be some uncertainty as to the precise possible procedures of iron and steel production at the time, and also specifically for mass-produced items like the munition armour: questions remain about the way the furnaces and fineries attributed to these processes were operated[51]. Whatever the *modus operandi*, a forgeable ferrous metal was obtained that was more or less heterogeneous in its composition in terms of microstructural phases and inclusions[52]; key characteristics that affected its working life performance[53] and subsequent corrosion[54].

During the 14th century in Italy, larger metal plates emerged and they were generally of steel[55]. However, the subsequent centuries progressively witnessed a regression in the quality of Italian munition armour. Studies by Williams demonstrate that the mass-produced Italian steel armour of the 16th century contained less carbon than of the previous century and armour of the 16th-17th centuries further worsened in quality "…as iron becomes commoner for munition armour, and its slag

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[45] Silicates and oxides inside the iron ore: 2.1.2.1.1 Direct process: bloomery furnace

[46] Magro Conti, 2007, pers. comm.

[47] Discriminating analysis techniques of inclusions (Dillmann et al., 2002) and applications to armour are developing (Williams, 2003, p. 891).

[48] Low-carbon steel is classified, by contemporary terminology, as containing <0.30% carbon (Chandler, 1998, p. 32).

[49] Vella et al. 2004, pp. 221-222, 230

[50] Williams, 2003, p. 5

[51] Ibid., pp. 886-889

[52] 2.1.2.1.1 Direct process: bloomery furnace & 2.1.2.1.2 Indirect process: blast furnace & finery

[53] Williams, 2003, p. 879

[54] Chandler & Hudson, 2000, p. 5

[55] Williams, 2003, p. 56

content increases"[56]. Steel's superior hardness over iron is attributable to its increased carbon content. Based on the literature review below on metal smelting processes and on an admittedly small sample of eight munition armour from the Palace Armoury investigated by Vella et al.[57], the metallurgy of the PA armour appears to fall within the quality trends outlined by Williams. The fabrication processes for this wrought heterogeneous product with inclusions made it less like contemporary steel, which lacks slag and features far greater homogeneity[58, 59].

2.1.2.1.1 Direct process: bloomery furnace

Historically, metal extraction from the iron ore (*gangue*) as a liquid was not initially achievable since the melting point (MP) for iron (1535°C) was not easily attainable[60]. The direct, or bloomery process, managed to extract a metal, but in a non-liquid state. The process involved heating granulated iron ore in a masonry furnace of 1-2 metres height[61]. Oxygen (O_2) necessary for combustion was supplied from the exterior with pipes (*tuyeres*) that were fed by bellows[62]. Charcoal, wood and the mostly enclosed shaft furnace structure provided the fuel and reducing atmosphere (i.e. sufficiently deficient in oxygen) to reduce (*smelt*) the iron from the iron ore (Equation 2-1).

$$FeO_{(s)} + C_{(s)} \rightarrow Fe_{(s)} + CO_{(g)}$$

Equation 2-1 Simplified smelting representation of iron oxide reduction to elemental iron[63]

Iron ore reduction to iron was achieved at circa 700-800°C. However, higher temperatures were required to liquefy the slag; facilitating its physical separation from the reduced iron[64]. Slag is known to lessen mechanical resistance properties required for armour[65, 66]. Slag is very common in bloomery iron but, "…high quality products may show very little evidence of slag content"[67]. At 1205°C the MP of the most common slag species, iron silicate (*fayalite*, $2FeO.SiO_2$), was reached and

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[56] Ibid., p. 889
[57] Vella et al. 2004
[58] Buchwald & Wivel, 1998, pp. 76, 94-95
[59] Gale, 1969, p. 7
[60] Scott, 1989, p. 8
[61] Williams, 2003, pp. 4, 877 & Buchwald & Wivel, 1998, p. 73
[62] Buchwald & Wivel, 1998, p. 76
[63] Williams, 2003, p. 879
[64] Ibid., p. 4
[65] Ibid., p. 879
[66] The effect of slag on corrosion is later discussed: 2.2.3.3 Uneven local to uneven general corrosion
[67] Scott, 1991, p. 102

limited separation occurred by settling or tapping out the slag from underneath the bloom furnace[68, 69]. Figure 2-6 demonstrates the schematic layout of some earlier bloomery furnaces.

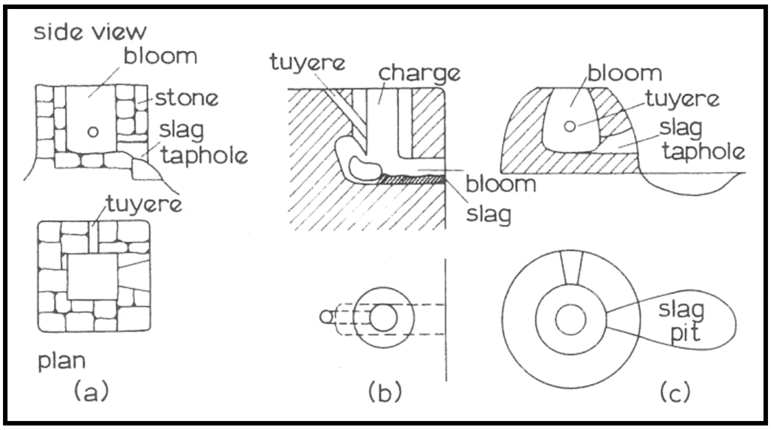

Figure 2-6 Section and plan perspectives of three bloomery furnaces dating from the Middle Ages[70]

The result coming from the bloomery furnace, when operated under direct process conditions, was the *bloom*: a porous, semi-solid mass of heated iron containing high and varied amounts of encapsulated inclusions[71]. A host of non-ferrous metal oxides present as slag inclusions in non-contemporary direct process-derived iron has been reported in the literature, including oxides of sodium, magnesium, aluminium, silicon, phosphorus, sulphur, potassium, calcium, barium, titanium, vanadium and manganese[72]. Inclusions came from remaining unreduced iron ore, added flux or developed via formation with the furnace walls[73]. *Physically* decreasing the impurities using the bloomery furnace, via liquid slag & solid metal viscosity differences at elevated temperatures, has already been described. C*hemically* decreasing the slag present in the direct bloom was achieved via more reducing conditions in the furnace when carbon could reduce some, but not all, of the non-elemental iron in slag to iron. The result would simultaneously increase (at least locally) the carbon content of an iron (i.e. *ferrite*[74]) bloom thereby making a steel

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[68] Williams, 2003, p. 4

[69] Tylecote, 1976, p. 88

[70] Tylecote, 1992, p. 76

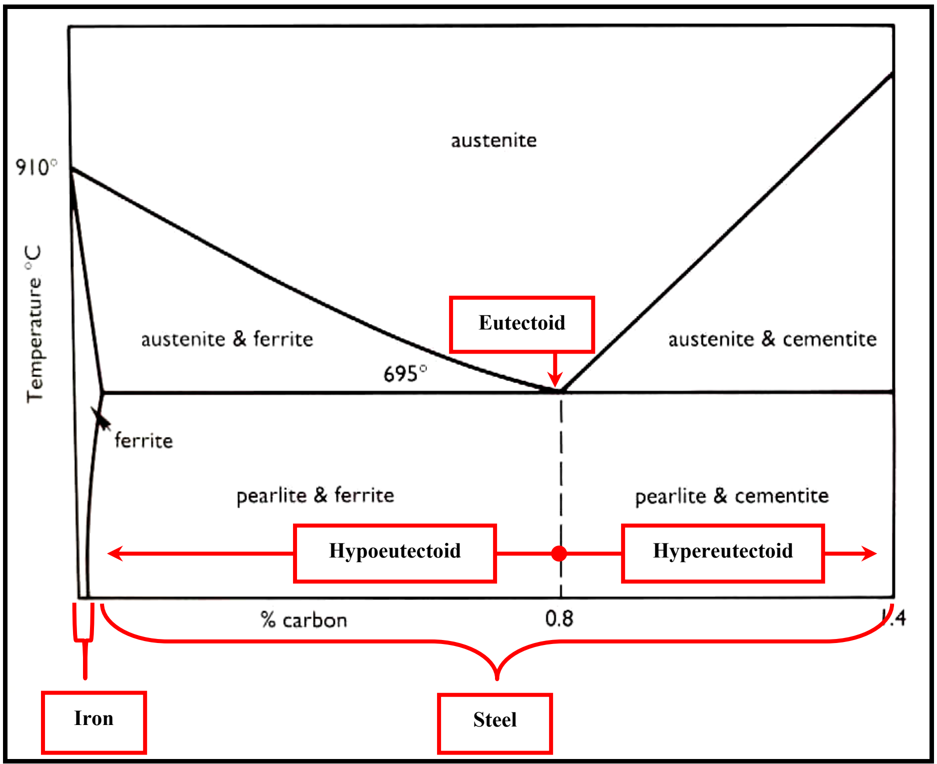
[71] Ibid., p. 96 & Williams, 2003, pp. 4, 879

[72] Buchwald & Wivel, 1998, pp. 80-81

[73] Williams, 2003, p. 4

[74] *ferrite* = a solid solution in body centred cubic iron, and carbon being the typical solute (Chandler, 1998, pp. 38-39).

(e.g. *pearlite*[75] with *cementite*[76], i.e. hypereutectoid[77] or pearlite with ferrite, i.e. hypoeutectoid[78])[79] (Graph 2-1).



Graph 2-1 The iron and steel section of the iron-carbon phase diagram[80]

The bloomery or shaft furnace is largely attributed to have only made iron and not steel, but it is known from remnant excavated fragments and experimental archaeology that carbon steels, even cast iron (if only accidentally) could be made from such furnaces[81]. Neither a homogenous iron, nor a homogenous steel product was obtainable in the time span that a bloomery furnace could burn. Some parts of the bloom were fully reduced to iron and contained parts richer in carbon (0.4-0.7%); these areas were identified and separated for production of articles that benefited from the harder properties of this steel product[82].

The generally negligible or lower carbon content of bloomery iron (especially when compared to cast iron[83]), made it malleable for forge work and it is for this reason it is also referred to as wrought iron. Wrought iron contains circa 0.03%

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[75] *pearlite* = Fe/Fe_3C (i.e. ferrite and cementite laminations) (Spence, 2005, p. 43).
[76] *cementite* = Fe_3C (Spence, 2005, p. 43).
[77] Brandt, 1992, p. 149
[78] Ibid.
[79] Williams, 2003, p. 879
[80] Scott, 1991, p. 132
[81] Williams, 2003, p. 877 & Hawthorn & Stanley Smith footnote citation in Theophilus, 1979, p. 183
[82] Buchwald & Wivel, 1998, p. 86
[83] 2.1.2.1.2 Indirect process: blast furnace & finery

carbon and 1-3% slag, the latter being physically mixed rather than chemically[84]. An important step for lowering slag content was performed out of the furnace and was undertaken by hammering out some slag (*bloom consolidation*). The quality of this work would determine the amount of slag as inclusions still trapped inside the resultant ingot or *billet*[85]. This process elongated the remaining slag perpendicular to the forging action[86].

The small size of a bloom obtained from the direct process in a bloomery furnace, and the fact that it was made by a batch process (i.e. stopping and starting the furnace) made it unsuitable for mass production of plate armour; such as was probably required for the Palace Armoury's munition armour. Large plates of armour between 2.5-4.5kg required a billet of at least 10kg making such production via the direct process difficult[87]. It was also preferable to make a plate of armour from one single billet since forge-welding numerous plates together was wasteful of the metal: due to oxidation and increased risk of inclusion entrapment from the forge[88].

2.1.2.1.2 Indirect process: blast furnace & finery

The second method available at the time for possibly producing ferrous metal used in armour fabrication took a lengthier, more circuitous route than the direct process: hence the appellation *indirect process*. Despite greater fuel consumption, the advantages of the indirect process over the direct included: continuous operation; greater ore to metal conversion efficiency; and ability to smelt inferior ores[89].

The indirect process comprised two steps in separate furnaces and hearths that yielded different ferrous materials of varying carbon content[90]:

1. Blast furnace → cast iron (circa 4.0 C%)
2. Finery hearth → steel (circa 0.1-0.8 C%)

BLAST FURNACE

The earliest claimed European blast furnace is attributable to Sweden and dates to the mid-late 12th century[91]. Normally, the blast furnace comprised a top feeding chimney and a hearth with two openings: an upper one for the air source; and

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[84] Schweitzer, 2004, p. 646
[85] Dillmann et al., 2002, p. 327
[86] Scott, 1991, p. 7
[87] Williams, 2003, p. 56
[88] Ibid., pp. 56, 878
[89] Ibid., pp. 880-881 & Tylecote, 1992, p. 96
[90] Buchwald & Wivel, 1998, p. 74
[91] Ibid., p. 87 & Tylecote, 1992, p. 76

a lower one for accessing the reduced and liquefied metal. The continuous blast of air came from bellows that were typically powered by watermills located in adjacent streams (Figure 2-7 & Figure 2-8)[92]. Biringuccio attested to the use and benefits of hydraulic power for bellows during the characteristically large-scale operations of the blast furnace[93].

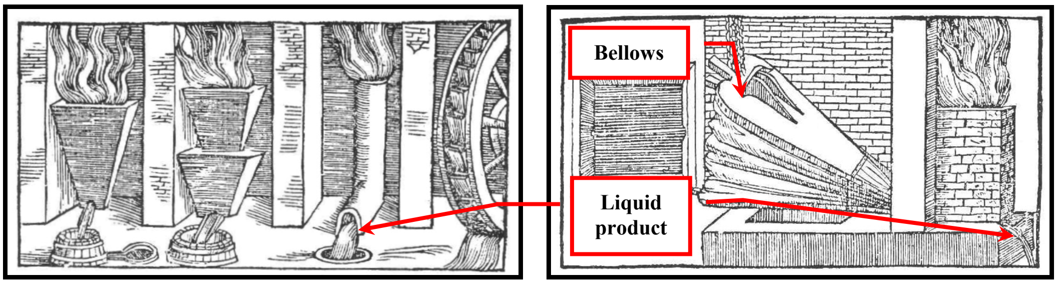

Figure 2-7 Left: Sixteenth century illustrations of Italian blast furnaces of various shapes powered by a watermill[94] Right: A bellow and blast furnace[95] Note all furnaces are producing liquid material

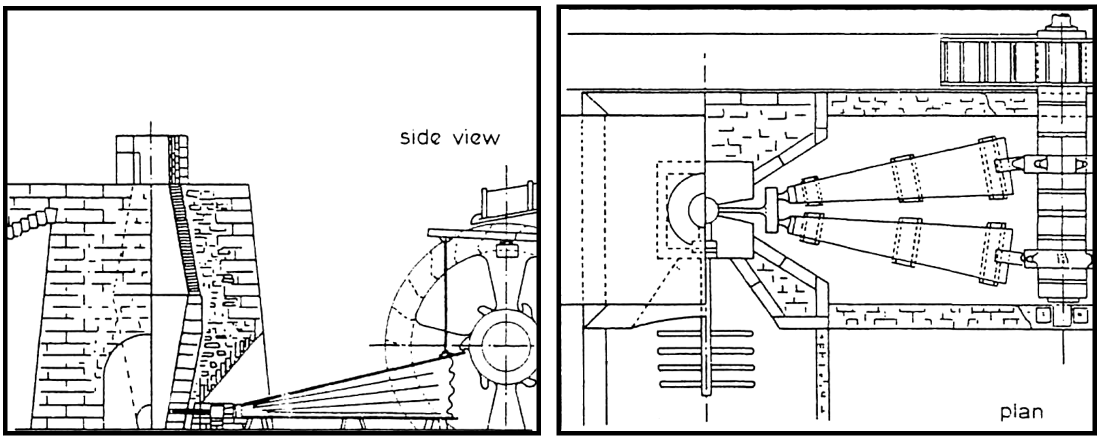

Figure 2-8 Left: & Right: Contemporary technical elevation and plan of a hydraulic blast furnace (circa 16th century)[96]

By smelting granulated iron ore with fuel in a bigger and taller furnace that was blasted with more air, higher temperatures and more transformations could occur to the reduced iron: notably an increased carbon content. As the carbon content increased towards 2.0%, the MP of the fraction further decreased (to a minimum of 1147°C) thereby encouraging even greater absorption of carbon (Graph 2-2)[97]. As a liquid metal, the carbon could then more easily diffuse into the metal thereby potentially creating even higher carbon concentrations (circa 4%)[98].

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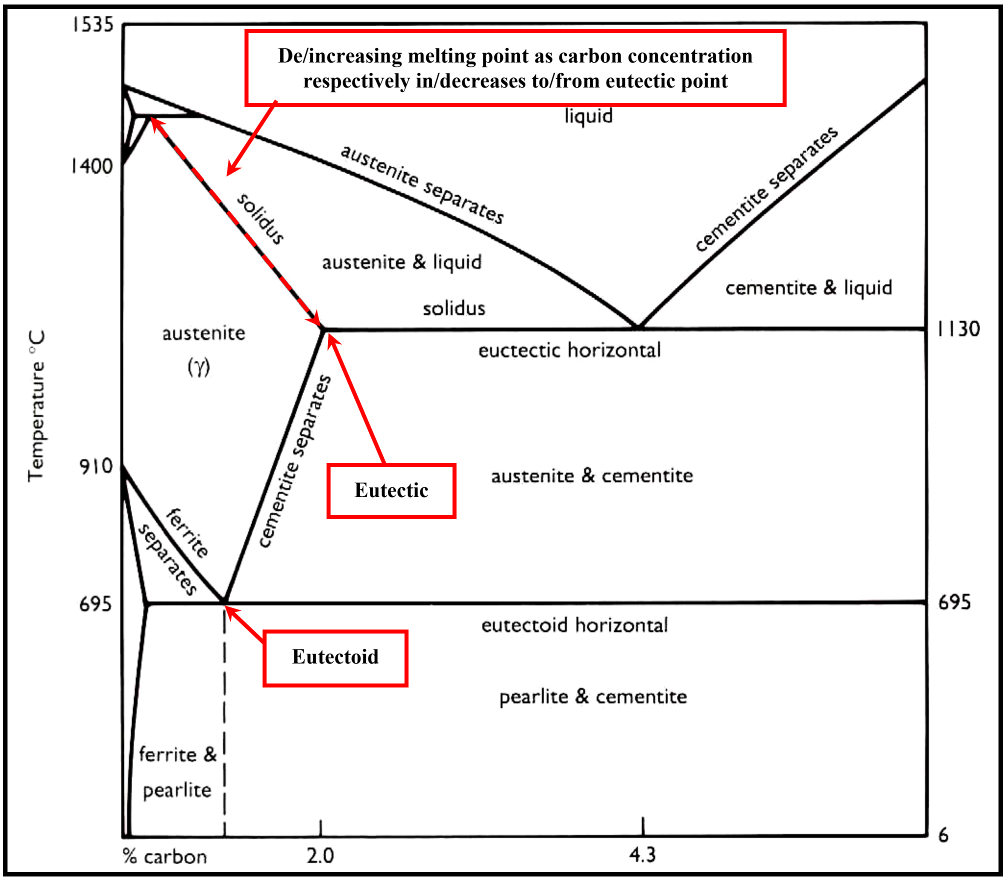
[92] Tylecote, 1992, p. 97
[93] Biringuccio, 1990, pp. xiv, 22
[94] Ibid., p. 150
[95] Ibid., p. 64
[96] Tylecote, 1992, p. 97
[97] Williams, 2003, p. 880 & Buchwald & Wivel, 1998, p. 74
[98] Buchwald & Wivel, 1998, p. 74 & Dillmann et al., 2002, p. 327



Graph 2-2 The iron-carbon phase diagram including, iron, steel and cast iron phases[99]

The molten metal (with infused carbon) was easily drained away from the less dense slag. As a result the cast iron, at this stage, was almost free from slag inclusions and unreduced components[100]. This increased carbon concentration and little slag marks a contrast with bloomery iron. However, the elevated concentrations of carbon resulted in embrittlement: making steel unsuitable for the forge work required for armour plate production[101].

FINERY HEARTH

To make cast iron from the blast furnace forgeable, its carbon content would have been lowered by oxidation[102]. This process was performed with small lumps of cast iron in an open oxidising finery hearth at circa 1150°C[103]. As the metal lumps lost carbon content the metal resultantly solidified (due to the rising MP as carbon

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[99] Scott, 1991, p. 132
[100] Dillmann et al., 2002, p. 327
[101] Williams, 2003, p. 881
[102] Buchwald & Wivel, 1998, pp. 88-89 & Dillmann et al., 2002, p. 327
[103] Buchwald & Wivel, 1998, p. 89 & Williams, 2003, p. 882

concentration decreased: as per Graph 2-2) and were then consolidated into one mass[104].

Negatively, while the fining process involved the subtraction of carbon, it also coincided with the formation of a heterogeneous metal that was "…just as likely to be full of slag…" as bloomery iron[105]. Elements such as phosphorous, silicon and iron in the previously relatively slag-free cast iron were oxidised and therefore became inclusions[106]. These inclusions were partly extracted via hammering that also flattened the resulting bloom before its cutting and distribution[107]. The use of hydraulic power was here again drawn upon: this time as automated trip-hammers to produce sheets of plate metal[108].

2.1.2.1.3 Blast furnace-direct process

Williams cites some scepticism towards the fining stage of the indirect process. He states that the practical achievement of enabling decarburisation to occur at an intermediate level between cast iron and iron would have been difficult to achieve due to instability of the finery hearth temperature[109]. Williams has suggested the possibility of the blast furnace being operated like a bloomery furnace[110]. In brief, Williams supposes that blast furnaces supplying Italian armourers were not used to create cast iron *indirectly* for armour, but instead to *directly* create the larger blooms necessary to make armour plates[111]. It is unclear whether the ironmaster *certainly* limited the carburisation occurring in the blast furnace so as to attain a forgeable carbon steel suitable for armour and to avoid formation of liquid cast iron and the subsequent finery process: Williams believes ironmasters had such capabilities[112].

2.1.2.1.4 Cofusion-indirect process

Alternatively, Biringuccio describes an indirect steel-making process, *cofusion*, which involved the repetitious addition of masses of bloomery iron (negligible or low carbon content) to a continually heated receptacle of molten cast iron (high carbon content). The process ended when the mixture became "…soft and

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[104] Williams, 2003, p. 882
[105] Ibid., & Buchwald & Wivel, 1998, p. 89
[106] Dillmann et al., 2002, p. 328
[107] Buchwald & Wivel, 1998, pp. 74, 89
[108] Williams, 2003, p. 881 & Biringuccio, 1990, pp. xiv, 22
[109] Williams, 2003, p. 888
[110] Ibid., p. 889
[111] Ibid., p. 878
[112] Ibid., p. 881

pasty…" whereby it appears this might have been caused by the dilution of its carbon content; as a result, the MP rose, thereby beginning to solidify the mass[113]. To increase even carbon distribution, the carburised material was periodically extracted cooled and broken up and returned to the bath[114].

2.1.2.2 Munition armour forming

The various anatomical parts that comprise half-armour are given in Figure 2-9.

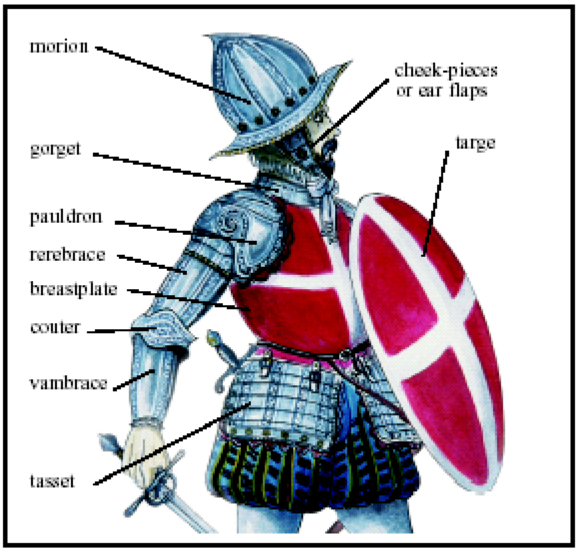

Figure 2-9 Left: Annotated appellation of worn etch-decorated[115] half-armour (breast and backplates are covered by a surcoat marked by the Order of St. John ensign)[116]

The Palace Armoury's collection of munition armour under study is present in three distinct relative sizes; small; medium; and large: supporting the notion that mass-produced munition armour were not custom-fitted to particular soldiers[117].

To help briefly outline some of the processes necessary to transform the metal billet to fabricated armour, the munition armour of this study are further described here. The munition armour are relatively lightweight (0.8-1.2mm in thickness[118]) and would have been hammered from sheets. The concave shaping of the sheets was wrought, probably hot, by hammers on anvils, stakes, dishes etc[119] (Figure 2-10).

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[113] Graph 2-2

[114] Biringuccio, 1990, pp. 68-69, Tylecote, 1992, p. 105 & Williams, 2003, p. 887

[115] The etched surfaces depicted are not representative of the armour in this study.

[116] Spiteri, 2003, pp. 55, 384

[117] Magro Conti, 2007, pers. comm.

[118] As measured by the present author on the various lames on 8 different munition armour assemblies

[119] Biringuccio, 1990, p. 370 & Williams, 1978, p. 132

Figure 2-10 A 15-16th French manuscript depicting hot forming of a breastplate or backplate by hammer on an anvil[120]

Shears would have made the final cut, trimming away excess metal. The outer surfaces of munition armour at the PA are largely plain and undecorated, while the decorations that do exist are modest. The most common decorative forms of this typology include spirals (*volutes*) and edging formed by repoussé (surface embossing by hammering reverse of sheet metal), roped edges (outer edges of ferrous plates have been rolled over drawn wire then hammered or filed to give a cord-effect) (Figure 2-11).

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[120] Price, 2000, p. 60

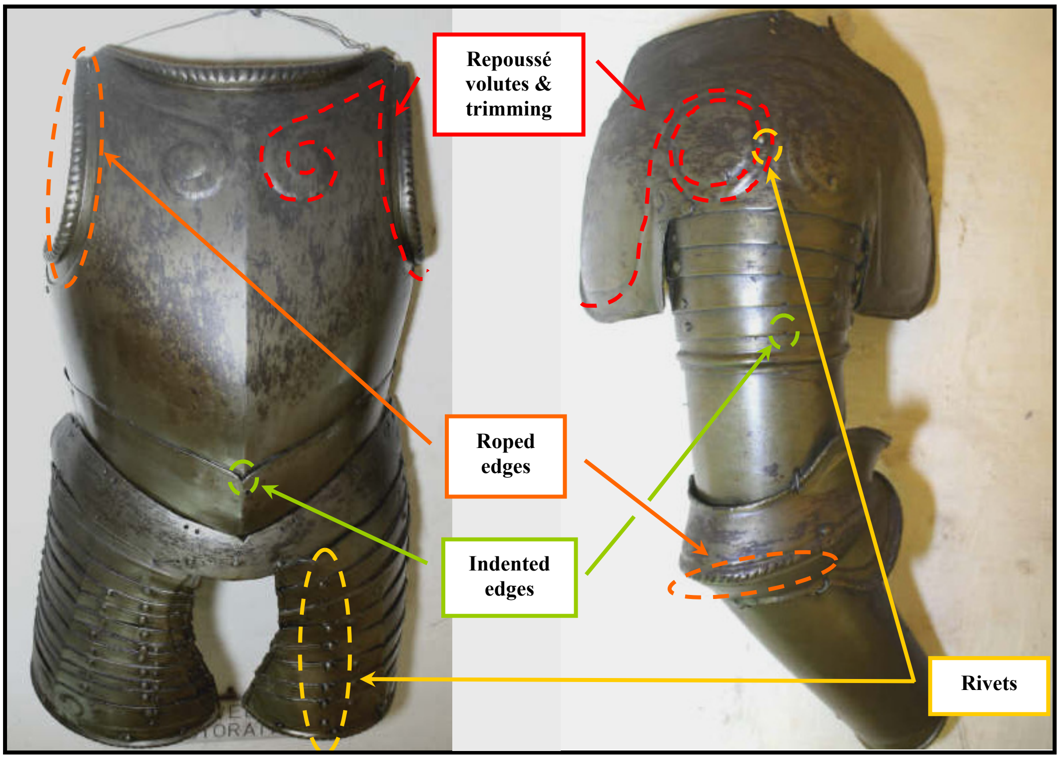

Figure 2-11 Typical mid 16th-mid 17th century northern Italian-style munition armour at the Palace Armoury[121]. Left: Breastplate and tasset. Right: Pauldron, upper cannon (rerebrace), couter and lower cannon (vambrace)

More rarely, single acid-etched or chisel-engraved lines appear as trimming or centrelines. These might have been used for evolving symmetry during pattern making and forming. Some lame edges were cut in an indented manner thereby providing positioning for adjacent lames[122].

2.1.2.3 Munition armour heat-treatment

In addition to the hardness imparted by carbon structures of cementite in steel, this carbon presence permitted armourers to further increase hardness of steels via *quenching*[123]. Quenching could have been carried out by rapidly cooling the hot metal by immersion in a liquid: water for a hard-quench; or oil for a slack-quench, for example. The hardness increased with the quicker rate of cooling, and unless later tempered, quenching could lead to embrittlement[124]. The improved physical properties were attributable to microstructural changes to *bainite* (acicular shape) or *martensite* (lath shape)[125]. According to Williams, pre-1530 hardening of undecorated Italian armour seldom occurred, while post-1530 the practice was

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[121] Crawford, 2005-2007, pers. photog. permission courtesy of E. Magro Conti
[122] Stroud, 2006-2007, pers. comm.
[123] Williams, 2003, p. 879
[124] Tylecote, 1992, p. 52
[125] Williams, 1978, p. 132

discontinued[126]. A sample of six undecorated late 16th-early 17th century northern Italian armour studied by Williams supports this theory since all of the samples were classified as being air-cooled low-carbon steel (i.e. hardening was neither achieved, nor attempted)[127]. All of the seven *steel* samples of 16th-17th century northern Italian-style munition armour from the Palace Armoury examined by Vella and Williams appear to have been air-cooled: remaining consistent with the hypothesis that hardening of munition armour in Italy was not performed post-1530[128].

2.1.2.4 Munition armour surface finishing

For munition armour a series of three basic manufactured outer surface finishes[129] has been proposed by Robert Smith[130], a prominent authority on armour conservation and restoration:

1. "Rough from the hammer: The piece was hammered into shape and was then *planished* (smoothed to a greater or lesser extent using a flat hammer and a stake)."
2. "Rough filed: This is not common, but surfaces exist which have been planished and then rough filed smooth: file marks are still evident."
3. "Polished: The piece would have been planished, rough filed and then polished to a bright finish using successively finer abrasives" (Figure 2-12).

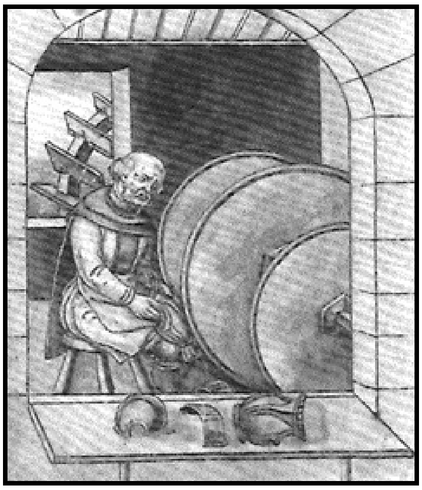

Figure 2-12 An illustration from Hausbuch der Mendelschen Zwölfbrüderstiftung (circa 1571) depicting an armourer using a hydraulic powered polishing/grinding wheel[131]

In a foreign collection, other half-armour of strikingly similar typology (Pisan), period (1560-1570) and provenance (northern Italy) has been shown to bear

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[126] Williams, 2003, p. 211

[127] Ibid., p. 209

[128] Vella et al. 2004, p. 230

[129] Exclusive of decorative applied and depletion techniques (gilding, etching etc)

[130] Author and former Head of Conservation, Leeds Armoury, United Kingdom and currently in private practice

[131] Price, 2000, p. 264

so-called *browned* surfaces (intentional oxide layers[132]) that underneath still exhibit *rough from the hammer* marks (Figure 2-13). This particular armour present at the Kunsthistorisches Museum is believed to be that used by an infantry foot soldier; however earlier in the mid 1500s nobility sometimes wore armour of this description[133]. This Kunsthistorisches Museum armour is in contrast to the Palace Armoury armour in this study, which *currently* have smooth, non-facetted metallic finishes[134]. The outer surfaces *from manufacture* of the PA munition armour are believed to be of a brilliant metallic finish and therefore belong to the third surface classification above: i.e. polished[135].

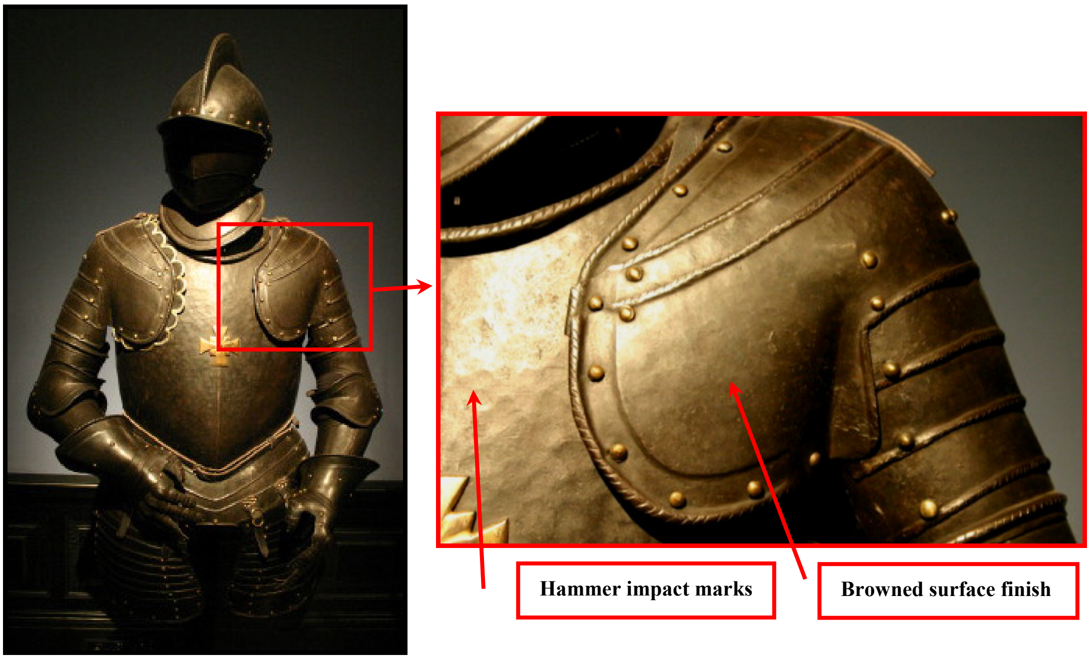

Figure 2-13 "Northern Italian foot soldier/infantry armour (c. 1560-1570)" [136] at Vienna's Kunsthistorisches Museum[137]

Since the PA munition armour have been highly intervened over the last centuries the probable modification of the armour surfaces since manufacture is not disregarded[138]. The exposed outer surfaces present today do not testify such browned surfaces and without further study of a larger corpus of these armour (in particular between lames and under rivets) it is supposed for now that the outer surfaces of the armour in this study were more likely to have been fabricated with the polished

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[132] Smith, 2006, p. 28
[133] Anon. Display caption. Inv No A 1045
[134] i.e. the still metallic uncorroded surfaces
[135] Stroud, 2006-2007, pers. comm. & Smith, 12/06/2007, pers. comm.
[136] Anon. Display caption. Inv No A 1045
[137] Crawford, 2005-2007, pers. photog.
[138] 2.1.3 History of the Palace Armoury's 16th-17th century northern Italian-style munition armour

finish. In contrast, it is supposed that the inner surfaces of armour were not polished of their hammer-scale oxides[139].

A conservator's awareness of the various manufacture surface finishes of armour is of high significance to detecting and acting on preserving any such remnant original or modified original surfaces. Armour's manufactured surface finishing is an area of metallurgy requiring further investigation that would help inform the armour conservator[140].

2.1.2.5 Munition armour assembly & articulation

Finally, the separate metal plates comprising the half-armour would have been assembled with ferrous rivets often capped with copper alloy plating (brass with minor and trace metals[141]) and embossed rosettes. Originally, armour inner surfaces featured leather strapping to facilitate their assembly and articulation and padded textile to improve the comfort of the wearer[142]. Only very rarely, and in very small quantities do organic components of the Palace Armoury munition armour inner surfaces remain[143].

2.1.3 HISTORY OF THE PALACE ARMOURY'S 16TH-17TH CENTURY NORTHERN ITALIAN-STYLE MUNITION ARMOUR

Here an attempt is made to outline the probable history of the mid 16th - mid 17th century northern Italian-style munition armour currently present at the Palace Armoury. This account importantly includes some documentation regarding the corrosive effects of the environment and some approaches to corrosion product removal through the armour's history. Indeed it is possible (or almost doubtless) that some of the many and separable multi-component armour bear surfaces that are testimony to the history that each piece has passed through: from the mid-late Early Modern Period to contemporary times[144].

The arms and armour that now constitute the PA collection, some spanning almost 500 years, have almost always been of high prominence and remained under the administration of the governing or occupying state[145]. As a result, a relatively

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[139] Stroud, 2006-2007, pers. comm. & Degrigny et al., 2007b, p. 38
[140] Smith, 29/07/2007, pers. comm.
[141] Degrigny et al., 2007a, pp. 27, 29
[142] Smith, 1982, pp. 9, 12
[143] Stroud, 2006-2007, pers. comm.
[144] Magro Conti, 2007, pers. comm.
[145] Spiteri, 2003, p. 17

continuous line of information is present, though this is still dependent on the records kept by each successive ruling administration and external documentary resources. The *individual* documentation identifying *each article* of munition armour and its location since manufacture to the present-day is non-existent, as it seems that the Order of St John and subsequent administrations did not pay attention to record the individual details of each article. The former individual wearers of each munition armour are not known and these armour are thus treated as an assembly. Early records do show however numerous events where control of military equipment dissemination was a problem and the Order's Artillery Commander was placed personally responsible to account for the arsenal's whereabouts[146]. The *definitive* history of each munition armour piece, especially when outside the Palace Armoury, hence remains open to speculation. As a concession, thanks to the significant numbers of munition armour (as required for the numerous troops), this collection category can be traced through numerous inventories (listing only *article categories*) and historical sources (e.g. written memoirs, graphic representations) associated with the collection's time at the prominent PA (17th century onwards). Such Palace Armoury-related resources could not cover all the history of the munition armour since some armour predates the establishment of the PA, and because the PA later formed an integral part of a larger network of armouries throughout the Maltese Islands. It can be expected that transfers between armouries, as needs arose, would have formed a part of the armour's strategic management[147]. For example, it is known that up until the 18th century three armouries existed in Valletta, including the Palace Armoury, St James Cavalier and Strada Forni[148]. The munition armour could have also possibly been stored in one of the many decentralised village or town armouries in the Maltese Islands[149].

The controlled issuing of equipment from the Palace Armoury by the Order ended in 1798 with their eviction by the French and it is uncertain how much equipment trickled back to the PA since then[150]. So, despite this indefinite history, it can be reasonably speculated that much of the remaining quantities of munition

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[146] Ibid., pp. 80-83

[147] Magro Conti, 2007, pers. comm.

[148] Spiteri, 2003, pp. 13, 103

[149] Ibid., p. 103

[150] Ibid., p. 118

armour have had a long connection with the Palace Armoury environment: a minimum 210 years from present (2008) and reaching just over 400 years[151].

The various roles that the numerous 16th-17th century munition armour have taken over these centuries is described next. Written accounts of visits and inventories of the armoury form the basis of the historical evidence during its original administration by the Order, while documentation of subsequent rule is further supported by pictorial evidence.

It is illustrated in the following subsection that the munition armour have consistently assumed a significantly lower status especially when compared to the individual, more elaborate and technically complex armour of the Grand Masters. Also, in the Palace Armoury's early history under the Order's administration, the strategically significant and numerous guns further diminished the attention paid to the munition armour. The prioritised attention towards other items in the collection probably influenced the munition armour's conservation state; similarly to the present-day[152].

2.1.3.1 Mid 16th century-1798, Order of St John: functional, symbolic & obsolete arsenal

2.1.3.1.1 Mid-late 16th century, Order of St John: pre-Palace Armoury

The munition armour dating to the mid-late 16th century evidently antedate the 1604 establishment of the Palace Armoury in the Grand Masters' Palace. It is possible that such armour, presuming direct importation from the Italian manufacturer to Malta, were stored either in Fort St Angelo in Vittoriosa (*Birgu*)[153, 154], or, after the establishment of Valletta, in either of the armouries located in Strada Forni or later in Piazza San Giorgio[155, 156]. The Mdina armoury could have also been another possible, yet distant, storage location during the late 16th century[157, 158].

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[151] Magro Conti, 2007, pers. comm.

[152] 2.1.4.2 Ground floor location, 1975-present

[153] Spiteri, 2003, pp. 65, 71

[154] Figure 2-2 Upper left

[155] Spiteri, 2003, p. 12

[156] Figure 2-3

[157] Spiteri, 2003, p. 200

[158] Figure 2-2 Upper left

2.1.3.1.2 1604-1798, Order of St John: Palace Armoury

The transferral of the armoury in Piazza San Giorgio to the Grand Masters' Palace[159] in 1604 marked a paradigm shift regarding the management of the Order's military equipment[160]. Notably, the wall hanging arrangement of static arms and armour previously worn by the Grand Masters' appears to have transpired early in the 1600s[161]. Whereas the date for the institution of trophies of common arms and munition armour at the Palace Armoury is not known, but probably occurred from the mid 17th century[162]. Trophies of arms or *panoplies* were commonplace in Europe's palaces and castles, but more so during the romantic revival of the 19th century (Figure 2-14).

Figure 2-14 Examples of trophies of arms across Europe. Left: Hertford House (circa 1873-1897), Sir Richard Wallace, United Kingdom[163]. Centre: Pierrefonds (published 1867), Viollet-le-Duc, France[164]. Right: *Cabinet des armes et armures* (n.d.) of Prince Soltykoff in St Petersburg, Russia[165].

It will be seen in the following subsections that the open wall-display of panoplies of munition armour at the Palace Armoury increased after the Order's rule and persists to a lesser extent until the present day. The wall panoplies are of high significance at the PA, even today, to the conservation implications of their contents[166]. It is notable that during the time of the Order, the number of wall-hung armour (either as a means of storage or on display as trophies), appears to be

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[159] Figure 2-3
[160] Spiteri, 2003, pp. 69-70
[161] Spiteri, 2006, p. 32
[162] Spiteri, 2003, p. 200
[163] Edge, 2006, p. 45
[164] Faton-Boyancé et al., 2006, p. 13
[165] Ibid., p. 12
[166] As explained in 2.2 Indoor atmospheric ferrous corrosion & control

insignificant when compared to its apparent peak during the British rule of the 20th century[167].

From the beginning of the management of the military equipment at the Palace Armoury, two parallel states seem to have formed for different classes of equipment: the *dynamic* (use) state; and the *static* (display) state. The static state continues to present day for all the collection, and on balance is inherently favourable to the collection's preservation when compared with the former embattled and dynamic period of the arsenal.

The initial primary state of the PA was of course as a dynamic arsenal: a central functional storehouse for maintaining and issuing pieces of offensive and defensive equipment to the Order of St John's troops and Knights[168]. An account of a room supplementary to the main armoury hall, published in 1679 by Sieur de Bachelier, testifies to an abundant yet orderly arrangement of arms and armour:

> "In this room we find laid out in the same order 6000 muskets, and as many bandoliers (musket ammunition belts), 2000 helmets and an equal number of breastplates"[169].

There is no early pictorial evidence available to support this description, but this categorised arrangement of similar equipment would be suitable for quickly issuing items at the time of alarm. The vast quantities suggest most of this equipment was reserved for the numerous troops, not the relatively few personnel of the upper ranks[170]. Sieur de Bachelier's description of the Palace Armoury possibly reflects a categorised arrangement depicted in an illustration of the Royal Armoury in Bastille, Paris, dating to the same period (Figure 2-15). Breastplates and backplates mounted high on the beams and the guns on the more central and more accessible racks along the floor and walls are to be noted. This speculated possible early configuration is echoed in pictorial evidence of the configuration at the PA much later during the mid 19th century[171].

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[167] 2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques

[168] Spiteri, 2006, p. 70

[169] Bonello, 2001, p. 41

[170] Stroud, 2006-2007, pers. comm.

[171] Later presented in 1798-1964, French & British occupation: decorative romantic trophies to academic antiques & Figure 2-17 Left: Detail of trophies of arms from Right: *Armoury in the Governor's Palace in Valetta*, lithograph by Charles Frederick de Brocktorff, circa 1840.

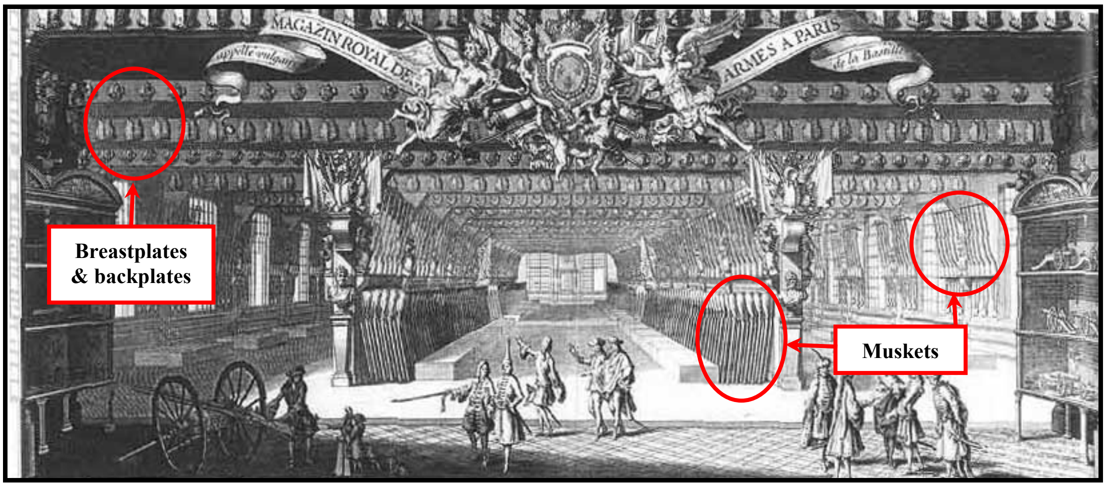

Figure 2-15 ***Le Magazin Royal des Armes à Paris*****, circa 1686**[172]**.**

Given that the armour of this study were manufactured in the mid 16th-mid 17th centuries, it can be presumed that at least during the early years of the armour's installation at the Palace Armoury (i.e. 1604 onwards) the majority of this arsenal would have been relatively new and had a state that could be classified as being *dynamic*; especially taking into account the numerous alarms and mobilisations of the troops and militia in the late 16th & early 17th centuries. There were at least nine incidents between 1598-1629, while the 1614 Turkish invasion of a force of 5 000 men prompted the call-up of the Order's militia[173] and troops[174] to confront the invaders. Another alarm, later in 1638, required the despatch of 200 troops[175] to reinforce the Cittadella in Gozo[176].

The succession of new and improved military technologies inevitably rendered dynamic parts of the Palace Armoury arsenal obsolete. Records indicate the removal of obsolescent items, specifically guns, on several occasions (1640, 1703 & 1763)[177]. Although not explicitly found in the literature concerning the PA collection, it is assumed that obsolescence would have also occurred for the thin Palace Armoury munition armour, especially at a time when increasing efficiency and use of firearm technologies compelled improved armour defensive capabilities via *bullet-proofing*[178]. Generally, armour use began to decline in the late 16th century, while obsolescence (at least for defensive purposes) was largely complete by the end of the

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[172] Faton-Boyancé et al., 2006, p. 8
[173] Spiteri, 2003, p. 70
[174] Stroud, 2006-2007, pers. comm.
[175] Ibid.
[176] Spiteri, 2003, p. 146
[177] Ibid., pp. 104, 107 & 119
[178] Ibid., p. 60

17th century[179]. The decline in armour use was protracted since often the slow reloading of firearms during siege warfare would ultimately lead to hand-to-hand combat where armour was useful[180]. However, by the latter half of the 18th century the defensive capability of ferrous armour against firearms was surpassed and armour was rendered totally obsolete as a functional piece of equipment[181].

The secondary, yet significant (in terms of historical evolution and conservation), and parallel state of the arsenal installed at the Palace Armoury, was not functional and dynamic, but instead symbolic and static. In just thirteen years after Grand Master Wignacourt's installation of the armoury in the Palace, a 1617 account by Count George Albrecht of Erbach describes his tour led by the German Knights. The Knights presented the battle suits of Grand Masters adjacent to their portraits and numerous other arms and armour[182]. From this early observation it is clear that the Knights retained equipment that was not of continued functional military value, but also of historic, symbolic and decorative value. A specialist in Malta's military history, Stephen Spiteri, uses Erbach's 1617 account to support his claim that the Palace Armoury:

> "…quickly began to assume the character of a showpiece reflecting the military power and glory of the Order, capturing the attention and imagination of many a distinguished visitor to Malta… it also began to acquire the qualities of an antiquarian collection and as such, became an instrument of propaganda exalting the Order's heroic past"[183].

It is supposed, by the present author, that the static display in elaborate trophy panoplies (as opposed to the more practically accessible rows) of munition armour occurred to some armour after they were rendered technologically obsolete. The retention of the more common equipment, such as the munition armour covered in this study, for static use in decorative displays is only well attested during the latter part of the Order's management of the collection. The Order's Commander of Artillery, St Felix, described in 1785 the distribution of items in the armoury. His inventory demonstrated the previously described dual statuses (i.e. dynamic and static) of items in the Palace Armoury. The account included almost 20 000 guns of various types including nearly 18 000 muskets that were held on 4-metre high wooden racks in the centre of the room and along the walls that were intended to be

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[179] Smith, 1982, p. 7
[180] Spiteri, 2003, p. 60
[181] Galizea, 1906, p. 11
[182] Spiteri, 2001, p. 127
[183] Ibid., p. 127

functional (i.e. dynamic)[184]. Meanwhile antique arms and armour were displayed (i.e. static) along the walls in 24 elaborate panoplies of trophies-of-arms below the cornice, and with some suits on the floor[185]. The cornice included armour of 254 breastplates & backplates and 124 helmets[186].

The specific arrangement of the cited decorative panoplies is unclear, but it seems possible the inspiration could have been drawn from heraldry/blazons, decorations on architectural features[187] and even from some types of armour (Figure 2-16). These dated armour surface etchings indicate that composing arms and armour in symmetrical formations was established even before the 1604 founding of the PA.

Figure 2-16 Acid-etched decorations on more elaborate armour (circa 1590) indicate trophy of arms display formations[188].

MAINTENANCE & RESTORATION

The responsibility of keeping arms and armour functional at the time of the Order was bestowed on the *Capomastro del Armeria* who led armourers, skilled labourers and sometimes slaves[189]. Such maintenance work was performed in the

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[184] Ibid., p. 129
[185] Spiteri, 2003, p. 109
[186] Ibid.
[187] Ibid., pp. 125-127
[188] Ibid., p. 290
[189] Spiteri, 2001, p. 128

Armourer's workshop (*Ufficina dell'Armeria*); a room next to the armoury hall[190]. The concern of the Order for the condition of the arsenal was exemplified by a decree in 1648 that required, "…a commission of knights was to inspect the Armoury at least once or twice a year and draw up a detailed list indicating the quantity, quality and state of preservation of the weapons and armour"[191]. However it is believed that these condition reports were not undertaken at the decreed regular intervals and only one such list has been found, dating much later (1782)[192]. A variety of repair work was undertaken, but several accounts (1769, 1782, 1795) of rusted equipment and cleaning procedures would have made corrosion product removal a significant task during the latter part of the Order's management of the arsenal[193].

Oil and emery (*olio e smeriglio*) were used as cleaning materials during the time of the Order. Emery's abrasive qualities were not only understood for their efficiency in removing corrosion products, but caution to the armourers was given to not overclean and consume the underlying metal; otherwise reducing the efficacy of the armour in active service[194]. The oil was presumably used as a lubricant for the emery's physical action and for possible corrosion protection. Sand is reputed, not documented, to have substituted emery at times of low stock in the late 18th century and was applied in a mixture of vinegar (chemical action by acidic dissolution) with a cloth. The finishing polish appears to have been a form of burnishing performed with deer horn and wine spirits[195]. Records of the works performed in the Armourer's workshop were supposed to be kept[196]. The details of these were probably scant and more intended to account for the payments made to the armourers[197], rather than for treatment documentation purposes that are presently required for recording conservation treatments.

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[190] Ibid.

[191] Spiteri, 2003, p. 81

[192] Ibid.

[193] Ibid., pp. 11, 147, 154

[194] Spiteri, 2006, p. 74

[195] Ibid., p. 74

[196] Spiteri, 2003, p. 160

[197] Ibid., pp. 158-162

2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques

The ever decreasing military value and increasing aesthetic value of the armoury perpetuated its changing role from active arsenal to gallery of antiques and curios; *form as function & symbolism* was being exchanged for *form as decoration*. It is seen here that the early part of this period truly cemented the status of the munition armour as being functionally obsolete and decorative, especially in comparison to the firearms. Later, scholarly interest in the Palace Armoury collection grew, but this attention was not directed towards the munition armour.

When Napoléon I and his forces occupied Valletta without resistance in 1798, the rapid dissolution of the Order's rule over the Maltese Islands and their eviction ceased the Order's management of the Palace Armoury. The strategic military importance of the PA was recognised at the time of invasion: in fact, most of Malta's armouries fell under French control[198]. An inventory made one year after occupation listed literally thousands of firearms categorised as "new models (totalling 9234)", "old models (965)", "to clean (749)" or "unspecified (2950)". It would appear that these firearms were being classified according to potential continued use. It is therefore not surprising that some suspicion falls upon Napoléon's ship, *L'Orient*[199], for thousands of these now unaccounted firearms[200]. Meanwhile, the French perception of the armour as being non-functional or ornamental is clearly seen in their inclusion of the armour in a list entitled, "*Décorations de la Salle d'Armes*". Two phrases describe the arrangement of 255[201] *cuirasses* (breast/backplates) hanging in rows above and on the cornice-coving and a series of fourteen symmetrical trophies with unspecified contents[202]. Napoléon's forces seemed uninterested in documenting the serviceable state of the munition armour. Unlike the firearms, it appears that the munition armour's technological obsolescence, perhaps coupled with their inherently non-exquisite nature, was their saving grace from pilfering by the French occupation.

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[198] Spiteri, 2003, p. 118

[199] Bound for the war campaign in Egypt (Spiteri, 2003, p. 118).

[200] Spiteri, 2003, p. 118

[201] Almost corresponding (i.e. 255 versus 254) to the quantities previously mentioned in the 1785 Order of St John inventory

[202] Spiteri, 2003, pp. 115-116

Later however, under British rule (1800-1965), "…quantities…" of Italian munition armour were pilfered by the British and taken to London's Tower Armouries in 1826 and 1846 making it "…an important centre for the study of this type of armour"[203]. Yet, another account of the British occupation details the positive attention given to a derelict collection by the British colonial Governor (1858-1864) Sir John Gaspard Le Marchant, himself a "…great amateur and connoisseur of antiquities"[204]:

> "The old Armoury of the Knights of St. John had been long neglected, and its contents thrown aside like useless lumber. Sir Gaspard (Le Marchant) set himself to work to recover these valuable relics of a bygone age. Under his personal direction they were duly restored, classified, and arranged to the best advantage in one of the finest halls of the Palace"[205].

At this time the decorative, static nature of the hall was accentuated by developing a late romantic style. The number of wall panoplies increased and mannequins bearing armour and papier mâché shields were installed[206]. Figure 2-17, Figure 2-18 and Figure 2-19 demonstrate the increasing use of symmetrical formations of trophies of arms during the first part of the British period.

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[203] Spiteri, 2001, p. 131

[204] Żygulski, 1970, p. 70

[205] Laking, 1903, p. xiv

[206] Żygulski, 1970, p. 70

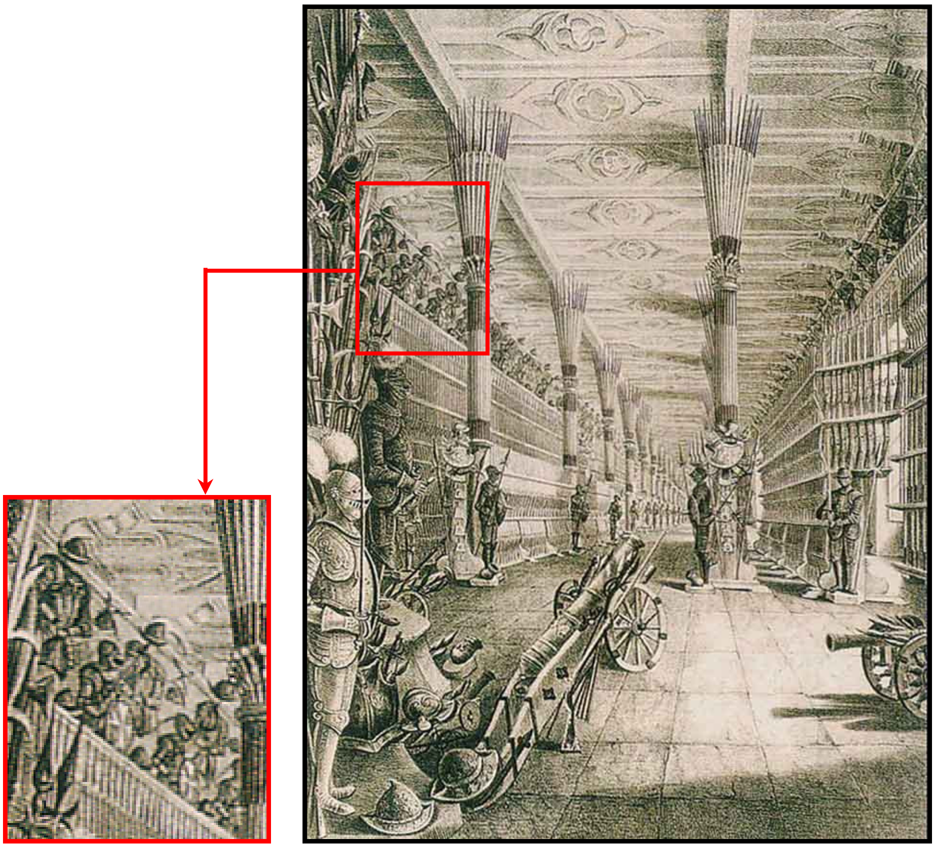

Figure 2-17 Left: Detail of trophies of arms from Right: *Armoury in the Governor's Palace in Valetta*, lithograph by Charles Frederick de Brocktorff, circa 1840[207].

The establishment of the Palace Armoury as a museum in 1860 marks its transition to a more academic profile[208]; although, it can be said that museums of the Victorian era were more characteristic of curiosity cabinets than the more educational museums of the present-day. The increasing role of the Armoury as being of scholarly interest came at the turn of the 20th century with the arrival of Sir Guy Francis Laking, Keeper of the British King's armoury. Lord Grenfell, the then Governor of the Maltese Islands, requested Laking's study of the collection and this published work can be seen as the first pseudo-academic or scholarly interpretation of the PA collection[209]. Laking counted hundreds of 16th-17th century armour on the walls, however, his descriptive cataloguing was prioritised to 464 articles of the 5286[210] articles counted. He stated that the "…more ordinary armaments…", presumably such as the munition armour of this present study, were not the focus as he justifies:

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[207] Ganado, 2001, p. 18
[208] Spiteri, 2003, p. 9
[209] Laking, 1903, Żygulski, 1970, p. 70 & Spiteri, 2003, p. 9
[210] Żygulski, 1970, p. 71

> "Each specimen would, had time and space permitted, have had its individual place in the Catalogue, but as it is, the more ordinary armaments will be found mentioned in round numbers, and the important pieces fully recorded in the Catalogue"[211].

This again demonstrates that the collective munition armour was held in less regard and attention was prioritised elsewhere.

Galizea, the Palace Armoury curator at the turn of the 20th century confirms the location and decorative status of the munition armour at the turn of the century noting that, "The plainer suits of the men at arms have been left for the decoration of the walls of the gallery…"[212].

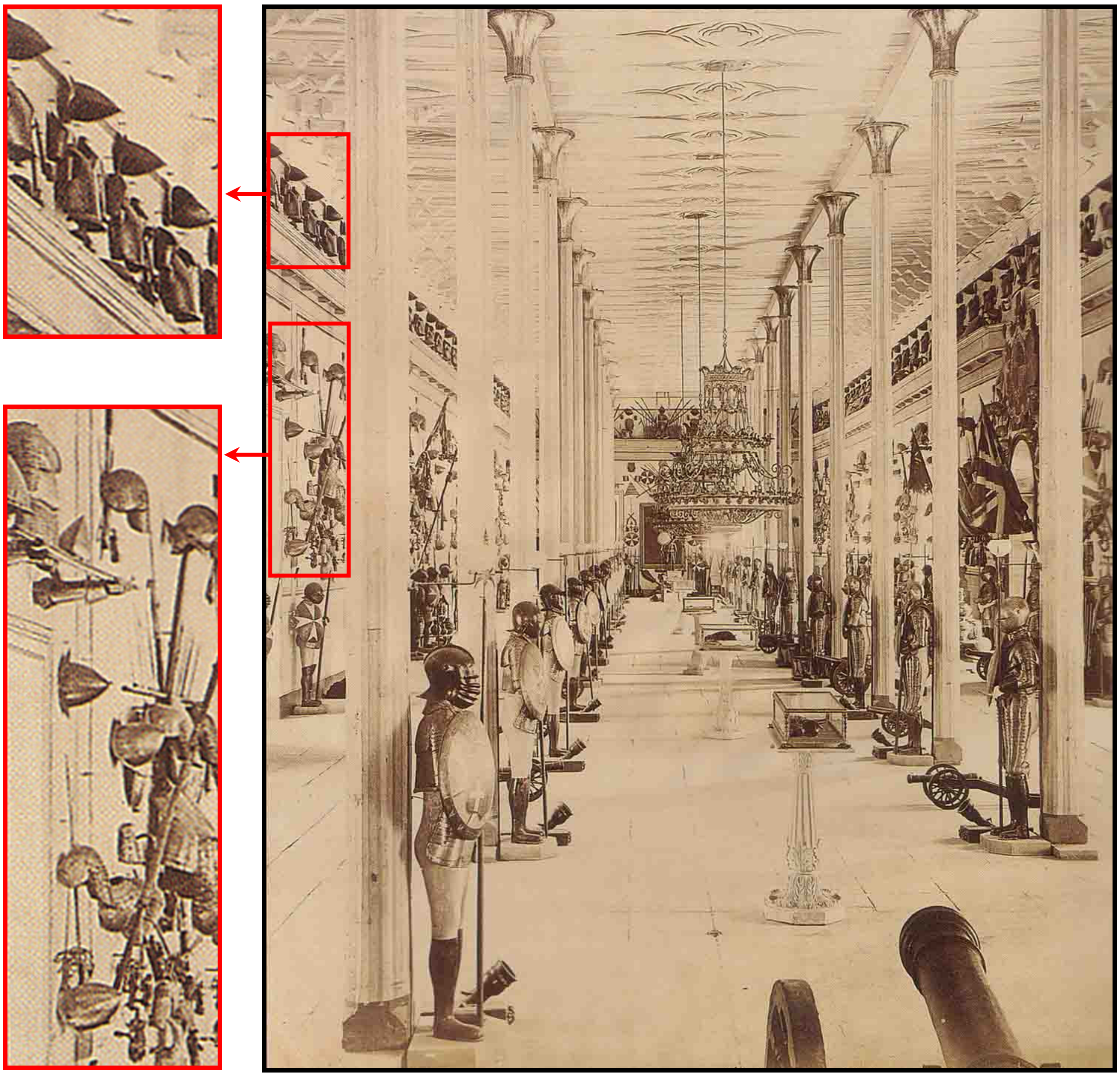

Figure 2-18 Upper and lower left: Details of trophies of arms from Main: The Palace Armoury circa 1900[213]

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[211] Laking, 1903, p. xiv
[212] Galizea, 1906, p. 20
[213] Spiteri, 2001, p. 138

Laking's display interpretation remained until a bombing of the Palace during the Second World War[214]. The collection was then transferred to underground shelters[215] where some damage was sustained due to the "…unfavourable conditions"[216] (presumably corrosion from the typically elevated humidities of subterranean spaces). After the war the collection was returned to the Palace Armoury and entrusted to the Governmental Museums Department[217]. The Museums Department was slow to effectively manage the Palace Armoury. Criticism of an attention bias towards other museums under their directorate has been cited[218], along with a lack of resources[219], as causes for insufficient attention to the PA.

Figure 2-19 Postcards depicting the Palace Armoury during the British period of the 20th century[220]. Note the multitudes of trophies of arms (and armour) on walls and furnishings

2.1.3.2.1 Restoration

It is apparent that a period of significant neglect leading to corrosion passed during the middle of the British period. Prior to the opening of the Palace Armoury as a museum in 1860, three months of armour cleaning was undertaken[221]. And after the Second World War armour were again polished[222] (Figure 2-20).

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[214] Czerwinski & Żygulski, 1969, p. 6
[215] Żygulski, 1970, p. 71
[216] Czerwinski & Żygulski, 1969, p. 6
[217] Spiteri, 2001, p. 131
[218] Magro Conti, 2007, pers. comm.
[219] Spiteri, 2003, p. 225
[220] Courtesy of L. Sciberras & C. Zammit
[221] Spiteri, 2003, p. 207
[222] Ibid., p. 224

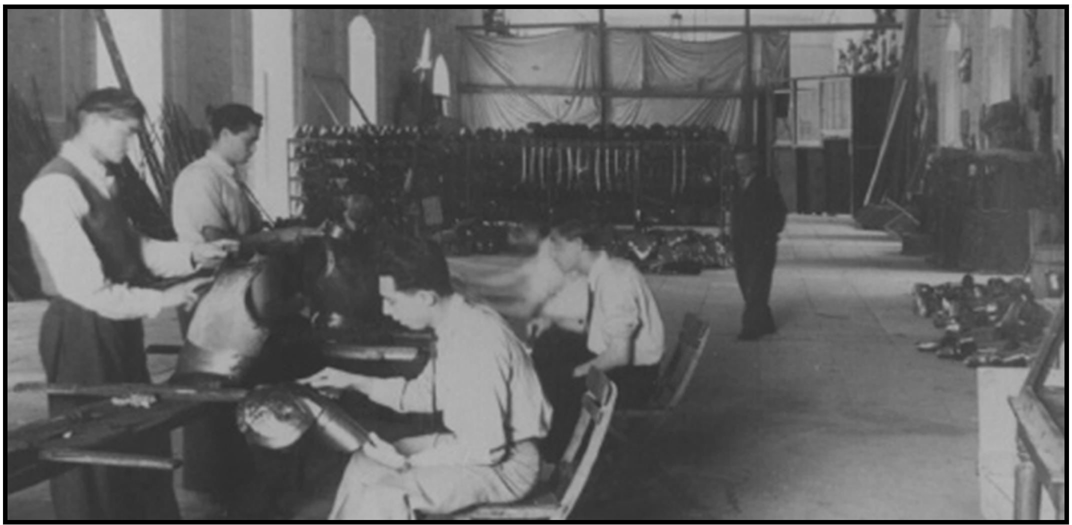

Figure 2-20 Armourers polishing armour at the Palace Armoury after the Second World War[223]

2.1.3.3 1964, Independence: remnants of a colonial history

The independence of Malta from British administration was enacted in 1964, and 1979 saw the end of Britain's military presence in Malta[224]. Another study of the Palace Armoury collection was performed in 1969, this time by United Nations Educational, Scientific & Cultural Organization (UNESCO) representatives Czerwinski and Żygulski. Again, it seems the munition armour were ignored, "All objects, except for those hanging on the walls … have had their condition examined"[225]. The UNESCO visit came at a time when Malta was in transition from colonial to independent federated state. For the PA collection, the independence from colonial rule was indelibly marked by a significant political decision that imposed a further decline in the already tenuous welfare of the collection: its relocation to the Grand Masters' Palace's former stables[226]. The potential conservation implications of this act are described in 2.1.4.2 Ground floor location, 1975-present.

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[223] Ibid., p. 224

[224] Attard, 2004, pp. 133-134

[225] Czerwinski & Żygulski, 1969, p. 9

[226] Spiteri, 2003, p. 227

Figure 2-21 The Palace Armoury arrangement before its 1975[227] ground floor transferral[228]. Note the relative absence of wall-displayed armour when compared with Figure 2-19

2.1.3.3.1 Restoration

Czerwinski and Żygulski the UNESCO representatives, noted that "…the largest group" of the Palace Armoury collection was "…objects of bright steel partly attacked by rust… especially from among the exhibits hanging on the walls"[229]. These are believed to be the munition armour. Czerwinski and Żygulski demonstrated to PA staff a series of restoration treatment options. Those deemed suitable at the time for undecorated objects were "…jellied…" or "…liquid rust remover, steel wool and fine wire brushes". Electrochemical "…reduction in zinc and caustic soda" was also recommended for objects without ornaments "… covered with thick layers of old rust"[230]. Of note was the demonstration for "Mechanical finishing of a cleaned object: brushing, polishing with fine abrasive cloth no. 00 or emery powder and oil"[231]. The extent of the subsequent application at the Palace Armoury of these demonstrated restoration procedures is unknown[232].

2.1.3.4 Recent history: museum typological collection & tourist site

The most recent developments at the Palace Armoury have occurred since the inception of Heritage Malta (HM) in 2002, a governmental agency entrusted with the conservation and management of Malta's cultural patrimony. The representation and

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[227] Stroud, n.d. p. 1
[228] Spiteri, 2003, p. 224
[229] Czerwinski & Żygulski, 1969, p. 10
[230] Ibid., p. 14
[231] Ibid.
[232] Stroud, 2006-2007, pers. comm.

interpretation of the PA collection arranged by chronological and typological format is being continued after its initiation and revision during the last years of the former Museums Department[233]. The focus of recent refurbishment works has been to improve visitor facilities and interpretation of the display cases. Meanwhile, comparatively little resources have been allocated to maintaining the continued display of armour in the wall panoplies[234]. The attention bias away from the munition armour has thus been demonstrated to continue until present day.

2.1.3.4.1 Restoration

It is known that until the early 1990s a phosphoric acid-based *rust converter* was in use at the Palace Armoury for removing corrosion products[235]:

> "Very deep rusting is best treated with orthophosphoric acid which helps loosen the corrosion without actually affecting the solid metal. Controlled immersion is by far the best method but successive brush/swab application often proves sufficient"[236].

The detection (by milli-x-ray fluorescence (XRF) spectrometry) of quantities of phosphorus on decorated PA armour helmets[237] has been supposed to be either attributable to the metal constituents or phosphoric acid residue[238]. The current approaches to munition armour CPs at the Palace Armoury are explored in detail as a part of this research's experimental component and are therefore presented in Chapter 3 Experimental methods & materials and Chapter 4 Results.

2.1.4 ENVIRONMENT OF THE PALACE ARMOURY'S 16TH-17TH CENTURY NORTHERN ITALIAN-STYLE MUNITION ARMOUR

The past and present natural and anthropogenic environmental influences on the Palace Armoury collection during its history are briefly introduced here. The mechanics and implications of such environmental aspects are expanded upon in 2.2 Indoor atmospheric ferrous corrosion & control.

2.1.4.1 First floor location, 1604-1975

The original location of the Palace Armoury was on the first floor at the Merchants Street end of the Grand Masters' Palace (Figure 2-2). The Order of St

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[233] Magro Conti, 2007, pers. comm.
[234] Further described in 2.1.4.2.1 Current display & storage method
[235] Kitto, 2006, p. 59
[236] Stroud, c.1993, p. 2
[237] Degrigny et al. 2007a, pp. 28, 31
[238] Ibid., pp. 29-33

John was all too aware of the indoor natural environment and the effects of metal corrosion on their arsenal. Appropriate architectural planning motivated by the knowledge of the susceptibility of arms and armour to corrosion by *rising damp* is given in Romano Carapecchia's (-1738) *Compendio Architettonico*[239]. The implementation of such architectural theory by the Order was evidenced in Malta by the placement of armouries on non-ground floor locations in buildings at Mdina, Birgu and Vilhena Palace[240]. Nonetheless, several separate accounts (1769, 1782[241], 1858[242], 1903[243]) of the corrosive effects on the collection were made in the period that the Palace Armoury was located on the first floor of the Grand Masters' Palace. A late assessment of the first floor environment by Czerwinski and Żygulski (1969) comments that while the gallery presented "…a rather dry microclimate" external dust and humidity could penetrate the gaps in the windows and a source of dust was the unsealed limestone (essentially calcium carbonate, $CaCO_3$) floor[244]. Even so, they reported the condition of the artefacts as being "…on the whole good, in many cases – very good" and attributed this to the application of protective varnish[245]. However, this is in contrast to the corrosion they noted on the wall-displayed armour[246].

2.1.4.2 Ground floor location, 1975-present

Waves from the socio-political events of the 1970s in Malta were felt by the Palace Armoury collection when an order was issued (1974) by the then Prime Minister Dom Mintoff to relocate the PA from its original site on the first floor to the ground floor site immediately below: the former stables of the Grand Masters' Palace[247] (Figure 2-22).

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[239] Spiteri, 2003, p. 188
[240] Ibid., p. 125
[241] Ibid., p. 200
[242] Ibid., p. 206
[243] Laking, 1903, p. vii
[244] Czerwinski & Żygulski, 1969, p. 9
[245] Ibid.
[246] 2.1.3.3 1964, Independence: remnants of a colonial history, Restoration
[247] Spiteri, 2003, pp. 224-226

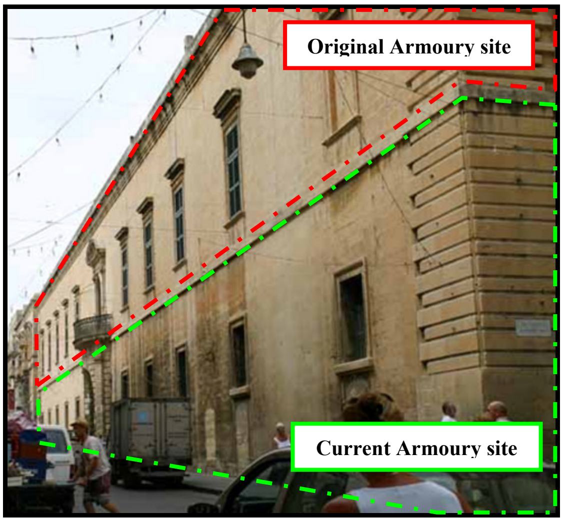

Figure 2-22 Original and current Palace Armoury locations[248]

The subsequent curatorial order in 1975 for relocation was three days and the move was carried out in this time[249]. This left insufficient time for adequate immediate organisation and some armour lay on the floor unattended for four years[250]. It is presumed that this armour would have most likely included the less prestigious munition armour of this study: not the parade armour of the Grand Masters[251].

2.1.4.2.1 Current display & storage methods

At present the armour displayed at the Palace Armoury can be categorised into three display types: display cases; open floor display; and open wall displays (Figure 2-23). Each display types presents its own environmental characteristics. The munition armour under study here are exclusively represented on the open wall (119 armour elements) and floor displays, while many more that were once hanging on the walls, comprise a large number of artefacts in the storage reserve where some 1025 further single armour pieces or armour assemblies are kept[252].

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[248] Crawford, 2007a, p. 9, permission courtesy of E. Magro Conti

[249] Stroud, n.d, p. 1

[250] Stroud, n.d. & Magro Conti, 2007, pers. comm..

[251] Ibid.

[252] Argyropoulos, in press, Chapter 5, p. 17 & Magro Conti, 2007, pers. comm. & Vella et al., 2005a, p. 5

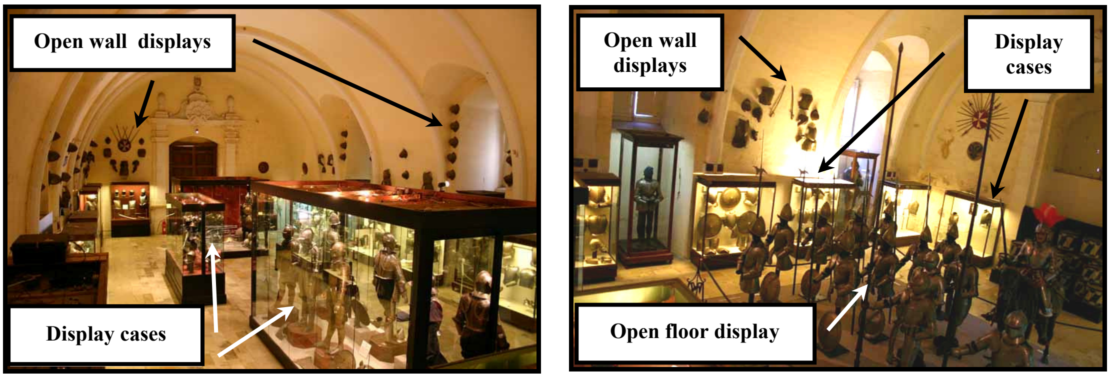

Figure 2-23 Palace Armoury Armour Hall exhibition space in 2006 marked with display types[253]

Figure 2-24 A selection of the wall-displayed trophies of arms in the Armour Hall in 2006[254]

The open wall displays are relatively inconspicuous and form no part of the current period and typological museological classification that the arrangements in display cabinets feature. No educational interpretation attempt is made for the museum visitor (e.g. in the form of lighting, signage, captions or audio guides). As a result, the focus of attention by the visitors does not fall on these wall displays. Maintenance efforts seem to correspond with this lack of visitor attention and are attributable to a lack of appropriate staff[255]. Instead the armour lies, literally and figuratively, on the periphery of the hall in their bygone symbolic and decorative formations.

Inspections of the wall-displayed armour in the Palace Armoury Armour Hall in 2005 showed the prevalence of corrosion products on their upper surfaces[256]. The reasons for this corrosion behaviour are attributable to their display characteristics and are explained in the subsequent section to exemplify the principles of corrosion in this case study.

From these historical and contemporary accounts it is clear that corrosion has plagued the arms and armour at the Palace Armoury, whether they were located on

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[253] Crawford, 2007a, p. 11, permission courtesy of E. Magro Conti
[254] Ibid., p. 12
[255] Stroud, 2006-2007, pers. comm.
[256] Vella et al., 2006b, p. 3

the original first floor location or as present in the former Palace stables. Any difference in the extent of corrosion occurring between the two locations was not ascertainable from the literature. Even though it is evidenced in the next section[257] that the present unfiltered and ventilated ground floor environment is unfavourable to the munition armour's conservation, good housekeeping is also important for such a large and vulnerable ferrous collection and is later outlined in 2.2.4.1 Preventive conservation methods. When the PA was located on the original first floor site inappropriate housekeeping could explain why Czerwinski and Żygulski noted occurrences of corrosion on wall-displayed armour, but not other armour[258].

2.2 INDOOR ATMOSPHERIC FERROUS CORROSION & CONTROL

The causes of ferrous metal corrosion in a non-air conditioned and cyclically ventilated indoor atmospheric environment such as that characterised by the Palace Armoury are examined here. In accordance with the research topic, the role of corrosion products as one factor in the complex interdependent material-environment system is included, as well as their morphologies and the hypothetical mechanisms behind their evolution. The resulting corrosion mechanisms are of significance to preserving or destroying traces of *modified original surfaces* as explained in subsection 2.3.1 What is the original surface & why determine its presence?

Since there are many similar corrosion characteristics between iron and carbon steels[259] they are largely treated as a whole group[260]. Their "…interactions with corrosive atmospheres demonstrate more similarities than differences…"[261] and "…many of the reactive atmospheric species and many corrosion products are the same"[262]. It is recognised that the Palace Armoury environmental-corrosion system is further complicated by Early Modern Period ferrous materials and by the presence of protective organic coatings, which must be surmounted before corrosion ensues. Appropriate corrosion and environment examples from separate recent studies at the PA are cited in the following sub-sections to exemplify certain points.

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[257] 2.2 Indoor atmospheric ferrous corrosion & control

[258] 2.1.4.1 First floor location, 1604-1975

[259] Carbon steels (i.e. not necessarily low-carbon steel) contain, by this citation and contemporary definition, ≤1% carbon and also small varying amounts of Mn, S, P and Si (Leygraf & Graedel, 2000, p. 281).

[260] Leygraf & Graedel, 2000, p. 281

[261] Ibid.

[262] Ibid.

Based upon the subsequent information sourced from the literature and these case study examples, it will be suggested that:

> The Palace Armoury's current building and environmental management, coupled with the inherent location on an urbanised peninsula adjacent to industry and on an island in the centre of the Mediterranean Sea is not advantageous to preventing atmospheric ferrous metal corrosion (Figure 2-25).

Figure 2-25 The coastal, urban and industrial regional environment of the Palace Armoury, Valletta[263]

Lastly, appropriate means for corrosion prevention in a cultural heritage context are briefly summarised so as to emphasise the priority from the outset to minimise corrosion occurrences, and to limit development should it occur.

2.2.1 FERROUS CORROSION: BASIC DEFINITIONS & CONCEPTS

By definition, "Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment", meanwhile the term *rusting* is specific to corrosion of iron or ferrous alloys[264]. Corrosion processes are most often electrochemical and are driven by the thermodynamic instability of the metals to revert to the more stable energy states they possessed prior to extraction from the mineral ore[265]. Thus, on an observational basis, metal corrosion is evidenced by the

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[255] Virtual Tourist, 2006, http://members.virtualtourist.com/m/7cf39/6ecb5 – accessed 04/06/2006

[264] Uhlig & Revie, 1985, p. 1

[265] Ibid., p. 6 & Selwyn, 2004, p. 19

transformation of an often brilliant lustrous metallic appearance to a non-reflective mineralised aspect[266]. On a fundamental basis, metal corrosion involves a transfer of electrons. A loss of electrons from the metal occurs (termed oxidation and occurring at the negatively charged pole, or *anode*), with a simultaneous acceptance of electrons by other chemical species present in the metal, in the corrosion products or in the environment (termed reduction, occurring at the positively charged pole, or *cathode*)[267] (Equation 2-2).

$$M \rightarrow M^{z+} + ze^{-} \quad \text{..} \quad (a)$$
$$EA^{z+} + ze^{-} \rightarrow EA \quad \text{..} \quad (b)$$

M = metal
z = valence/number of electrons
EA = electron acceptor

Equation 2-2 Conceptual half reactions for metal oxidation (a) and reduction of other chemical species (b)[268]

It is important to emphasise the distinction between the terms *corrosion* and *corrosion products*: two terms that are often confusingly interchanged. It is here specified that *corrosion* is referred to as a process that produces corroded areas in metal (i.e. lost metal), while corrosion products are mineralised metal that have been converted by the corrosion process and are positioned in the corroded area or elsewhere (in solid states or in liquid solutions).

2.2.2 INDOOR ATMOSPHERIC FERROUS CORROSION: DEFINITION, PROCESSES & FACTORS

2.2.2.1 Definition

Atmospheric corrosion is distinguishable from the broader previously given definition of corrosion since it is further specified as the "…the corrosion or degradation of material exposed to the air and its pollutants, rather than immersed in a liquid"[269], and it does not concern high temperature gaseous oxidation since it relates to ambient temperatures, as found in a museum.

The atmospheric environment is complex. It consists of gaseous, liquid and solid phases where electrochemical, chemical and physical processes can occur either within these phases or at the interfaces between them[270].

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[266] Leygraf & Graedel, 2000, p. 24
[267] Uhlig & Revie, 1985, p. 9
[268] Tretheway & Chamberlain, 1998, p. 76
[269] Pohlman, 1998, p. 80
[270] Leygraf & Graedel, 2000, p. 9

2.2.2.2 Processes

Atmospheric corrosion, whether it occurs indoors or outdoors, follows the same physicochemical processes including: "…adsorption of water [H_2O], deposition of gases and particles into the liquid layer, proton- and ligand-induced (metal) dissolution, ion pairing, and precipitation, and growth of corrosion products"[271]. The notable difference between indoor and outdoor atmospheric corrosion is a less corrosive indoor environment where "…variations in relative humidity (RH) are less dramatic indoors than out, and deposition velocities and concentrations of gas or particle corrodents are generally lower"[272]. However, corrosivity increases with high indoor-outdoor air exchange rates[273] and this effect on corrosion is therefore of importance to the cyclically ventilated and unfiltered Palace Armoury environment. This subsection outlines the sequence of stages required for atmospheric corrosion to occur.

2.2.2.2.1 <u>Surface hydroxylation & water adsorption</u>

Instantaneously, under atmospheric exposure, metal surfaces react with water vapour and normally cause disassociation of the water molecules and mainly initially result in forming bonds with metals or metal oxides (Figure 2-26)[274].

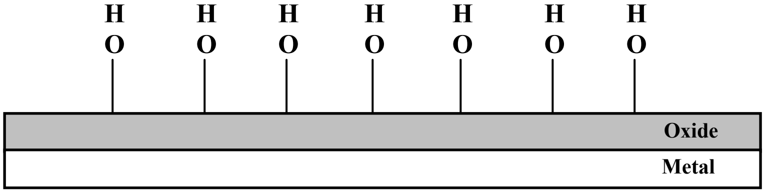

Figure 2-26 "A schematic depiction of surface hydroxyl (OH^-) groups on a metal oxide surface" after Leygraf & Graedel[275]

Subsequently, further water vapour is adsorbed in superior layers, but as complete molecules. The thickness of this water layer increases with increased humidity[276] and hygroscopic aerosol pollutants[277, 278]. The water's lateral distribution is more localised as clusters rather than as a uniform distribution. The composition

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[271] Ibid., p. 126
[272] Ibid.
[273] Ibid., p. 109
[274] Ibid., pp. 9-10
[275] Ibid., p. 10
[276] 2.2.2.3.2 Atmospheric water
[277] 2.2.2.3.3 Atmospheric pollutants
[278] Leygraf & Graedel, 2000, pp. 9-11, 17

and topographies of ferrous surfaces affects the amount of water present[279]. Importantly, the adsorbed water layer also acts as a solvent for gaseous and solid aerosols and is subsequently referred to as the *liquid* layer, rather than the *water* layer[280].

At the interface between the adsorbed liquid layer and the solid substrate (i.e. metal and/or corrosion products) electrochemical reactions can occur. In atmospheric ferrous corrosion, the predominant anodic and cathodic reactions are respectively metal dissolution and oxygen reduction[281], as follows in Equation 2-3.

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \ldots\ldots\ldots\ldots \quad (a)$$
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad \ldots\ldots\ldots\ldots \quad (b)$$

Equation 2-3 Predominant anodic (a)[282] and cathodic (b)[283] reactions in atmospheric ferrous corrosion

The liquid layer is in close proximity to atmospheric oxygen, which is normally easily dissolved by the adsorbed liquid layer[284]. This scenario typically makes the anodic reaction the rate-limiting step, instead of the cathodic reaction[285]. In the case of metals coated with protective coatings such as organic polymers, atmospheric water and oxygen must first access the metal. To do this they must diffuse through coatings, and/or facilitate the coating's degradation (more achievable if in an oxidising or acidic environment such as that caused by pollution e.g. ozone, O_3, sulphur dioxide, SO_2)[286, 287].

2.2.2.2.2 Proton- & ligand-induced metal dissolution

Ions such as protons (H^+) and ligands (e.g. bisulphite (HSO_3^-), bisulphate (HSO_4^-)) present in the liquid layer are known to exchange with the previously described hydroxyl ions[288] under the adsorbed liquid layer. This replacement is said to be one of the most important initial corrosion stages since it can weaken the bonded metal and adjacent metal[289]. Protons are allegedly involved in the detachment of the metal ions (*cations*) since if at least two protons are bonded to the metal they

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[279] Ibid., p. 283
[280] Ibid., p. 13
[281] Ibid..
[282] Chandler & Hudson, 2000, p. 3
[283] Asphahani & Silence, 1998, p. 113
[284] Tretheway & Chamberlain, 1998, p. 281
[285] Leygraf & Graedel, 2000, p. 13
[286] Hess & Bullett, 2000, p. 43
[287] 2.2.2.3.3 Atmospheric pollutants, Gaseous aerosols
[288] Figure 2-26 "A schematic depiction of surface hydroxyl (OH^-) groups on a metal oxide surface" after Leygraf & Graedel
[289] Leygraf & Graedel, 2000, p. 17

can cause weakening of its bond via polarisation[290]. The departure of the metal ion into the liquid layer creates a vacant site on the surface, which is then hydroxylated, thereby freeing more protons that are in turn capable of facilitating further metal dissolution via polarisation[291].

2.2.2.2.3 Ion-pairing

The metal's cations dissolved into the liquid layer are reactive with counterions also present there and form covalent bonds with those counterions that possess similar valence electron properties. Likely paired species follow the Lewis acid-base concept where soft acids (e.g. Cu^+) are more likely to bond with soft bases (e.g. R_2S). Relevant to ferrous corrosion, hard acids (e.g. the ferric ion, Fe^{3+}) prefer to bond with hard bases (e.g. H_2O, OH^-)[292]. The ferrous ion (Fe^{2+}) is classed as an intermediate acid and its probable intermediate basic counterparts include sulphite (SO_3^{2-}) and nitrite (NO_2^-) anions[293].

2.2.2.2.4 Corrosion product precipitation

The formation of solid phase corrosion products occurs via the precipitation of the ion pairs out of supersaturated liquid layer solutions and can emerge via a colloidal state[294]. Defects in the solid surface (i.e. metal, metal corrosion products) provide nucleation sites for this precipitation to occur. The overall CP precipitation formation rate is governed by the rate of growth rather than the nucleation rate[295].

2.2.2.2.5 Corrosion product coalescence

Given time, cycling of the previously outlined steps of metal dissolution, ion pairing and corrosion product precipitation initiate enough nucleation sites, which propagate in sufficient size to eventually cover the metal surface with CPs[296]. These corrosion products "…play a most important role for the behaviour of any material in a given environment"[297] as detailed in subsection 2.2.2.3.4 Ferrous corrosion products. Providing that the CPs are not protective and the liquid layer is not too

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[290] Ibid.
[291] Ibid., pp. 17-18
[292] Ibid., p. 18
[293] Ibid.
[294] Ibid., p. 20
[295] Ibid.
[296] Ibid., p. 22
[297] Ibid., p. 21

thick then the anodic reaction (i.e. metal dissolution, Equation 2-3a), continues to be the rate-limiting step[298].

2.2.2.3 Factors

This subsection describes the various major factors influencing atmospheric corrosion processes.

2.2.2.3.1 Atmospheric oxygen

As mentioned previously[299], oxygen in the atmosphere normally acts as the electron acceptor in the cathodic reaction of atmospheric corrosion. Equation 2-3b represents near neutral or alkaline conditions, while Equation 2-4 summarises neutral to acid conditions in the presence of oxygen, which is also reduced.

$$H^+ + \tfrac{1}{4}O_2 + e^- \rightarrow \tfrac{1}{2}H_2O$$

Equation 2-4 Cathodic half equation for aerated, acidic to neutral atmospheric conditions[300]

Iron corrosion can even occur in deoxygenated conditions where acidity provides an alternative reduction reaction: proton reduction to produce hydrogen gas (Equation 2-5)[301]:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2$$

Equation 2-5 Cathodic half equation for deaerated, acidic atmospheric conditions[302]

Acidic conditions might occur when pollutants like sulphur dioxide are present in high concentrations[303, 304] or due to hydrolysis of ferrous ions in confined spaces like corrosion pits or crevices (Equation 2-6)[305].

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$

Equation 2-6 Hydrolysis of ferrous ions to form acidic conditions[306]

2.2.2.3.2 Atmospheric water

The three subdivisions of atmospheric corrosion conditions are determined by the level of atmospheric water present and are called dry, damp and wet corrosion[307].

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[298] Ibid.
[299] 2.2.2.2.1 Surface hydroxylation & water adsorption
[300] Cornell & Schwertmann, 2003, p. 492
[301] Ibid.
[302] Ibid.
[303] 2.2.2.3.3 Atmospheric pollutants, Gaseous aerosols
[304] Pohlman, 1998, p. 81
[305] Kruger, 1990, p. 151
[306] Ibid.
[307] Pohlman, 1998, p. 80

Dry corrosion atmospheres (characterised by an absence of ambient moisture) have negligible rates on iron and are mainly of concern to copper and silver (referred to as *tarnishing*, such as with the presence of hydrogen sulphide, H_2S)[308].

Ferrous metal atmospheric corrosion is attributable to the latter categories of damp & wet corrosion[309]. Water in the atmosphere is actively implicated in many reduction reactions (e.g. Equation 2-3b, Equation 2-6) and the overall corrosion process since water provides a conductive means for transporting current and is referred to as the *electrolyte*.

It has been measured that the atmospheric corrosion of iron is circa 2000 times greater outdoors than indoors, and it is not simply attributable to water from rainfall (or other climatic precipitation)[310] as indicated earlier[311]. Laboratory studies show "…the main reason is the extremely high dependence of the iron corrosion rate on relative humidity"[312]. On normally clean metal surfaces (i.e. no corrosion products or pollutants) a relative humidity of around 70% is sufficient to support a thin invisible surface film of moisture in atmospheric conditions. The amount of adsorbed moisture required to form the electrolyte for the current transfer necessary for damp corrosion to occur is known as the *critical relative humidity*[313]. The critical RH for iron is 60% and is when rust slowly forms[314]. The RH for metals in a museum environment is recommended to be as low as possible, while 35-55% RH can be tolerated as a compromise for mixed collections containing organics susceptible to embrittlement via dehydration[315, 316]. As relative humidity increases, the ferrous corrosion rate increases. For example, between 75-80%RH a sharp increase in corrosion rate occurs, while at 90% another rate increase can be observed[317]. Increasing corrosion rates are associated with the moisture film thickness, underlying material surface and pollutant properties. A maximum corrosion rate is observed when the moisture layer exceeds 150µm[318]. Relative humidity is largely governed by natural climatic conditions: increases and decreases

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[308] Uhlig & Revie, 1985, p. 165, 171 & Pohlman, 1998, p. 80

[309] Pohlman, 1998, p. 81

[310] Leygraf & Graedel, 2000, p. 124

[311] 2.2.2.2 Processes

[312] Leygraf & Graedel, 2000, p. 124

[313] Pohlman, 1998, p. 82

[314] Ibid.

[315] CCI, 1995, p. 1

[316] Not to forget museum staff and visitor comfort

[317] Pohlman, 1998, p. 82

[318] Ibid.

in temperature respectively decrease and increase RH due to air's temperature dependent capacity for moisture retention[319]. The indoor architectural environment not only plays a sheltering role from wet atmospheric corrosion by precipitation such as dew and rain, but can also play an insulating role from outdoor atmospheric temperature and humidity, and their fluctuations[320]. Yet, the architectural environment can have its own influence on increasing RH: it too can contain moisture in the building-fabric and air[321]. Water sources from plumbing, roofing leaks, or groundwater sources cannot be overlooked[322] and have been revealed at the Palace Armoury, which is located on a ground floor without an insulating damp course and with walls exhibiting soluble salt efflorescence, typical of rising damp[323].

Wet atmospheric corrosion involves the local presence of visible water in crevices and condensation traps[324]. Such water has been noted on ferrous surfaces at the Palace Armoury[325]. Notably, the multi-component armour constructions, with their many overlapping metal plates and rosettes, probably make ideal interfacial condensation traps and ensuing local wet corrosion possible.

TIME OF WETNESS/DAMPNESS & HUMIDITY CYCLES

An important factor governing the corrosion rate is the time a corroding surface is above the critical RH for corrosion to occur, and is referred to as the *time of wetness*[326].

Iron and steel are very sensitive to relative humidity fluctuations[327]. Often fluctuations in T & RH are seen to affect corrosion more than their absolute values. The most important effect temperature has on atmospheric corrosion (such as at indoor ambient temperatures) is indirect, but can still be significant due to its influence on relative humidity[328]. Dry-damp cycles are well known to accelerate corrosion since they induce the precipitation-dissolution cycles that occur as moisture is respectively lost, gained and lost[329]. Corrosion accelerated by dry-damp cycles is usually less common indoors, but again such a generalisation becomes less

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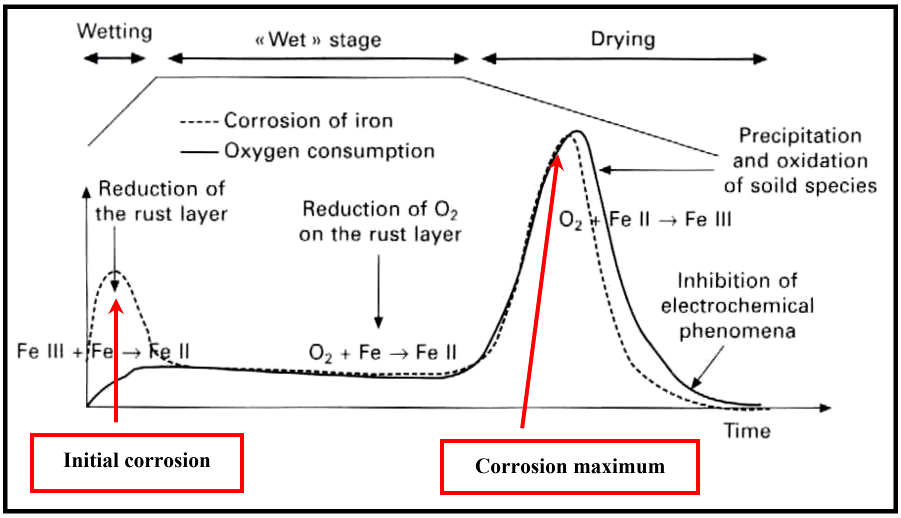
[319] Uhlig & Revie, 1985, p. 173 & Rowlinson, 1977, p. 23
[320] Pohlman, 1998, p. 81
[321] Cassar, 1995, p. 45
[322] Getty Conservation Institute, 1994, p. 86
[323] Magro Conti, 2007, pers. comm.
[324] Pohlman, 1998, p. 80
[325] Vella et al., 2006b, p. 12
[326] Pohlman, 1998, p. 82 & Uhlig & Revie, 1985, p. 174
[327] Leygraf & Graedel, 2000, p. 71
[328] Ibid., p. 195
[329] Ibid., pp. 126, 194

applicable with buildings featuring high indoor-outdoor air exchange rates[330]. While RH fluctuations are expected to be less than outdoors, they might still be appreciable[331]. Relative humidity and temperature fluctuations in the uncontrolled indoor environment of Palace Armoury are likewise dependent on the ventilation with the outdoor environment. Quantifying the Palace Armoury air exchange rate was not determinable from the literature[332], but it is known that each extraction fan in the two exhibition halls is used for daily air-exchange that functions in conjunction with the external doors, which are opened daily[333].

Studies on lightly rusted iron, by corrosion scientists, Stratmann and Streckel, demonstrated that during the drying phase of the adsorbed moisture layer the corrosion rate "…shows a pronounced maximum"[334]. This is due to the increased access oxygen has to corrosion product pores previously more occupied by water ("Corrosion maximum" in Graph 2-3)[335].



Graph 2-3 Consumption rates of iron and oxygen during a wet-dry cycle (after Stratmann)[336]

The drying phase is also of significance to corrosion since the concentration of dissolved species in the adsorbed liquid layer can increase by several orders of magnitude thereby causing more corrosive pH levels to develop[337].

Half of the annual temperature and relative humidity compiled in 2006 inside the Palace Armoury is presented in Graph 2-4[338]. It is immediately observable from

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[330] Ibid., p. 126

[331] Ibid., p. 110

[332] Though air-exchange rates can be calculated.

[333] Stroud, 2006-2007, pers. comm.

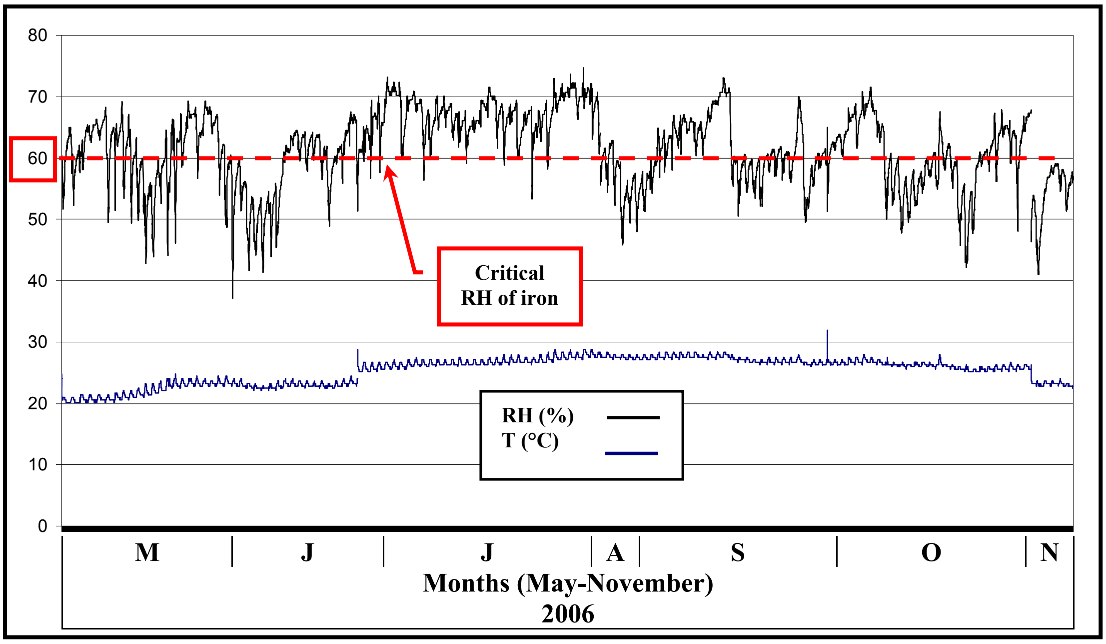
[334] Stratmann & Streckel, 1990, p. 695

[335] Maréchal et al., 2007, p. 23

[336] Ibid., p. 22

[337] Leygraf & Graedel, 2000, p. 14

the graph alone that the RH is predominantly above the critical RH of iron, where this time of wetness must also be influencing the corrosion rate, as previously mentioned. Additionally, it appears the temperature fluctuations (25.20±2.12°C = mean±1 standard deviation) corresponded with relative humidity fluctuations (63.13±6.61%RH = mean±1 standard deviation)[339] that are in close agreement with the psychrometric chart (Graph 2-5) and are potentially favourable for iron corrosion, since on numerous occasions the RH fluctuates around the critical relative humidity.



Graph 2-4 Temperature and relative humidity in the Palace Armoury Armour Hall around the summer months[340]

Upon analysis of the raw data[341] for Graph 2-4, it can be summarised that the Palace Armoury's inherent building dampness (e.g. damp building foundations) and daily ventilation is likely to be inducing the relative humidity fluctuations. To briefly explain, following afternoon closing time (i.e. window extraction fans off and entrance doors closed), the RH steadily increases (probably due to an interior moisture source such as rising damp), while temperatures remain nearly constant or constant[342]. In the morning (i.e. window extraction fans on and entrance doors

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[338] RH and T in the PA for the year November 2006 – October 2007 will be published in Degrigny, Chapter 7, (in press), p. 28

[339] Argyropoulos et al., 2007a, p. 11

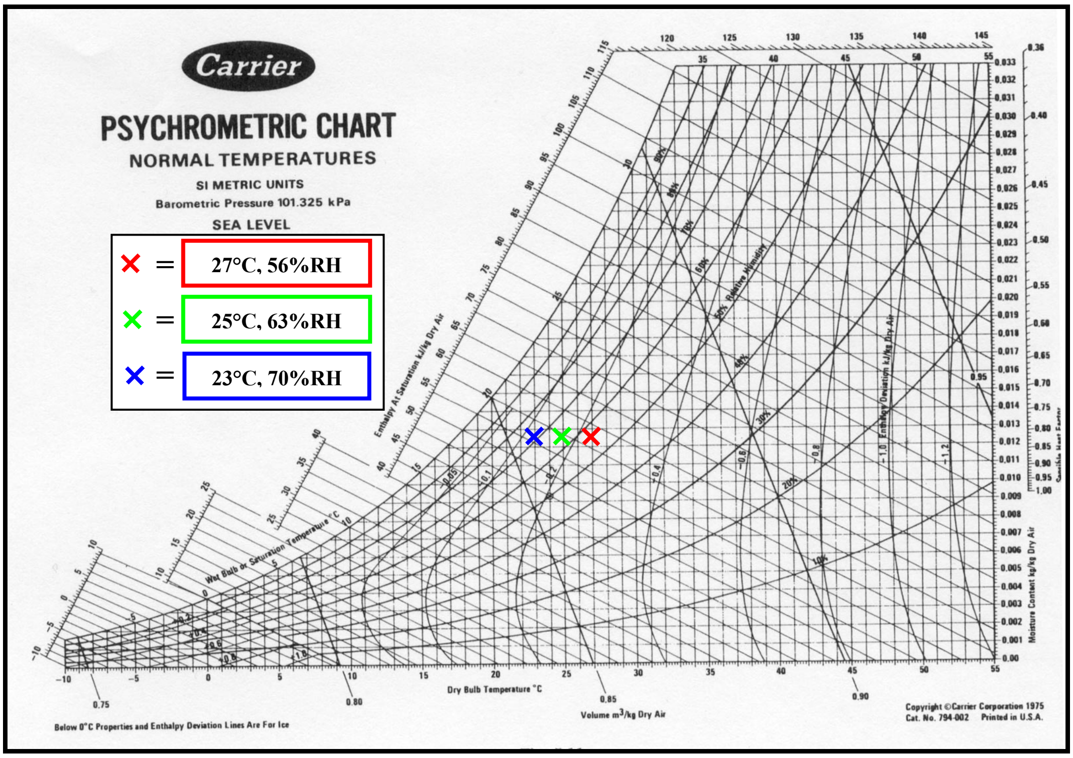
[340] Ibid., p. 12

[341] Examined by the present author, available courtesy of D. Vella, conservation scientist, Diagnostic Science Laboratories, Heritage Malta, Bighi, Malta.

[342] In one overnight example (20-21/09/2006), despite a constant temperature and closed indoor space, a recorded 7.6% RH increase in the closed Armour Hall was noted in the raw environmental

opened) the RH dramatically drops as this interior, more humid air is displaced and/or heated by the normally warmer (over the summer months) and drier exterior air (but rarely falls below 40%RH in Malta[343]).

At already elevated relative humidities it only takes a small temperature change to produce a large RH fluctuation. For example, at 63% RH & 25°C (the mean T & RH in the PA Armour Hall during summer[344]) a decrease of 2°C increases the RH to circa 70%RH (Graph 2-5).



Graph 2-5 Psychrometric chart exemplifying the effect on relative humidity by temperature change[345]

2.2.2.3.3 Atmospheric pollutants

Many forms of natural and anthropogenic airborne species in the atmosphere contribute to indoor corrosion mechanisms[346]. These polluting airborne species are referred to as aerosols, and are defined as "…suspension(s) of small liquid and/or

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monitoring data of the graph published in Argyropoulos et al., 2007a, p. 12 examined by the present author, courtesy of D. Vella.

[343] Malta Weather Services, 2006, http://www.maltaweather.com/climate.shtml – accessed 14/01/2006

[344] Graph 2-4 Temperature and relative humidity in the Palace Armoury Armour Hall around the summer months

[345] Howard University, 2006, http://howard.engr.siu.edu/staff1/tech/MET/ET401/LAB/psychro_carrier_si.jpg – accessed 12/08/2006

[346] Leygraf & Graedel, 2000, pp. 110, 115

solid particles in a gaseous medium"[347]. They can either come from indoor sources or be introduced by air currents from outdoor sources. Aerosols, gaseous or solid, deposit on surfaces by either dry or wet deposition. The former occurs when aerosols collide into and adhere to a dry surface[348], while the latter occurs when the aerosols dissolve into atmospheric humidity or into water already adsorbed onto surface aerosols[349]. The manner by which some atmospheric pollutants react to induce corrosion are outlined and it is important to note that their interrelationship with the metal and environment is complex and can only be cursorily covered here.

SOLID AEROSOLS

Outdoor types of solid aerosols include soil, sea-salt, construction dust and hydrocarbon combustion pollution[350]. Meanwhile indoor solid aerosols can emanate from the building fabric (e.g. concrete, stone, marble)[351].

Due to the sheltered indoor environment, indoor solid aerosols have deposition velocities of one to two orders of magnitude less than in outdoor environments[352]. The size of the particles also affects their transportation: very small particles have high diffusion rates and follow atmospheric movements more, while large particles are affected less since they have their own greater momentum[353]. Large particles deposit easily on non-inverted surfaces, whereas they do not deposit easily on inverted surfaces. Deposition of small particles is much less affected by surface orientation since they move more like gaseous aerosols[354].

A metallic surface partly covered with solid aerosols, such as particles from architectural masonry or earth sediment, can cause corrosion via the formation of *differential aeration cells* due to the relative difference in access to atmospheric oxygen[355] (Figure 2-27).

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[347] Ibid., p. 55
[348] Ibid., p. 40
[349] Ibid., pp. 40, 57
[350] Ibid., pp. 59-60
[351] Stolow, 1987, p. 18
[352] Leygraf & Graedel, 2000, p. 56
[353] Ibid., p. 55
[354] Ibid., p. 57
[355] Pohlman, 1998, p. 81, Fyfe, 2000, p. 35 & Leygraf & Graedel, 2000, p. 63

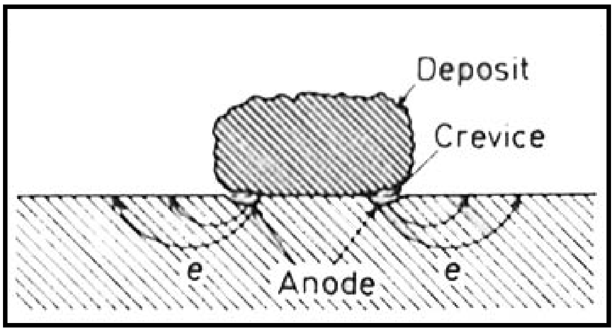

Figure 2-27 Schema of differential aeration corrosion caused by a surface deposit particle[356]

Hygroscopic particles can either simply increase atmospheric water adsorption or participate further in electrochemical reactions. For example, carbon soot from combustion, highly present in urban zones, increases surface moisture adsorption[357], whereas sodium chloride is more implicated. Sodium chloride is not only hygroscopic, and therefore increases the amount of adsorbed surface moisture, but additionally, is conductive, thereby increasing corrosive conditions through the electrolyte's conductivity[358]. Salt-water coastal environments, such as the peninsula where the Palace Armoury is situated, are known to be corrosive and this is largely due to the prevalent water-soluble salt sodium chloride (NaCl) that comes from breaking waves on saltwater seas and oceans[359]. The chloride ion (Cl^-) is highly corrosive to both iron and steel and is also known to degrade protective coatings[360].

The effect of solid aerosols on ferrous corrosion at the Palace Armoury is evidenced and pronounced, and is therefore elaborated here. Despite the sheltered indoor environment, using scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Vella documented sodium chloride crystals on surfaces exposed to the Palace Armoury atmosphere during the European Commission Promet project. It is presumed that such salts came in the form of sea-spray from the natural environment and were drawn through the museum's cyclically open ventilation[361]. Later SEM-EDS studies by the same research group, showed a year-round accumulation of calcium and silicon materials. Chlorine was also heavily

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[356] Shreir, 2000, p. 155
[357] Fyfe, 2000, p. 35 & Leygraf & Graedel, 2000, p. 63
[358] Fyfe, 2000, p. 35 & Leygraf & Graedel, 2000, p. 283
[359] Fyfe, 2000, p. 35 & Leygraf & Graedel, 2000, p. 59
[360] Leygraf & Graedel, 2000, p. 38 & Pohlman, 1998, p. 81
[361] Vella, 2006 – An extended interpretation of this raw data acquired by Vella is made later in the context of 4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

evidenced. These findings presumed a correlation of the calcium with limestone, the silicon with clay [earth] and the chloride [*sic*] with marine salts[362].

Accordingly, an apparently significant indoor source of solid aerosols at the Palace Armoury is the traditional limewash applied to cover the limestone walls[363]. Limewash has historically been and is contemporarily still in use at the Palace Armoury[364] and throughout Malta[365] to provide a layer to areas where rising damp is problematic. Salt efflorescence destroys this thin superficial layer that is periodically replaced at lesser expense than the construction stone[366]. The necessary porosity of this material engenders its friability and its susceptibility to becoming an atmospheric pollutant. Lime for producing limewash is produced from the Upper and Lower Coralline Limestones, not the Globigerina Limestone[367]. Meanwhile a limestone is the construction stone of the Palace Armoury[368], and more specifically Lower Globigerina, is the predominant construction stone for Valletta[369].

A correlation between the deposition of solid aerosols on ferrous surfaces and corrosion has been noted on artefacts, and also on contemporary samples of low-carbon steel, of which their history is more confidently known (Figure 2-28)[370].

Figure 2-28 Left: Rack containing low-carbon steel coupons exposed at an inclination of 30° to the vertical in the Palace Armoury, Armour Hall[371]. Centre: Very corroded particle-collecting upper side of unprotected coupon after 17 months exposure[372]. Right: Slightly corroded inverted side of corresponding unprotected coupon, which is collecting less particles[373].

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[362] Degrigny (in press), Chapter 7, pp. 29-30
[363] Magro Conti, 2007, pers. comm.
[364] Stroud, 2006-2007, pers. comm.
[365] Chetcuti 30/10/2007, pers. comm.
[366] Ibid.
[367] Cassar, 01/11/2007, pers. comm. & Cassar & Scerri, 2007, pp. 4-6
[368] Magro Conti, 2007, pers. comm.
[369] Cassar 2004, p. 12
[370] Vella et al., 2006b, pp. 2-4, 13
[371] Ibid.
[372] Crawford, 2007c, coupon 48
[373] Ibid.

It should be noted that some particles retard corrosion: notably via the neutralisation of acidic surfaces with alkaline particulates[374]. The calcium carbonate-derived limewash wall and ceiling finish at the Palace Armoury could potentially fall within this category of alkaline materials[375]. However, in practice, surfaces are contaminated with mixtures of particles[376] and it is experimentally evident from Figure 2-28 that the overall presence of this atmosphere's solid aerosols facilitates corrosion processes.

GASEOUS AEROSOLS

In an indoor environment, with still air, gaseous aerosols are transported by molecular diffusion and convection[377]. However air currents caused by fans and ventilation would have a greater influence on transport. Actual surface deposition is dependent on the gas transport rate and also the transformation ability after collision[378]. Gaseous aerosols do not have significant size differences that affect their transport like the case for solid aerosols[379].

Sulphur and nitrogen dioxides (NO_2) are the most notable gaseous pollutants cited as having a corrosive effect on metals: they increase surface acidity[380] by transformation to sulphurous (H_2SO_3), sulphuric (H_2SO_4) and nitric (HNO_3) acids[381]. The corrosive effect and rates depend on the metal type, but generally increase with increasing RH[382]. Iron and steel are both known to be highly sensitive to sulphur dioxide[383]. The oxidising property of ozone (produced in photochemical smog) enables oxidation of nitrogen oxides (NO_xs) to nitric acid and thus has an indirect corrosive effect on metals[384].

Gaseous hydrogen chloride (HCl) occurs in marine environments by dechlorination of sea salt aerosols. Gaseous hydrogen chloride dissolves readily in atmospheric water, allowing the chloride ion to disassociate and participate as a

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[374] Tidblad & Kucera, 2002, p. 234
[375] Trench, 2000, p. 283
[376] Vella, 2006
[377] Leygraf & Graedel, 2000, p. 110
[378] Ibid.
[379] Ibid. p. 55
[380] Pohlman, 1998, p. 81, Tidblad & Kucera 2002, pp. 234-235 & Leygraf & Graedel, 2000, p. 44
[381] Leygraf & Graedel, 2000, pp. 14, 42, 45 & Evans & Taylor, 1972, p. 228
[382] Tidblad & Kucera, 2002, pp. 233-234
[383] Leygraf & Graedel, 2000, p. 38
[384] Tidblad & Kucera, 2002, p. 22

corrodent[385]. Sources of gaseous HCl are known to be associated with industrialised coastal regions exposed to nitric or sulphuric acids[386].

All of the above mentioned anthropogenic pollutants are mainly products (e.g. SO_2, NO_2) or by-products (e.g. O_3) of fossil fuel combustion in the outdoor environment[387]. Some of the possible sources relevant to the Palace Armoury region include automated road traffic, cruiseships, cargoships & Marsa's oil-fuelled power station (Figure 2-25). Importantly, the possible interaction of these regional anthropogenic (and other natural) atmospheric pollutants on the PA collection is dependent on the relative locations of the pollutant sources and naturally variable climatic conditions, such as wind direction and speed[388].

Meanwhile, the more immediate urban environment of the Palace Armoury is also consistently populated by fossil fuel consuming activities. Merchants Street (*Triq-il Merkanti*) (Figure 2-2, Lower right), where the Armoury is located, is subjected to 6-times weekly fossil fuel powered vehicles transporting merchandise to the shops opposite and open-air street markets.

Some gaseous aerosols that come from indoor environments and are detrimental to iron are volatile organic compounds (VOCs) such as formaldehyde (HCHO), acetalaldehye (CH_3CHO), formic acid (HCOOH) and acetic acid (CH_3COOH). These are often in higher concentrations indoors than outdoors due to their indoor material sources[389]. Display case materials are a common indoor source cited in museum contexts[390]. Construction timber (i.e. fibres and adhesives) provides sources of these volatile corrodents and iron, in addition to tin and lead, are deemed to be the metals most susceptible to formaldehyde[391].

Maximum advisable gaseous aerosol pollutant exposure concentrations specific for indoor museum ferrous metals could not be sourced. However, guidelines have been established for copper in indoor museums[392]. The maximum average concentrations for gaseous aerosols such as SO_2, NO_2 and O_3 were respectively $1.01\mu g.m^{-3}$, $5.03\mu g.m^{-3}$ and $25\mu g.m^{-3}$ and were published in reference to gaseous aerosol investigations in the Palace Armoury Armour Hall. It was

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[385] Leygraf & Graedel, 2000, p. 46
[386] Ibid., pp. 46, 51
[387] Ibid. pp. 40-41, 44
[388] Boubel, et al., 1994, p. 233
[389] Leygraf & Graedel, 2000, p. 197
[390] Stolow, 1987, p. 18
[391] Hatchfield, 2002, p. 33
[392] Knotkova et al. 2007, pp. 64-65

summarised in that reference that only for one month (August) was SO_2 above the advised maximum threshold, while NO_2 was consistently above. The level of O_3 was above the advised maximum during the summer months[393].

Two important points are necessary regarding this overview of the advised maximum gaseous pollutant exposures when applied to ferrous metals in the PA collection:

1. These maximum exposure guidelines are for copper, not iron or steel.
2. The established recommended maximum concentrations do not account for the "possible corrosion effects of particulates in indoor atmospheres"[394], important when considering the PA's particle-polluted environment[395].

As a consequence of these factors and unquantifiable synergisms with RH and other pollutants[396], the net effect of the theoretically permissible exposure limit of PA ferrous metals to these gaseous aerosols cannot be determined here. Nonetheless, it is clear that these polluting gaseous aerosols are at least periodically present in the environment at levels excessive for some other metals that also feature on the armour (e.g. cupreous rivet heads and rosettes)[397], and the susceptibility of ferrous metals to these gaseous aerosols would probably be increased by the presence of particles.

2.2.2.3.4 Ferrous corrosion products

As outlined here, ferrous corrosion products themselves can play various roles by either retarding or furthering atmospheric corrosion. However, on the whole, their presence is considered undesirable for corrosion prevention and hence provides a dilemma for cultural heritage artefacts where their preservation might be required[398]. The way some common ferrous CPs generally affect corrosion processes in atmospheric environments is outlined here, while their types, some of their specific effects and their formation are outlined shortly afterwards in the subsequent subsections, Types of atmospheric ferrous corrosion products & Formation of atmospheric ferrous corrosion products.

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[393] Degrigny, (in press), Chapter 7, p. 28

[394] Knotkova et al. 2007, p. 70

[395] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[396] Hatchfield, 2003, p. 5

[397] 2.1.2.5 Munition armour assembly & articulation

[398] 2.3 Metal heritage artefact conservation & corrosion products: philosophy & practice

Atmospheric ferrous corrosion products frequently appear as non-adherent orange-brown or black voluminous masses[399]. Following the same differential aeration corrosion mechanism caused by a surface deposit particle[400], ferrous CPs can induce corrosion, providing the environment is conducive (Figure 2-29)[401].

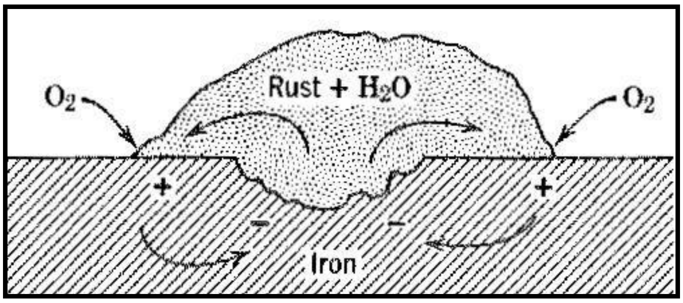

Figure 2-29 "Differential aeration cell formed by rust on iron"[402]

Beneficially, corrosion products entirely covering ferrous surfaces normally slow the corrosion rate. Moreover, the formation of dense CPs is also known to limit further corrosion[403]. The corrosion rate slows as the thickness or density of the CP layer increases, since reactive species in the liquid layer now need to migrate inwards through the corrosion product layer to react with the metal. Singly charged ions (e.g. Cl^-) or protons, rather than doubly charged species like sulphates (SO_4^{2-}), are more easily transported through this layer. In addition, the outward migration of the dissolved metal's ions needs to occur for corrosion to continue[404]. The transport of electrons generated at the anode, and consumed at the cathode, must also be achieved for corrosion to continue. Thicker, denser and non-conductive CP layers can retard this migration, thereby assisting electron transport to be the rate-limiting factor[405].

The possible imparted corrosion protection of a corrosion product film is dependent on its coherency and the volume ratio of the formed corrosion product and the corroded metal[406]. "Rust layers on iron and carbon steel are porous and poorly adherent"[407]. Cracks are typically present in the outer corrosion product layers while nanometric (circa 3-15nm) pores permit ingress of adsorbed liquid to promote further

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[399] Cornell & Schwertmann, 2003, p. 499
[400] Figure 2-27
[401] Uhlig & Revie, 1985, p. 11
[402] Ibid.: Depicting conventional current direction not electron current direction
[403] Stratmann, 1990, p. 51
[404] Leygraf & Graedel, 2000, p. 21
[405] Ibid.
[406] Cornell & Schwertmann, 2003, p. 496
[407] Leygraf & Graedel, 2000, p. 282

corrosion of underlying metal[408]. Iron's metal to corrosion product volume ratio is at least 1:2.1, therefore explaining why stresses and defects occur in the forming CPs[409]. Also, the separate locations of anodic and cathodic sites means that the CPs form away from the anodic site and do not provide a protective layer[410]. Decreases in corrosion rate attributable to ferrous surface corrosion product coverage[411] are less pronounced on pure iron than on low-alloy steel since the former propagates more powdery and looser products[412]. Unalloyed steel also features porous non-adhering films[413].

Relating this information to the Palace Armoury munition armour, which are not expected to be like contemporary low-alloy steel[414], and of which a small corpus is known to be unalloyed steel and iron[415], it is likely then that non-protective corrosion product layers feature and further corrosion would be active due the high RH and polluted environment[416, 417]. Furthermore, in the practical case of the historic armour at the Palace Armoury, this proposed slowing of corrosion rate attributed to surface corrosion products is probably not as pronounced throughout since the armour surfaces are only partly covered with CPs, leaving susceptible adjacent metal exposed.

TYPES OF ATMOSPHERIC FERROUS CORROSION PRODUCTS

Iron's cations, produced from the anode, might commonly form corrosion products of oxides (e.g. Fe_3O_4, magnetite) or oxyhydroxides (FeOOH)[418], while many other compounds are possible, depending on the environmental constituents. Commonly occurring steel corrosion products in outdoor environments are phases of lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite[419]. A more precise description of iron and steel CP occurrence and distribution includes a dense inner

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[408] Ibid.
[409] Cornell & Schwertmann, 2003, p. 496
[410] Ibid. p. 493 & Evans & Taylor, 1972, p. 227
[411] 2.2.2.3.4 Ferrous corrosion products
[412] Uhlig & Revie, 1985, pp. 166-167
[413] Pohlman, 1998, p. 80
[414] Low-alloy steel definitions vary, but as a general indication low alloy steels can be regarded as alloy steels (by ISO definition) containing between 1 and less than 5% of elements deliberately added for the purposes of modifying properties (IMMA, 1988, p. 4)
[415] Excepting one phosphoric (circa 0.1-0.5%wt) iron from ten samples investigated (Vella et al. 2004, p. 230)
[416] Leygraf & Graedel, 2000, p. 281
[417] 2.2.2.3.2 Atmospheric water & 2.2.2.3.3 Atmospheric pollutants
[418] Turgoose, 1989, p. 30
[419] Antunes et al., 2003, p. 27

layer of so-called *amorphous iron oxyhydroxides* with magnetite and an outer loose layer of maghemite (γ-Fe_2O_3) with a lepidocrocite/goethite layer[420].

The Promet project's recent short-term corrosion of contemporary low-carbon steel in the laboratory[421] and *in-situ* at the Palace Armoury[422] respectively produced corrosion products of ferrihydrite & magnetite (determined with µx-ray diffractometry (µXRD) & µRaman spectroscopy)[423], and also ferrihydrite, goethite and lepidocrocite (determined with µRaman spectroscopy only)[424]. These metals were corroding indoors and are therefore more relevant, in terms of materials and environment, to the scenario of this study.

Other studies from indoor environments, but on older materials, also detected the typical main phases of outdoor atmospheric ferrous corrosion products: magnetite; goethite; and lepidocrocite. This work involved synchrotron radiation µx-ray diffractometry (SR-µXRD) characterisation of crystalline CPs from pre-contemporary hypoeutectoid ferrous metals aged 120-1600 years[425, 426].

As an extension of the same research group, Neff et al. recently published Raman spectroscopy studies on various atmospherically corroded indoor irons from the 13-18th centuries. This work proposed a ferrous corrosion product stratum that was predominated by goethite as the main phase, together with unspecified poorly crystallised hydrated iron oxyhydroxides, and smaller amounts of lepidocrocite and occasionally akaganéite (ß-FeOOH)[427].

Monnier et al's recent continuation of Neff's et al.'s work determined a similar CP stratigraphy to her predecessor. Transverse-section stratigraphies of samples extracted from wrought iron bars (dating 1498) were investigated by µXRD, SEM, µRaman spectroscopy and µx-ray absorption spectroscopy (µXAS)[428]. A main corrosion product phase of goethite featured with local presences of "a type of

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[420] Leygraf & Graedel, 2000, p. 285

[421] 24 hours at 30°C/100%RH + 24 hours at 25°C/50-60%RH + 24 hours at 30°C/100%RH (Degrigny, in press, Chapter 7, pp. 6-7)

[422] 12 months exposed at variable ambient conditions (Degrigny, in press, Chapter 7, pp. 6, 8-9) and oriented as per Figure 2-28

[423] Degrigny, in press, Chapter 7, p. 8

[424] Ibid., p. 11

[425] Dillmann et al., 2001, pp. 318, 332

[426] This citation marks one of a series of research papers presented here by the successive research colleagues and teams of corrosion scientist, Philippe Dillmann, Laboratoire Pierre Süe, CEA/CNRS Saclay, Gif Sur Yvette, France, who are investigating the factors of atmospheric ferrous corrosion, for contemporary application: in the prediction of long-term corrosion behaviour in nuclear waste storage systems.

[427] Neff et al., 2006, pp. 1230, 1232, 1236

[428] Monnier et al. 2007, p. 48, 52

ferrihydrite”, lepidocrocite and akaganéite (nearer the surface) (Figure 2-30)[429]. Notably, magnetite was not reported despite the detection capabilities of the instrumentation used.

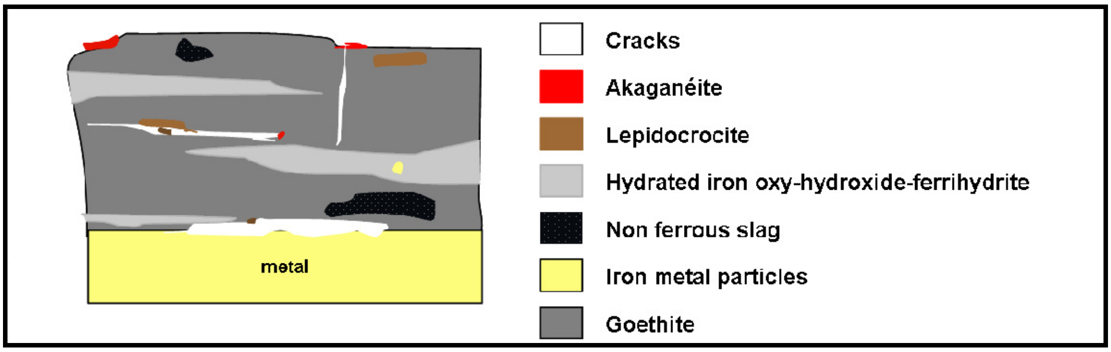

Figure 2-30 “Schematic view of the corrosion layer developed on the Amiens iron chains”[430].

In much closer correlation with this study (in terms of artefact genre), crystalline (only) corrosion product characterisation (i.e. via XRD) by Biasini & Cristoferi on 16th-17th northern Italian century armour also demonstrated the presence of akaganéite, goethite, lepidocrocite and, in lesser frequency, hydrated ferric chloride ($2FeCl_3.5H_2O$) and siderite ($FeCO_3$)[431].

Crystalline corrosion product characterisation has also recently been performed on munition armour from the Palace Armoury and falls in line with the predominant species previously cited. These analyses were performed with synchrotron radiation µXRD in transmission mode on extracted particle samples at station 9.6 of the synchrotron radiation at Daresbury Laboratory, United Kingdom[432]. Iron oxyhydroxides (goethite, akaganéite and lepidocrocite), and to a lesser extent, magnetite dominated the samples (total 52) that were extracted from the inner and outer surfaces of three armour (PA RC 166, PA 316, PA 329[433]) (Table 2-1). Compositional variation between the inner and outer surfaces of the armour was minor[434].

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[429] Ibid. p. 52

[430] Ibid., p. 53

[431] Biasini & Cristoferi, 1995, p. 253

[432] Degrigny et al., 2007b, p. 36

[433] These three armour are those studied by the present research more specifically in: 4.1.3.2 Armour corrosion cross-section observations & analyses, and also together with other armour in 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

[434] Monnier, 2006, p. 1

	Corrosion product species (n = 52)	
	Mean frequency	**Standard deviation**
Goethite	79%	±3%
Akaganéite	77%	±4%
Lepidocrocite	62%	±4%
Magnetite	42%	±2%
Wüstite	13%	±2%
Hematite	6%	±1%

Table 2-1 Frequency of crystalline corrosion product types from a selection of three Palace Armoury munition armour (PA RC 166, PA 316, PA 329)[435]

The properties of iron oxyhydroxides are known to significantly favour corrosion processes due to their affinity for water and aggressive gases and negative ions (*anions*)[436]. At the surface of FeOOH crystals, hydroxyls and oxygen defects react highly by chemisorption of vapours of water or sulphur dioxide and increase the electrical conductivity of the oxyhydroxide; respectively by direct or indirect donation to it of an electron[437]. The attraction of iron oxyhydroxides to aggressive anions is demonstrated by strong adsorption of sulphates onto surface hydroxyls of goethite, while chlorides are presumed to be electrostatically adsorbed, by majority, to the surfaces of goethite and lepidocrocite, and inside akaganéite[438].

Akaganéite is formed in seacoast environments[439] and contains chlorides and water in its tunnel-like structure[440]. Akaganéite is seen to be a symptom of active corrosion and is often located at the iron/iron corrosion product interface[441]. Much has been summarised about akaganéite on ferrous heritage artefacts, more particularly archaeological[442] iron artefacts[443] where chloride concentrations and corrosive effects would be expected to generally be much greater than on *historical*[444] iron[445]. Akaganéite participates or contributes to ferrous corrosion

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[435] Statistical compilation tabulated from Monnier, 2006, p. 1
[436] Kaneko, 1989, p. 55-56, 62-63
[437] Ibid., pp. 62-63
[438] Ibid., p. 64
[439] Cornell & Schwertmann, 2003, p. 499
[440] Ibid. p. 105
[441] Selwyn et al. 1999, pp. 225-226
[442] Archaeological artefacts are, in this context, classified as being excavated from burial (terrestrial or marine) conditions.
[443] Zucchi, et al., 1977, pp. 217-232 & Selwyn et al. 1999, pp. 217-232
[444] Historical artefacts are, in this context, classified as those that have not been buried and instead have been atmospherically exposed.
[445] Differentiating between archaeological and historical artefacts is an important means of artefact classification that not only implies their general environmental characteristics, but also anthropogenic influences such as accessibility.

processes since it is perceived to act as a catalyst, release chlorides, behave hygroscopically and like the other iron oxyhydroxides physically damages structures during precipitation formation[446]. Akaganéite often appears as hollow beads of yellow-brown precipitate[447].

Ferrihydrite, a lesser-mentioned, poorly crystalline[448] or nano-crystalline, natural mineral or corrosion product species of disputed molecular formula[449] is reddish-brown and unstable, so much so that it has been referred to as "…an important precursor of more stable and better crystalline Fe oxides"[450].

Lepidocrocite, an orange corrosion product[451], has been theorised to play an active role in the atmospheric corrosion cycle as proposed by Stratmann. During the wetting phase of a wet-dry cycle, lepidocrocite (with its +3 oxidation state) initially oxidises the metal by receiving the latter's electrons (lepidocrocite simultaneously being reduced to a +2 oxidation state, to form magnetite, Fe_3O_4)[452] ("Initial corrosion" in Graph 2-3 & Equation 2-7). Such a corrosion reaction can be classified as being *galvanic* in mechanism, as discussed later[453], and research by Antony et al. "…indicates that (the) iron/γ-FeOOH galvanic coupling is possible"[454].

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

Equation 2-7 Reduction of ferric ions to the ferrous state during wetting of a corrosion product layer[455]

Recent preliminary studies by Neff et al. (on a statistically low number of 6 samples)[456] and later on a further 50 sites of interest[457] initially questioned Stratmann's theory's long-standing dependence on lepidocrocite as a corrosion product active in atmospheric ferrous corrosion. However, this contradiction was erroneous (as confirmed in more recent personal communications with co-author Dillmann[458]) because it was based upon the unfounded "…condition that

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[446] Selwyn et al. 1999, pp. 225-226
[447] Ibid., pp. 221-222
[448] Neff et al., 2006, p. 1229
[449] Michel et al., 2007, p. 1726
[450] Cornell & Schwertmann, 2003, p. 6
[451] Ibid., p. 5
[452] Stratmann, 1990, p. 47
[453] 2.2.3.3.2 Galvanic corrosion mechanism
[454] Antony et al., 2005, p. 751
[455] Leygraf & Graedel, 2000, p. 150
[456] Neff et al., 2006, p. 1229
[457] Dillmann, 07/12/2007, pers. comm.
[458] Dillmann, 05/02/2008, pers. comm.

lepidocrocite is in contact with the metal"[459] and their analyses that had "…shown that lepidocrocite is never in contact with the metal."[460]. Dillmann's team is currently investigating the electrical conductivity of corrosion products to potentially understand the role of lepidocrocite that is not in direct contact with the metal core[461].

The location of Stratmann's cited reduction reaction in corrosion product layers is important since it demonstrates that the reduction can occur away from the metal/atmosphere interface, which can be in areas of low oxygen concentration[462]. Additionally, further electrochemical reactions are provoked since the reduced CPs (highly doped with Fe^{2+}) are electronically conductive and form part of the corrosion product/electrolyte interface that determines the rate of oxygen reduction[463].

Magnetite, the black corrosion product[464] reduced from lepidocrocite according to Stratmann's wet-dry cycling model, is an electron conductor and is known to be a significantly greater reductant of oxygen than the metal and is said to be one reason why incomplete corrosion product removal before protective coating application encourages failure[465]. Magnetite, a semi-oxidised CP can also be formed from the metal as an oxidation product at the metal/corrosion product interface since there is less oxygen available in this area for full oxidation[466]. In cases of restricted oxygen access maghemite can also result[467].

Goethite, a yellow-brown corrosion product[468], can be formed directly as a corrosion product precipitate or via other CP phases such as lepidocrocite[469] and is "…extremely stable and is often the end member of transformations of other iron oxides"[470]. Indeed, a simple measure of the ability for corrosion product layers to provide protection of the underlying metal from further corrosion has been termed as the *protective ability index* and has been defined, for example, by Hœrlé et al. as a ratio of goethite to lepidocrocite, α-FeOOH/γ-FeOOH: the greater the proportion of

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[459] Neff et al 2006, p. 1236
[460] Ibid.
[461] Dillmann, 05/02/2008, pers. comm.
[462] Ibid.
[463] Stratmann, 1990, p. 51
[464] Cornell & Schwertmann, 2003, p. 6
[465] Ibid., p. 500
[466] Ibid., p. 499
[467] Chandler & Hudson, 2000, p. 4
[468] Cornell & Schwertmann, 2003, p. 4
[469] Ibid., p. 497
[470] Ibid., p. 6

goethite to lepidocrocite the more protective the CP layer[471]. More recently in a continuation of similar research activities, Antony et al. proposed an alternative method of characterising the corrosivity of corrosion product layers towards iron[472]. They suggested replacing the *protective ability index* with *reduction reactivity*[473]. By studying the electrochemical reactivities of synthesised[474] ferric ion-based powders a relative order of reduction reactivity towards metallic iron was deduced: magnetite < goethite α1 < goethite α2 < maghemite < lepidocrocite < akaganéite < ferrihydrite[475]. In essence this work studied the potential of galvanic coupling[476] effects that ferric minerals could have on iron[477]. Ferrihydrite is considered to be the species of the series that is most reactive to reduction with the iron metal[478]. In a second part of the same work, the reduction reactivity of real hypoeutectoid steel corrosion product layers (aged 200, 400, 600, 800 years in indoor atmospheres) was proven to decrease with the age of the samples: the 800 year old sample was considered to have "… a very low reactivity" and possibly reached a stable composition consisting almost exclusively of goethite[479]. An increased presence over time of ferric-based CP species, which are less reactive to iron, might be a more interesting discovery for the conservation of metals that are totally covered in corrosion products and have had sufficient time to age. But considering the case of the Palace Armoury munition armour where the metal surfaces are only partly covered and the armour themselves are only about 400 years old (not the outer surface CPs), such results suggested by Antony et al.'s study might not be so applicable for these heritage artefacts.

FORMATION OF ATMOSPHERIC FERROUS CORROSION PRODUCTS

The oxidation of metallic iron can be a three-stage process according to combinations of the two valence states of the iron ions: ferrous (+2); and ferric (+3). Firstly, iron is oxidised to the ferrous oxidation state, then to an intermediate corrosion product including a combination of both ferrous and ferric cations and,

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[471] Hœrlé et al., 2004, p. 1441

[472] Antony et al, 2007, pp. 7754-7759

[473] Ibid., p. 7757

[474] This experimentation does not account for some physical properties (such as thickness and porosity) of naturally formed corrosion product layers and possible effects therein (Ibid., p. 7759).

[475] Antony et al, 2007, p. 7757

[476] 2.2.3.3.2 Galvanic corrosion mechanism

[477] Antony et al., 2007, p. 7758

[478] Ibid., pp. 7757, 7759

[479] Ibid., pp. 7756-7757

then finally the fully oxidised ferric ion is formed[480]. Ferrous corrosion products are largely composed of hydrous ferric oxides[481] (i.e. including iron oxyhydroxides[482]). The overall oxidation of iron (0 oxidation state) to its +3 oxidation state as an iron oxyhydroxide is summarised by Equation 2-8.

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH$$

Equation 2-8 Complete oxidation of iron and corrosion product formation summary[483]

A simplified process of iron oxidation in *mild*[484] steel is presented next so as to demonstrate the transition from the unoxidised metal species to the fully oxidised ferric ion. In a humid atmosphere the normally protective oxide layer on mild steel decomposes and results in the loss of electrons (Equation 2-3a)[485]. In alkaline and neutral conditions the typical reduction reaction of oxygen has been presented in Equation 2-3b. The produced hydroxides then react with further ferrous ions from Equation 2-3a and produce ferrous hydroxides (Equation 2-9) that are then further oxidised to form ferric hydroxide ($Fe(OH)_3$)[486].

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

Equation 2-9 Reaction of ferrous ions with hydroxides[487]

Corrosion product evolutions and transformations are many, complex and, as outlined previously[488], the CPs themselves can alternate between the two oxidation states of the iron cations (Equation 2-3a & Equation 2-7).

2.2.2.3.5 Ferrous metal type

Last, but certainly not least, the type of ferrous material undergoing atmospheric corrosion is of importance. The type of ferrous metal determines the susceptibility to corrosion since some ferrous metals have self-protecting or *passivating* layers (e.g. stainless steels[489] and low-alloy weathering steels[490]). Those ferrous metals that are generally more susceptible to corrosion are cast iron, wrought

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[480] Leygraf & Graedel, 2000, p. 286

[481] Uhlig & Revie, 1985 p. 1

[482] Chandler & Hudson, 2000, p. 3

[483] Maréchal et al., 2007, p. 132

[484] *Mild steel*, also containing up to 0.3% carbon, is synonymous to low-carbon steel and is simply non-engineering commercial terminology referring to low-carbon steels without further standard specifications (IMMA, 1988, p. 3).

[485] Chandler & Hudson, 2000, p. 3

[486] Ibid.

[487] Ibid.

[488] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[489] Leygraf & Graedel, 2003, p. 281

[490] Chandler & Hudson, 2000, p. 3

iron and steels[491]. The nature of these metals not only affects the rate of corrosion (e.g. wrought iron atmospherically corrodes 30% slower[492] than the less corrosion resistant mild steel[493]), but more importantly can also affect the manner in which it corrodes (e.g cast iron corrodes via graphitisation[494] and some stainless steels corrode via pitting or intergranular corrosion[495]).

A varying metallurgical structure of even the same metal type can affect corrosion susceptibility. For example, contained metalloids or local composition variations of metallic phases each have their effects[496].

The way in which wrought iron and wrought low-carbon steels corrode is of high significance to this research's determination of the limitos and is described in the next subsection.

2.2.3 ATMOSPHERIC FERROUS CORROSION, CORROSION PRODUCT MORPHOLOGIES & CORROSION MECHANISMS

Under atmospheric corrosion conditions, like elsewhere, ferrous corrosion and corrosion products can manifest themselves in a wide variety of ways that can be classified according to the "…visual characteristics of the *morphology* of attack"[497]. Their forms are dependent on many interdependent factors such as the metal's composition, homogeneity, construction and surface coatings. The complexity and interrelation of each corrosion process scenario is too great to always be able to confidently draw conclusions on distinct, all-inclusive corrosion *mechanisms* involved in the metal loss and CP formation that becomes evident to the observer[498]. Nonetheless, in many cases labelled morphologies are indicative of, and indeed result from, their corrosion mechanisms, which can then at least be hypothesised from the material and environmental indications.

From a metallic heritage conservation perspective, it is imperative to understand the corrosion mechanisms so as to facilitate the development of

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[491] Ibid.
[492] Ibid., p. 5
[493] Gale, 1969, p. 7
[494] Figure 2-45 "Longitudinal cross-section through the wall of a cast iron pipe, exhibiting severe graphitic corrosion, i.e. dissolution of the iron from the cast iron pipe leaving behind layers of intact graphite"
[495] Asphahani & Silence, 1998, pp. 113-114 & Steigerwald, 1998, p. 124
[496] Steigerwald, 1998, p. 123
[497] Craig & Pohlman, 1998, p. 79
[498] Ibid.

conservation strategies[499]. In the case that corrosion has already occurred, it is similarly important to identify the various corrosion mechanisms since they should influence determination of the limitos and selective corrosion product removal procedures[500].

Little was found in the literature regarding specific reference to corrosion/corrosion product morphologies and corrosion mechanisms of wrought iron and wrought low-carbon steel provenancing the mid-late Early Modern Period. This might be due to a combination of factors; possibly being that these materials are/feature:

1. Not as relevant today as contemporary industrial materials, which are of greater current economic concern[501];
2. Corrosion phenomena similar to pre- and post- mid-late Early Modern Period wrought iron and low-carbon steel, and thus do not require further temporal specification; and/or
3. Simply an understudied/underpublished area.

It is unclear then which corrosion mechanisms, if any have been ascertained, are considered responsible. The few references specific to "wrought iron" corrosion are most probably regarding materials and processes from the industrial revolution (late 18th - early 19th century) onwards. Until 1860 "…wrought iron was the most important structural metal available"[502] possibly explaining their inclusion in engineering texts (e.g. "Conservation of Bridges"[503] or generic engineering handbooks, such as published by American Society for Metals (ASM) International[504]). No references could be cited regarding corrosion of pre-contemporary wrought low-carbon steel and it is presumed that such a steel classification would have been ambiguously encompassed by the classification of "wrought iron"; at the time, a misnomer for steel.

In order to communicate a more complete description of corrosion of mid-late Early Modern Period wrought iron and low-carbon steel it is therefore necessary to cautiously combine potentially applicable theory from research on similar contemporary materials with corrosion examples on primary sources of 16th-17th century armour at the Palace Armoury.

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[499] Neff et al., 2006, p. 1228
[500] Bertholon, 2001a, p. 244
[501] Gale, 1969, p. 9
[502] Brandt, 1992, p. 39
[503] Tilly et al., 2002
[504] Davis, 1998

Two main corrosion/corrosion product surface morphologies are described here since they predominate the examples found at the Palace Armoury. It is important to note that the vast majority of morphology evaluation of the PA munition armour has been made on a visual *surface-only* assessment. The assessment and extent of subsurface corrosion/corrosion product morphologies (e.g. pitting, intergranular, transgranular) can only be determined by cross-section observation and this has been undertaken during a preliminary study of an admittedly small corpus of ten samples[505] due to the undesirably invasive nature of such procedures on valued cultural heritage artefacts. While understanding any corrosion of the internal metal core is of importance to the artefact as a whole, and its structural integrity (the majority of PA armour are structurally sound), the surface and near surface subsurfaces are more particularly relevant to selective corrosion product removal due to their observability and potential accessibility.

Two types of fundamental corrosion mechanisms that drive the various resulting morphologies are hypothesised: differential aeration and galvanic corrosion cells.

2.2.3.2 Filiform corrosion/corrosion product morphology

Filiform corrosion is most commonly associated with metal (e.g. steel, zinc aluminium[506]) surfaces that have an organic coating (circa 0.1mm thick[507]) that has failed under conditions of relative humidity exceeding 65%[508]. Corrosion ensues and the:

> "…pattern of attack is characterized by the appearance of fine filaments emanating from one or more sources in semi random directions. The source of initiation is usually a defect or mechanical scratch in the coating"[509].

An example of filiform corrosion occurring on the coated Palace Armoury munition armour is given in Figure 2-31.

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[505] Vella et al., 2005b

[506] Uhlig & Revie, 1985, p. 257

[507] Hahin, 1998, p. 104

[508] Shreir, 2000, p. 170

[509] Hahin, 1998, p. 104

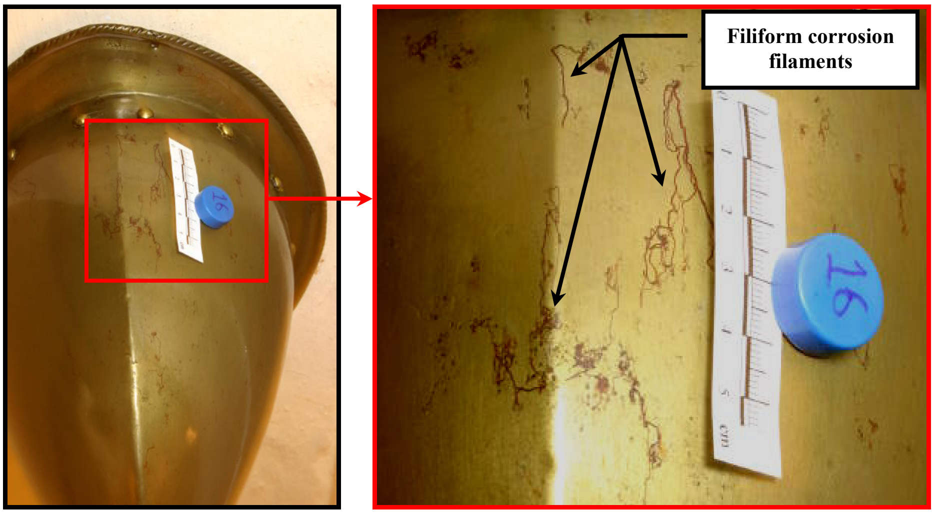

Figure 2-31 Left: *Varnished*[510] helmet *in-situ* on a wall display at the Palace Armoury. Right: Detail of the same helmet featuring filiform corrosion[511]

The morphology of the filiform filament is anatomically separated into the advancing head and the trailing tail or body (Figure 2-32).

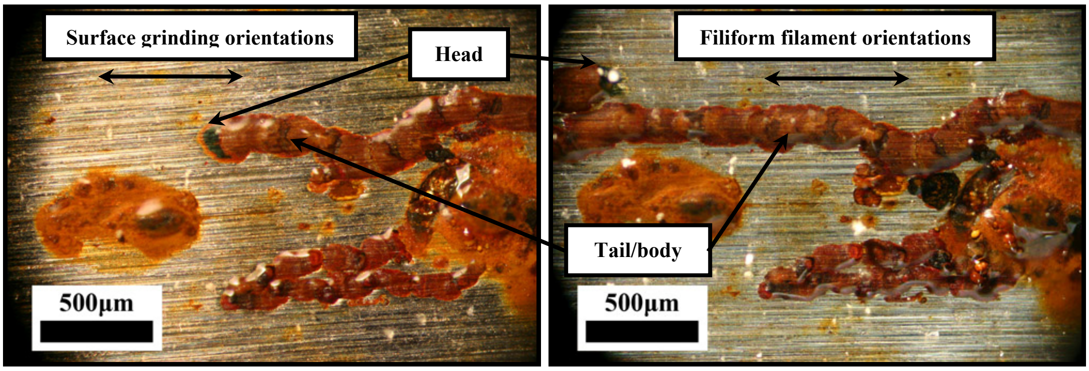

Figure 2-32 Filiform corrosion progressing on contemporary low-carbon steel coated with Paraloid B-72™ [512] (15%m/v in acetone) during laboratory-based accelerated corrosion protective system efficiency tests. Left: Filament after 14 daily cycles & Right: Same filament after 22 daily cycles[513]

The filiform head is characteristically blue, grey or green and features low pH (1-4, due to hydrolysis) and high chlorine concentration (Figure 2-33)[514]. The tail consists of characteristically brown corrosion products[515]

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[510] A transparent yellow-green "varnish" is anecdotally known to have been used in the recent past and is characteristic of a type of polyurethane identified by Fourier transform infra-red spectroscopy (FTIR) analyses on different Palace Armoury armour (Lemasson et al., 2004, p. 11).

[511] Crawford, 2007a, p. 23, permission courtesy of E. Magro Conti

[512] Copolymer of ethyl methacrylate-methylacrylate (Horie 1987, pp. 106-107).

[513] (Crawford in) Degrigny, in press, Chapter 7, p. 19

[514] Hahin, 1998, pp. 104-105

[515] Ibid, p. 105

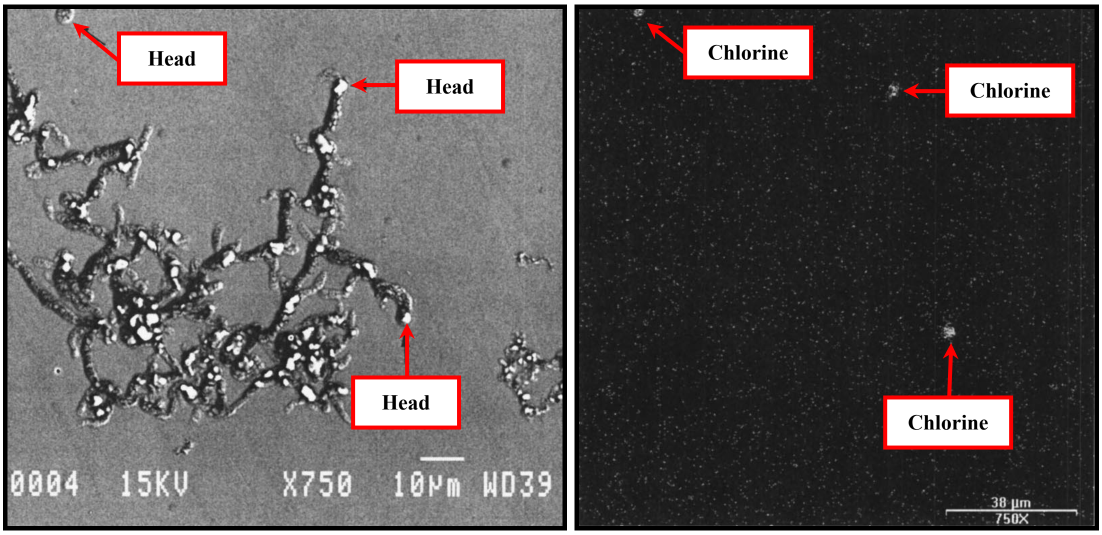

Figure 2-33 Left: Scanning electron microscope image of filiform corrosion on iron. Right: Filiform heads enriched with chlorine as determined by corresponding mapping with energy dispersive spectrometry[516]

Corrosion of the metal by filiform corrosion is restricted to the upper areas of a metallic substrate and can corrode metal up to 15µm deep and create filaments about 20µm in height and 0.05-3mm in width[517]. Higher RH supposedly results in thicker corrosion product filaments due to "…more vigorous corrosion…"[518].

2.2.3.2.1 Filiform corrosion mechanism

Filiform corrosion is considered a specialised form of differential aeration cell that is driven by differences in oxygen concentration between the head and body of the filament[519]. The oxygen concentration difference occurring induces the potential difference, which causes the current flow associated with corrosion processes[520].

Figure 2-34 demonstrates the filiform corrosion mechanism on coated steel.

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[516] Weissenrieder & Leygraf, 2004, p. 168
[517] Hahin, 1998, p. 104
[518] Weissenrieder & Leygraf, 2004, p. 167
[519] Hahin, 1998, pp. 104, 106
[520] Uhlig & Revie, 1985, p. 12

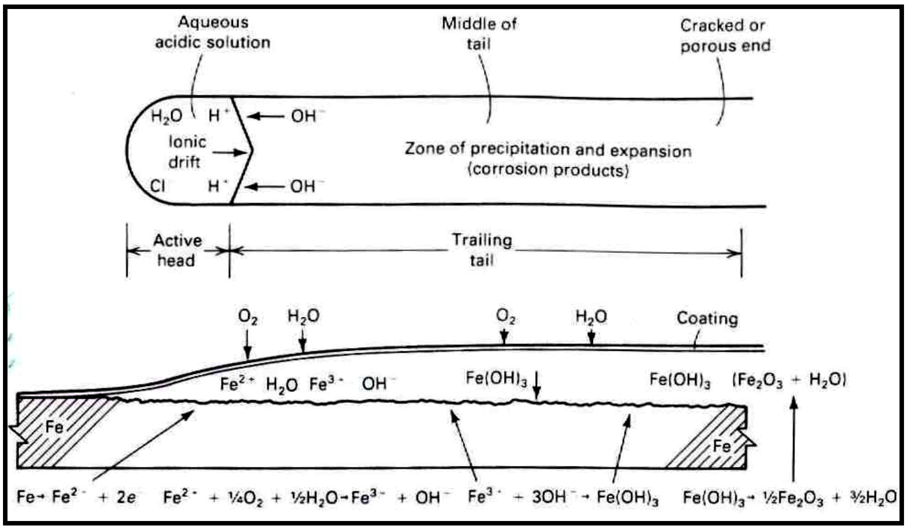

Figure 2-34 Plan and profile of filiform corrosion mechanism on coated steel[521]

The head and tail are where oxygen and water permeate the coating, and the centre of the head is where the anodic site generating ferrous ions is located. The differential aeration cell is established between the centre of the head (relatively less oxygen) and the periphery of the head and its junction with the tail, where oxygen access is greater[522]. The hydroxides produced from the cathodic oxygen reduction reaction (Equation 2-3b) react with the Fe^{2+} thereby forming $FeO.H_2O$, which is then oxidised by further oxygen to form $Fe_2O_3.H_2O$ (or FeOOH)[523]. The result is a vertically displaced corrosion product tail with the superimposed coating[524]. Hahin describes this important part of the corrosion mechanism, which is strongly related to this research:

> "The head literally tunnels through the substrate, separating the coating from the steel and bulging it out by expansion of corrosion products or by hydrogen gas evolution if the head is very acidic."[525]

This conversion, and physical displacement, of the former metal surface with corrosion products is vital to Section 2.3 Metal heritage artefact conservation & corrosion products: philosophy & practice and is also vital to the interpretation of the experimental phenomena recorded in Chapter 4 Results.

A coating's film strength and bonding to the metal substrate is affected by both the head's and tail's physical and chemical properties: the tail's CPs are typically alkaline causing coating cracking and debonding via softening and

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[521] Hahin, 1998, p. 106
[522] Weissenrieder & Leygraf, 2004, p. 170
[523] Uhlig and Revie, 1985, p. 259
[524] Weissenrieder & Leygraf, 2004, p. 170
[525] Hahin, 1998, p. 106

weakening of the film[526] , while blistering of the head due to hydrogen evolution can occur due to low pH (circa 1-2) (Equation 2-5)[527]. Rupturing of the swollen coating by considerably expanded corrosion products at the head or tail permits a new initiation site for further filament propagation[528]. Filiform initiates perpendicular to the defect in a coating (i.e. where the oxygen concentration is lowest, thereby forming the anode) and it is reported that filiform tends to propagate in the direction the metal was rolled or burnished[529]. Similarly, from the author's personal observation of actual examples with filiform corrosion product morphologies on steel, the predominant orientation of filaments are parallel to any polishing direction/*micro-grooves*, as has been observed on contemporary steel examples (Figure 2-32 & Figure 2-35) and on many of the PA's ferrous armour (Figure 2-36).

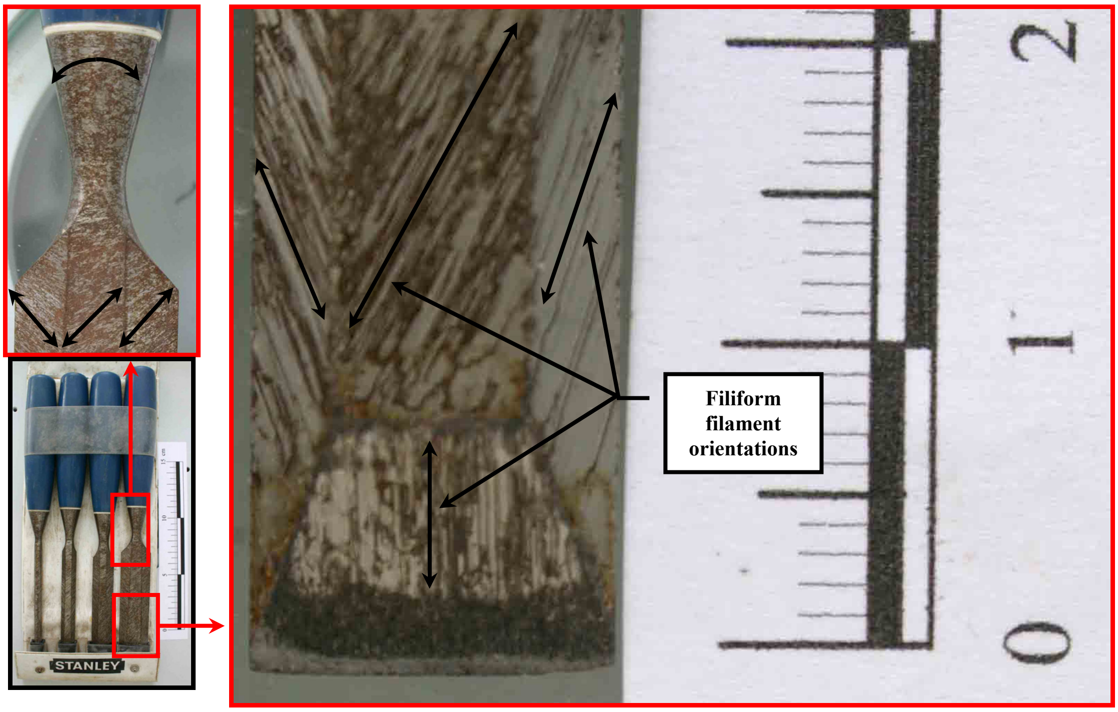

Figure 2-35 Lower left: Contemporary set of four varnished steel carpentry chisels[530] featuring filiform corrosion products oriented parallel with the grinding directions on each facet. Top left and right: Details of a single chisel's facets and filament orientation

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[526] Ibid.

[527] Ibid.

[528] Ibid.

[529] Ibid., p. 104

[530] Courtesy of J. Camilleri-Polidano

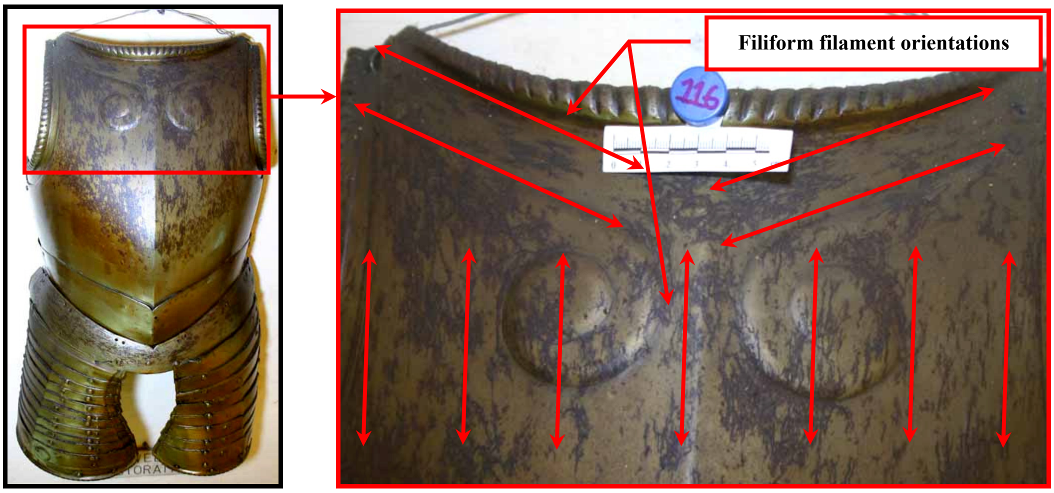

Figure 2-36 Corrosion product filaments that are oriented parallel in respective areas on Palace Armoury munition armour[531]

It is conjectured from Figure 2-36, and numerous other armour examples that the last corrosion product removal and/or metal polishing procedure left similarly oriented surface irregularities that then influenced the direction of coating failure and filiform CP propagation.

It is observed later[532] that the undermining of the coating on Palace Armoury armour becomes so extensive that the filament corrosion morphology becomes less localised and spreads outwards becoming non-filament like and more generalised. Similarities exist between the filiform head and pitting[533] corrosion, since filiform corrosion is effectively an uninterrupted lateral succession of multiple shallow differential aeration cells with corrosion pits that migrate over the surface of the metal rather than remaining immobile and extending in depth[534].

The intentional creation of filiform corrosion products can be performed by coating depletion techniques[535]. Note that many of the densely packed filaments in Figure 2-37 have either deflected or terminated after interception with other filaments: typical behaviour of filiform corrosion[536].

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[531] Crawford, 2007a, p. 23, permission courtesy of E. Magro Conti

[532] 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

[533] 2.2.3.3.1 Pitting corrosion mechanism

[534] This citation refers to filiform corrosion of aluminium (Huisert, 2001, p. 88).

[535] Cebelcorr, n.d., http://www.cebelcor.org/activities.htm – accessed 02/01/2006

[536] Weissenrieder & Leygraf 2004, p. 167 & Hahin, 1998, p. 106

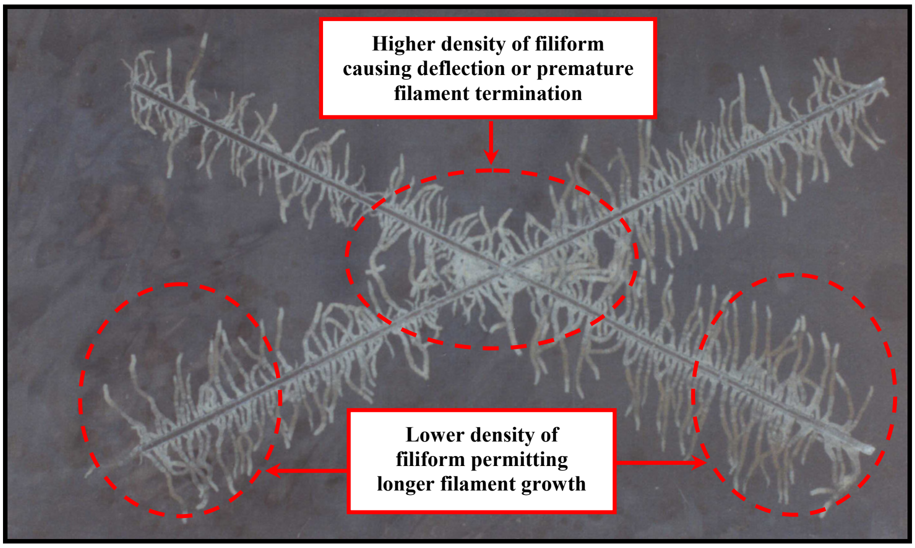

Figure 2-37 A coated unspecified metal with filiform corrosion propagating from deliberate coating incisions[537]

Filiform corrosion has been documented (to a much lesser extent) as occurring on iron surfaces without coatings, but instead lightly coated with pollutants, particularly sodium chloride salts (Figure 2-38)[538]. While the material cause differs (i.e. coating versus deliquesced salts), the corrosion mechanism of differential aeration and its resulting filament CP morphology is fundamentally similar[539].

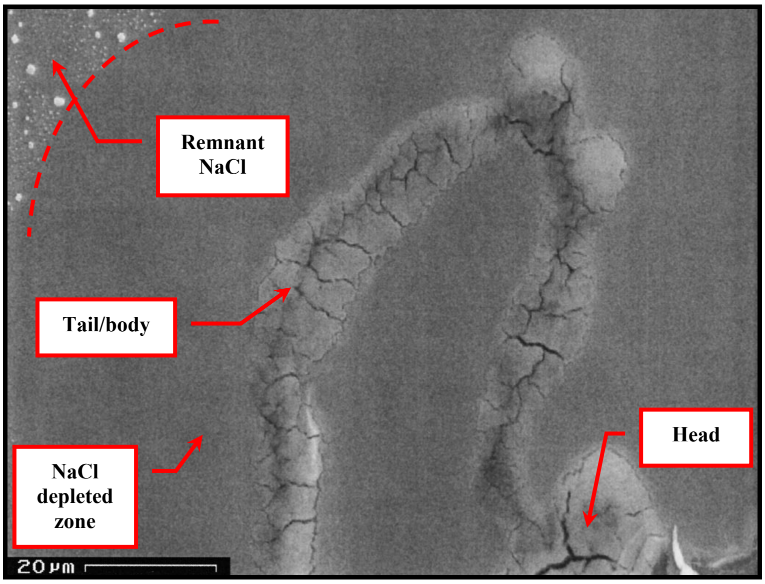

Figure 2-38 Scanning electron microscope image of a small filiform corrosion filament on iron coated with halite, rather than a coating[540]

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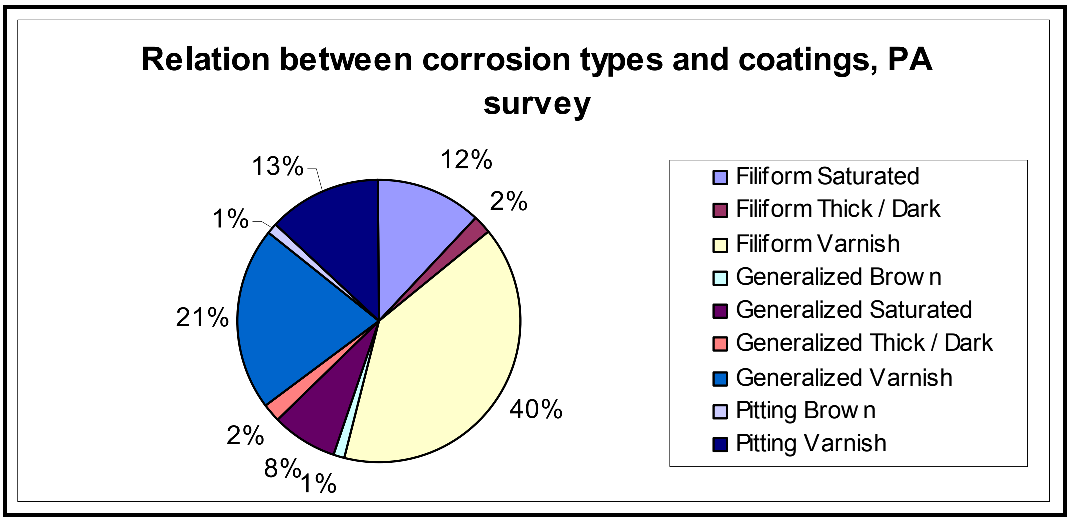
[537] Cebelcorr, n.d., http://www.cebelcor.org/activities.htm – accessed 02/01/2006
[538] Weissenrieder & Leygraf, 2004, pp. 165-171
[539] Ibid, p. 169
[540] Ibid, p. 170

The specification of *underfilm* filiform corrosion has been previously used to describe filiform associated with protective coatings[541]. Although, previous studies[542] have proven the presence of chlorides on the Palace Armoury armour artefacts, it is proposed that in this case the filiform corrosion is mainly attributable to the protective coatings (in conjunction with high RH) applied to the armour and can therefore be specified as most likely being underfilm filiform corrosion.

Recently the documentation of various types of surface CP formations was undertaken in a corrosion survey of display cases and open-air exhibited armour at the PA[543]. Graph 2-6 shows a sample of the acquired data and a trend of filiform corrosion (40%) being mainly associated with a characteristic varnish (Figure 2-31) on the armour, while a generalised corrosion product surface coverage (associated with the same varnish) follows next in frequency[544]. It is unclear whether this statistical analysis takes into account the fact that there are inherently more artefacts with this varnish type, thereby possibly leading to skewing of the data.



Graph 2-6 Relationship between surface corrosion product typologies and coatings on armour at the Palace Armoury[545]

2.2.3.3 Uneven local to uneven general corrosion/corrosion product morphology

In order to present the second corrosion and corrosion product morphology classification relevant to the Palace Armoury, observation of cross-sections of corroded munition armour from the PA is required (Figure 2-39).

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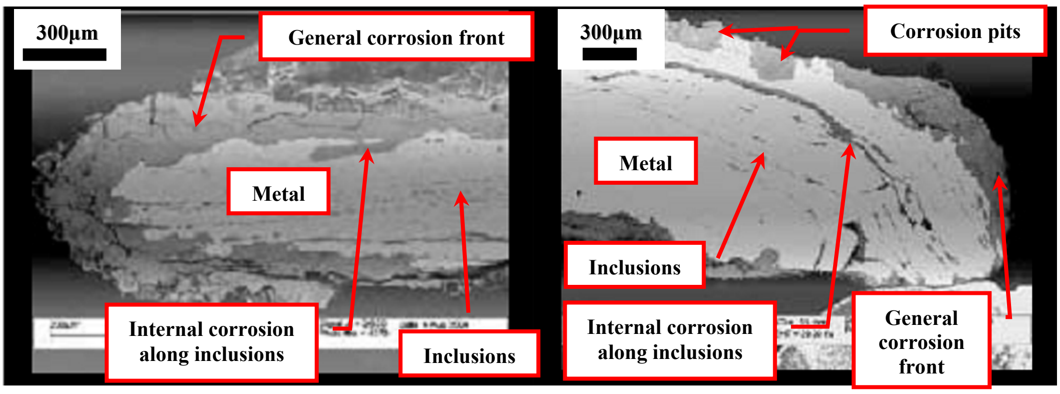
[541] Uhlig & Revie, 1985, p. 257

[542] Table 2-1 (Monnier, 2006, p. 1) & Vella et al. 2005b, p. 322

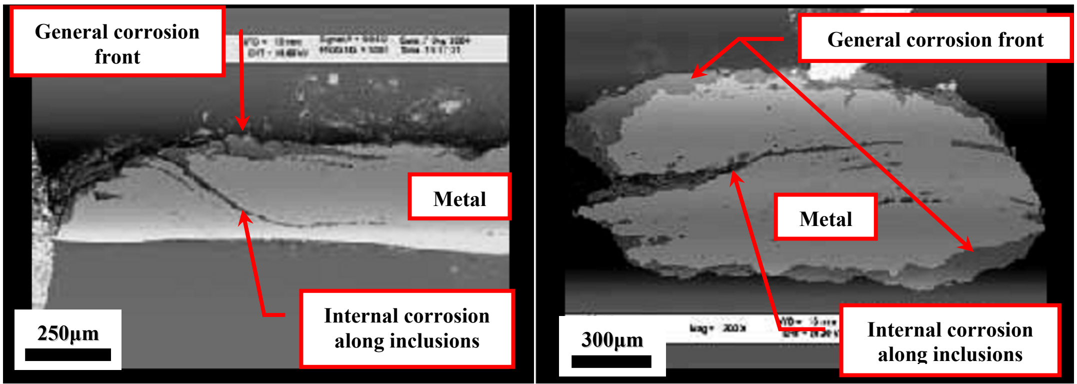
[543] Argyropoulos, in press, Chapter 5, p. 17

[544] Ibid.

[545] Ibid, p. 25



Iron part of tasset – PA RC 29 [546] Iron part of pauldron fragment – PA RC 166 [547]



Steel part of tasset – PA RC 80 [548] Steel part of full arm – PA RC 88 [549]

Figure 2-39 Scanning electron microscope backscatter electron (BSE) detector images of cross-sections of corroded munition armour from the Palace Armoury

On the whole, it can be seen from Figure 2-39 that corrosion appears to have occurred heterogeneously through the cross-sections, but predominantly towards the atmosphere/armour surface interface. In each case presented in Figure 2-39 the surface layers are more corroded than the internal areas. It appears that this could be due to an inherently greater access of necessary reactants like atmospheric oxygen. The corroded metal surface and corrosion product distribution is characterised by a combined morphology of *uneven local* and *uneven general corrosion* (Figure 2-40) strata that is sometimes characterised by wide corrosion pits.

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[546] Vella & Degrigny, 2004b, p. 7
[547] Ibid., p. 8
[548] Ibid., p. 11
[549] Ibid., p. 15

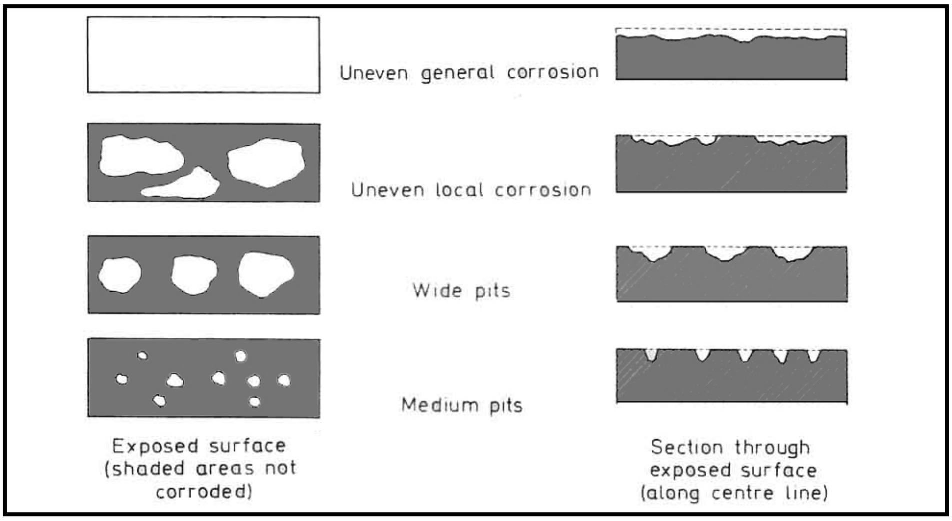

Figure 2-40 Schematic classification of types of metal corrosion: excluding corrosion products[550]

Oxygen and iron detected by energy dispersive spectrometry on these cross-sections in Figure 2-39 indicated oxides of iron, presumably corrosion products, but possibly also slags, especially for the cases where silicon or non-ferrous metals also featured with oxygen around the elongated features[551]. The corrosion appears to have taken an internal path along these inclusions[552] and along general surface corrosion fronts parallel to the armour lame's surface and supposed working direction. This internal corrosion could be compared, if only much less pronounced, with the "…laminated or stringy longitudinal texture" that becomes more obvious in severe corrosion cases of structural wrought iron (Figure 2-41)[553].

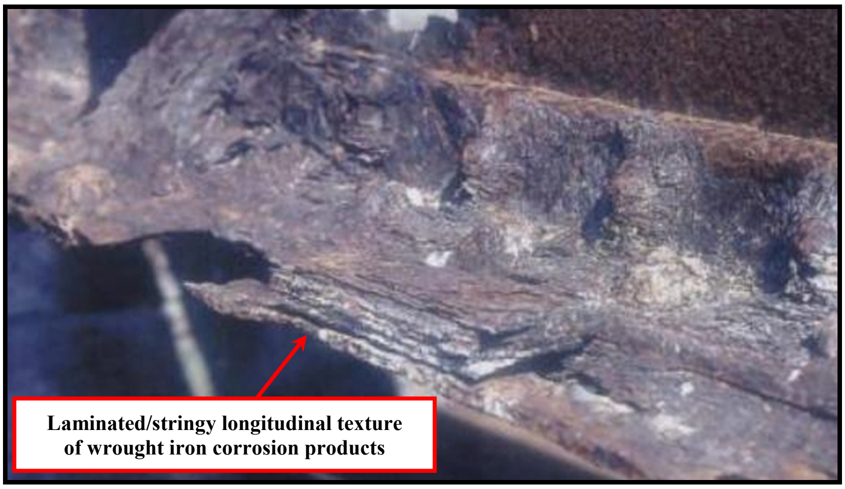

Figure 2-41 Excessive corrosion to a wrought iron construction beam[554]

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[550] Shreir, 2000, p. 152

[551] Vella & Degrigny, 2004f, p. 5, Vella & Degrigny, 2004j, pp. 4, 8, Vella & Degrigny, 2004h, pp. 2-3, Vella & Degrigny, 2004g, pp. 6-7

[552] Vella & Degrigny, 2004j, pp. 3, 5

[553] Tilly et al., 2002, p. 181

[554] Ibid.

One found reference regarding the corrosion of wrought iron appears to substantiate the apparent internal longitudinal corrosion on the cross-sections depicted in Figure 2-39:

> "The atmospheric attack of wrought iron can sometimes progress along the internal planes formed during rolling and cause swelling of the material. For this reason it is best not to cut across the grain boundaries and leave the face exposed to the environment"[555].

Such severe delaminations are not present on the armour and this is possibly simply due to its less corroded state or also since slag was ideally minimised in armour[556].

From the cross-sections presented in Figure 2-39 and others not presented[557], two separate types of corrosion mechanisms are inferred to be operational on the same material: again differential aeration cells (but this time of the pitting/crevice type)[558]; and possibly galvanic corrosion cells (caused by semi-conductive phases of corrosion products and also possibly by some types of slag inclusions). Further justification is warranted to further substantiate the case for galvanic corrosion via semi-conductive impurities since this assertion is later supported by a small amount of published research[559].

2.2.3.3.1 Pitting corrosion mechanism

Pitting corrosion, i.e. where corrosion is more localised than in adjacent areas, is associated with differential aeration cells and can occur when a porous or defective protective coating covers the metal[560]. The high ratio of cathodic to anodic areas, and auto-catalytic formation of acid isolated in the pits are factors of the pitting corrosion mechanism[561]. In the case of pitting corrosion, these differential aeration cells are formed between areas that are less accessible to oxygen (due to insoluble corrosion product deposits, more impermeable coating) and areas that are more accessible to oxygen (absent CPs, less protective coating)[562]. The pitting corrosion products on carbon steels at the surface environment interface are

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[555] Pohlman, 1998, p. 82
[556] 2.1.2.1.1 Direct process: bloomery furnace
[557] Vella & Degrigny, 2004a-j
[558] 2.2.3.3.1 Pitting corrosion mechanism
[559] 2.2.3.3.2 Galvanic corrosion mechanism
[560] Uhlig & Revie, 1985, p. 12 & Cornell & Schwertmann, 2003, p. 497
[561] Shreir, 2000, p. 175
[562] Uhlig & Revie, 1985, p. 12

characterised by a hemispherical/domed membrane that inhibits diffusion of dissolved oxygen to the metal beneath[563] (Figure 2-42). This membrane is of great significance to the later discussion about formation of modified original surfaces[564] and interpreting the experimental phenomena recorded in Chapter 4; where it is documented in reality that the membrane can *also* be discontinuous, cracked and irregularly ordered[565], as per previous descriptions of iron and steel corrosion products[566] and unlike the simplified schematic depiction below.

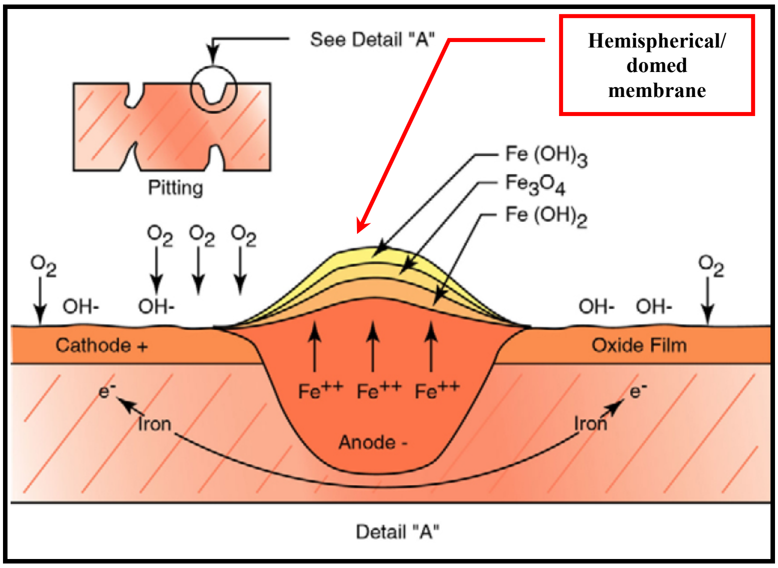

Figure 2-42 Schematic depiction of pitting corrosion by differential aeration on a ferrous metal with a previous oxide layer[567]

The corroding bottom of the pit is anodic (Equation 2-3a), while the cathodic area where oxygen is reduced (typically Equation 2-3b), is adjacent to the surface. The production of the positive ferrous ions (cations) in the pit from the corroded metal requires charge balancing and this is achieved with anions, typically chlorides from the environment[568].

The physically separate locations of the cathodic and anodic sites permit differences in pH and solution composition. Around the anode a lower pH (profusion of acid, H^+) can result due to the hydrolysis of the formed cations or by precipitation of oxides[569]. These subsequently hydrolysed products form metal hydroxides and

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[563] Shreir, 2000, p. 182

[564] 2.3 Metal heritage artefact conservation & corrosion products: philosophy & practice

[565] Figure 4-50, Figure 4-51, Figure 4-54 & Figure 4-55

[566] 2.2.2.3.4 Ferrous corrosion products

[567] NSA, n.d., p. 7

[568] Asphahani & Silence, 1998, p. 113

[569] Turgoose, 1989, p. 30

free acid (Equation 2-6)[570]. The free acid continues the corrosion pit's propagation[571]. Meanwhile around the cathode, pH is greater due to the alkalinity imparted by the relative magnitude of hydroxyl ions produced by the reduction reaction (Equation 2-3b) and oxyhydroxides[572].

It is very important, on the one hand to emphasise that the presence of slag in wrought iron is most often cited to be the ground for its good corrosion resistance. The extent of pitting corrosion occurring in wrought iron can be limited by the presence of the non-metallic amorphous slag stringers since they often form a physical and non-conductive barrier between other metallic areas and pitting corrosion cannot proceed past them[573]. It is thought that in these cases where slag inhibits corrosion, the authors might refer to the most common slag species: fayalite, a glassy, insulating i.e. non-conductive material at room temperature and pressure[574]. A possible example of this corrosion inhibition by slag in the Palace Armoury munition armour is noted later in the experimental part of these investigations[575].

On the other hand, applying the theory of pitting corrosion via differential aeration cells to the cases of wrought armour at Palace Armoury, corrosion could also involve the development of corrosion pits that extend longitudinally into the metal via its internal planes, rather than vertically (transversally). This can be seen in the cases given in Figure 2-39 and might be considered more akin to *crevice corrosion*. Crevice corrosion is another closely related form of differential aeration corrosion cell, but its definition includes its occurrence along unintentional metallurgical seams/defects of metal-to-metal or non-metal-to-metal interfaces[576]. The internal seams demonstrated in Figure 2-39 could be attributable to slag and/or the internal interfaces created on wrought ferrous metals during consolidation of bloom iron[577] or armour forging[578].

Another cross-section of Palace Armoury armour (Figure 2-43) demonstrates corrosion pits with increased chlorine concentrations and a much lesser presence of

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[570] Asphahani & Silence, 1998, p. 113

[571] Ibid.

[572] Turgoose, 1989, p. 30

[573] Brandt, 1992, p. 39 & Gale, 1969, p. 5

[574] Cococcioni, 2003, pp. 1, 5

[575] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron (part) PA RC 166

[576] Kain, 1998, pp. 108, 110

[577] 2.1.2.1.1 Direct process: bloomery furnace

[578] 2.1.2.2 Munition armour forming

slag inclusions. Notably, these inclusions are also discontinuous and relatively short, rather than the long stringers that would otherwise isolate layers of metal from further downward corrosion: pitting corrosion has been able to proceed past these discontinuous inclusions.

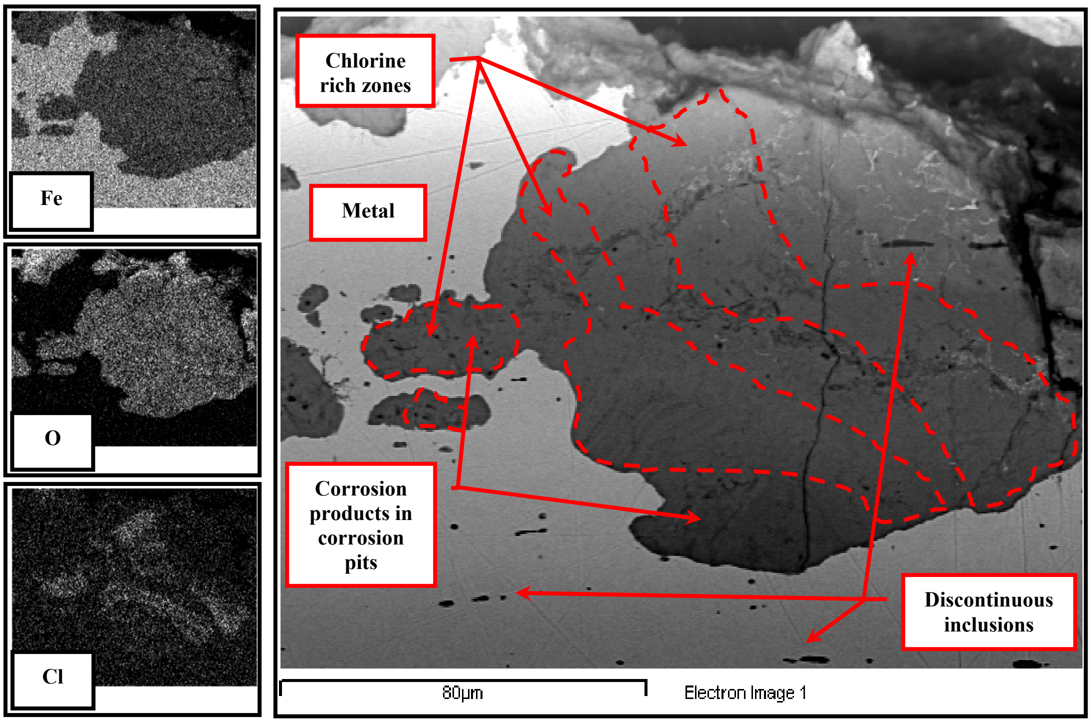

Figure 2-43 Left: Energy dispersive spectrometry mapping of a cross-section of more heavily corroded Palace Armoury armour (PA RC 20) with increased chlorine concentration inside a corrosion pit below the adjacent metal. Main: Corresponding SEM BSE image[579].

2.2.3.3.2 Galvanic corrosion mechanism

Galvanic, or bimetallic, corrosion can occur when two conductive materials of dissimilar potential are coupled together in a corrosive environment, such as an atmospheric environment where humidity and possibly also pollutant levels are sufficiently corrosive[580]. The material with the more negative potential (i.e. less electrochemically noble) becomes the anode and corrodes in preference to the material with the more positive potential, which becomes the cathode[581]. The oxidation sites in galvanic corrosion necessarily occur on a metal, whereas the sites for reduction need only occur on a material (metallic or conducting non-metallic), which is connected electrically to the metal and in the same electrolyte[582]. The flow

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[579] Vella et al. 2005, p. 322
[580] Leygraf & Graedel, 2000, p. 181
[581] Pryor & Astley, 2000, p. 213
[582] Baboian, 1998, p. 83

of electrons from the anode does not pass via the electrolyte[583] and must pass through a solid-state material[584].

The rate of galvanic corrosion is largely influenced by less readily polarised cathodes[585]. Polarisation of anodes and cathodes occurs due to the current flowing between them that causes their potentials to shift towards each other. A galvanic cell featuring a less easily polarised cathode features a potential shift of the anode closer to the cathode and results in greater corrosion of the anode when compared with a corresponding cell of opposite cathodic and anodic polarisation behaviour. Differences in polarisation behaviour significantly affect the ability and extent of galvanic corrosion[586].

Galvanic couples featuring non-metallic conductors as cathodes are less reported in the literature than galvanic couples with metal cathodes[587]. Magnetite is a semi-conductive iron oxide that is considered to display "…almost metallic properties"[588] and is known to participate in galvanic corrosion of steel[589], while lepidocrocite's galvanic action on iron has already been detailed[590]. To be semi-conductive the "…separation between the valence band of orbitals and the conduction band is less than 5eV"[591]. There are many ferrous minerals that satisfy this requirement: wüstite (FeO) (band gap 2.3eV); maghemite (2.03eV); hematite (Fe_2O_3) (2.2eV); goethite (2.10eV); lepidocrocite (2.06eV); akaganéite (2.12eV); and magnetite (0.1eV)[592]. The low band gap of magnetite results in its greater conductivity (10^2-10^3 Ω^{-1} cm^{-1}) when compared with goethtite, lepidocrocite and akaganéite (circa 10^{-9} Ω^{-1} cm^{-1}) at room temperature[593].

As mentioned previously[594], the determination of conductive iron oxides (particularly corrosion products, rather than residual mineral oxides) contributing to ferrous corrosion is one of the present themes of interest for the research team of

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[583] Selwyn, 2004, pp. 20-21
[584] Dillmann 05/02/2008, pers. comm.
[585] Pryor & Astley, 2000, p. 231
[586] Baboian, 1998, p. 83
[587] Ibid., p. 84
[588] Cornell & Schwertmann, 2003, p. 115
[589] Baboian, 1998, p. 84
[590] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products
[591] Cornell & Schwertmann, 2003, p. 115
[592] Ibid. p. 117
[593] Ibid.
[594] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

Dillmann et al.[595]. Such semi-conductive ferrous oxide species might not only be present as products of corrosion, but could also be products of manufacture (e.g. wüstite or hematite as high temperature oxides formed from smithing[596] or wüstite as an unreduced slag species from the iron ore[597]). Wüstite-based slags prevail in ferritic iron, while fayalite-based slags prevail in the pearlite phase of steels. Wüstite slags have dendritic microstuctures[598]. Of the three ferritic irons of Palace Armoury armour observed by Vella et al. no dendritic structures in the "high slag content"[599] were reported[600]. This does not necessarily conclude these oxides on the samples are all products of corrosion: dendrites might have simply not been observed since morphologies more likely to be representing corrosion products than slag were the focus of that study on corrosion product morphologies[601].

A list of non-ferrous metal oxides (including titanium) present as slag inclusions in bloomery iron has been given previously[602]. Kaneko suggests that, "The FeOOH crystals produced on iron antiquities may exhibit a high surface activity which originates from the higher electronic conductivity due to impurities" [603] and "The introduction of foreign cations of a valency different from the parent cations leads to a distinct change in electrical conductivity"[604]. For example, doping with Ti^{4+} enhances the electrical conductivity of goethite, while Al^{3+} accordingly has no effect[605]. This influence of non-ferrous oxides on the semi-conductor properties of ferrous corrosion products and their potential influence on galvanic corrosion of wrought iron/steel is poorly represented in the literature; raising questions about the awareness or certainty of this phenomena or simply whether it has been underinvestigated.

In conclusion to this matter on the possible galvanic corrosion effect of semi-conductive ferrous and non-ferrous inclusions, it seems far less proven than the galvanic effect that has been established and published for certain ferrous corrosion products: namely magnetite; and lepidocrocite.

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[595] Dillmann, 05/02/2008, pers. comm.
[596] Degrigny et al., 2007b, pp. 36, 38
[597] Buchwald & Wivel, 1998, p. 77
[598] Dillmann et al., 2002, p. 329
[599] Vella et al., 2004, p. 230
[600] Vella et al., 2005b, pp. 319, 322, 324
[601] Vella et al., 2005b
[602] 2.1.2.1.1 Direct process: bloomery furnace
[603] Kaneko, 1989, p. 61
[604] Ibid.
[605] Ibid.

2.2.4 ATMOSPHERIC CORROSION CONTROL

The control of corrosion in the museum environment is briefly mentioned here as a reminder that there are many possible strategies available for avoiding corrosion in the first instance, thereby avoiding the periodic interventions on formed corrosion products. The methods for controlling atmospheric corrosion on metallic cultural heritage artefacts are less obvious than those permissible for commercially/industrially employed metals and are described here in two subsections. Often, for successful corrosion control, preventive and interventive conservation methods must be employed in tandem[606]. Recently, maintenance efforts, or lack thereof, have been cited as an influential factor contributing to metal corrosion at the Palace Armoury[607].

It is necessary to therefore assess the material-environment system (Figure 2-44), rather than simply consider the materials separately from the environment and follow instinctive prejudices to remove corrosion product materials from an artefact.

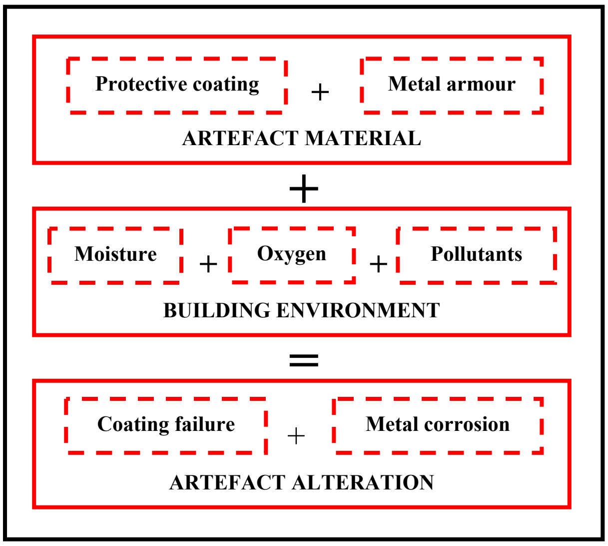

Figure 2-44 A conceptual representation of the principal components of the material-environment system contributing to the metal artefact alteration by corrosion

Certain norms and guidelines have been established for ferrous metals for varying states of pollution and environments. For example, as stated earlier[608], unpolluted and uncorroded iron has a critical relative humidity of circa 60%[609], while corroded and chloride polluted archaeological iron has a critical relative humidity of

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[606] Hockey & Shearman, 2006, p. 33

[607] Argyropoulos, in press, Chapter 5, p. 25

[608] 2.2.2.3.2 Atmospheric water

[609] Pohlman, 1998, p. 82

as low as 15% and a rapidly increasing corrosion rate when above 30%RH[610]. It would be expected that the armour at the Palace Armoury would fall between these two extreme scenarios since it is less corroded and has not been exposed to burial conditions where soluble salt concentration and penetration could be much higher.

2.2.4.1 Preventive conservation methods

Preventive conservation methods have long been known to be the most desirable form of action since they aim to avoid deterioration in the first instance: effectively demonstrating the adage that prevention is better than the cure[611]. Normally, preventive conservation methods function by removing (or reducing) one or more of the factors responsible for a deterioration process. Such processes are more respectful of the artefact materials since they involve procedures that are less intimately related to the artefact.

2.2.4.1.1 Environmental control

If an environment is considered to be corrosive, controlling the overall ambient atmosphere (in terms of relative humidity, pollutants) of a museum airspace via passive means (e.g. landscape/architectural design/construction, door/window seals)[612] or active means (e.g. building management, air conditioning, dehumidification, filtering)[613] are respectively the most desirable means of preventing/limiting degradation processes[614]. However, often the initial capital and/or ongoing running costs are perceived to be financially prohibitive[615], and museums are in inherited historic buildings requiring innovative installation of modern air-control systems[616]. The Palace Armoury is one such historic building and collection.

2.2.4.1.2 Display cases

The enclosure of sensitive materials inside appropriately constructed display cases potentially provides a protective microclimate extending material longevity by

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[610] Thickett & Luxford, 2007, p. 106
[611] Thompson, 1977, p. 46
[612] Cassar, 1995, pp. 33-52
[613] Ibid. pp. 77-108
[614] Gilroy & Godfrey, 1998, p. 113
[615] Cassar, 1995, p. 86
[616] Ibid. p. 85

limiting pollutant deposition and buffering environmental fluctuations[617]. The installation of larger showcases at the Palace Armoury occurred in 1957 for the "outstanding pieces of arms"[618] (i.e. not for the munition armour), while other smaller cases have even been in longer use (>100 years), as evidenced by pictorial documentation (Figure 2-18, Figure 2-19 & Figure 2-21).

2.2.4.1.3 Dusting regime

For artefacts too large, too numerous, or deemed of lesser priority (like the PA's munition armour) a scheduled regime of dust removal by physical processes (clean and soft cloth and brushes with portable vacuum) should help limit corrosion of artefacts that must remain on display and outside cases[619].

By 1969 Czerwinski and Żygulski, the invited UNESCO representatives, had already suggested these simple cleaning procedures and some of the above-cited architectural measures so as to preserve the arms and armour collection at the Palace Armoury[620].

2.2.4.2 Interventive conservation methods

Unfortunately, it follows that interventive conservation methods are often employed to treat the symptoms of inadequate or ineffective or non-existent preventive conservation practice, but there is little point in reinstating the artefact into its previously damaging environment[621]. Those interventive conservation methods only relevant to their possible application to the ferrous armour at the Palace Armoury are described here.

2.2.4.2.1 Applied barrier coatings

The use of an applied barrier coating helps to isolate the metal from its environment[622] in a similar way as a display case, but on a much more intimate level: by adhesion[623]. Barrier coatings suitable for indoor environments are typically organic compounds such as resins and waxes with very low water permeability[624]

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[617] Ibid. p. 109
[618] Czerwinski & Żygulski, 1969, p. 6
[619] Gilroy & Godfrey, 1998, p. 8 & Butcher-Younghans, 1993, pp. 133-135, 137
[620] Czerwinski & Żygulski, 1969, p. 15
[621] Gilroy & Godfrey, 1998, p. 1 & Hatchfield, 2002, p. 55
[622] Grossbard, 1992, p. 101
[623] Horie, 1987, p. 4
[624] Chatterjee et al., 2001, p. 67

and are preferably as inert, removable and visually inconspicuous as possible[625]. Coatings should only be perceived as an interim protection means until the next scheduled dust removal and themselves require maintenance according to the material longevity and efficacy determined by its properties and the environment[626]. Recently surveyed coating practices across Europe and the Mediterranean basin show that acrylic resins or waxes, used separately or in conjunction, are common for ferrous archaeological artefacts, while oils are also used on historical ferrous artefacts[627]. Importantly for armour and their multiple-joined components with defined edges, complete and uniform coating coverage is a far from achievable ideal[628].

2.2.4.2.2 Stabilisation

Stabilisation of metals is the term used to prevent recurrences of active corrosion. In an interventive conservation context, this can either be achieved by removal of the corrodent species (e.g. soluble salts) or by surface film forming or complexing with corrosion inhibitors[629]. These approaches are largely avoided for historical ferrous artefacts like armour since they commonly involve immersion in solutions. Tannic acid is the corrosion inhibitor most commonly used on ferrous artefacts[630] in Europe[631]. Tannic acid application is renowned for its black aspect[632], which might not be considered technologically or aesthetically sympathetic with the armour genre.

2.2.4.2.3 Corrosion product removal

Corrosion products are often removed from metallic cultural heritage artefacts. The possible motivations are many and case dependent. Importantly for the context of armour's (and other historical artefacts') conservation, it is their non-metallic mineral colours that make aesthetics an issue. Meanwhile, their hardness, adhesion and intimate proximity to the metal substrate pose risks by any

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[625] Horie, 1987, p. 7 & Grossbard, 1992, p. 104

[626] Grossbard, 1992, p. 104

[627] Argyropoulos et al., 2007b, pp. 168-169

[628] Bradford, 1993, p. 226

[629] Hatchfield, 2002, p. 125

[630] It was not specified if these artefacts treated with tannic acid are archaeological and/or historical iron

[631] Argyropoulos et al., 2007b, p. 168

[632] Gilroy & Godfrey, 1998, p. 123

interventions that might inadvertently affect metallic areas. The next section explores in depth the interventive conservation practice of corrosion product removal.

2.3 METAL HERITAGE ARTEFACT CONSERVATION & CORROSION PRODUCTS: PHILOSOPHY & PRACTICE

The development of conservation approaches for metal cultural heritage artefacts, like any material artefact type, follows a continuing evolution of thought and action over time. This evolution is governed by the material nature of the artefacts and their environment, societal perceptions of these artefacts and available sciences[633, 634]. Corrosion is the particular threat and form of degradation most relevant[635], but not necessarily unique[636] to metal cultural heritage. Accordingly, metal conservation research efforts to prevent this phenomenon have understandably, in the past and present, reflected this particularity. But how have these corrosion processes modified an artefact from its so-called *original* state and how do conservation professionals approach an artefact already with corrosion products?

Philosophical and practical approaches to corrosion products emanating from metal artefacts, and their contribution to the conservation or destruction of modified original surfaces on metal artefacts, are a major area of such continual development and are described here. This section initially explains the deeper relevance and concepts of the determination of the modified original surface in CPs on metallic artefacts; as developed and currently continued by conservator, conservation researcher and lecturer, Dr Régis Bertholon, with his emphasis on archaeological metal artefacts. Bertholon's work in the last two decades has involved a holistic step-by-step approach of:

- reviewing the work of past scientists and conservators on archaeological metal artefacts with modified original surfaces[637];
- constructing a standard vocabulary and an annotation system to describe corrosion product and metal stratigraphy features[638];
- defining valid markers useful for delimiting materials and interfaces on corroded artefacts[639]; and
- establishing research methodologies to characterise corrosion typologies and possible modified original surfaces therein[640].

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[633] Bertholon, 2001b, p. 172
[634] Hockey & Shearman, 2006, p. 32
[635] That is to say that metals are subject to other major conservation threats such as neglect, theft etc but these are not particular to metals
[636] Glass and plastics also suffer from corrosion degradation mechanisms (Bertholon, 2001c, p. 11)
[637] Bertholon, 2000, Bertholon, 2001b & Bertholon 2001c
[638] Bertholon, 2000
[639] Ibid.

The adaptation and restrictions of these findings and approaches from archaeological metal artefacts is later related to the historical artefacts found at the Palace Armoury[641]. Lastly, for a worldly perspective specific to the munition armour genre, international conservation practices on armour with corrosion products are subsequently examined via a literature review and questionnaire[642].

2.3.1 WHAT IS THE ORIGINAL SURFACE & WHY DETERMINE ITS PRESENCE?

The interest in determining a supposed *original* surface is driven by the direct[643] appreciation (by academics and the public) of a surface that represents an artefact's shape, fabrication method, decoration, evidence of use or surface details[644]. The artefact and its surface are thus a source of primary information and are irreplaceable. The artefact is only complemented by secondary information resources such as archival records; predominantly unavailable for archaeological[645] materials, and possibly available in greater or lesser extents for historical[646] artefacts. Correspondingly, a lack of secondary resources, especially unambiguous ones, on armour manufacture and surface finishing motivates direct metallurgical research investigations on real armour artefacts[647]. After corrosion of a metal surface it is clear that the actual original surface is no longer present; e.g. the characteristic lustrous metallic appearance and hardness are lost forever. However, some characteristics of the original surface, e.g. shape, marks, can still remain as features of the now modified original surface[648].

The graphitisation of grey cast-iron (such as for military cannon) is a well-recognised example of corrosion products representing, in a modified way (e.g. loss

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[640] Neff et al., 2003

[641] 2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour

[642] 2.4 International munition armour conservation philosophy & practice: literature review & laboratory questionnaire

[643] Radiographic techniques such as, x-ray radiology and x-ray tomography are increasingly valid forms of indirect observation, however at present and in the near future their use is, at best, mostly limited to necessity and to museum professionals. They therefore rarely facilitate artefact appreciation by the public who are until recently only accustomed to direct appreciation of museum tangible objects and not virtual reproductions. Though improvements and lowering costs will make technologies more affordable by museums it is not expected, in the present author's opinion, that the bulk of collections will be ever duplicated for exclusive appreciation in virtual forms.

[644] Bertholon, 2007a, p. 31

[645] Archaeological artefacts are again in this context classified as coming from burial conditions and are often dating prehistory and commonly do not accompany written records.

[646] Historical artefacts are again classified as those that have not been interred and are also typically of more recent periods.

[647] Williams, 2003

[648] Bertholon, 2000, pp. 218-219 & Bertholon, 2004, p. 228

of hardness) the shape of the original metal. The ferrite and pearlite content in grey cast iron corrodes, preferentially to the non-metallic carbon network in a more or less even corrosion front and preserves the original shape, producing little or no change in thickness[649] of the material in these graphitised layers[650] (Figure 2-45).

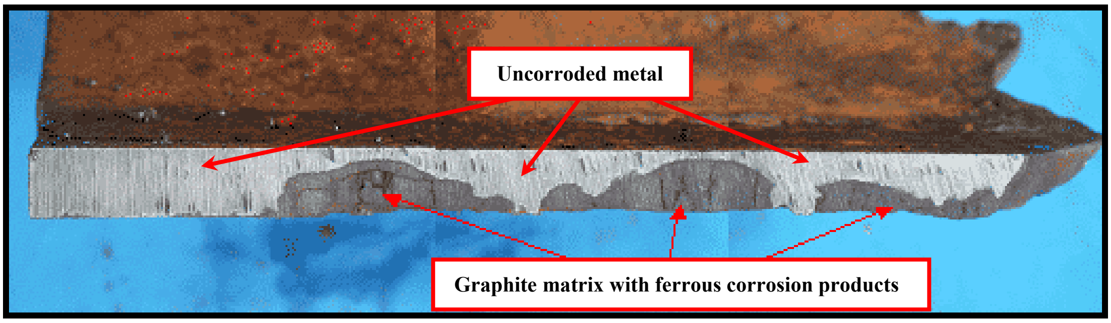

Figure 2-45 "Longitudinal cross-section through the wall of a cast iron pipe, exhibiting severe graphitic corrosion, i.e. dissolution of the iron from the cast iron pipe leaving behind layers of intact graphite"[651]

Surface information can be within corrosion product layer crusts as mineralised material that represents the modified metal's original surface features or encapsulates other preserved materials like *organic pseudomorphs*[652] (more applicable to more corroded artefacts like archaeological artefacts).

Alternatively, this surface information can remain as still uncorroded metallic surfaces that are underneath corrosion product layers that have deposited from adjacent corrosion sites (more applicable to less corroded materials like historical artefacts). Notably, if a surface has altered over time, as is often the case with corroded artefacts, the reliability of information gained from corroded artefacts depends on the knowledge of the given alteration mechanisms[653]. The extent of alteration of an artefact's surface, from that moment before abandonment at the end of its useful life until its conservation examination, can be considerable depending on the artefact material, environment and duration. In fact, evidence of the original surface *per se* can be irretrievably corroded and this was a common, unquestioned and sometimes incorrect conservation diagnosis on many metal artefacts until the latter part of the 20th century. Removing all corrosion products (*stripping*, Figure 2-46) was common practice because the CPs did not bear a resemblance of a

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[649] Steigerwald, 1998, p. 133

[650] Turgoose, 1989, p. 30 & Cornell & Schwertmann, 2003, p. 497

[651] Testlabs, n.d., www.testlabs.ca/tech-ref.html – accessed 20/08/2007

[652] Structures of decomposed organic material that have been preserved by corrosion products that have migrated from adjacent metals and impregnated the organic cell structures (Cronyn, 1990, pp. 183-184).

[653] Bertholon, 2007a, p. 32

recognisable metallic surface or they were deemed to have destroyed the original surface upon expansion[654].

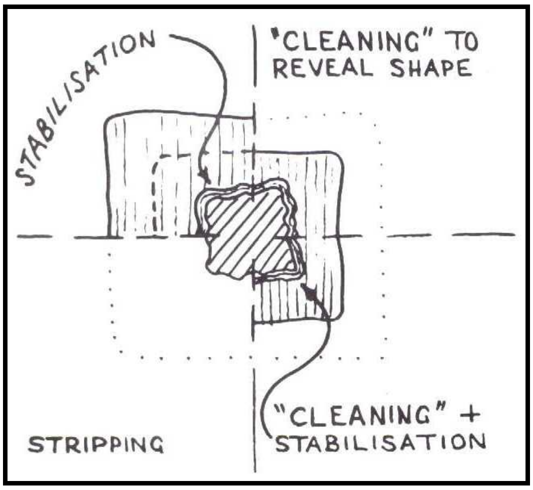

Figure 2-46 "Diagram showing four options the conservator may choose in cleaning a bronze object"[655]

However, the practice of stripping has largely been discontinued[656] since there is increasing realisation that corrosion products can potentially retain modified original surfaces[657]. Now that more support has grown from the evidenced cases where CPs can preserve surface information, the current challenge is how to correctly diagnose if original surface information remains in other as yet undetermined cases.

2.3.1.1 Development of the original surface concept

The concept of the *original surface* is not a new area of interest for conservation, nor is it exclusive to metal artefacts. To describe the conceptual development of the original surface for metals, particularly archaeological ones, Bertholon reviewed the published conservation literature from authors of the 20th century[658].

The development of the original surface concept for archaeological metals was classified accordingly:

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[654] Bertholon, 2001c, p. 10
[655] Organ, 1977, p. 125
[656] Bertholon, 2001b, p. 168
[657] Bertholon, 2001c, p. 11
[658] Bertholon, R. (2001b). The location of the original surface, a review of the conservation literature. Metal 2001: Proceedings of the International Conference on Metals Conservation, Santiago, Chile, I. D. MacLeod, J.M. Theile, C. Degrigny (eds.). Perth, Western Australian Museum. 167-179.

1. Emergence;
2. Conceptualisation; and
3. First definitions and extensive conceptual application[659].

Of concern to this present dissertation on historical ferrous metals, it should be emphasised here that the subjects of the articles reviewed by Bertholon[660] seem to be predominated by metals and environments differing to the Palace Armoury and this could lead to differing corrosion product formations and original surface preservation mechanisms. The focus of Bertholon's reviewed literature was on archaeological metals and with a majority ratio of circa 5:2, of non-ferrous versus ferrous metals/alloys[661]. The proportion of non-ferrous metals was circa 4:1, Cu versus Ag/Sn/Pb/Au.

While the term *original surface/surface originelle* has been used widely used in the literature, other terms have also been expressed. A selection of terms from a wider group of texts reviewed in the doctoral work of Bertholon were used to describe the artefact's former or present day existence (Table 2-2):

original shape	original form/forme originelle	original contours
original appearance	distinctive form	surface primitive
forme primitive	forme initiale	patina/patine
original volume	surface features	surface markings
surface details	skin/peau	epidermis/épiderme
authentic surface	pseudomorphic replacement	pseudomorphic substitution

Table 2-2 Summary of *original surface*-related terms used to describe surfaces of artefacts as reviewed by Bertholon[662]

A reappraisal of the context of these terms used in the numerous texts reviewed by Bertholon is out of the scope of the present work. The broad point is that Bertholon found many authors had realised the original surface of their subject matter could have been transformed into corrosion products and was therefore no longer in existence[663]. They consequently used other terms to describe the traces of the former original surface. Some of these terms are referred to in the following sections outlining the development of the original surface concept. Later, efforts were made to organise the semantics related to the concept of the original surface.

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[659] Ibid., p. 168
[660] Ibid., pp. 172-174
[661] Ibid.
[662] Bertholon, 2000, Microsoft Excel file "IndexSO" on attached CD-ROM
[663] Ibid., p. 192

2.3.1.1.1 Emergence: late 19th century-1960s

At the end of the 19th century Rathgen, German scientist renowned for his discovery of x-rays, recognised that the ancient surface of an artefact could be preserved in the smooth patina. Rosenberg (1917), Danish Museum[664], is attributed as being, "…the first to extensively use the concept of the original surface" as he proposed the possible presence of original surfaces under some corrosion products and also suggested the use of markers from the environment (namely sand/quartz) to demarcate the original surface[665]. Of relevance to locating the modified original surface, Rosenberg noted the corrosion layers as being externally or internally relative to the original surface[666]. This relative positioning infers that he must have been aware of examples where he could locate the original surface. Research scientists, Fink and Eldridge, pursued ways of approaching the CPs and original surfaces of bronze artefacts and were sympathetic of conservation ethics that dictate the objective is not to *make like new*. In their 1925 report, as cited by Bertholon[667], "…bringing out details in design and yet not making the object appear as though it were of recent origin" was the approach to be respected. In spite of these philosophical considerations, initially Fink and Eldridge attempted to revert the artefact's oxides back to the metallic state. Plenderleith, via his landmark conservation handbook Conservation of Antiquities and Works of Art (1956)[668] concentrated on describing the "original form", not the "original surface", and did not specify if the latter was present or indeed recoverable[669].

2.3.1.1.2 Conceptualisation: 1960s-1980s

Jedrzejewska (1964) considered the original surface concept by focussing on bronzes and what she designated the "surface layer", discussing its properties, distribution, structure, composition and its cleavage properties (of relevance to physical cleaning)[670]. The application of new analytical instrumentation by scientists (Gettens, 1970) to corrosion product layers facilitated greater theorising about corrosion mechanisms and strata together with correlations with pre-abandonment

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[664] Ibid., p. 21
[665] Bertholon, 2001b, p . 168 & Bertholon, 2001c, p. 6
[666] Bertholon, 2001c, p. 6
[667] Ibid.
[668] Bertholon, 2000, p. 50
[669] Bertholon, 2001b, p. 168
[670] Ibid., pp. 168-169

artefact surfaces. Meanwhile, the cleaning practices by conservators (France-Lanlord, 1965; Organ, 1977) reflected the new perception that original surfaces remained within CP layers[671]. However, of notable relevance to the present research focussing on the ferrous metals of iron and low-carbon steel, Organ explicitly cites his perception that the original surface of iron does not exist, at least in its *trueness*:

> "I do not believe there is ever a true original surface preserved in rusted objects. Many of my colleagues in Europe, however, believe that there are and that they can find them. I am not convinced of this at all, although a lower layer of black oxide can usually be found"[672].

Exactly what Organ meant by a "*true* original surface" is unclear, but it is supposed that he implied at least one of the two following meanings, more probably the first:

1. Simply, the original surface had modified from a metallic state to a corrosion product state; or
2. The original surface could not be recreated or *sculpted* by inference (i.e. compared with adjacent surface levels of inlays[673]).

In this same publication Organ provides the basic and useful conceptual schematic cross-section of an incompletely corroded bronze artefact (Figure 2-46). He uses the diagram to demonstrate that the CP layers are both above and below the artefact's "shape". The diagram also shows the results of other possible conservation intervention options on the CP strata.

2.3.1.1.3 First definitions & extensive conceptual application: 1990s & onwards

The last two decades have witnessed a surge in activity on the original surface topic, largely driven by Bertholon with his work continuing the focus on archaeological metal artefacts. Importantly, this period is seen as one that helped properly define the precise terminology relating to original surfaces.

A broader definition from Bertholon and colleague Relier (1990) on any archaeological artefact (not necessarily metallic) was also given:

> "The original surface of an archaeological object is the limit between what make up the object (metallic parts and other mineral or organic parts) and the environment at the time of its abandonment"[674].

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[671] Ibid., p. 168

[672] Organ, 1977, p. 137

[673] Ibid., pp. 137-138

[674] Bertholon, 2001b, pp. 168-169

This definition has intentionally represented the original surface as "a non-material limit (or interface) between two layers," rather than a tangible material[675].

In Bertholon's doctoral thesis (2000) on "La limite de la surface d'origine des objets métalliques archéologiques, caractérisation, localisation et approche des mécanismes de conservation"[676], he coined revised definitions for the original surface in temporal and spatial terms:

> "The original surface is the surface of the metallic object at the time of its abandonment. The abandonment, voluntary or involuntary, marks the end of the anthropogenic phases of its existence before its discovery (e.g. excavation)."[677]
>
> "The original surface constitutes the volume starting from the interface with the abandonment environment until the lower limit of the metal zone, which differs to the core metal in composition, in physical-chemical properties or in metallurgical structure."[678]

The first definition clarifies the *point in time* that the artefact surface is classified as "original". Since the fabrication date does not account for changes to the artefact occurring during its useful life (i.e. evidence of human use that can be of historical significance) and during its burial period (i.e. when alterations were induced after its human interaction), the original surface is thus defined as the point in time when human contact was last made and burial environment alterations have not started: i.e. the moment of abandonment.

The second definition clarifies the *point in space* in the artefact where the surface is classified as "original". The original surface must therefore be at or just below the interface with the abandonment environment. The depth of the original surface has characteristics that can vary according to the artefact's inherent material nature (e.g. roughness, shine, colour, profile, thickness) at the time of abandonment. This second definition differed from the one made a decade earlier by Bertholon and Relier since this original surface was defined as possibly having a material volume as well as an abstract limit or interface[679].

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[675] Ibid., p. 168

[676] Bertholon, 2000

[677] Translated, courtesy of A-C. de Poulpiquet, from: "La surface d'origine est la surface de l'objet métallique lors de son abandon. L'abandon, volontaire ou involontaire, marque la fin des phases anthropiques de son existence avant sa découverte" (Bertholon, 2000, p. 217).

[678] Translated, courtesy of A-C. de Poulpiquet, from: "La surface d'origine constitue le volume partant de l'interface avec l'environnement d'abandon jusqu'à la limite inférieure de la zone du métal différente du métal de base en composition, en propriétés physico-chimiques ou en structure métallurgique" (Bertholon, 2000, p. 217).

[679] Bertholon, 2001b, p. 171

2.3.1.2 The limit of the original surface: the limitos

Bertholon required a third and ultimate definition to differentiate the previously defined *original surface* between the *surface of the modified artefact* that emerges after its abandonment period. After corrosion the original surface can be transformed forever. The *limit* (i.e. not necessarily the location or appearance) of this former original surface can at best be possibly located. Thus, the *limit of the original surface* was Bertholon's chosen term to describe this modified surface after corrosion. The *limit of the original surface* is a conceptual term that attempts to encompass a variety of modified original surfaces depending on the metal and environment. This definition takes into account that the original surface of metallic artefacts can alter its position and/or composition over time. The modified original surface now consisting of corrosion products can either be different in its aspect (e.g. colour) and profile/form (e.g. expansion or vertical displacement). However, surface features from the original surface, such as texture, can persist. For ease of reference the *limit of the original surface* will hereafter often be referred to as the *limitos*, as proposed by Bertholon[680].

2.3.1.2.1 Localisation of the limitos

Bertholon remarked that in spite of increased acceptance of the possible preservation of modified original surfaces (or the limitos), subsequent research activity, explicit and comprehensive evidence and rational published discussion was limited:

> "In most of the works mentioning the original surface, little is said about the ways it can be located among the corrosion stratigraphy; the original surface position is assumed but rarely argued"[681].

This significant *lacuna* in the metals conservation field appears to have driven the research motivation of Bertholon to pursue the area in a progressive rational manner that attempts to not only fill this gap in theoretical knowledge, but importantly, also in conservation practice.

Corrosion scientist, Turgoose (1989) stated some cautious optimism towards the feasibility of determining original features of artefacts:

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[680] Bertholon, 2000, p. 219

[681] Bertholon, 2001b, p. 169

> “Potentially it is possible to obtain information concerning the original shape and internal structure of metal artefacts. However, it is not to be expected that this will be possible for every object”[682].

Turgoose also stated that, “The possible preservation of some marker of the original surface has attracted considerable debate”[683].

Bertholon categorised the many features cited in the literature that were deemed by authors to be *indicative* or even *reveal* the original surface/limitos (Table 2-3).

	Features that act as “clues” to locate, or not, the original surface	**Features that act to “reveal” the original surface**
1.	Striking[684] surface profile	Decorations
2.	Striking[685] interface surface profile	
3.	Tool marks and use marks	
4.	Corrosion layer cohesion	
5.	Corrosion layer hardness	
6.	Compactness or porosity of corrosion layers	
7.	Compactness or density of the x-rays pictures	
8.	Cleavage and parting of corrosion layers	
9.	Physical properties of corrosion layers, crystal and metallurgical structures	
10.	Colour and shine	
11.	Chemical composition	
12.	Presence of metal core or metallic nodules	
13.	Presence of sand in corrosion layers	
14.	Presence of calcium carbonate in corrosion layers	
15.	Presence of organic materials or organisms	

Table 2-3 Summary of artefact features cited in the literature that are deemed indicative or indeed reveal the original surface[686]

These features that help localise the position of the limitos on corroded artefacts have been termed as *markers*[687]. Markers can be distinguishable by their material composition and structure, shape and appearance. It is important to see that most markers in Table 2-3 are considered only as “…*clues* to locate the original surface”. To exemplify this point, one “clue” particularly worthy of elaboration is “colours and shine”; qualities that are readily observable to a conservator and, like others, are open to proper use or misuse according to their interpretation. The application of colours alone to recognise specific corrosion product *species* (which might then be associated with the limitos) has been used by conservators in the past,

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[682] Turgoose, 1989, p. 30

[683] Ibid.

[684] It is presumed that *striking* is meant to imply *prominent* or *obvious*

[685] Ibid.

[686] Bertholon, 2001b, pp. 175-179

[687] Bertholon, 2004, p. 227

but is now considered unreliable[688]. For the case of archaeological wrought iron, the uncovering of the black layer by conservators has led to their assumption that it contains magnetite and to their subsequent conclusion that the limitos is present there[689]. Bertholon refers to the case of this black layer on terrestrial archaeological wrought iron:

> "The description of the corrosion form is far from being precise enough and the same for our knowledge of the limitos location. In fact the location of the limitos is not always the interface of this black layer with other layers."

Colours should only be used in conjunction with other properties (e.g. porosity, hardness) for identifying corrosion product *forms*[690] so as to be able to relate them with existing comparable corrosion forms that have had their limitos previously defined[691]. Notably, corrosion products can be arranged in CP mixtures, thus giving differing net colours according to the relative concentrations, varying particle sizes, shapes and refractive indices of the species present[692]. Manual, sensitive cleaning has been cited as potentially useful for determining tactile differences between corrosion product layers[693].

The exceptional marker listed in Table 2-3 that might be used alone to define the limitos is decorations. The inlaid decorations, on an excavated archaeological wrought iron artefact after selective corrosion product removal, testify the location of the limitos, which in this case has not only been converted into CPs, but has been vertically displaced; albeit in an irregular manner (Figure 2-47), as Bertholon recounts again for terrestrial archaeological wrought iron:

> "As the corrosion continues, the thickness of the corrosion layers increase. The formation of corrosion products under or within the layer of magnetite may cause swelling of the corrosion layers that contain the original surface. Therefore the original surface[694] is no longer at its original level. That is the reason why the original surface is not always flat and smooth as would have been expected on such objects"[695]

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[688] Bertholon, 2007b, pers. comm.

[689] Ibid.

[690] *forms* = "a combination of some corrosion strata or layers disposed in a specific corrosion structure" (Bertholon, 2007b, pers. comm.).

[691] Bertholon, 2007b, pers. comm.

[692] Cornell & Schwertmann, 2003, p. 131 & Elias et al., 2006, pp. 73-74 & Selwyn et al. 1999, p. 220

[693] Bertholon, 2001b, pp. 170-171

[694] Here *original surface* is meant to imply the *limitos*. Despite being defined earlier by Bertholon (2000) the term limitos was not used in this reference – perhaps an intentional avoidance of jargon in this more introductory paper written for material engineers.

[695] Bertholon, 2001a, p. 244

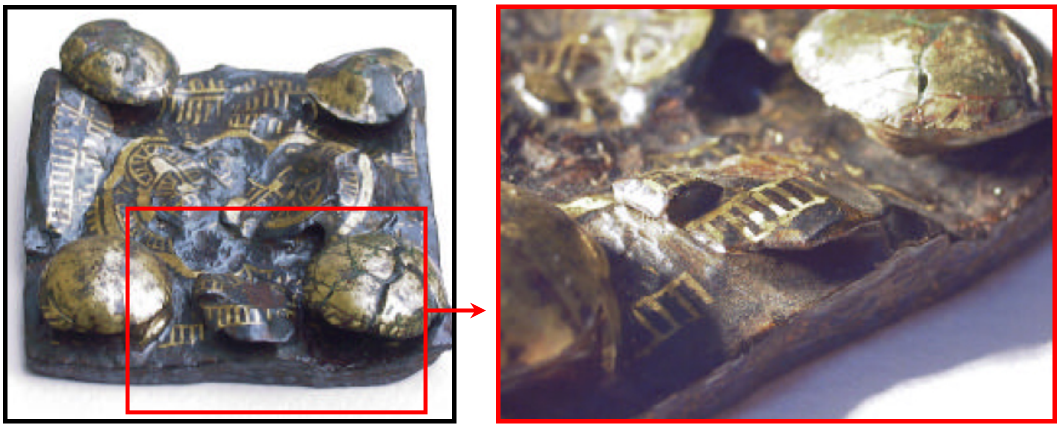

Figure 2-47 Left: Overall view of a Merovingien (5-8th century AD) wrought iron plate inlaid with brass[696]. Right: Detail demonstrating the vertical displacement of the corroded iron and contained brass.

The given example of a decorated ferrous archaeological artefact is made so as to clearly demonstrate, via the contrasting brass, the extent of surface displacement in a burial environment. Later, this research pursues identifying which markers on undecorated atmospherically corroded wrought ferrous metals could be useful for determining any limit of the original surface in that material-environment[697].

Markers have been classified according to their position relative to the limitos[698]:

- *Superior limitos marker*: such a corrosion stratum character indicates that the limit of the original surface is below the given corrosion stratum, but does not specify its exact location[699]. It is a relative marker[700];
- *Inferior limitos marker*: such a corrosion stratum character indicates that the limit of the original surface is above the given corrosion stratum, but does not specify its exact location[701]. It is a relative marker[702]; and
- *Corresponding limitos marker*: such a corrosion layer interface character indicates that the limit of the original surface corresponds to the given interface, definitively localising the limitos[703]. It is an absolute marker[704].

Superior limitos markers are materials exogenous to the artefact and are often a deposit of burial material such as sand in soil sediment[705, 706], which cannot penetrate the lower matrix of CPs and therefore remains superior to the limitos. The

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[696] Courtesy of Unité Municipale d'Archéologie de Saint-Denis (Bertholon, 2000, p. 220)
[697] Chapter 3 Experimental methods & materials, Chapter 4 Results & Chapter 5 Discussion
[698] Bertholon, 2000, p. 221
[699] Bertholon, 2004, p. 238
[700] Bertholon, 2000, p. 222
[701] Bertholon, 2004, p. 238
[702] Bertholon, 2000, p. 222
[703] Bertholon, 2004, p. 239
[704] Bertholon, 2000, p. 222
[705] Ibid.
[706] Bertholon, 2001b, p. 171

CPs permeate this environmental material forming a matrix referred to as the *transformed medium*, or TM (Figure 2-48). Figure 2-48 schematically shows the relative positions of superior and inferior limitos markers in a buried and corroded wrought ferrous metal. For the latter environment and metal it would normally be supposed that the limitos could be preserved at the interface of areas marked *dense product layer* (DPL) and the TM[707], or unusually in the case of this simplified schematic representation, the limitos could be within the DPL since the internal and external markers do not meet.

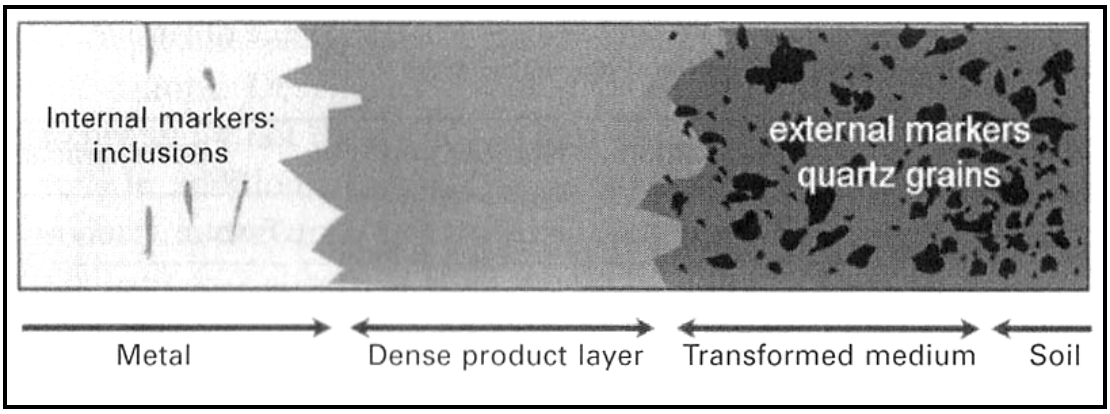

Figure 2-48 Schematic representation of internal and external marker locations on a wrought ferrous metal in a burial environment[708]

An example demonstrating the practical application of the theory of superior limitos markers is given in Figure 2-49 & Figure 2-50 where quartz markers on a formerly buried wrought iron artefact were used to delimit the corrosion products superior to the limitos during selective mechanical CP removal.

Figure 2-49 Left: Wrought iron axehead dating from the Middle Ages after terrestrial excavation with corrosion products fixed into sediment. Right: Same axehead after removal of sediment fixed with corrosion products[709]

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[707] Neff et al. 2004, p. 743
[708] Reguer et al, 2007, p. 174
[709] Crawford, 2003

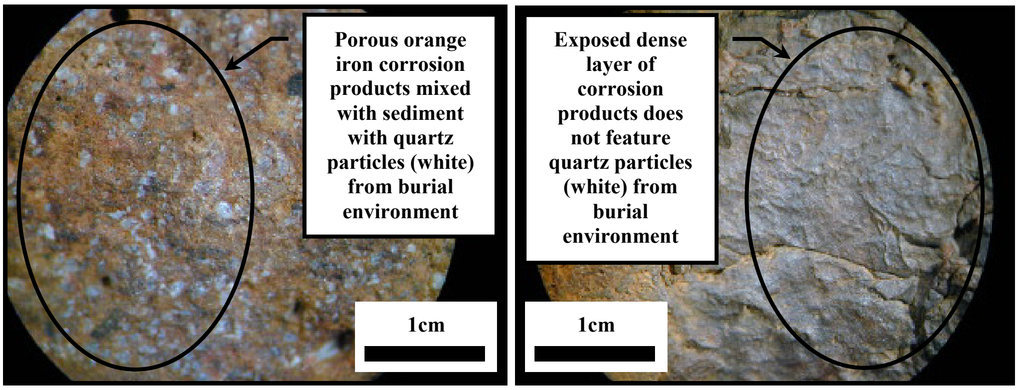

Figure 2-50 Details from during corrosion product removal stages of axehead in Figure 2-49. Left: Quartz sediment superior limitos markers in external corrosion product layers. Right: Determined limitos of axehead without quartz sediment superior limitos markers[710]

As later investigated[711], a potentially comparable superior limitos marker in an atmospheric exposure context might include particulate aerosols from the indoor or outdoor environment that are distinguishable from the corrosion products or other pollution.

Inferior limitos markers are materials endogenous to the artefact and can be metallurgical features[712] such as *ghost* grain microstructures (Figure 2-51) like dendrites, or resilient inclusions such as slag (Figure 2-52)[713]. Slag inclusions offer a superior permanence that makes them particularly useful (at least in cross-section) as inferior limitos markers. From the point of manufacture or even before, they are essentially composed of an oxidised thermodynamically stable state, an inertness that the ferrous metal seeks to attain since its moment of extraction by smelting.

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[710] Ibid.

[711] 4.1.2 Armour Hall aerosol pollutants: scanning electron microscopy-energy dispersive spectrometry & 4.1.3.2 Armour corrosion cross-section observations & analyses

[712] Bertholon, 2000, p. 222

[713] Ibid., p. 338

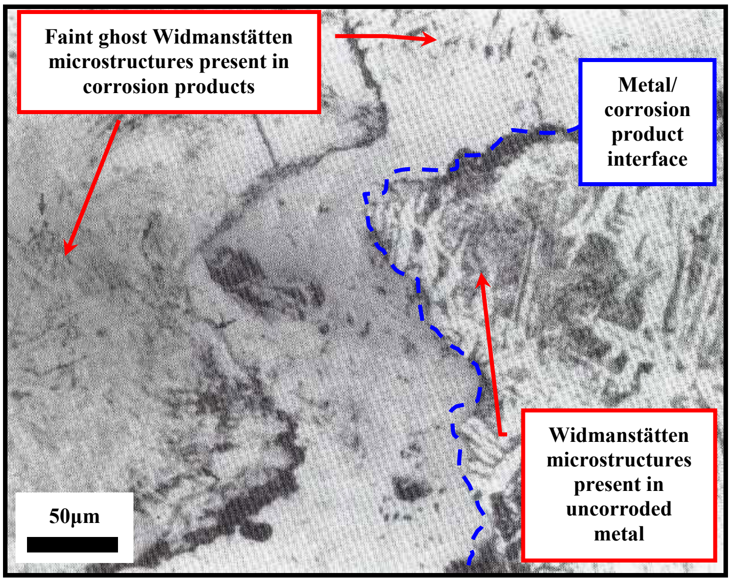

Figure 2-51 Widmanstätten microstructures present in metal[714] and corrosion products (200x)[715]

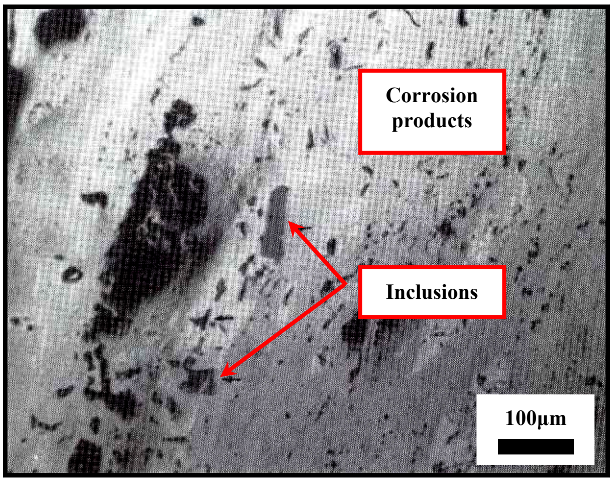

Figure 2-52 "Slag inclusions wholly surrounded by corrosion products (100x)"[716]

The corresponding limitos marker can be a surface or interface between CPs layers and can include physical or tactile properties such as cleavage between layers[717].

Bertholon has asserted the need to use a simultaneous combination of the superior, inferior and corresponding markers to more definitively determine the location of the limitos[718]. Figure 2-53 schematically demonstrates an ideal situation where the sequential presence of all these labelled limitos markers and their interfaces are noted through the CP stratigraphy. The ideal presence of superior limitos markers in layers 1 and 2 and at interface 1/2 of Figure 2-53 indicates that the

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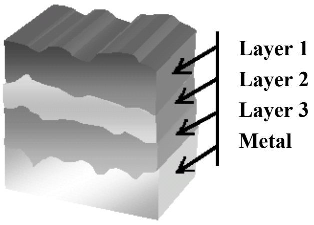
[714] Metal type not specified
[715] Scott, 1989, p. 13
[716] Ibid., p. 11
[717] Bertholon, 2000, p. 222 & Bertholon, 2001b, p. 171
[718] Bertholon, 2000, p. 224

limitos must be beneath these layers. Meanwhile, the presence of inferior limitos markers in layer 3 and the metal and at interface 3/metal indicates that the limitos must be above these layers. Finally, the presence of a corresponding limitos marker at the interface between layers 2 and 3 determines that the limitos is located in here[719]. If justifiable the upper two corrosion products layers and interface could then be removed to reveal the limit of the original surface in the CPs.

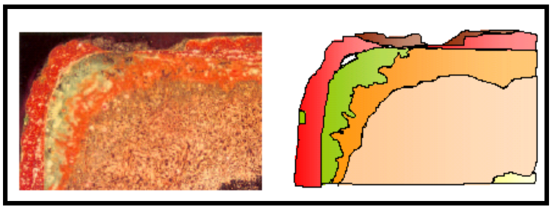


Corrosion product layers	**Superior limitos marker**	**Corresponding limitos marker**	**Inferior limitos marker**
Layer 1	*Present*	Absent	Absent
Interface 1/2	*Present*	Absent	Absent
Layer 2	*Present*	Absent	Absent
Interface 2/3	Absent	*Present*	Absent
Layer 3	Absent	Absent	*Present*
Interface 3/Metal	Absent	Absent	*Present*
Metal	Absent	Absent	*Present*

Figure 2-53 Conceptual localisation of the limitos using Bertholon's limitos marker system[720]

CORROSION/CORROSION PRODUCT STRATIGRAPHY TERMINOLOGY

Bertholon devised an annotation system, involving an extensive vocabulary, coding and framework for describing CP features and distribution, to effectively communicate between conservation professionals the corrosion strata observed on artefacts[721]. A simple introduction to the layout is given in Figure 2-54.



Sediment	**Corrosion product**	**Void**	**Corroded metal**	**Metal**
S	CP (1, 2, 3, 4)	V	CM	M

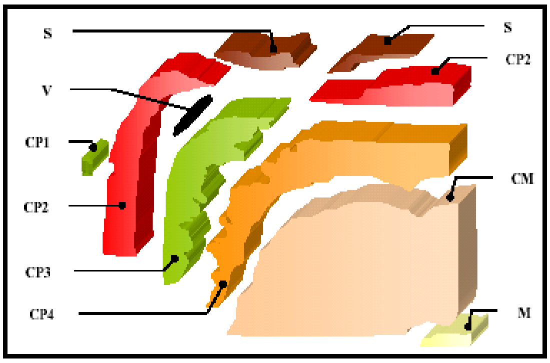


Figure 2-54 Cross-section of corroded Chinese bronze with schematic representation of same area with labelling of the various strata[722]

2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour

It is necessary to define a meaning of the limitos that is appropriate the context of the mid 16th-mid 17th century northern Italian-style plate munition armour.

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[719] Ibid.
[720] Ibid., p. 223
[721] Ibid., p. 307
[722] Ibid., p. 240

To do this it is essential to relate the previously established historical events that have caused the armour's transformations through time[723].

There is common recognition that the long-term accessibility of armour on display in museums has led to centuries of cleaning and restorations that have removed much of the possibly remaining original surfaces[724] and added new materials[725]. As such, the previously described history of the Palace Armoury munition armour collection[726] includes important periods of the armour's existence that have dictated the possible survival of any original surfaces from manufacture and other features from use.

According to Bertholon:

> "The history of most artefacts can be divided into four main periods of time: the creation period (the object's fabrication or production), the use period, the abandonment period (with or without burial, in various environments) and the post-excavation period"[727],

…while each period can further be subdivided into phases relating to events in each period. Bertholon considers that variations of this framework are possible[728] and it is here that we consider its adaptation to the case of the Palace Armoury munition armour.

For the munition armour, the *creation period* (mid 16th-mid 17th century) is clearly the purported time of manufacture in northern Italy. This period was divided into many successive phases: from mineral ore smelting, forge work, surface finishing and assembly[729].

After a transitional transportation period to Malta, the armour began its >100 to 200-year *dynamic use period* (mid 16th-mid 17th century to the mid 18th century) during its existence in active service as worn by troops of the Order of St John. The armour most probably experienced one or more cycles of alert, preparation, battle, maintenance (e.g. repair and polishing) and relative peace when complacency slackened maintenance procedures[730, 731]. This use period is specified with its dynamic status so as to differentiate it from its subsequent static display use

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[723] Ibid, p. 199

[724] Starley, 2006, p. 2 & Smith, 2006, p. 55

[725] Starley, 2006, p. 4

[726] 2.1.3 History of the Palace Armoury's 16th-17th century northern Italian-style munition armour

[727] Bertholon, 2007a, p. 31

[728] Ibid.

[729] 2.1.2 Munition armour fabrication: materials & techniques

[730] Spiteri, 2003, pp. 11-12

[731] 2.1.3.1 Mid 16th century-1798, Order of St John: functional, symbolic & obsolete arsenal

(effectively a continued symbolic use, if not practically functional)[732]. It is reminded that the munition armour reached dynamic obsolescence in the time of the Order, and thus the Knights were the first to put it on display as trophies of arms (circa mid 17th onwards[733]). The Order therefore probably polished them for aesthetic reasons; in a similar manner as during their service life.

The so-called *abandonment period* and *post-excavation period* classifications are more applicable to archaeologically interred artefacts and are not as easily adaptable to historical armour[734], since the armour were under permanent custodianship and accessibility. The *abandonment period* and *post-excavation period* classifications are adapted here and respectively retermed as the *obsolescence & neglect period* and the *static use (display) & storage period*.

The *obsolescence & neglect period* for the munition armour is proposed to reflect the *abandonment period* since the armour's dynamic use was eventually discontinued due to irreparable battle-damage or later technological obsolescence as previously described[735]. The obsolescence of the armour permitted its static use on display as trophies of arms and other wall arrangements. It is supposed that most/all heavily damaged munition armour would not have been displayed. The *static use (display) & storage period* is proposed to represent the *post-excavation period* since interest in the armour would have included phases of restoration, display/exhibition and possible study, as previously described[736].

Compared with archaeological artefacts, historical artefacts, as exemplified here by the munition armour, do not necessarily have sequential *use*, *abandonment* and *post-excavation periods*. Instead these historical armour, treated as an ensemble or collection due to their imprecisely documented individual histories, have an almost simultaneous commencement of the two latter periods of their history. Indeed, the *obsolescence & neglect period* and the *static use (display) & storage period* started around the same period: circa mid 17th-mid 18th century onwards depending on the age and use of the particular munition armour. Numerous accounts have previously been cited when the static display armour suffered from neglect as it

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[732] 2.1.3.1.2 1604-1798, Order of St John: Palace Armoury

[733] 2.1.3.1.2 1604-1798, Order of St John: Palace Armoury

[734] Hockey & Shearman, 2006, p. 31

[735] 2.1.3.1 Mid 16th century-1798, Order of St John: functional, symbolic & obsolete arsenal

[736] 2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques, 2.1.3.3 1964, Independence: remnants of a colonial history & 2.1.3.4 Recent history: museum typological collection & tourist site

repetitively fell out of favour due to other priorities and attractions[737]. The armour's static use (display) was thus marked by times of neglect and inattention resulting in corrosion. When attention was cyclically cast back onto the munition armour on display their corrosion products were removed[738].

More recently, similar to when the munition armour were in a supplementary storage room (as per Sieur de Bachelier's 1679 account)[739] during their *dynamic use period* in functional service, those armour deemed superfluous, or possibly unfit for continued display, have been stored in the reserve collection rather than on display.

So what do the implications of historical accessibility with cyclical interventions mean for the original surfaces and limits of the original surfaces of the mid 16th-mid 17th century northern Italian-style plate munition armour at the Palace Armoury?

Since the *static use (display) and storage period* has lasted up to 350 years, featuring numerous documented corrosion episodes and corrosion product removal campaigns, it cannot generally be expected that much of the original surfaces (as for the uncorroded areas) or the limits of the original surfaces (as for the corroded, corrosion product covered areas) dating to the armour's Italian manufacture or its last dynamic service (or static display use) by the Order of St John have survived.

Inaccessible surfaces such as those found between lames or under rivets might have evaded periodic cleaning campaigns. If uncorroded these localised areas could therefore possibly retain some original surfaces, or potentially some limits of the original surfaces, if corroded. Any unaltered remaining original surfaces of the armour therefore have to be defined as the surfaces on the munition armour that have been historically untouched, inaccessible and/or uncorroded i.e. metallic. Since armour are riveted together, making them impossible to non-destructively disassemble, and since the far majority of the plate surface areas are accessible, this study focuses on these exposed and accessible areas with corrosion products. Meanwhile, the potential limitos of the armour must be defined as the surfaces or interfaces found in any CPs. This potential limitos area might represent an original surface, perhaps from manufacture or use in service or from display, that has been modified by corrosion processes. More likely and relevant to these historical

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[737] 2.1.3 History of the Palace Armoury's 16th-17th century northern Italian-style munition armour

[738] 2.1.3.1 Mid 16th century-1798, Order of St John: functional, symbolic & obsolete arsenal & 2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques

[739] 2.1.3.1.2 1604-1798, Order of St John: Palace Armoury

artefacts, the limitos might correspond to the CPs formed from a metallic surface that was previously created by any one of a number of CP cleaning interventions that occurred during its *obsolescence & neglect* and *static use (display) & storage periods*[740].

The last intervention on the majority of munition armour was typically 30 or more years ago. This intervention is most likely to have featured the removal of a failed protective coating, practically all CPs from affected areas and the reapplication of a protective coating[741]. As a result, any possibly determined limitos corrosion products might come either from these more recently created metallic surfaces or from any other time since fabrication. The imprecise dating of the munition armour's current surfaces is attributable to the lack of documentation.

After the last corrosion product removal intervention on the armour, corrosion on certain areas has ensued. The unanswered questions remain:

1. How have any limits of the original surfaces on the munition armour been formed by corrosion since the time of its last CP removal intervention?
2. And have these corrosion processes preserved any evidence of the limitos from the former metallic surfaces?

These are the principal practical questions this dissertation seeks to answer.

2.4 INTERNATIONAL MUNITION ARMOUR CONSERVATION PHILOSOPHY & PRACTICE: LITERATURE REVIEW & LABORATORY QUESTIONNAIRE

The international literature on armour conservation and restoration is reviewed here. No attempt is made to detail the maintenance of armour when it was still in use since this point has been addressed in detail specifically for the case of the Palace Armoury munition armour[742]. Notably the researched literature is rather limited in number and scope, and even less so when detailing approaches to corrosion products.

To supplement and update the scarce information provided by the literature, a questionnaire focussing on CPs and munition armour conservation, was designed by

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[740] Vella et al., 2005b, p. 318

[741] Stroud, 2006-2007, pers. comm.

[742] 2.1.3 History of the Palace Armoury's 16th-17th century northern Italian-style munition armour

the present author and disseminated to international armour conservation workshops and laboratories.

2.4.1 LITERATURE REVIEW ON FERROUS ARMOUR CORROSION PRODUCTS

The researched literature can be broadly categorised into discussions about the issues and philosophies concerning corrosion products on armour, and secondly into case studies that report the technical procedures employed towards these CPs. These case studies also reflect upon the reasoning behind the approaches taken.

As with many aspects of conservation practice in general, over recent years CP removal approaches have changed considerably for armour (and arms). More scientifically informed preventive and interventive actions have become the preferred and performed treatment options by later generations of conservation professionals. The developing approaches towards CPs on archaeological metal artefacts over the last century preceded this sea change[743]. Of note is the recent amount of examination, documentation, and analytical work used to inform conservation proposals on historical artefacts including armour[744]. Interventive approaches towards armour have generally become more conservative. Previously, ex-servicemen or artisans undertook the caretaking of arms and armour[745]. These personnel bore a traditional restoration approach that removed all CPs. "The aim of restoration is now to physically support or enhance the legibility of an object without attempting to 'recreate' the original appearance"[746].

2.4.1.1 Philosophy

Stipulated ethics form the common foundation stone of contemporary western conservation practice. Various national and international codes of conduct and/or ethical guidelines are now available for conservation professionals to follow[747]. Of particular note and contention with some ethical guidelines is the issue of *reversibility* and that any intervention should ideally be reversible[748]. The guidelines

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[743] Bertholon, 2001b & Bertholon, 2001c

[744] Hockey & Shearman 2006, p. 33

[745] Ibid., p. 31

[746] Ibid., p. 33

[747] ECCO, 2002, http://www.ecco-eu.info/matador/eccosite/ecco_contents.php?doc_id=170 – accessed 03/02/2007 UKIC, n.d., http://sul3.stanford.edu:10001/ukic/ukic_ethics.doc – accessed 03/02/2007 & AIC, 2004, http://aic.stanford.edu/pubs/ethics.html#six – accessed 03/02/2007

[748] "The Conservator-Restorer shall strive to use only products, materials and procedures which, according to the current level of knowledge, will not harm the cultural heritage, the

offer a dramatic contrast with times past, but difficulties remain in their interpretation and application as they depend on the genre of artefact, its condition, its environment and its use. In the context of armour conservation, Smith has raised the inherent irreversibility of any corrosion product removal[749]. Meanwhile, Oddy, more experienced in the archaeological domain concurs, "…removal of corrosion products is certainly irreversible and certainly compromises the integrity of the object"[750]. Edge suggests that the removal of CPs falls neither within the categories of conservation nor restoration activities[751]. Edge contends that "…insensitively 'cleaned' or inaccurately 'restored'…" work on armour risks the loss of decoration, evidence of construction or use and the original form[752]. Furthermore, Edge feels that over-cleaning of CPs from armour "…in an effort to make an object shiny and visually appealing…" and the removal of metal around corrosion pits in an attempt to restore armour "...to an appearance it never actually had…" is a kind of restoration that is "…of course completely unacceptable"[753].

Figure 2-55 shows how an undocumented former cleaning process appears to have extracted the majority of CPs from the corrosion pits on a piece of Palace Armoury munition armour.

Figure 2-55 Detail of Palace Armoury munition armour tasset with corroded surface area largely devoid of corrosion products[754]

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environment or people. The action itself and the materials used should not interfere, if at all possible, with any future examination, treatment or analysis. They should also be compatible with the materials of the cultural heritage and be as easily and completely reversible as possible" (ECCO, 2002, Article 9).

[749] Smith, 1998, p. 7

[750] Oddy, 1999, p. 3

[751] Edge, 1994, p. 153

[752] Ibid., p. 154

[753] Ibid., pp. 154-155

[754] Crawford, 2007a, p. 31 permission courtesy of E. Magro Conti

Despite such criticism of how *not* to perform corrosion product removal, suggested appropriate levels of CP removal are rarely discussed. Smith details the extent of his cleaning undertaken:

> "By carefully removing the corrosion products it is often possible to recover a reasonably smooth clean surface though dotted with black corrosion spots" that "…can, in many cases, recover some of the 'original' surface surviving *between* the corrosion pits"[755].

Smith highlights that the so-called original surface is highly unlikely to be that related to the "…working lifetime (i.e. period of use) of the object… as all objects will have been extensively cleaned throughout the centuries"[756]; an important point that was previously outlined and is later discussed[757].

The literature's discussion about armour CPs and any need for preserving original surfaces largely centres around the requirement to avoid damaging surface treatments such as browning, gilding, etching, or features like stamps[758] that are mostly on the armour outer surfaces. While, Manella mentions intentionally keeping "…la patine intérieure d'origine…" in his cleaning treatment of an armour[759]. Undecorated outer metal surfaces, such as those in this study, are less frequently mentioned[760], let alone discussed in much detail. Smith states, "Of course many pieces of armour are just plain iron or steel but even here care must be exercised to preserve any surviving surface"[761]. It is unclear whether Smith is referring to a surviving metal surface or a surviving modified surface retained in the CPs. But from his earlier statements about the "…'original' surface surviving *between* the corrosion *pits*"[762, 763], it is assumed he means the unmodified metal surface. It seems then that, according to Smith, modified original surfaces *within* corrosion *products* are not sought after in CPs. But, also according to Smith, the retention of some corrosion products can provide some other information since they, "…can indicate the presence, or absence, of other materials or parts of the object and the pattern of

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[755] Smith, 2006, p. 54

[756] Ibid., p. 55

[757] 2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour & 4.2.3 Armour analogues, limitos application: corrosion product removal to the limitos

[758] Smith, 2006, pp. 53-54, Edge, 1994, p. 155, Hockey & Shearman 2006, p. 33 & Paulitsch, 1992, p. 385

[759] Mannela, 1998, p. 187

[760] Smith, 2006, p. 54 & Hockey & Shearman 2006, p. 33

[761] Smith, 2006, p. 54

[762] Ibid.

[763] As cited previously at greater length in quote referenced by footnote 755.

pitting can indicate past use"[764] and might retain indications of former display characteristics[765].

Aesthetics are deemed by Smith to be of importance to the motivations behind the amount of CPs removed from armour:

> "Basically arms and armour were originally intended to have bright smooth surfaces which reflected light strongly. Thorough and total cleaning of the surface of an iron object, that is removing all the corrosion products from every corrosion pit, results in a dull grey surface which does not reflect the light."[766]

Reference is made in the literature to the possible adverse effects of keeping CPs on armour. In order to develop informed restoration procedures, Biasini and Cristoferi used cross-sections of samples taken from 16th-17th century Italian armour to study the corrosion morphology. They found, via energy dispersive spectrometry, deep pits filled with corrosion products featuring chlorine concentrated at the metal/CP interface[767]. This discovery, and the presence of akaganéite (the ferrous CP containing chlorides[768]) detected by XRD on extracted CP samples influenced their cleaning approach. Biasini and Cristoferi realised that:

> "…the corrosion product layer does not have any protective effect on the underlying metal; on the contrary the corrosion process is very active, especially inside pits and cavities, and can compromise the good condition of the object"[769].

As a result, the restoration method had,

> "…the aim of removing the corrosion products as completely as possible, without damaging the original surface… One cannot think however, of removing every trace of corrosion because this would compromise the surface of the ancient artefact"[770].

In their approach, it is clear that even though the corrosion products were recognised as harbouring corrosive species, which would have been desirable to entirely extract, their physical cleaning approach was tempered by respecting the adjacent uncorroded metal. Notably their account does not conceive CPs as possibly containing modified original surfaces and the extent of cleaning appears to be quite subjective as a balance between aesthetics and minimising metal surface damage was sought.

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[764] Smith, 1999, p. 7
[765] Smith, 2006, p. 52
[766] Ibid. p. 54
[767] Biasini & Cristoferi, 1995, p. 254
[768] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products
[769] Biasini & Cristoferi, 1995, p. 255
[770] Ibid.

The last justification cited for removing corrosion products from armour is the prevention of degradation caused by CPs on organic components like leather strapping that assembles the armour[771].

In favour of some corrosion product retention, Smith states that armour from unburied environments[772] that still have "…black corrosion spots…" after cleaning can be kept at moderate relative humidities (<50%RH); even with the retention of these corrosion products[773]. The reasoning behind this practice is not stated, but it is assumed that Smith makes the distinction between archaeological and historical armour due to the greater reactivity of archaeological CPs caused generally by a more concentrated presence of soluble salts. Such salts are more likely to be found in burial conditions. Edge also mentions black corrosion products that "…are often completely stable"[774]. No mention was made of other coloured corrosion products (e.g. ochres).

Regarding corrosion product morphologies, Smith is not the only author to cite corrosion of armour with pitting[775]. Biasini and Cristoferi also determined the presence of deep pitting as the corrosion morphology present on their armour[776].

Of relevance to stability and the previously cited material-environment system[777], Paulitsch's summary of a conservation treatment on an engraved and painted 16th century armour, describes that his level of corrosion product removal is dictated by the future environmental conditions of the armour. When the conditions in the exhibition space and reserves are suitable for the armour, Paulitsch asserts that it is not necessary to remove all CPs. Like Biasini and Cristoferi, Paulitsch states a preference to not remove all CPs since doing so can damage the metal and provides new contact surfaces for corrosion to occur[778].

2.4.1.2 Practice

The practices followed to achieve the armour conservation or restoration approaches of the past were generally by physical (abrasion) and/or chemical (dissolution/chelating) means, but today physical approaches predominate. The

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[771] Smith, 2006, p. 51
[772] i.e. historical, not archaeological
[773] Smith, 2006, pp. 54-55
[774] Edge, 1994, p. 155
[775] Smith, 2006, p. 54
[776] Biasini & Cristoferi, 1995, p. 254
[777] Figure 2-44
[778] Paulitsch, 1992, p. 384, translation courtesy of S. Michael

similar physical and chemical sensitivity and intimate positioning between a metal and its various possible corrosion products makes the selective treatment of one of these materials a challenging task to achieve without undesirable effects on the other.

According to the literature, alternative approaches to ferrous corrosion products, as applied to some other genres of metal artefacts, were determined not to be suitable for armour. Use of chemical conversions (e.g. tannic or phosphoric acid) and more complex treatments such as electrochemical reduction or electrolysis or innovative techniques such as CP removal via laser were not found in the armour literature.

Only one reference was made to corrosion product removal assisted by magnification: Paulitsch performed local cleaning of CPs from a painted armour by scalpel under binocular microscope[779].

Whichever technique is applied, its success is cited to be determined by the experience of knowing how to apply it and knowing how far to go before stopping[780].

2.4.1.2.1 Physical removal

Due to their controllability, manual and mechanical means of physically abrading away corrosion products with tools and materials are now the preferred means of CP removal from armour[781]. Smith cited a variety of manual tools including hard-steel scrapers, fine abrasive papers, wire wool and abrasive pastes that would be selected according to the corrosion and condition of the armour[782].

Biasini and Cristoferi used air-abrasive equipment using glass microspheres (50-100μm) at 0.5-1.5kgcm^{-2} to remove ferrous corrosion products from armour since they felt it was the most selective means[783]. Rotating brushes were deemed inappropriate since they either damaged the metal surface, because they were not localised enough, or "…exerted too much force for the areas with light surface corrosion products and not enough force in those areas with deeper corrosion"[784]. A dental descaler was used for reduction of thicker layers[785].

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[779] Ibid., p. 383, translation courtesy of S. Michael.

[780] Smith, 2006, p. 54

[781] Hockey & Shearman 2006, p. 33, Smith, 2006, p. 54, Biasini & Cristoferi, 1995, p. 254 & Mannela, 1998, p. 187

[782] Smith, 2006, p. 54

[783] Biasini & Cristoferi, 1995, p. 255

[784] Ibid., p. 254

[785] Ibid., pp. 254-255

Paulitsch also performed removal of heavy CPs using air-abrasive with walnut shell and glass microspheres at 1 bar pressure. He also cites the use of sandpaper[786].

2.4.1.2.2 Chemical removal

The full immersion of artefacts in chemical solutions (e.g. corrosive acids) has mostly been discontinued. And if any chemical treatments are justifiable then they are performed on a localised basis[787]. Incorrectly applied or unsupervised corrosion product removal via chemical means can overclean a surface by emptying corrosion pits and also etch any remaining metal[788].

2.4.1.3 Literature review summary & conclusions

From this literature review an observation and a prime conclusion can be drawn regarding corrosion products on armour and original surfaces. They are that:

1. The literature is predominantly concerned with decorated armour, not the mainly undecorated armour of this study; and
2. The literature discusses broader issues of ethical interest, especially the irreversible nature of CP removal procedures and there are many reasons for justifying the removal or justifying the preservation of corrosion products on armour, but there does not seem to be any perception that traces of modified original surfaces can exist in corrosion products. Instead it seems that original forms are recreated by inference with adjacent uncorroded surfaces.

2.4.2 LABORATORY QUESTIONNAIRE ON FERROUS ARMOUR CORROSION PRODUCTS

As outlined in the literature review on armour conservation-restoration[789], information relevant to this research dissertation is inadequate and thereby prompted the need for a complementary information source. Practical and philosophical literature covering ferrous armour conservation has been published, but specific approaches to their corrosion products are not very detailed. The information given is often in the context of individual case studies where technical procedures and underlying rationales for a specific armour conservation treatment are presented. Not only does published information rarely cover the simpler relatively undecorated munition armour, it also does not attempt to assess international trends in munition armour conservation. It was deemed appropriate to gain a current and simultaneous

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[786] Paulitsch, 1992, p. 383, translation courtesy of S. Michael

[787] This citation refers to archaeological arms and armour (Hockey & Shearman 2006, p. 33).

[788] Hockey & Shearman 2006, p. 33

[789] 2.4.1 Literature review on ferrous armour corrosion products

overview on armour conservation trends from a wide variety of armour conservation professionals at an international level via a questionnaire.

The delivered questionnaire and the quantified respondent results with analyses are respectively in Appendix A[790] & Appendix B[791], while a largely qualitative summary of the questionnaire findings is presented next.

2.4.2.1 Laboratory questionnaire summary & conclusions

Results compiled from the "Ferrous Armour Corrosion Product Questionnaire" outlined the prevailing international trends in approaching ferrous corrosion products on plain undecorated ferrous armour. The wide international representation of countries (14) by the reasonable number of respondents (24), of whom the majority (70.8%) have an armour specific professional background in predominantly armour (and arms) collecting organisations, is deemed to be sufficient to draw fairly confident conclusions from the philosophy and practices surveyed. Before concluding on the questionnaire's seven main findings, it is important to reiterate here that *trends were surveyed*, and clarify that the aim was not to attempt to document all the individual approaches and influencing conditions possible for each and every individual armour: an immeasurable and impossible task for any research methodology. Consideration of the individuality of each armour's *use* (dynamic and static) and environment (climatic, fiscal), past and future, is recognised by some respondents who elected to emphasise these important aspects.

The questionnaire's seven main conclusions are as follows:

1. Corrosion product removal is unanimously the approach *most commonly* taken to ferrous CPs on undecorated ferrous munition armour. So-called CP conversion with chemicals is still practiced as an option, but to a much lesser degree. Unlike some approaches taken to archaeological ferrous artefacts, leaving CPs in place on armour and not intervening is uncommon practice: only one respondent did this and this was on armour inner surfaces only;
2. The level of corrosion product removal was less decisive, but a clear majority take a relatively conservative approach by "Removing red-brown corrosion products, leaving most/all dark grey/black corrosion products in/above the corrosion pits". Completely stripping a surface of CPs appears to be largely, but not entirely, a discontinued practice;

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[790] Appendix A – Laboratory questionnaire on ferrous armour corrosion products: delivered questionnaire

[791] Appendix B – Laboratory questionnaire on ferrous armour corrosion products: results & analyses

3. The factors for determining which corrosion products are removed are ranked here in order of receiving the respondents' highest degrees of influence:

    i. Corrosion prevention;
    ii. Armour surface information; and
    iii. Aesthetics.

i. Corrosion prevention

Corrosion prevention is the highest-rated factor influencing which corrosion products are removed. The majority of respondents did not make any differentiation between any possible effects of different CP types (colours, forms) and any specific influences on *which* CPs are removed and kept. Armour conservation professionals do not seem to make a distinction between ferrous CP species/phases, although specific questions on this topic would be required to confirm or disprove this supposition. One respondent specified, "Active corrosion may be removed, but on the whole the objects are coated in wax and put into controlled environments and left". It is unclear how "active corrosion" can "be removed" and it is thought that this refers to the weeping corrosion products that are symptomatic of active corrosion rather than the root cause of corrosion. Preventive conservation practices were not surveyed, but these approaches must obviously play an integrated overall role in limiting the corrosion evolution-corrosion product removal cycle. Unsurprisingly suggesting that these preventive conservation practices do indeed exist in parallel, a respondent specified that the philosophy was: "Minimal intervention" and the "Aim: protection and preventive conservation".

ii. Armour surface information

The second highest-rated factor that influences which corrosion products are removed is "Armour surface information". For this factor, the CP removal procedure is cited as being used to reveal original surface features, while at the same time the approach taken is tempered by not removing too much material since this could paradoxically remove the features that the procedure endeavours to reveal. It is unclear if this information is preserved in the CPs or in the adjacent uncorroded metal. This is of high relevance to the research dissertation since there were no cited examples of CPs retaining such former surface information. This either suggests that the phenomenon does not exist, or at least is not perceived to exist, on atmospherically corroded ferrous armour. A specific question is required to elicit these data.

iii. Aesthetics

The third highest-rated factor that influences which corrosion products are removed is "Aesthetics". Here the motivation for selecting which CPs are removed is mentioned as improving, "as much as possible", the uniformity or evenness of the surface. Making improvements is a *relative & subjective* concept where boundaries are defined by the *before treatment* condition and the subsequent level of cleaning performed, and of course by human opinion. Approaching full restoration by attempting to obtain a new state for aesthetic purposes is not possible without removing all CPs and the far majority do not attempt this practice.

In practice, these three influential factors would not be treated in isolation and the overall decision to select which CPs to be removed would be determined by making a simultaneous assessment of these and other factors. One respondent aptly specified, "You have to do a balance that is dependent on the factors in play at the time - in conservation the only golden rule is that there is no golden rule!"

4. Concerning the types of equipment/materials used to remove corrosion products, a wide variety is in use. The most commonly cited categories of equipment/materials in use are summarised below in order, and are notably all physical and manual methods[792]:

   i. Handheld implements (91.7%);
   ii. Steelwool handtools (66.7%); and
   iii. Abrasive pastes liquids (58.3%).

   Some respondents who have preferences for *manual*, rather than *automated* (i.e. mechanical) physical tools, made this distinction, "However I do almost all my work now using abrasive methods by hand so that the process is highly controlled", "I have, in the past, used a range of polishing machinery, but I would not advocate that approach now at all", and "…always manual (no motor, etc)".

   The strong preference for physically based equipment/materials is further made clear when compared to chemically based equipment/materials in use (acid solutions (29.2%), chelating agents (16.7%)). One respondent specified their unambiguous perception of a specific acid:

   > "One of the worst treatments used on armour which has caused irreparable damage in many European collections has been the application of acid, most commonly phosphoric acid. Mechanical methods I believe are much superior because the conservator has control of the level of corrosion removal. Acid is not very controllable, destroys the total surface of the object-often leaving the surface dead."

   The same respondent preceded this statement however with an important point that is in fact applicable irrespective of any technique, physical or chemical:

   > "Often it is not so much the type of abrasive/technique used, but the actual knowledge/method & skill of the conservator that is the defining factor in producing a sympathetic treatment or a damaging one".

   More complex and innovative techniques (e.g. laser, local electrolysis) have been tested by several respondents, but it appears that the simpler traditional techniques remain in predominant use; probably logically since they are perceived, at least until present, the most effective and affordable. Laser and local electrolysis are in continued use by one respondent each.

5. Before corrosion product removal procedures, protective coatings are in the majority removed and done so with solvents.

6. The finding that the majority (70.0%) of respondents polish adjacent metallic surfaces after corrosion product removal (in order to homogenise the overall appearance) has implications for the long-term conservation of armour surfaces. The depletion of metal from armour is in these cases a two- or possibly three-stage process that would vary in severity on a case-by-case basis:

   i. Before treatment intervention: corrosion of metal by oxidation,
   ii. During treatment intervention: erosion of metal by polishing, and
   iii. After treatment intervention: corrosion or repassivation of previously passivated metal by oxidation.

   It appears from the data that the treatment techniques applied to remove CPs from munition armour could be, at the outset, insufficiently localised to avoid such initial metal contact and metal surface polishing. The level of assisted magnification, if any, could have beneficial implications on insufficiently localised CP removal procedures.

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[792] Although non-physical actions of constituents in proprietary abrasive pastes/liquids are open to question.

7. Respondents unanimously remove corrosion product residues from surfaces after CP removal procedures, while they all use solvents and fibre/cloths to achieve this. This practice is believed to occur so as to improve the corrosion resistance of a surface, and coverage of any coating; although motivations were not specifically asked.

2.5 SUMMARY TO HISTORICAL, SCIENTIFIC & CONSERVATION CONTEXT

Chapter 2 has demonstrated that the mid 16th-mid 17th century northern Italian-style wrought ferrous munition armour has experienced a diverse history, assuming roles that have implicated its corrosion and removal of subsequent corrosion products. Current philosophical and practical approaches to CPs on metal artefacts including armour have evolved to account for many of the considerations required in a contemporary museum context. Of significance is the current development of the conservation of modified original surfaces in corrosion products on archaeological artefacts.

The following chapters seek to experimentally ascertain if it is indeed possible to determine the presence of modified original surfaces in the corrosion products of Palace Armoury munition armour and on atmospherically corroded materials similar to this armour. Any traces of the limitos could activate international discussion regarding the approaches taken to armour conservation and possibly other historical ferrous artefacts.

In other words, is there a surviving limit of the original surface on atmospherically exposed mid-late Early Modern Period wrought iron and low-carbon steel armour artefacts? If there is a limitos, how does one determine its location? And lastly, how does one practically reveal it?

3 EXPERIMENTAL METHODS & MATERIALS

The experimental methods and materials employed to determine and reveal any limits of the original surfaces present in the corrosion products on the mid 16th-mid 17th century[793] northern Italian-style wrought plate munition armour at the Palace Armoury are presented in this chapter.

The application of these methods was divided between the two major components of the experimental investigations: firstly, during non-invasive[794] or non-destructive[795] investigations on *authentic munition armour* artefacts and secondly, during extensive invasive[796] investigations performed on *armour analogues* designed to simulate the characteristics of the authentic armour.

3.1 OVERVIEW OF THE EXPERIMENTAL FRAMEWORK

Case studies on the authentic munition armour were used to define the metal, corrosion and corrosion product morphologies present on these cultural heritage artefacts. Defining the CP morphologies and their extent of development relative to the uncorroded metal was integral to determining their association, and determining how the limit of the original surface[797] might be preserved within these CPs. The metal surfaces did not require much further investigation since their identification was apparent from their metallic appearance, but the surfaces' influence on corrosion morphologies was noted. The determination of evidence for the former original metal surfaces in the corrosion products on armour was the focus of this research.

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[793] i.e. mid-late Early Modern Period

[794] Non-invasive investigations are defined as where investigations do not cause any artefact alterations.

[795] Non-destructive investigations are defined as where investigations cause alterations to a surface site or sample, but permit reinvestigation since the site/sample is not destroyed.

[796] Invasive investigations are defined as where investigations cause irreversible alterations. Invasive investigations might be wholly destructive of a surface or sample or they might be non-destructive; thereby permitting reinvestigation.

[797] As a reminder, the *limitos* (limit of the original surface) can be considered here as the last metallic surface that has become modified over time during corrosion processes. The limitos manifests itself as metal corrosion products, not metal. The surfaces of uncorroded metal can be considered as the *original surface* according to the definitions given in 2.3.1 What is the original surface & why determine its presence?

The methodology to study the authentic munition armour began on a global level during a macroscopic, *in-situ* corrosion condition survey of the collection displayed in the Armour Hall at the Palace Armoury. This macro perspective of a large quantity of armour enabled determining the major trends in CP surface distribution and morphologies. Next, surfaces on a smaller selection of munition armour were observed in the laboratory at macro- and microscopic levels. From these armour, three extracted and embedded samples (made available from previous studies) were selected for non-destructive cross-section investigations. Each of these samples provenanced munition armour featuring surfaces hypothesised to represent differing historical interventions or non-interventions. The stratigraphy of this local area on each armour could then be determined in terms of its metal core, inclusions, corrosion products, protective coatings and surface pollution. Amongst these stratigraphies, the localisation of the limitos on several zones of interest (ZOIs) for each sample was then proposed.

The case studies of authentic munition armour informed the subsequent manufacture of the simulated armour: the *armour analogues*, otherwise also simply referred to as *coupons*. These contemporary analogues, made from similar but non-identical materials to the armour, were prepared to create the corrosion product morphologies simulating those previously observed on the authentic armour.

Since the research question revolves around the interventive, destructive and therefore totally irreversible conservation-restoration practice of metal corrosion product removal, it was anticipated that the experimental questions would require quantities of suitable experimental material to destructively investigate. Conservation ethics dictate the requirement to minimise testing on authentic artefacts, especially when at an initial research phase. In this way, destructive research interventions on authentic armour during these preliminary investigations would be avoided while accepting the limitations of indirect comparability.

The armour analogues were destructively used for a series of three principal and consecutive objectives, which were to: determine the presence, or indeed absence, of the limitos; investigate current corrosion product removal practice at the Palace Armoury; and finally demonstrate the level of selective CP removal required to respect the previously determined limitos (if any).

3.2 PALACE ARMOURY ENVIRONMENT, MUNITION ARMOUR & CORROSION PRODUCT CASE STUDIES: NON-INVASIVE & NON-DESTRUCTIVE INVESTIGATIONS

The methodologies followed, the justification for the selection criteria, and the various levels and means of observation and analyses made on the Palace Armoury environment and munition armour, are presented here.

The main objectives of the laboratory investigations of the Palace Armoury's environmental pollution and corroded munition armour were to:

1. Assess the potential use of environmental pollution as a superior limitos marker in the armour corrosion products;
2. Propose potential corresponding and inferior limitos markers in the armour corrosion products; and
3. Interpret the development of corrosion products on the armour surfaces and their internal structures, so as to better simulate representative corrosion on the armour analogues.

As a consequence, of particular interest was the presence of: particulate aerosols within the PA environment and the armour's corrosion products; the distribution of the armour's corrosion product morphology types and their extent of development; and the armour's metallurgical features.

The genre of undecorated munition armour of the Palace Armoury, once worn by the field troops of the Order of St John, was chosen since it represents the majority of armour in the collection that requires attention in terms of corrosion product prevalence. This genre conveniently provides a less complicated material construction being less decorated (i.e. no gilding, bluing, browning, limited etching etc) than the Knights' or Grand Masters' field or parade armour[798].

In this research, focus was made to determining the limitos of the outer armour surfaces. The armour surfaces are defined by their orientation to the former wearer: *outer* surfaces are those that face outwards when worn and are visible, while *inner* surfaces are those that face towards the body of the wearer. Identifying the inner and outer surfaces has important implications towards interpreting the respective surface histories of the armour. Armour have historically been appreciated for their aesthetic appeal whether in active service or static display. As a result the

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[798] Opportunely starting with fewer construction variables reduces the complexities introduced by these materials and can be more easily simulated by contemporary analogues. In this way the studies on the munition armour and their analogues could form the basis of future studies on decorated historical ferrous artefacts, which feature this greater number of variables.

outer surfaces, rightly or wrongly, have been and continue to be, given greater attention to maintain their observed appearance[799].

3.2.1 ARMOUR HALL WALL DISPLAY: *IN-SITU* CORROSION SURVEY

The objective of the Palace Armoury Armour Hall wall display *in-situ* corrosion survey was to gain an understanding of how the environment has been affecting the corrosion of this munition armour. Of particular interest was correlating environmental factors and corrosion protection coatings with the presence, morphologies, distribution and extent of ferrous corrosion and corrosion products.

Wall-displayed armour were inspected via ladder access while still *in-situ* on the wall in the PA[800]. Handling was prohibited and low ambient illumination was supplemented by a headlamp. This impractical documentation scenario limited possibilities to study the surfaces in detail, but provided an opportunity to gain a macro perspective of the corrosion condition of all the munition armour hanging as wall panoplies in the Armour Hall. In addition to recording the evident environmental effects later outlined[801], the particular armour component and constituent materials including protective coatings were noted. The inner surfaces of the armour were not documented primarily due to their inaccessibility and also because this research focuses on outer surfaces. The total number of armour assemblages investigated in this way was 119. The corresponding Arms Hall featured a similar quantity, which was only viewed from the floor and not photographed, as it was deemed unnecessary to effectively duplicate the survey.

3.2.2 ARMOUR HALL AEROSOL POLLUTANTS: SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY (SEM-EDS)

To further investigate which, if any, of the materials deposited at the Palace Armoury could act as potential superior limitos markers it was necessary to explore the immediate atmospheric environment so as to identify their presence and gain a

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[799] The attention given to the armour inner surfaces appears to have included repeated application (over existing materials) of coatings for protection and has resulted in a multi-layered organic stratigraphy with metal corrosion products and possible high temperature oxides remaining from fabrication (Degrigny et al., 2007b, p. 38). This complex stratigraphy can be considered a time capsule of valuable information (e.g. fabrication, maintenance) warranting a larger collaborative conservation research project between metals and paintings conservators. Nonetheless, the inner armour surfaces were not entirely overlooked in this research since they formed a part of these three-dimensional artefacts and because they sometimes provided useful comparisons with the information provided by the outer surfaces.

[800] 3.5.1.1 *In-situ* macrophotography

[801] 4.1.1 Armour Hall wall display: *in-situ* corrosion survey

better understanding of the potential interactions of these artefacts' material-environment system. An understanding of the PA's environmental composition would facilitate interpretation of materials unassociated with the metal and corrosion products.

To gain an overview of the elements comprising the aerosol pollutants at the Palace Armoury, particles actually deposited on experimentally exposed surfaces other than armour were observed and elementally analysed with SEM-EDS by Vella[802]. The present author interpreted these data. These particles had been manually collected (by means of SEM copper backed adhesive tape) from exposed and previously clean experimental surfaces located adjacent to armour on a wall display in the Armour Hall. The samples were analysed without a preparatory carbon coating, as this was unnecessary for conductivity of these thin layers already mounted on the conductive copper tape. It is important to note that point analyses were not performed randomly; indeed they aimed to identify the range of materials present, not their statistical quantities. A range of morphologies was analysed.

To confidently use exogenous materials as superior limitos markers, they should ideally not be inherently present in the artefact material itself, making attribution between the two sources possible. If such an ideal superior limitos marker is not found, then discrimination between materials of similar elemental composition might still be possible, via justification with major differences in morphology or quantity. Since such material characterisation is here based on SEM-EDS[803], morphology and elemental composition can only be used, as opposed to the more definitive structural characterisation methods such as x-ray diffractometry or Raman spectroscopy.

3.2.3 AUTHENTIC MUNITION ARMOUR CORROSION/CORROSION PRODUCT MORPHOLOGIES: LABORATORY INVESTIGATIONS OF SURFACES & STRUCTURES

The methodologies followed to perform the various laboratory investigations on the surfaces and cross-sections of the authentic munition armour are subsequently presented here. Justification of the instruments and approaches followed and sample selection criterion is emphasised.

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[802] Vella, 2006

[803] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

3.2.3.1 Armour surface observations

Laboratory examinations of a selection of these munition armour was required for a greater understanding of the corrosion and corrosion products, since superior illumination, magnification and surface cleanliness greatly facilitated observation, circumstances that were unachievable *in-situ* at the Palace Armoury.

3.2.3.1.1 Munition armour selection

Ten armour, mostly formerly displayed on the Palace Armoury walls, but now stored in the PA reserve collection, were made available for more detailed study in the laboratory[804]. Images of the ten available armour for selection are provided in Appendix C[805].

From the ten armour available, six were selected for further *surface* documentation. They were chosen for their representativeness of the majority of the munition armour collection. Since there is no current inventory of the Palace Armoury collection, the selection was based on the data and experiences obtained from the *in-situ* observation of the armour on the wall displays and a previous inspection of the collection held in the reserve collection.

Four of these available armour[806] were excluded from the surface observation selection since the armour surfaces were either:

- Covered (i.e. PA RC 29 Tasset & PA RC 88 Full arm) with black paint. The opaque black paint limited observation of any possible underlying metallic surfaces and the type and extent of corrosion product morphologies. Transparent coatings were preferred since the paint might have had a possibly different, even if minor, effect on the corrosion surface properties and moreover since transparent coatings permitted greater surface observations without destructive probing of these coating layers. More significantly, armour with transparent coatings such as the yellow-green polyurethane[807] varnish were deemed more representative of the collection[808]; or
- Decorated largely with acid-etching (i.e. PA RC 20 Cannon & PA RC 25 Gorget). Etched armour, as previously explained[809], represent non-munition armour materials and present more complex material structures not under study here.

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[804] The curators of the Palace Armoury made these armour available for the Promet project and subsequently for this research dissertation.

[805] Appendix C – Ten Palace Armoury armour available for laboratory study

[806] Appendix C – Ten Palace Armoury armour available for laboratory study

[807] Lemasson et al., 2004, p. 10

[808] 4.1.1 Armour Hall wall display: *in-situ* corrosion survey

[809] 3.2 Palace Armoury environment, munition armour & corrosion product case studies: non-invasive & non-destructive investigations

Although these four artefacts had altered surfaces, their metal cores were still of potential interest; thus they were not totally excluded from enquiries concerning the metal composition.

3.2.3.1.2 Armour surface macrophotography & photomicroscopy

Photographic documentation of the surfaces of the six representative munition armour began on a macroscopic scale[810] by looking globally at the corrosion product distribution over the varying orientations of the armour surfaces. The objective of performing armour surface *macrophotography* was to assist documentation of trends in the types, distribution and extent of corrosion products present on the surfaces of the six selected armour.

The armour available for laboratory examination had mostly previously been cleaned of its particulate layer, thereby allowing unobstructed inspection of the surface CPs. This unobscured observation (together with greater illumination and magnification) further confirmed the probable causes (assumed from the Palace Armoury *in-situ* wall display examination) why corrosion had ensued on certain surfaces yet was almost non-existent on other surfaces. Further to this confirmation, close-up surface inspections, still on a macro scale, enabled classifying a possible evolution or transition of the types of corrosion product morphologies on the metal surfaces. The differing CP morphologies and their extent of development supported a hypothetical proposition of how the CPs possibly evolved and even interacted to provoke different morphologies over time.

The objective of the subsequently performed *photomicroscopy*[811] was to complement the macro perspective observations by determining how these normally macro-viewed surfaces are microscopically constructed. The surface morphology of the metal, not only the CPs, was deemed to be of interest since this would provide a reference point of the surface conditions before corrosion. and possibly determine how the metal surface influences, or not, the development/morphology of the corrosion products. Such surfaces might then be mimicked in the CPs and therefore behave as a corresponding limitos marker (i.e. indications of the limitos in corrosion products)[812]. Information from these microscopic surface investigations would also

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[810] 3.5.1.2 Laboratory macrophotography

[811] 3.5.1.3 Laboratory photomicroscopy

[812] 2.3.1.2.1 Localisation of the limitos

provide the basis for the informed manufactured surface finishing of the armour analogues.

3.2.3.2 Armour corrosion cross-section observations & analyses

The main aim of the cross-section observation and analysis of the armour was to determine if, by this unique internal core perspective, evidence exists within the corrosion products for diagnostically defining the limitos. It was anticipated that some exogenous materials (i.e. pollution, coatings) might be used as superior limitos markers. Simultaneously, some endogenous materials (i.e. metal, inclusions) might be used as inferior limitos markers. Lastly, any corresponding limitos markers, the definitive marker, were sought. All of these markers were expected to help highlight the boundary between the CPs containing the superior and inferior limitos markers.

As a secondary objective, the cross-section observation assisted in understanding the nature of the CP stratigraphy in order to enable the more accurate reproduction of the armour analogues.

Characterising corrosion products and their pollutants would also assist in determining the likely stability of these CP layers and their reactivity towards the metal. While it was not the research focus, the implications these corrosion product layers have on the underlying supporting metal are paramount when considering their material conservation implications, and also the attitudes held by museum staff towards ferrous CPs.

While the primary research question was to diagnostically determine the limits of the original surfaces, it was also useful to consider the type of any evidence found. This consideration was necessary in order to see if such micrometric-scaled evidence[813] could then later be extrapolated, and applied, onto the scales of a macroscopic artefact. In other words:

> How could any evidence, which is found on such a small scale and in cross-section, be useful to a conservator who is attempting to reveal, via a plan perspective, the original surface limits from a complete armour artefact with a coating and corrosion products?

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[813] As given by optical microscopy, micro-Raman spectroscopy, scanning electron microscopy-energy dispersive spectrometry

3.2.3.2.1 Armour cross-section sample selection

To facilitate the subsurface assessment of the armour, one cross-section[814] from each of the ten pieces of Palace Armoury armour was made available for this study[815]. To prepare a shortlist of candidate samples for further study, the results from previously published studies[816] and project reports[817] (predominantly using SEM-EDS) of these armour samples by Vella et al. were used in conjunction with the present author's preliminary application of reflected optical microscopy (standard optical and metallographic microscopes[818]). To focus these studies on a more feasible quantity, a selection of three from these ten armour and corresponding cross-sections was made.

A summary of the ten armour's characteristics, and more particularly the characteristics of their accompanying cross-sections, are given in Appendix D[819]. Particular reference is given to the representativeness of the samples and the armour, especially their corrosion and corrosion products. Again, the presence of paint layers and decorative etching precluded four of these armour from being selected[820].

All the armour sample extraction locations were previously decided with curatorial consultation so as to minimise the impact of such invasive sampling[821]. Mainly due to the concurrence between visible outer surfaces and those featuring corrosion products, it was not possible to obtain samples from these aesthetically prominent surfaces. These prominent surfaces are of more promising research potential due to their representiveness of the bulk material and the surface conditions not always found at the armour edge. Sampling from damaged areas of armour was elected for the minority of the armour. Despite localised damage possibly making a sample unrepresentative of the remaining armour and collection, one such sample was chosen since the highly developed corrosion and retained corrosion products were deemed of high investigative potential.

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[814] Cross-sections previously created during the Promet research project were reused for the current research.

[815] 3.2.3.1.1 Munition armour selection

[816] Vella et al., 2004 & Vella et al., 2005b

[817] Vella & Degrigny, 2005b

[818] 3.5.1.3 Laboratory photomicroscopy

[819] Appendix D – Ten Palace Armoury armour and cross-section samples: comparative summary

[820] 3.2.3.1.1 Munition armour selection

[821] Degrigny et al., 2007b, p. 36

The small number and localised nature of the cross-sections from the numerous and multi-component pieces of armour makes claiming full statistical representativeness impossible. Due to the heterogeneities inherently introduced by the wrought ferrous plate manufacture technology[822], homogeneity of composition between separate plates or across individual plates is not assumed. Nonetheless, these samples provided indispensable insights into the armour's internal composition and condition.

Generally, the extracted samples contained the metal core with corrosion products, organic coatings and surface pollution. The investigative potential of both the sample and corresponding armour were influential on the sample selection criteria. Also, the influence of the specific variant of wrought ferrous metal (i.e. iron or steel) on CP formation, and its possible effect on any limitos markers and the limitos position, was seen to be of potential investigative interest.

Images of the three armour, PA RC 166, PA 316 and PA 329, selected for further investigations in cross-section, are given in Figure 3-1.

PA RC 166 Pauldron (part) **PA 316 Pauldron** **PA 329 Backplate**

Figure 3-1 The three munition armour accompanying the cross-section samples selected for further laboratory study[823]

As an extract of Appendix D – Ten Palace Armoury armour and cross-section samples: comparative summary, Table 3-1 provides a comparison of the attributes of each of the three chosen armour, and their corresponding samples; in terms of representativeness of the originating artefact itself and also the Palace Armoury collection.

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[822] 2.1.2 Munition armour fabrication: materials & techniques

[823] (Crawford in) Vella et al., 2005a, pp. 8, 10

	Palace Armoury ID no. & date		**PA RC 166 – 1600-1650**	**PA 316 – ca. 1570**	**PA 329 – ca. 1570**
	Armour component name		**Pauldron (part, proper right?)**	**Pauldron (proper left)**	**Backplate**
Armour macroscopic examinations	**Whole armour corrosion description: typology, extent and distribution**	**Outer surface**	Highly developed general surface CPs throughout	Moderately developed general CPs throughout oblique surfaces & highly developed filiform corrosion throughout oblique surfaces	Moderately developed general CPs throughout oblique surfaces & highly developed filiform corrosion throughout oblique surfaces
		Inner surface	Highly developed general surface CPs throughout	Highly developed general surface CPs throughout	Moderately developed general surface CPs throughout
	Armour sample site description: corrosion typology and extent (surface assessment only), between lames, damaged edge, etc.	**Outer surface**	Highly developed general surface CPs	Not observable: between lames	Mildly corroded surfaces with no CPs evident
		Inner surface	Highly developed general surface CPs	Highly developed general surface CPs	Moderately developed general surface CPs
	Number of lames & sampling location notes		One lame from one. Physically damaged edge.	One lame from nine. Edge between dynamic lames	One lame from two. Physically damaged edge
	Representativeness of artefact		Yes, in respect to corrosion typology and extent. No, in respect to damaged edge	Yes, in respect to corrosion typlogy and extent. Determinable for inner surface only	Outer – Yes, in respect to surfaces exhibiting pitting but few CPs. No, in respect to corrosion typologies and extent of corrosion. Inner surface – Yes, in respect to corrosion typology and extent
	Representativeness of collection		No, in respect to physically damaged and highly corroded state with no adjacent metallic areas	Yes	Yes
Armour sample microscopic examinations	**Metal type & microstructure**		Ferrite[824]	Ferrite with carbides[825]	Widmanstätten ferrite-pearlite[826]
	Corrosion products (CPs) observable by optical microscope	**Outer surface**	Present	Present	Present in partly emptied pits
		Inner surface	Present	Present	Present

Table 3-1 Attributes of the metal and corrosion products comprising the three munition armour and corresponding samples selected for further study

The key cross-section sample selection prerequisite was the presence and extent of corrosion and/or corrosion products. As indicated by the armour surface

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[824] Vella et al. 2004, p. 223 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[825] Ibid., p. 227 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[826] Ibid., p. 224 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

conditions of PA RC 166, PA 316 and PA 329, and their respective extracted samples (Table 3-1), the selected armour most probably had non-identical histories. That is to say their present day condition (i.e. presence or absence of corrosion pits and/or corrosion products) suggested a variety of information indicating their histories might be retrieved from each sample cross-section and associated armour surface. The potential contribution of each sample for these studies varies according to the amount of CPs remaining. A request for resampling of new sites featuring greater corrosion and CP prevalence was considered in order to acquire samples more suited to this experimental question. This was decided against however due to its inherently invasive nature.

The proportions of the previously determined[827] microstructures of the eight[828] remaining munition armour (i.e. 3 iron, 37.5% & 5 steel, 62.5% steel) were used to determine a proportionally representative sample of three (one iron, 33.3% & two steel, 66.7%) cross-sections.

The chosen ferritic armour was PA RC 166 (Appendix E[829]). Although it would not eventually be possible to use a single-phased ferritic iron for the armour analogue material, it was deemed appropriate to investigate the possibility of any corrosion product strata differences between iron and steels; especially in terms of the limitos. In turn, two *steels* of differing microstructures (ferrite with carbides, Pauldron PA 316 (Appendix E[830]); and ferrite-pearlite, Backplate PA 329 (Appendix E[831]) were selected to indicate possible corrosion differences between varying steel microstructures[832].

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[827] Vella et al., p. 230

[828] The etched armour (PA RC 20 Cannon & PA RC 25 Gorget) were excluded since they are not considered munition armour (Figure 2-5 Left: Northern Italian-style etched Knight's Armour (circa 1570-1580) Right: Northern Italian Pisan style gilt parade armour of Grand Master Verdelin (circa 1580)).

[829] Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[830] Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[831] Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[832] 2.2.2.3.5 Ferrous metal type

3.2.3.2.2 Armour cross-section sampling site surface macrophotography & photomicroscopy

The plan surfaces adjacent to the sampling site were recorded via macrophotography[833] and photomicroscopy[834]. The purpose of retrospectively recording the magnified appearance of the surfaces adjacent to the cross-sections' sampling sites was to enable a comparison with the subsurface condition of the subsequently observed cross-sections. When faced with surfaces of similar aspect, that do not have the benefit of a complementary cross-section observation, it might be possible to assume cautious preliminary assessments about a possible range of conditions to expect inside an armour's corrosion products. Inspecting the sampling site would also aid greater understanding of how its provenance from the specific location on the armour artefact might have affected its current internal condition.

3.2.3.2.3 Armour cross-section sample preparation

The samples were previously extracted and embedded by Vella et al. for metallographic[835] and subsequent corrosion morphology[836] studies[837].

Upon receipt of the three samples by the current author, minor pitting and superficial corrosion products on the metal cross-section were removed by polishing with 2400 and 4000 grit silicon carbide paper for 20-30 seconds each. White spirit was used as a polishing lubricant to avoid flash rusting and/or dissolving the thicker coating system that covered two of the samples and their CPs. Between investigations, samples were stored in sealed boxes desiccated with dry silica gel to limit corrosion reactivation.

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[833] 3.5.1.2 Laboratory macrophotography

[834] 3.5.1.3 Laboratory photomicroscopy

[835] Vella et al., 2004

[836] Vella et al., 2005b

[837] The procedure is stated to involve manual cutting from the armour with a jeweller's saw and embedding in Buehlers Epoplast epoxy resin (Vella et al. 2004, p. 221). It was noted that the corrosion product layers on PA RC 166 "…might have been disturbed during cutting/embedding procedure" (Vella et al., 2005b, p . 319). The embedded samples were ground and polished with 100-200-300-400-600-1000 grit silicon carbide paper on a specimen preparation wheel. Finally 3µm and 1µm diamond pastes were used to achieve a higher polish. These samples had previously been acid-etched for metallography, but were subsequently repolished for the preliminary studies of corrosion morphology (Vella et al., 2005b, p. 320).

3.2.3.2.4 Armour cross-section optical & metallographic photomicroscopy

Photomicroscopy[838] performed on the cross-sections was used to make preliminary observations of the various features of the sample stratigraphies resolvable at the low magnifications offered by these instruments. This enabled selection of zones of interest specifically appropriate for the investigations. Zones of interest were principally those regions that exhibited corrosion products.

Generally the samples were first surveyed at low magnifications (standard optical: 40x / metallographic: 64x) to gain an overview and context of the various features. Then higher magnifications (100/128x-200/256x) were used to further inspect zones of interest.

3.2.3.2.5 Armour cross-section scanning electron microscopy-energy dispersive spectrometry

To bridge the optical and metallographic microscope observations of the armour cross-sections low magnification (25-100x) observation with the scanning electron microscope[839] were performed first. A general indication of the applied detectors is given later[840]. Then using the higher magnification (200-2000x) and elemental characterisation capabilities of the SEM-EDS, the followed methodology correlated morphological and elemental compositional qualities occurring within the corrosion product layers or metal. Consistent boundaries (or interfaces) between the various features were sought in order to document any possible evidence for the limit of the original surface. Complementary to this, the absence or presence of superior or inferior limitos markers[841] was sought to assist the limitos determination on the armour.

3.2.3.2.6 Armour cross-section Raman micro-spectroscopy

It was anticipated that the Raman micro-spectroscopy [842], performed abroad by a second party[843], could provide information on the composition and distribution of the corrosion product species, or at least the majority phases (i.e. single or mixed

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[838] 3.5.1.3 Laboratory photomicroscopy

[839] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[840] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[841] Materials respectively exogenous or endogenous to the artefact, as per 2.3.1.2.1 Localisation of the limitos

[842] 3.5.3 Raman micro-spectroscopy

[843] Ms Judith Monnier, Laboratoire Pierre Süe, CEA (Commissariat Energie Atomique) Saclay, France

CPs). The distribution of CPs, vertical from the surface layers to the uncorroded metal, was of interest since this is the perspective the conservator has, when approaching armour.

The zones of interest corresponded with those investigated with the SEM-EDS; facilitating complementarity of investigation techniques.

It was via Raman micro-spectroscopy that indications regarding the possible activity or inactivity of these CPs on further corrosion of the metal could be made.

3.2.4 AUTHENTIC MUNITION ARMOUR CORROSION PRODUCT REMOVAL: THE PALACE ARMOURY TECHNIQUE

The current author made a request to the Palace Armoury curators to document the current corrosion product removal procedure being practiced on their munition armour. The CP removal approach on armour pending treatment was observed and documented.

One rationale behind documenting the armour cleaning process was to enable making an assessment of the comparability of the performed CP removal approaches subsequently applied to the armour analogues. The surface area of armour analogues later given to the Palace Armoury conservation personnel[844] was required to be small (2 x 2.5cm) to facilitate their subsequent examination on the various microscope stages. Such a small size might not favour comparable conduct that could occur with larger armour. Also it was suspected that corrosion product removal procedures between authentic armour and armour analogues might become incomparable if the respective coatings and CPs did not respond similarly to cleaning techniques. In this way any possible resulting differences in approaches to the analogues could be assessed for their significance.

The firsthand witnessing of the Palace Armoury's munition armour routine corrosion product removal practice also supported the information provided by the PA in their contribution to the Ferrous Armour Corrosion Product Questionnaire[845].

Prior to meeting for the documentation of the cleaning procedure in the PA conservation laboratory, the broad research rationale behind documenting the CP removal was outlined. Three backplates, formerly on wall display, had been selected

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[844] 3.3.2.3.2 Armour analogues, Palace Armoury technique: current armour corrosion product removal practice & 4.2.1.2.1 Summary of armour analogue corrosion cross-section investigations results

[845] Appendix A – Laboratory questionnaire on ferrous armour corrosion products: delivered questionnaire & Appendix B – Laboratory questionnaire on ferrous armour corrosion products: results & analyses

in collaboration with the Palace Armoury Curator from a collection pending treatment. The armour represented three relative degrees of CP development (Figure 3-2). A fourth, more heavily corroded backplate was available for selection, however this corrosion was deemed to not be representative of the greater munition armour collection (as established by the PA *in-situ* corrosion survey[846]).

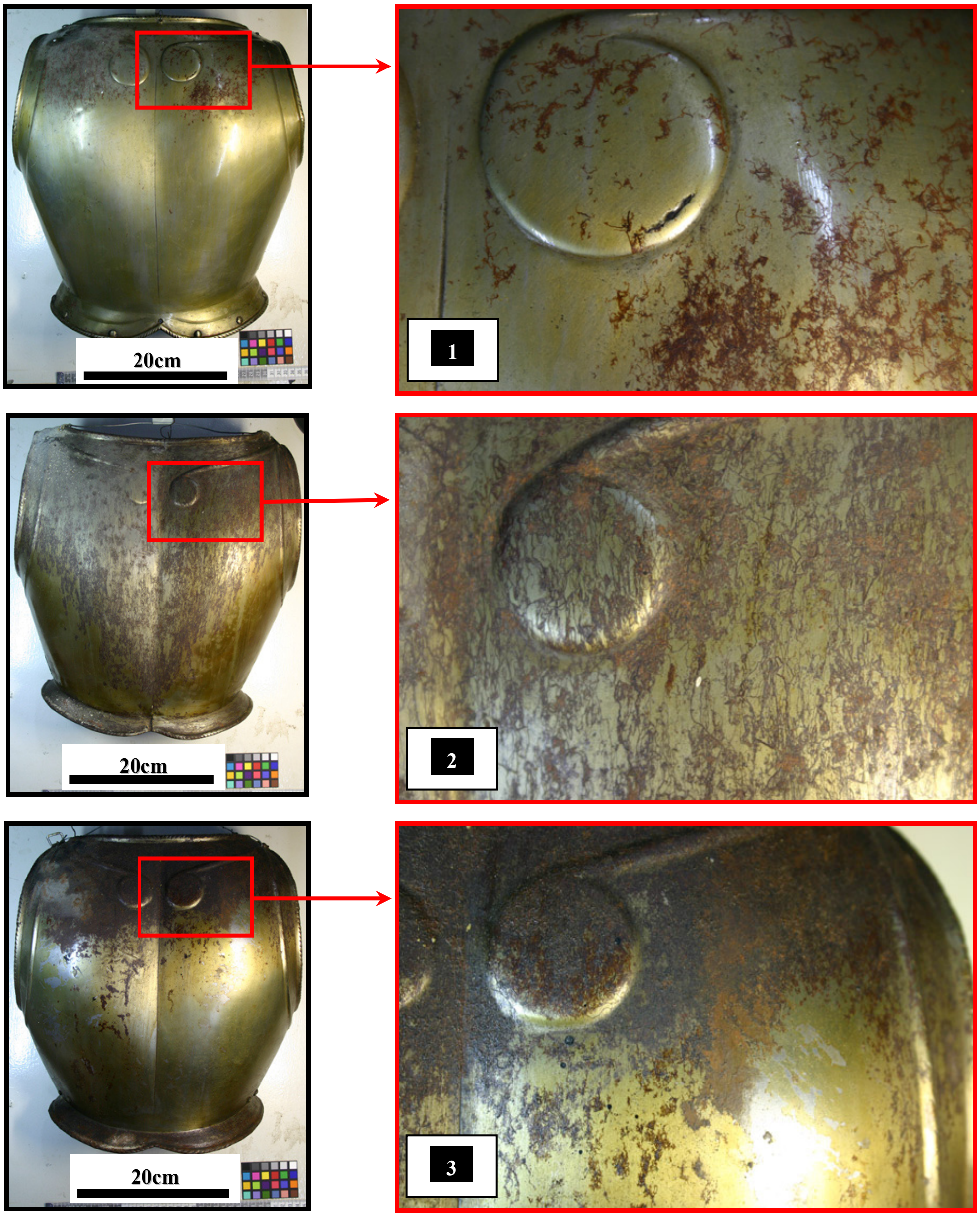

Figure 3-2 Three backplate armour selected to be representative of the corrosion extent on the wall displays

The armour with the least corrosion development (Figure 3-2, image 1) was selected to observe the Palace Armoury's cleaning technique since it was expected that it would be representative of the amount of corrosion realistically possible to later create in the laboratory on the armour analogues. It was not expected that the

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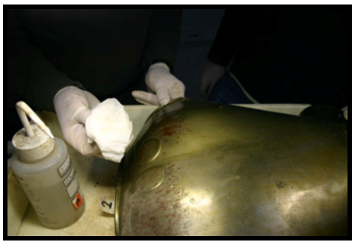
[846] 4.1.1 Armour Hall wall display: *in-situ* corrosion survey

armour analogues would have enough time to corrode as much as the third, and possibly second, corrosion extent classifications. A temporary vignette was selected for corrosion product removal and would form a comparative reference to the uncleaned areas on this symmetrically corroded armour.

The corrosion product removal technique only attended to the outer armour surface. Divided into the following stages, they were all performed manually and progressed downwards through the strata. The stated objective of the PA munition armour cleaning procedure is to "…treat it like a disease and to remove as much corrosion products as possible"[847]. However not all rust is removed for practical reasons since, "No brush or tool can take the rust in the pores of the metal out"[848]. Remarks by the Palace Armoury staff member describing the intention behind the performed actions are quoted below through the procedure:

1. Particle removal
    a. Loose particulate matter on surfaces was removed by dry cloth
2. Upper coating (i.e. grease[849]) removal
    b. Dried grease on surfaces was removed by white spirit solvent on toilet tissue
    c. Residual white spirit was removed by clean dry paper


2a.


2b.

3. Lower coating (i.e. yellow-green varnish) removal
    a. Toilet tissue with methylated spirits rubbed over surface
    b. Bristle brush with methylated spirits rubbed into the surface since this varnish had a "good strong coat". The coating became sticky. "Some varnishes dissolve immediately, but others, like this one, are more resilient and take too long to remove by methylated spirits alone".
    c. Bristle brush with commercial spray thinner (mixture of aromatic hydrocarbons) rubbed into the surface.
    d. Toilet tissue without solvent rubbed over surface to remove varnish. "Loose reddish rust" in coating removed during coating removal and thrown away to avoid scratching of the metal. Steps c. & d. were continued for circa 5 cycles until most varnish was removed
    e. Acetone on paper used to remove almost all isolated remnants of varnish (acetone evaporates too quickly for the bulk of coating removal and would have used twice as much paper)

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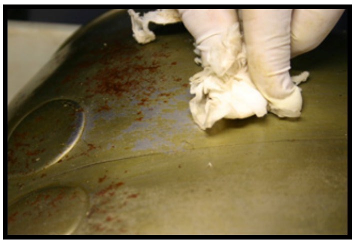
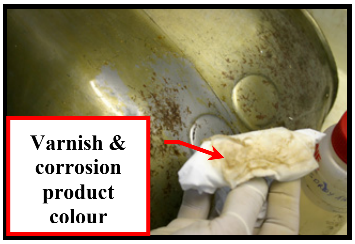
[847] This is in contrast with approaches to decorated armour (Stroud, 2006-2007, pers. comm.).
[848] Stroud, 2006-2007, pers. comm.
[849] Ibid.

3c.

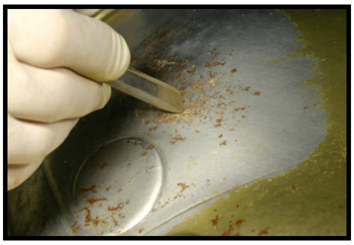


3d.

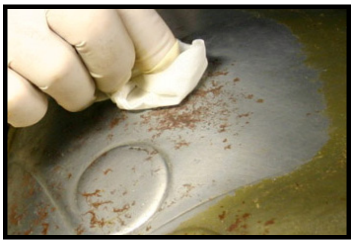


3d.

4. <u>Upper (i.e. positioned above adjacent metal profile) corrosion product removal</u>
    a. Adherence of “hard rust attached to the surface” checked by probing with the custom-made acrylic plastic wedge. This physical process also “removed varnish remnants trapped in the rust”. “Rust is hard, but shallow”, and the acrylic tool skimmed over surface without too much resistance. Acrylic tool applied in a manner to avoid scratching metal surface; as can occur if it picks up corrosion products and pushes them over the metal surface. Remaining CPs proved too resilient as it wore the acrylic wedge
    b. Acetone and toilet tissue used to clean surface for improved surface observation



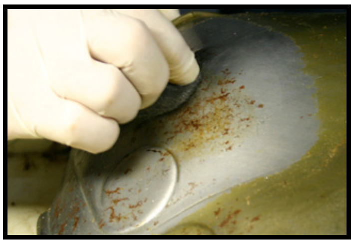
4a.



4b.

    c. Machine oil (3-in-1™) added to wad/ball of 0000 grade steel wool and armour for lubrication and limited abrasive action. Pressure with fingertips created a localised effect from the steel wool, while the “rest of wad just tickled the surface”. Generally, long hand movements are restricted to larger areas of corrosion products
    d. Acetone and toilet tissue used to clean surfaces for improved surface observation.

4c.

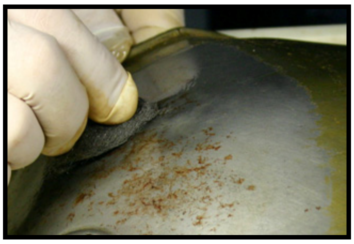


4c.

4d.

    e. Scalpel skimmed over surface leaving dark corrosion products in deeper pits. Care taken to not scratch adjacent metal since scratches would show. Blade inspected to see if serrated edges were created by CPs and blade was accordingly replaced. “Worming things” (i.e. filiform corrosion filaments) quite deep; scalpel unable to remove them
    f. 0000 steel wool wads and machine oil used “to remove grits left after scalpel stage”
    g. 0000 steel wool with machine oil applied with pressure on small areas with bamboo skewers to avoid rubbing whole area. A circular motion used to create a more diffuse, less polished area than from straight motions


4e.

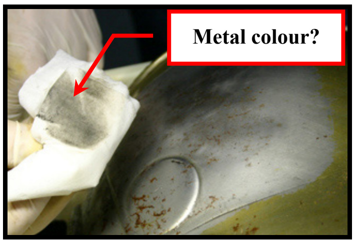

4f.


4g.

5. Lower (i.e. positioned in pits below adjacent metal profile) corrosion product diminution
    a. Wads of 0000 wool moistened with machine oil and dusted with rottenstone (silica-limestone powder) and applied in a circular motion. “Rottenstone teases out grit and dirt from holes, tones down blemishes left by rusting and blends in the previous interventions (e.g. “nicking etc from scalpel”)”. “Not using too much pressure from steel wool as it is used more as a carrier for the rottenstone”
    b. Acetone & toilet tissue were used to remove rottenstone, abraded “grit & dirt”


5a.

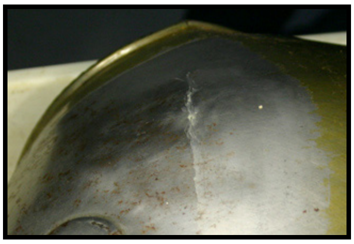

5a.



5b.

6. Surface polishing
    a. Pre-Lim™ polishing paste by Picreator applied with tissue in a circular motion “to give a shine and take off more dirt”
    b. Pre-Lim™ residue removed with acetone and toilet tissue


6a.


6b.

The equipment and materials used in the Palace Armoury’s outlined corrosion product removal procedure are given in Figure 3-3.


Top row from left: toilet tissue, 3-in-1 machine oil, rottenstone abrasive

Bottom row from left: bristle brush, acrylic scraper, 0000 steel wool, scalpels, steel wool on bamboo skewer, Pre-Lim™ polishing paste

From left: White spirit, methylated spirits, commercial thinner (mixture of aromatic hydrocarbons), acetone

Figure 3-3 Equipment and materials used during the Palace Armoury's documented backplate corrosion product removal (and associated) procedures

As routine, armour are then cold-waxed for corrosion protection with two coats of Renaissance Microcrystalline Wax™ by Picreator. This step was followed after macrophotographic surface documentation was performed[850].

3.3 MUNITION ARMOUR ANALOGUES: LABORATORY CORROSION CASE STUDIES: PREPARATION & DESTRUCTIVE INVESTIGATIONS

The methodologies followed and justification for the aging and selection criteria and various means of observation and analyses made on the munition armour analogues are presented here.

The broad aim of producing and studying armour analogues was to better understand the stratigraphies of corrosion product layers and interventions on materials similar to the munition armour. Of particular note was the potential determination of the limitos in such ferrous CP stratigraphies that would not be complicated by the indeterminable variables and ambiguities introduced by historical human interventions. By momentarily withdrawing this significant variable, the natural ferrous corrosion system could be investigated.

3.3.1 ARMOUR ANALOGUES: MANUFACTURE & CORROSION

The literature review on atmospheric ferrous corrosion[851] and direct studies of the surfaces of the armour[852] were used to inform the manufacture of the coupons designed to simulate the armour metal and its corrosion product morphologies.

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[850] 4.1.4 Authentic munition armour corrosion product removal: the Palace Armoury , Figure 4-43, Figure 4-44 & Figure 4-45

Before detailing how certain CP morphologies were encouraged, several general considerations regarding the fabrication of the armour analogues had to be respected. The major consideration was *time*. The corrosion of experimental analogues does not usually have the benefit of years or decades of CP evolution in the way historical artefacts do, albeit to their detriment.

Also, while the foundations for the armour analogue manufacture and corrosion were based on the literature and first hand observations of coated and corroded ferrous material, the end product coming from the subsequently formulated approaches were ultimately yielded from empirical approaches of trial and error. Differing series of strategies involving various materials were applied to corrode the coupons with morphologies comparable to the armour. Only those armour analogues of greatest experimental potential were selected for later investigation.

3.3.1.1 Metal selection & substrate preparation

The metal coupons used to fabricate the armour analogues were sourced from previous studies on protective coating efficiency[853]. Since wrought iron is no longer commercially produced[854], contemporarily produced steel was used as a substitute material[855]. Recycled wrought iron from specialist suppliers could have been considered if finances permitted and consequently a much larger group of samples would have been needed to mitigate/understand any effects of irreproducibility caused by such a variable source. The chosen substitute material, referred to as *grade A naval steel*, was hot-rolled above crystallisation temperatures during fabrication, rather than cold-rolled and tempered[856]. The rolling of the steel between successive mills implies that the metal was not wrought by folding and therefore does not feature the internal planes typical of non-contemporary wrought iron. The base material for all the armour analogues came from the same source and was analysed by a second party with atomic emission arc induced spectroscopy (AEAIS) and was

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[851] 2.2 Indoor atmospheric ferrous corrosion & control

[852] 3.2.3.1.2 Armour surface macrophotography & photomicroscopy & 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

[853] The coupons were made available from a previous laboratory testing corrosion protection performance of barrier coatings under the Promet project (Crawford et al., 2007).

[854] Lyons, 2005, p. 154

[855] Vella, 18/01/2006, pers. comm.

[856] Ibid. & Vella & Degrigny, 2005, p. 1

determined to be a hypoeutectoid steel[857] with minor alloying of manganese and silicon (Table 3-2)[858].

	Element	Measured concentration (% weight)[859]	Calculated concentration (% relative atomic weight)[860]
1.	Iron	98.9-99.9	99.1894-99.2202
2.	Manganese	0.5130-0.5190	0.5058-0.5119
3.	Silicon	0.1959-0.2012	0.0987-0.1014
4.	Carbon	0.1250-0.1572	0.0269-0.0339
5.	Copper	0.0572-0.0578	0.0652-0.0659
6.	Aluminium	0.0439-0.0444	0.0215-0.0212
7.	Chromium	0.0313-0.0314	0.0292-0.0293
8.	Nickel	0.0219-0.0220	0.0230-0.0231
9.	Sulphur	0.0087-0.0090	0.0050-0.0052
10.	Phosphorous	0.0066-0.0070	0.0037-0.0039

Table 3-2 Most prevalent alloying and trace element components of the armour analogues

With this established composition and according to the American Society for Metals[861] definition and also by those given earlier[862], this steel is a *carbon steel* (or *plain carbon steel*) as they contain, by definition, maximum concentrations of 1.65%wt manganese, 0.60%wt silicon, 0.05%wt sulphur and 0.05%wt phosphorus[863]. More specifically, the carbon content (C = 0.13-0.16%wt) of this particular carbon steel classifies it as a *low-carbon steel*[864] the same classification attributed to the majority of the steel armour (0.1-0.3%wt carbon) metallographically studied by Vella et al.[865]

"Low-carbon 'mild' steel…" is considered, by pre-eminent archaeometallurgist, R.F. Tylecote, as "…the modern equivalent of wrought iron"[866]. Although this is true, since low-carbon steel might have succeeded wrought iron in contemporary application, it is not identical to the so-called wrought iron produced in

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[857] Graph 2-1 The iron and steel section of the iron-carbon phase diagram

[858] Vella & Degrigny, 2005, p. 1 & Vella et al, 2006a, p. 1

[859] Surface Engineering Malta, 2005

[860] Converted from % weight into % relative atomic weight by the present author for comparison with later EDS data which is given in terms of %rel.at.wt (3.5.2 Scanning electron microscopy-energy dispersive spectrometry & 4.2.1.2 Cross-section perspective investigations)

[861] Now ASM International

[862] Chandler, 1998 in footnote 48 & Leygraf & Graedel, 2000, in footnote 259

[863] Roe, 1978, p. 183

[864] 2.1.2.1 Metal extraction & processing

[865] Vella et al., 2004, p. 230

[866] Tylecote, 1992, p. 145

the Early Modern Period, not least due to the relative freedom of inclusions in contemporary carbon steel and its relatively unworked structure[867].

Manganese and silicon are employed during production of contemporary low-carbon steels as *deoxidisers* of the metal. These two elements can be used simultaneously during fabrication to react with dissolved oxygen in the molten metal. The de-oxidation products formed are more stable than iron, and their removal as slag is facilitated prior to solidification[868]. Without these additives a greater proportion of these non-metallic particles would form from the oxygen and other elements present and impart undesirable properties in the manufactured metal[869]. The concentration of manganese in the armour analogues is too small to be classed as a manganese-steel (Mn = 1.2-1.8%wt) where depth of hardening, toughness and strength are thereby improved[870].

Potentially differing corrosion resistance between steels of dissimilar metal alloy (and carbon) content is not overlooked. An effect on corrosion resistance, increased or decreased, is likely, but it remains unknown if such behavioural differences are appreciable between the present research materials (i.e. authentic armour and armour analogues). For example, corrosion performance tests on two contemporary non-manganese steels of respectively varying carbon (0.12-0.17% versus 0.35-0.42%), manganese (0.40-0.60% versus 0.90-1.20%), silicon (0.18-0.28% versus 0.20-0.30%) and copper (0.20-0.25% versus [no stated value]) content showed a greater corrosion resistance of the latter steel (i.e. the steel with more carbon, more manganese, more silicon and no stated copper)[871].

In addition to the trace elements listed in Table 3-2 numerous other elements were detected, but with much lesser concentration. For micro-alloyed metals (including some carbon steels), the alloy component's concentration can be very small (together totalling only 0.005-0.10wt%): with elements like boron, vanadium and niobium cited as having an effect on useful properties at these small quantities[872]. The potential contribution of properties imparted by the amounts of these three micro-alloying elements on the armour analogues can be suggested by the amounts determined from the AEAIS. The concentrations of boron and vanadium

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[867] 2.1.2.1 Metal extraction & processing & 2.1.2.2 Munition armour forming
[868] Bodsworth, 1963, pp. 389-390, 400-401
[869] Ibid., pp. 389-390
[870] IMMA, 1988, p. 3
[871] Jekayinfa et al. 2005, pp. 286-292
[872] IMMA, 1988, p. 4

determined fell below the detection limits (respectively <0.0001%wt & <0.0010%wt), while nobium registered small amounts (0.0023-0.0027%wt)[873]. Taking the maximum registered possible values (i.e. boron 0.0001%wt, vanadium 0.0010%wt & nobium 0.0027%wt) the calculated amount is marginally less (24%) than the minimum amount expected to achieve a micro-alloying contribution to property changes. So according to these parameters, it is hypothesised that a micro-alloying effect in these contemporary analogues is unlikely: decreasing the possible dissimilarities between the metal of the armour analogues and the metal of the mid-late Early Modern Period armour.

The theoretical 30% increase in the corrosion rate of mild steel compared with wrought iron[874] is not considered to be of significance, but is nonetheless recognised and further separate research might be required to investigate this aspect in practice. To explain, the corrosion rate might not be considered to be as important, whereas the type of corrosion mechanism and resultant morphologies are more fundamental to these studies. The speculative claim that the difference in corrosion rate might be insignificant is also made on the proviso that the marginal increase does not entail disproportionately voluminous corrosion product surfaces. Since Palace Armoury munition armour metal generally appear to have relatively fewer and shorter inclusions[875] instead of multitudes of long stringers, and since the suggested predominant surface corrosion mechanisms appear[876] to be filiform[877] and pitting[878], rather than galvanic or crevice corrosion[879], a comparative decrease in corrosion rate for the analogues is not considered to be a very significant inadequacy.

Without simultaneous experimental studies in identical environments on the corrosion of Early Modern Period wrought iron and steel with this contemporary simulation material, it is difficult to categorically conclude on the possible the differences caused by their inherently differing material composition and structure. On the one hand, if such Early Modern Period wrought iron and steel were available then it would evidently be preferable to use this as the armour analogue simulation material. On the other hand however, these metals' corrosion phenomena appear

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[873] Surface Engineering Malta, 2005

[874] 2.2.2.3.5 Ferrous metal type

[875] 2.2.3.3 Uneven local to uneven general corrosion/corrosion product morphology

[876] 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy & 4.1.3.2 Armour corrosion cross-section observations & analyses

[877] 2.2.3.2.1 Filiform corrosion mechanism

[878] 2.2.3.3.1 Pitting corrosion mechanism

[879] 2.2.3.3.2 Galvanic corrosion mechanism

more similar than dissimilar, and knowing that unalloyed carbon steels are also subject to pitting and filiform corrosion[880] (rather than, for example, graphitic corrosion as for grey-cast iron, or intergranular and pitting corrosion as for stainless steels)[881], makes an unalloyed low-carbon steel a suitable best-available choice for these corrosion phenomena-based investigations.

Prior preparation of the metal by Vella et al. for the previously cited laboratory tests included first modifying the microstructure[882] (Appendix F[883]) and then preparing the surfaces and dimensions to standard-sized plates of metal (75 x 50 x 2-3mm) (Figure 3-4).

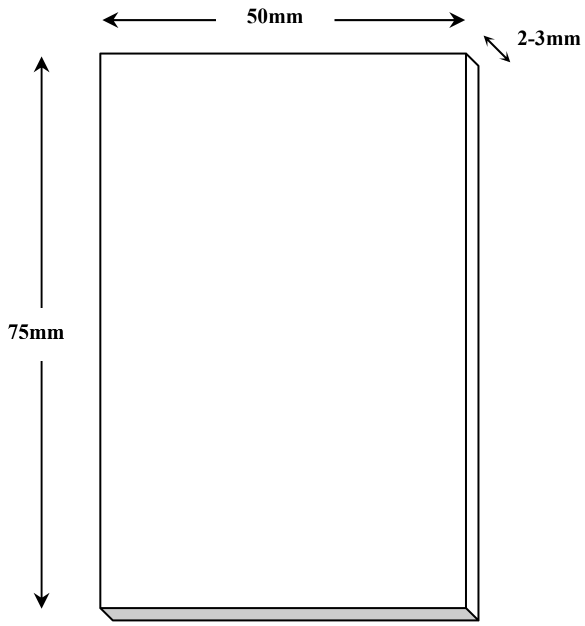

Figure 3-4 Dimensions of low-carbon steel armour analogues

The thickness of the coupons, 2-3mm, was not intended to represent the armour thickness (circa 0.8-1.2mm in the bulk areas[884]), but instead it provided a rigid practical support for the various experimental procedures to occur without

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[880] 2.2.3.2.1 Filiform corrosion mechanism & 2.2.3.3.1 Pitting corrosion mechanism

[881] 2.2.2.3.5 Ferrous metal type

[882] In brief, the microstructural treatment aimed to change the fine ferrite-pearlite into the Widmanstätten microstructures observed in a selection of previously studied armour (Vella et al, 2004). This involved heating guillotine-cut plates of the sheet metal in a furnace at 950°C for 4.5 hours and then rapidly cooling under a blast of compressed air. The intention was to approach a microstructure that might better simulate its corrosion susceptibility. Sandblasting, pressing, milling and grinding of surfaces to expose the metal core removed the mill scale and decarburised zones resulting from the furnace. The standard sized coupons were cut from the sheets of metal with a donkey saw (Vella & Degrigny, 2005a, pp. 2-8). The metallographic structures in the steel used for the armour analogues were established to vary from fine ferrite-pearlite microstructures to blocky ferrite and Widmanstätten ferrite platelets with pearlite microstructures (Crawford, 2007b, p. 19).

[883] Appendix F – Microstructures of munition armour analogues

[884] 2.1.2.2 Munition armour forming

introducing additional issues regarding flexing of the substrate. Such flexibility of the thin lames on armour might introduce fissures in the corrosion product layers, especially at local zones under stress from handling or storage/display. Further separate research would be required to investigate any significance of this aspect.

While the substrate material for each of the analogues came from the same source, the preparation of the surfaces purposely varied between each Coupon Series. Seven different series of coupons were prepared and the possible surface preparation variables between each series included:

- Pre-existing CPs and pits versus no CPs and pits;
- Extent and orientation of surface grinding and resulting micro-grooves;
- Presence or absence of sodium chloride;
- Composition of applied superior limitos marker; and
- Presence or absence of coating.

Table 3-3 presents a summary of the seven differently prepared armour analogue Coupon Series, and the corrosion and corrosion product morphology objectives that influenced their design. The duration of the respective Coupon Series' accelerated corrosion regime is also given.

Coupon Series	**Corrosion objectives**		**Surface preparation variables**					**Laboratory accelerated corrosion duration**
	Morphology	**Extent of development**	**Pre-existing corrosion products and pits**	**Micro-groove orientation & roughness**	**Sodium chloride & application method**	**Applied superior limitos marker**	**Paraloid B-72™ coating**	
1	Uneven local to general uneven corrosion	Primary-secondary	Yes	Lateral and weak	Yes, immersion	$BaSO_4$	Yes	4 months + 2 weeks
2	Uneven local to general uneven corrosion	Primary-secondary	No	Longitudinal and strong	No	$BaSO_4$	Yes	4 months
3	Uneven local to general uneven corrosion	Primary-secondary	No	Longitudinal and strong	No	$BaSO_4$	No	4 months
4	Uneven local to general uneven corrosion	Primary-secondary	No	Longitudinal and strong	Yes, immersion	ZnO/ $BaSO_4$	Yes	2 weeks
5	Filiform corrosion	Primary-secondary	No	Longitudinal and strong	Yes, locally	ZnO/ $BaSO_4$	Yes	2 weeks
6	Uneven local to general uneven corrosion	Primary-secondary	No	Longitudinal and strong	Yes, immersion	Au	Yes	2 weeks
7	Filiform corrosion	Primary-secondary	No	Longitudinal and strong	Yes, locally	Au	Yes	2 weeks

Table 3-3 Summary of the objectives and variables of the manufactured armour analogues

A minimum of three coupons (i.e. experimental replicates) was allocated per Coupon Series for purposes of statistical reproducibility. Due to financial limitations the armour analogues using gold as an applied superior limitos marker (Coupon Series 6 & 7) were limited to one coupon each. Due to their individuality, the results from the coupons with gold superior limitos marker could therefore only be considered as preliminary indications. A control coupon was also allocated to each Coupon Series. The controls were prepared simultaneously with the experimental replicates, but were not exposed to the corrosion duration, remaining instead in desiccated storage for possible comparison.

Since much of the armour analogue methodology was based on innovative approaches, extra coupons were prepared in parallel to serve as *methodology pilot coupons*. These coupons were used at stages of the investigation to trial approaches that, if successful, would be applied to the experimental replicates. This precautionary measure avoided the introduction of such variables into the experimental replicates.

3.3.1.1.1 Corrosion/corrosion product morphologies

It was decided, based on investigations of the munition armour[885], that the corrosion and corrosion product morphologies most representative of the collection *and* those that are present on the *surface* of armour would be reproduced for investigation. It was decided that filiform and uneven local to uneven general surface corrosion and corrosion product morphologies[886] would be reproduced for determination of their original surface limits.

The aimed extent of their development (Table 3-3) was decided to be *primary to secondary corrosion* (as later defined in Table 4-2 & Table 4-3). This extent would not only be more representative of the collection, but (as indicated initially[887]) in the given timeframe would be more achievable than the *tertiary corrosion* development classification.

The methodologies followed for each of the Coupon Series' preparation variables are given next.

3.3.1.1.2 Surface grinding

Two approaches were followed to prepare the surfaces of the previously used coupons:

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[885] 4.1 Palace Armoury environment, munition armour & corrosion product case studies: non-invasive & non-destructive investigations

[886] 2.2.3.2 Filiform corrosion/corrosion & 2.2.3.3 Uneven local to uneven general corrosion

[887] 3.3.1 Armour analogues: manufacture & corrosion

1. Removal of previous coating by immersion in appropriate solvent (either acetone or white spirit) and subsequent assistance by physical abrasion with cotton wool swabs. Removal of superficial corrosion products by rotating steel brush on hand held drill. As a result, the metal surface maintained the majority of the parallel and laterally orientated grinding lines/micro-grooves from initial coupon manufacture (Figure 3-5). Pits that were partly filled with CPs from previous corrosion remained. These irregularities were intended to act as defects to help initiate corrosion sites.

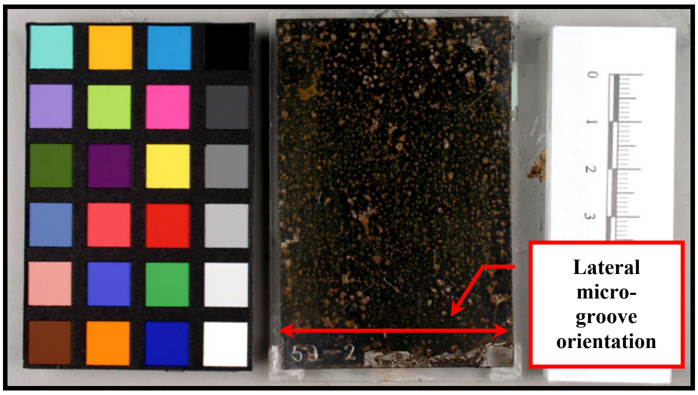

Figure 3-5 Armour analogue representative of Coupon Series 1 after pre-existing coating and partial corrosion product removal

These coupons can be considered similar to the armour surfaces where new corrosion products have propagated from formerly corroded and cleaned surfaces (Figure 3-6).

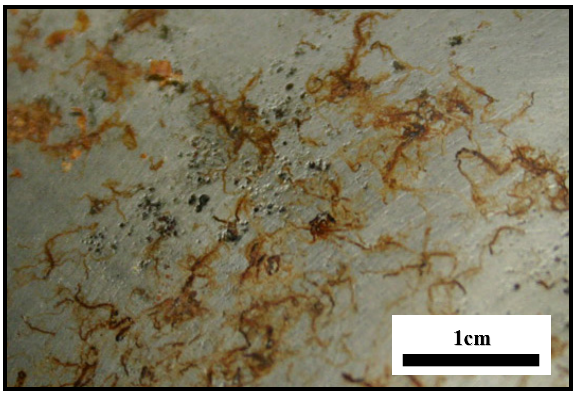

Figure 3-6 Filiform corrosion filaments (orange-brown) proposed to have initiated from former corrosion pits (black areas) on munition armour

2. Removal of all corrosion products and corrosion pits by an electric belt sander with 60-grit aluminium oxide sandpaper (Figure 3-7).

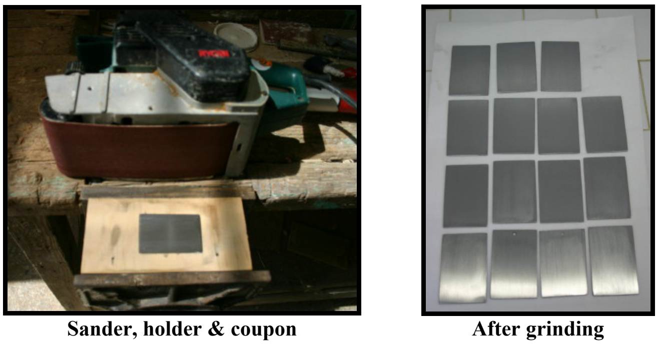
Sander, holder & coupon
After grinding

Figure 3-7 Armour analogues from Coupon Series 2-7 during and after surface grinding

As a result, this grinding removed the laterally oriented micro-grooves from initial manufacture. The final corrosion and corrosion product-free surface finish (Figure 3-8) of longitudinally oriented micro-grooves was achieved with 120-grit aluminium oxide sandpaper with the belt sander.

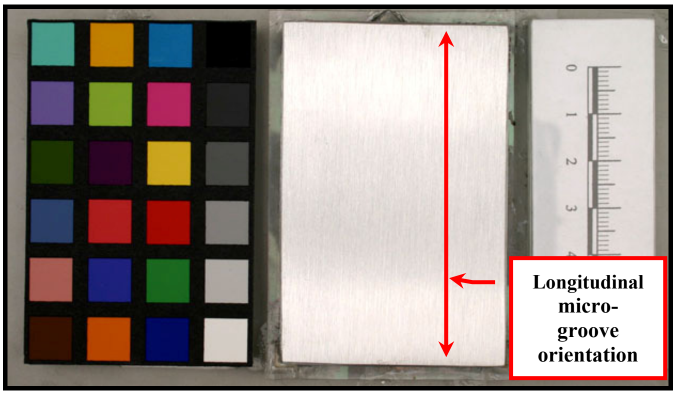

Figure 3-8 Armour analogue representative of Coupon Series 2-7 after pre-existing coating and corrosion product removal

These micro-grooves were intentionally created to help propagate parallel filiform (as documented on PA armour, Figure 3-9) longitudinally along the coupon. It was expected that the parallel micro-grooves would encourage filiform propagation by minimising self-termination and would facilitate simultaneous microscopic cross-section observation of numerous filaments. Cross-sectioning was anticipated to be performed transversally so as to be largely perpendicular these micro-grooves and any filiform filaments.

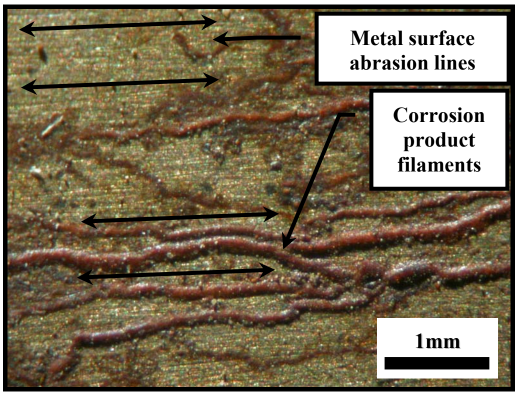

Figure 3-9 Filiform corrosion propagating along parallel metal surface abrasion lines on PA munition armour

The relatively coarse surface finishing of the coupons was executed for two main reasons. Knowing that rougher and unpolished surfaces provide corrosion initiation sites[888] a roughly ground surface was deemed desirable for encouraging corrosion in the given time span. The second, and more important motivation was borne from prior observations of other corroded steel surfaces that had shown that original surface features of the former metal could be emulated in corrosion products formed from these corrugated surfaces. Adding this minor corrugated third

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[888] Hess & Bullett, 2000, p. 50

dimension to the surface enabled its inclusion as a topographical marker that would help to characterise an otherwise flat and featureless surface. Since these micro-grooves are associated with the metal, they can therefore importantly be referred to as a corresponding limitos marker: the absolute or definitive limitos marker[889]. While armour also feature these micro-grooves (from manufacture, former maintenance or restoration intervention) their prominence, in quantity and quality, varies. Indeed some armour surfaces are very smooth. The micro-grooves on the armour analogues did not aim to represent the minutely corrugated surfaces of armour (although they clearly could have simulated them), but instead were anticipated to possibly provide a convenient diagnostic means of identifying an otherwise less distinguishable and flat surface topography.

To degrease the surfaces, and help remove any particles remaining from surface grinding (i.e. abrasives, metal & CPs), coupons were immersed in acetone and ultra-sonicated within an outer vessel of water for 20 seconds each (Figure 3-10).

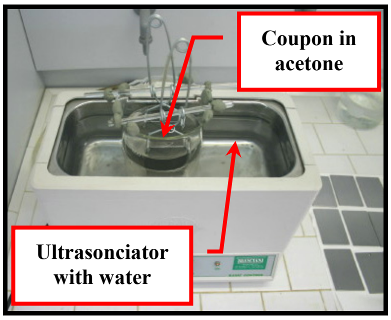

Figure 3-10 Removal of surface matter from armour analogues by ultrasonication

3.3.1.1.3 Corrosion accelerant

To increase the rate of corrosion, and subsequent corrosion product evolution, sodium chloride, was applied to some Coupon Series[890]. The salt was added to the coupons by one of two techniques depending on the targeted corrosion product morphology:

1. Uneven local to uneven general corrosion: momentary immersion of single coupon (still without applied superior limitos markers) in an aqueous sodium chloride solution (1.75%m/v) (Figure 3-11) and then desiccated horizontally in a chamber saturated with dry silica gel.

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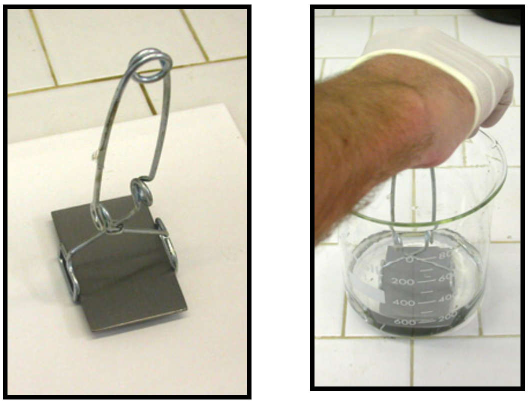
[889] 2.3.1.2.1 Localisation of the limitos

[890] As discussed, sodium chloride increases the conductivity of the electrolyte and is considered a known corrosion accelerant found in the Palace Armoury environment as per 2.2.2.3.3 Atmospheric pollutants, Solid aerosols.



Coupon & holder

Immersion in sodium chloride solution

Figure 3-11 Procedure for corrosion accelerant application by immersion

The sodium chloride concentration was empirically selected from previous experience. Previous studies using a 3.5%m/v solution proved to be so corrosive while under a laboratory accelerated corrosion regime that the surface became so disrupted that there would be little chance to track any modified original surfaces in CPs.

The addition of sodium chloride in a water solution resulted in a rapid superficial coating of corrosion products formed by *flash-rusting*. Even though such CPs are very thin, they were not desirable since it is supposed that it introduced an ambiguity between the CPs formed before and after the subsequently applied superior limitos marker. For future applications where prevention of preliminary corrosion is desirable it is recommended that solutions of sodium chloride in a non-corrosive solvent such as ethanol[891] be used.

To avoid unnecessary and untidy corrosion of the reverse coupon face, contact-adhesive tape was temporarily attached to act as a mask and prevent access to the surface by the sodium chloride solution during immersion.

2. Filiform corrosion: numerous local applications of single droplets of sodium chloride in aqueous solution (1.75%m/v) onto coupons that had been coated with their respective applied superior limitos marker[892] and coating[893]. To provide access to the metal surface for the sodium chloride, the coating was locally depleted mechanically by a handheld microdrill (Figure 3-12). After sodium chloride application the coupons were desiccated horizontally in a chamber saturated with dry silica gel.

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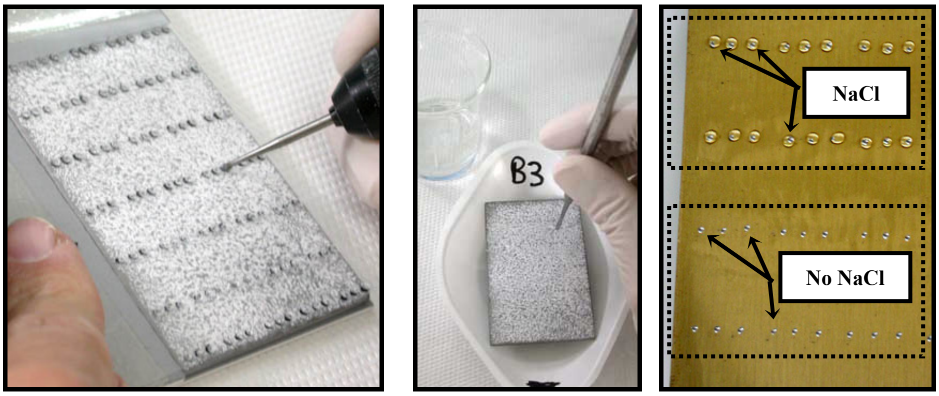
[891] In spite of sodium chloride's much lower solubility in ethanol (0.055 g/100g at 25°C) compared with in water (26.483g/100g at 25°C) (Pinho & Macedo, 2005, p. 30). Repeated applications would therefore be required.

[892] 3.3.1.1.4 Applied superior limitos markers

[893] 3.3.1.1.5 Protective coating



Coating incisions with template on a coupon from Series 5

Sodium chloride droplet application on a coupon from Series 5

Detail of sodium chloride droplet application in progress on a coupon from Series 7

Figure 3-12 Procedure for local corrosion accelerant application for filiform corrosion coupons

The design intention for Coupon Series 5 & 7 was for filiform corrosion filaments to initiate adjacent to the coating's incision with sodium chloride and to propagate parallel to the surface grinding direction (micro-grooves) (Figure 3-13).

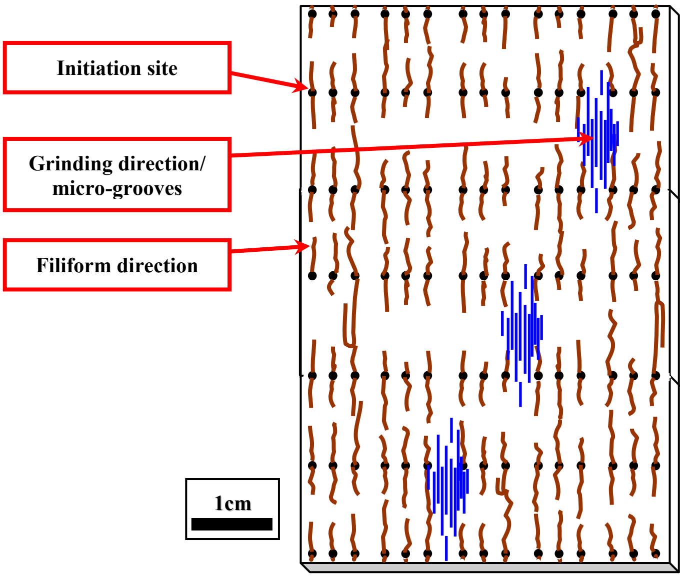


Figure 3-13 Schematic representation of coupons designed for filiform corrosion

3.3.1.1.4 Applied superior limitos markers

The deliberate application of superior limitos markers was made in an effort to provide identifiable markers that might contribute to the later attempt in determining the limitos. The markers were anticipated to prove useful if the corrosion product evolution became so locally prolific that it transfused into or deposited onto these markers. These applied superior limitos markers on the armour analogues were intended to act in a similar way to superior limitos markers like quartz sediment on archaeologically buried artefacts[894]. Unlike the exogenous particles to be studied on the authentic munition armour[895], the applied superior limitos markers did not attempt to mimic the position of solid aerosols from the natural environment that deposit on artefacts: they would be expected to be positioned more above the coating than below.

The ideal applied superior limitos marker would feature the following characteristics:

- Inert and neutral observer;
- Permeable structure and uniform surface coverage;
- Optically distinguishable from steel and corrosion products;
- Compositionally distinguishable from steel and corrosion products;
- Insoluble in water; and
- Non-toxic.

To avoid interference in the corrosion, and subsequent corrosion product formation processes, it was desirable that the applied superior limitos markers would be chemically inert and neutral observers of these processes.

Applied superior limitos markers permeable to corrosion products were chosen since they were required to permit CP evolution to pass through and deposit on top. Strong or coherent layers like metal foils, plastic or paint films were thus not deemed suitable since they would be more likely to trap all CPs, not letting them form and deposit freely. Notably, since polymer coatings are typically present on the munition armour any such possible effects from these constituents would be of valid consequence to the armour, but would be of hindrance to the diagnostic purpose of the armour analogues. The application of a coating to mimic this characteristic is discussed later[896]. The applied superior limitos marker should also be sufficiently permeable to water vapour and oxygen so as to not significantly impede corrosion.

To assist observation of the applied superior limitos marker in relation to the anticipated corrosion strata, several qualities were selected according to particular observation techniques. Since the primary available microscopic observation technique was anticipated to be optical microscopy, it was decided that applied superior limitos markers with colours that contrast with the metallic silver of the steel and the anticipated yellows, oranges, reds, browns and blacks typical of ferrous CPs would be appropriate. The secondary observation instrument and primary analysis

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[894] 2.3.1.2.1 Localisation of the limitos

[895] 4.1.3.2 Armour corrosion cross-section observations & analyses

[896] 3.3.1.1.5. Protective coating

instrument available for the armour analogues would be a scanning electron microscope coupled with an energy dispersive spectrometer. In terms of observation via the SEM (using the backscatter electron (BSE) detector), selected applied superior limitos markers would ideally be relatively radio-opaque compared to the iron in steel, and even more so to the ferrous corrosion products[897].

In terms of compositional analyses via the EDS, the applied superior limitos marker should not be composed of elements that could be confused with the other components of the armour analogue materials (i.e. steel coupon with minor alloying and trace elements, corrosion accelerant, coating). In this way the location of the applied superior limitos marker between evolved corrosion products could be confirmed (as suspected from observations of contrasting radio-opaqueness or particle morphology given by the SEM BSE detector).

Applied superior limitos markers being highly, or totally, insoluble in water were of preference for two reasons:

1. To minimise their dissolution and movement in the corrosion products during the projected highly humid accelerated corrosion regime[898]; and
2. To minimise loss of applied superior limitos marker during cross-section preparation while under abrasive polishing using water as a lubricant[899].

For health and safety reasons, toxic materials were disregarded for use as applied superior limitos markers.

Since this application of superior limitos markers is an innovative approach, markers of several materials and application techniques were tried. Three markers were finally selected and used on the armour analogues: particles of barium sulphate; zinc oxide; and gold.

None of the selected markers can be considered to be *ideal*, with each presenting their own advantages and disadvantages. Having a thin and/or porous material, regardless of its inertness, on a metallic surface such as the armour analogues, is likely to cause differential aeration of the surface and induce related corrosion mechanisms[900]. Conductive materials might be expected to behave electrochemically by way of galvanic corrosion[901]. Even if inert, such markers might be considered as catalysts and therefore not behave as neutral observers. Nonetheless

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[897] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry
[898] 3.3.1.1.6 Laboratory accelerated corrosion
[899] 3.3.2.2 Analogues: cross-section preparation
[900] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols
[901] 2.2.3.3.2 Galvanic corrosion mechanism

the selection of applied superior limitos markers that might be considered of limited influence was necessary.

Gold is highly renowned for its inertness[902] and is only dissolved in highly concentrated specific acid conditions[903], while barium sulphate is considered to be inert in both acidic and alkaline conditions[904] and has high insolubility in water ($0.00031 x 10^{20} g.100g^{-1} H_2O$)[905]. Although zinc oxide is also insoluble in water[906], its inertness is less satisfactory especially under humid atmospheric conditions when it can transform into soluble zinc carbonate[907] Moreover, zinc oxide is also amphoteric so readily dissolves in acidic (even diluted[908]) or basic solutions[909].

In terms of material compatibility, barium sulphate is known to be chemically compatible with all other pigments[910]. Zinc oxide is reported to typically be used in paints with lead white (lead carbonate hydroxide[911]), barium sulphate and titanium whites[912] (titanium dioxide[913]), however its compatibility was not established. Although gold is very unreactive, its high electrochemical nobility is expected to cause metal incompatibility due to possible galvanic corrosion of the steel coupons. There is a large potential difference between gold ($Au^{3+} + 3e^- \rightarrow Au$, +1.50V/SHE at 25ºC, 1M)[914] and iron ($Fe^{2+} + 2e^- \rightarrow Fe$, -0.440V/SHE at 25ºC, 1M)[915].

Barium sulphate and zinc oxide, both being brilliant white pigment powders, gave suitable optical contrast to the steel substrate and anticipated CPs. It was thought that gold would also contrast sufficiently.

No gold or barium was detected in the previous analyses of the coupon metal[916], making these elements suitable for discriminating between applied superior limitos markers and the ferrous metal and its corrosion products. The very low

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[902] Kettel, 1982, p. 5
[903] Aqua regia: 1 part nitric acid 3 part hydrochloric acid) – CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 14
[904] Feller, 1986, p. 51
[905] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 45
[906] Ibid, p. 4 – 95
[907] Eastaugh et al. 2004a, p. 407
[908] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 95
[909] Kühn, 1986, p. 175
[910] Feller, 1986, p. 50
[911] Gettens et al., 1997, p. 67
[912] Kühn, 1986, p. 178
[913] Lever, 1996, p. 295
[914] Uhlig, 1963, p. 28
[915] Ibid.
[916] Table 3-2

quantity of zinc (0.0037-0.0040%wt or 0.0043-0.0047%rel.at.wt[917]) in the coupon metal also made its source distinguishable since its concentration in the steel was circa two orders of magnitude below the expected detection limits of the EDS[918]). That is to say, if zinc were to be detected, then its source would have to be attributable to the superior limitos marker.

Barium[919] and gold, respectively having high atomic numbers of 56[920] and 79[921] versus 26[922] for iron give them potentially good atomic contrast with the SEM BSE detector, making their widespread identification with SEM rapid, rather than relying on EDS analyses for preliminary identification[923]. Zinc's atomic number (30)[924] was expected to be too low for SEM BSE visual discrimination, thereby requiring EDS for identification amongst ferrous corrosion products.

Zinc oxide was mainly chosen as an applied superior limitos marker due to its ready identification using ultra-violet (UV) light fluorescence microscopy. When subjected to UV light, zinc oxide auto-fluoresces a distinctive yellow light (evidently) observable in the visible light spectrum[925]. The peak emission at 520nm is a yellow-green[926]. Significantly in terms of the diagnostic potential of zinc oxide for these limitos studies, its fluorescence ability is inhibited by impurities or admixtures that affect the colour of its fluorescence[927]. The CPs of iron, themselves pigments, could also potentially be responsible for these undesirable phenomena, but a reference that specified which pigments affect the fluorescence of zinc oxide could not be found. For these diagnostic purposes, successful use of zinc oxide would require that zinc oxide fluorescence occurs when mixed with ferrous corrosion products.

The availability and demand for the anticipated scanning electron microscope-energy dispersive spectrometer fluctuates, so it was considered practical to have an applied superior limitos marker on the same Coupon Series that would be

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[917] Table 3-2

[918] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[919] The word *barium* derives from the Greek word *barys* meaning *heavy* (Feller, 1986, p. 46).

[920] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 5

[921] Ibid., p. 4 – 13

[922] Ibid., p. 4 – 17

[923] The principle of contrast by atomic numbers is outlined in 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[924] Ibid., p. 4 – 35

[925] Kühn, 1986, p. 172

[926] Eastaugh et al., 2004b, pp. 324-325

[927] Kühn, 1986, p. 172

potentially distinguishable via both optical and scanning electron microscopy. In this way the same Coupon Series could be investigated according to either means of observation. A mixture of zinc oxide and barium sulphate was formulated. To aid even composition (by volume) of the powdered mixture, the specific densities of zinc oxide and barium sulphate (respectively 5.6g.cm^{-3} [928] & 4.49g.cm^{-3} [929]) determined that a zinc oxide and barium sulphate mixture in proportions 4:5 by weight, was appropriate to approximate an equal formulation by volume (assuming comparable particle size and packing).

Despite their potentially beneficial diagnostic properties, the main undesirable quality that barium sulphate and zinc oxide bring to the experimentation is that they are known to act as pigments in anti-corrosion undercoats and paint systems[930]. Indeed, the naval colour *battleship grey* is formulated from 45% *blanc fixe* ($BaSO_4$), 45% *zinc white* (ZnO) and 10% *lamp black* (C)[931]. For this application, it was thought these pigments would not have a sufficiently protective effect since they would neither be *evenly* bound in a film suspension, nor *thickly* applied.

Barium sulphate is non-toxic due to its extreme water insolubility[932, 933]. Zinc oxide is considered to be "not particularly toxic"[934]. Gold as dust, the form present here, is considered to not be carcinogenic to rats, while skin implants of the metal sheet have proven to induce tumours[935]. Other candidate applied superior limitos markers based on white pigments with high atomic number like lead (Z = 82)[936] in the form of toxic lead white[937] pigment were not considered for health and safety reasons. To avoid skin contact, direct handling of the armour analogues was conducted with gloves. Indirect handling was made in dedicated plastic weighing trays. Inhalation during the application of the powdered white pigments was mitigated with a facemask, while inhalation during handling was not considered a significant risk to warrant facial protection.

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[928] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 95

[929] Ibid, p. 4 – 45

[930] Feller, 1986, p. 47

[931] Ibid., p. 50

[932] Ibid, p. 51

[933] Indeed barium sulphate, is ingested by human patients undergoing diagnostic medical procedures (i.e. barium enemas) as a radio-contrast agent for x-ray imaging of the digestive tract – the same principle applied here (Feller, 1986, pp. 51, 60)

[934] Kühn, 1986, p. 175

[935] Robles, 1998, p. 61

[936] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 18

[937] Eastaugh et al., 2004a, p. 233

The physical arrangement of the applied superior limitos markers was in particles so as to assist permeability by water, oxygen and the subsequently produced corrosion products. The barium sulphate and zinc oxide/barium sulphate mixture were applied by sieve in powdered form (Figure 3-14) from standard laboratory supplies (ZnO, 99.9%, Aldrich Chemical Company & precipitated $BaSO_4$, 99.9% BDH Laboratory Supplies).

Figure 3-14 Application of zinc oxide/barium sulphate applied superior limitos marker to armour analogue Coupon Series 5

Complete and uniform surface coverage for these two white applied superior limitos markers was problematic. Particles of barium sulphate and zinc oxide are reported in the literature to be small, respectively on average 0.5-2.0µm[938] and 0.25-1.0µm (nodular form used in this study)[939]. The problem however was the tendency for the particles to conglomerate together. Decreasing the assembly of particles was achieved by drying in an oven (105°C) until no mass loss was recorded. The powders were then ground further using a mortar and pestle. However, although it can be seen that the average conglomeration sizes are smaller, the particles did not fully separate from each other (Figure 3-15): probably due to the mesh diameter of the sieve. A sub-micron diameter sieve would have been preferable for separating particles thereby assisting greater uniformity of surface coverage.

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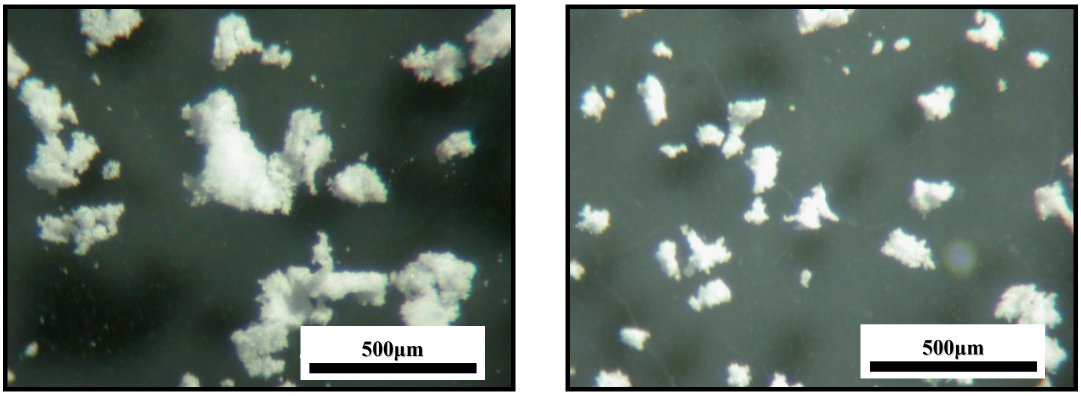
[938] Feller, 1986, p. 54

[939] Kühn, 1986, p. 179



From supplier and after sieving **From supplier and after heating, grinding and sieving**

Figure 3-15 Conglomeration of barium sulphate applied superior limitos marker particles

Gold was *sputter-deposited* onto the armour analogues using a SEM sample preparation sputter coater (Agar Automatic Sputter Coater B7341) (Figure 3-16). Since gold sputtering for SEM and/or EDS applications is designed to increase conductivity of the sample, while being *unobservable*, it was anticipated that it would be necessary to previously determine a sufficient quantity of sputtered gold that could indeed be *observable* under the SEM BSE mode (especially on a cross-section) and/or *detectable* under the EDS. According to the supplier of the gold sputter coater, the variable parameters (plasma current and time) required to apply a suggested standard application of gold to a sample normally destined for SEM-EDS investigations is 30mA for 120 seconds[940]. These parameters were applied as a preliminary test onto glass microscope slides, which were subsequently embedded in epoxy resin and polished in cross-section. Under optical microscope magnification (1000x) a lustrous gold reflection was faintly determinable, but very blurred and insufficient for diagnostic purposes. Energy dispersive spectrometry on a highly magnified (2000x) interface between the glass and the epoxy resin confirmed its presence. To increase the thickness of this gold layer, and therefore reduce the required observation magnification, *two* rounds of sputtering at the same amperage (30mA) and for 120 seconds were applied to the armour analogues representing Coupon Series 6 & 7 (Figure 3-16). The coupons were repositioned on the stage for the second sputtering application so as to gain a more even gold thickness throughout. The surface distribution of gold onto the analogues did not feature any observable lacunae.

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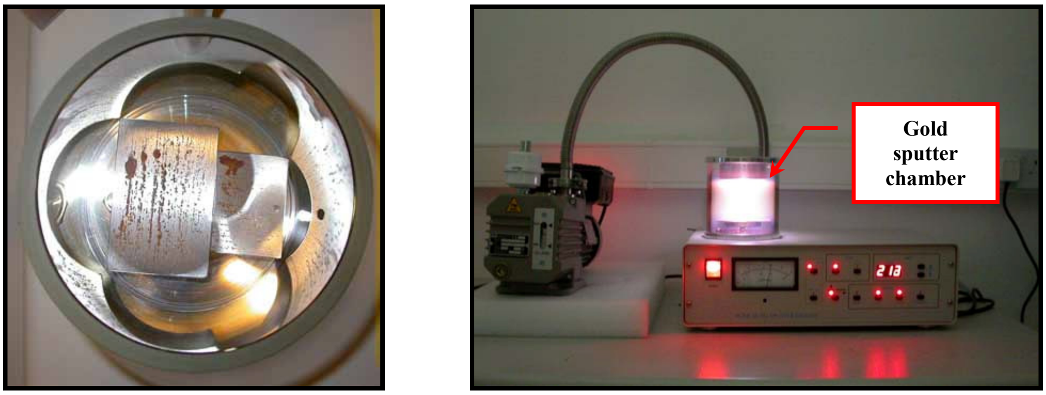
[940] Biella, 14/03/07, pers. comm.



Plan detail of coupons (experimental & control) from Coupon Series 6 on sputtering stage before sputtering

Gold sputtering application in progress in Agar Automatic Sputter Coater B7341

Figure 3-16 Gold superior limitos marker application onto armour analogues

The masses of each superior limitos marker applied to the coupons were calculated from before and after mass measurements recorded on an electronic microbalance (±0.0001g). The coverage of applied superior limitos marker was calculated in terms of the upper surface area (Table 3-4). To achieve greater surface coverage than the barium sulphate application made previously (on Coupon Series 1-3), the total amount of the barium sulphate and zinc oxide mixture was increased. The maximum quantity of gold applied was determined mainly by economic reasons.

Average mass and standard deviation of applied superior limitos marker applied to upper coupon surface area (mg.cm^{-2})		
$BaSO_4$ (<u>n</u> = 12)	**ZnO / BaSO4 (<u>n</u> = 12)**	**Au (<u>n</u> = 2)**
1.032 ± 0.225	6.559 ± 0.801	0.044 ± 0.025

Table 3-4 Mass range of applied superior limitos marker applied to coupons (75 x 50mm^2)

Despite gold's comparative scarcity by mass, its surface coverage attributed to small particles proved to be superior to that of barium sulphate and the zinc oxide/barium sulphate mixture.

3.3.1.1.5 Protective coating

A coating of acrylic resin (Paraloid B-72™, an ethyl methacrylate-methylacrylate (EMA/MA 70/30) copolymer by Rohm & Hass)[941] was applied to each Coupon Series (excepting Coupon Series 3) after the addition of their respective superior limitos marker.

The purpose of coating the armour analogues was to mimic the coated armour. Coatings, although not considered parts of the armour are certainly a part of

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[941] Horie, 1987, pp. 106-107

the munition armour's material-environment system[942] and their presence has clear consequences on the differential aeration corrosion mechanisms acting on the metal. The influence of coatings is testified by the corrosion product morphologies, most notably for filiform corrosion filaments, likewise referred to as *underfilm* filiform corrosion[943].

Coupon Series 3 was not coated due to concerns that the coating, despite its anticipated thinness, might at least to a certain extent impede the movement of evolving corrosion products through the applied superior limitos markers as reminded via personal communication with Bertholon[944]. So as to ascertain any effect the coating could have on corrosion product movement and the subsequent determination of the limitos, it was anticipated that after the accelerated laboratory corrosion regime Coupon Series 3 ($BaSO_4$/no NaCl/Paraloid B-72™) could then be compared with Coupon Series 2 ($BaSO_4$/no NaCl/Paraloid B-72™).

Paraloid B-72™ was selected as a coating material due to its ready solubility[945] in common solvents that would enable its subsequent removal from the coupons without significantly disturbing the corrosion product layers when assisted by physical action[946]. It was decided that such a coating would need to be sufficient to locally provide protection from atmospheric oxygen, and yet not be so thick and protective that it would significantly prevent corrosion and importantly the profusion of CPs through the coating should they evolve upwards as expected. The coating solution was prepared to a 7.5%m/v concentration[947]. The concentration was empirically selected from prior experiences with a 15.0%m/v concentration on similar low-carbon steel analogues[948].

The coating solution was applied by immersion in the same manner that the corrosion accelerant was applied to Coupon Series 1, 4 & 6 (Figure 3-11), although slower, so as to not disrupt the still loose applied superior limitos markers of barium sulphate and zinc oxide. An average and standard deviation mass of Paraloid B-72™

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[942] Figure 2-44

[943] 2.2.3.2.1 Filiform corrosion mechanism

[944] Bertholon 17/01/2007, pers. comm.

[945] Horie, 1987, p. 106

[946] The assisted removal, by physical means, of less soluble coatings present on armour might prove to have an extra effect on corrosion products on armour. Determining the extent and significance of this effect, if present, would require further experimentation

[947] i.e. 75g of Paraloid B-72™ *in* 1000mL of acetone, not *to make* a 1000mL solution

[948] Crawford et al., 2007, p. 9

applied to each surface (including all faces & sides) of the armour analogues (n=12) was calculated to be 0.8351±0.0966 mg.cm^{-2}.

3.3.1.1.6 Laboratory accelerated corrosion

In order to cause sufficient atmospheric corrosion of the metal, and create sufficient corrosion products in the relatively short timeframe of this research, accelerated corrosion regimes were designed and executed. Environmental parameters, in particular relative humidity, were selected and controlled. To accelerate the metal corrosion process, it was decided to fluctuate the humidity and thereby induce the wet and dry cycling forwarded by Stratmann's model of atmospheric corrosion of iron[949]. Condensing humidities (100%RH) were avoided as suggested by the atmospheric corrosion testing literature, which recommended 50-95%RH[950]. The targeted upper RH was chosen to be 90% since this would be sufficiently below dew point should the temperature drop significantly: e.g. 90%RH at 20°C becomes 100%RH with a 2°C drop[951]. Two accelerated corrosion regimes were followed: the first for over 4 months; and the second for 2 weeks. Normally, cycling was performed on a diurnal basis on working days. Over non-working days the analogues were left inside the chambers with elevated relative humidity. During the 4-month regime the containers were insulated inside polystyrene over-containers to limit fluctuations towards dew point. The 4-month regime involved cycling the relative humidity only, while the 2-week regime involved was more aggressive by cycling both relative humidity and temperature (Table 3-5).

	Accelerated corrosion regime			
	4 months		**2 weeks**	
	Relative Humidity (RH%)	**Temperature (TºC)**	**Relative Humidity (RH%)**	**Temperature (TºC)**
Working day (8 hours)	Ambient	Ambient	Glycerin box, circa 60%	Ambient
Night (16 hours) and non-working days	Glycerin box, circa 90%	Ambient	Glycerin box, circa 90%	Oven, circa 35º

Table 3-5 Summary of the anticipated temperature and relative humidity parameters and the executed accelerated corrosion regime durations

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[949] 2.2.2.3.2 Atmospheric water, Time of wetness/dampness & humidity cycles

[950] Leygraf & Graedel, 2000, p. 71

[951] As per the psychrometric chart (Graph 2-5)

In addition, during the last week of the 2-week regime, the conditions were cycled two times per 24 hours[952].

The targeted lower RH limit selected for the 2-week corrosion regime was 60%, the previously stated[953] critical RH of unpolluted iron[954]. In this way the coupons not polluted with sodium chloride would still have been likely to corrode at this lower RH. Furthermore filiform on steel is reported to occur at RH ranges of 60-95% in a temperature range of 20-35°C[955].

To achieve the desired relative humidity, the standard, "Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Glycerin Solutions ASTM D 5032 – 97"[956], was followed. This involved the placement of glycerin-water solutions of a predetermined concentration in closed containers whereby an equilibrium relative humidity was achieved. This solution functions on the principle that greater proportions of glycerin yields lower humidities. The predetermined concentration was ascertained by Equation 3-1, where the required relative humidity and expected temperature were inserted.

$$R = \left[\sqrt{(100 + A)^2 + A^2 - (H + A)^2} - A\right] \times 1/715.3 + 1.3333$$

$$A = 25.60 - (0.1950 \times T) + (0.0008 \times T^2)$$

R = refractive index
T = temperature (°C)
H = relative humidity (%)

Equation 3-1 Glycerin-water solution concentration calculation in terms of the solution's refractive index[957]

The equation's resulting refractive index (R) was then referred to in a set of standard data tables[958] with refractive index versus concentration of glycerin in water (mol glycerin/L water) at a given temperature (20°C). The molar concentration (mol/L) of the glycerin-water solution was converted to a mass per volume concentration and the solution was practically formulated. A summary of the various established parameters for obtaining the glycerin-water concentrations to achieve the targeted relative humidity in the closed chambers at the expected temperatures is given in Table 3-6.

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[952] Initially use of the oven by other personnel dictated that elevated temperatures could not be used during the day.

[953] 2.2.2.3.2 Atmospheric water

[954] Pohlman, 1998, p. 82

[955] Hahin, 1998, p. 105

[956] ASTM, 2003

[957] Ibid., p. 3

[958] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 8 – 66

	Required relative humidity (H)	**Expected temperature (T)**	**Calculated temperature co-efficient (A)**	**Calculated refractive index (R)**	**Concentration (mol glycerin.L^{-1} water)**	**Calculated concentration (g glycerin .L^{-1} water)**
Dry	60%	Ambient: circa 20°C	22.020	1.433	9.490	873.972
Damp	90%	35°C	19.755	1.378	4.252 [959]	391.584

Table 3-6 Summary of the parameters, data and key calculations to achieve targeted relative humidities

As suggested by the standard, copper sulphate (0.1% m/v) was added to the prepared glycerin water solution for biocide purposes[960].

Coupons were divided between two transparent polypropylene 8.4L Rubbermaid™ boxes featuring Eastover seals for improved hermiticness (Figure 3-17).

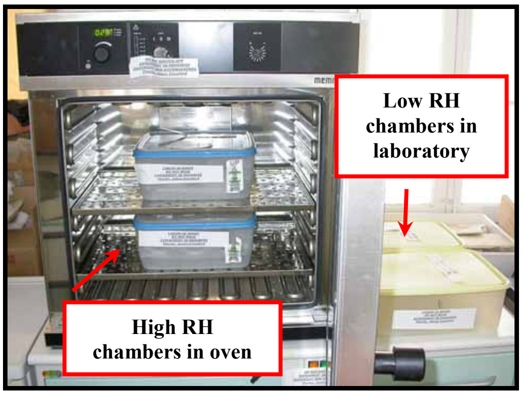

Figure 3-17 Polypropylene chambers and oven used for relative humidity and temperature cycling (2-week regime)

A Hobo™ data logger accompanied the armour analogues in one of the chambers to monitor and record the temperature and relative humidity. The data logger was supported with the software Boxcar Pro version 4.3, providing ±5% RH accuracy over the operating range of +5% to +50%°C[961]. Simple RH indicator strips were installed facing outwards through the containers as visual indicators for real-time RH spot-checking. The temperature and relative humidity data for the 4 month and 2 week acceleration corrosion regimes are presented respectively in Graph 3-1 & Graph 3-2. The difference between the targeted equilibrium RH and the RH actually recorded during the four-month corrosion regime was initially non-existent or very low (-2 to 0%RH). The progressive decrease in the equilibrium relative humidity achieved over the four month corrosion regime could be attributable to water loss

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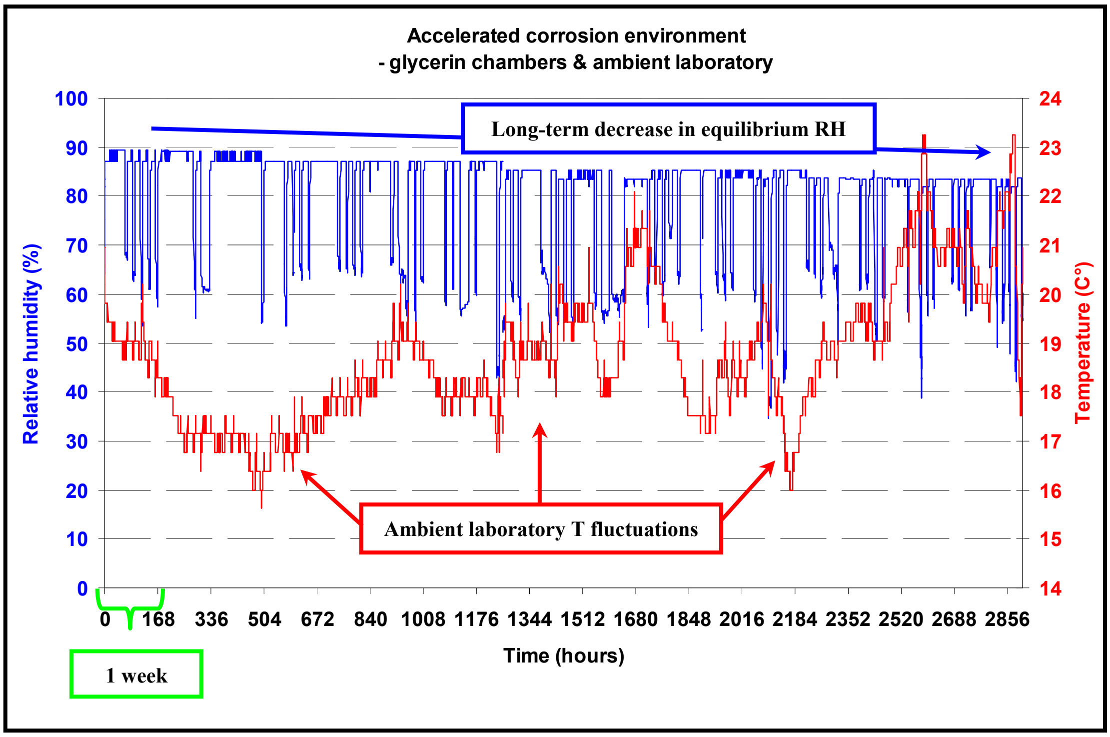
[959] Concentration of glycerin/water solution when with 1.3785 RI (at 20°C) (Ibid.). Data at 35°C could not be sourced.

[960] ASTM, 2003, p. 2

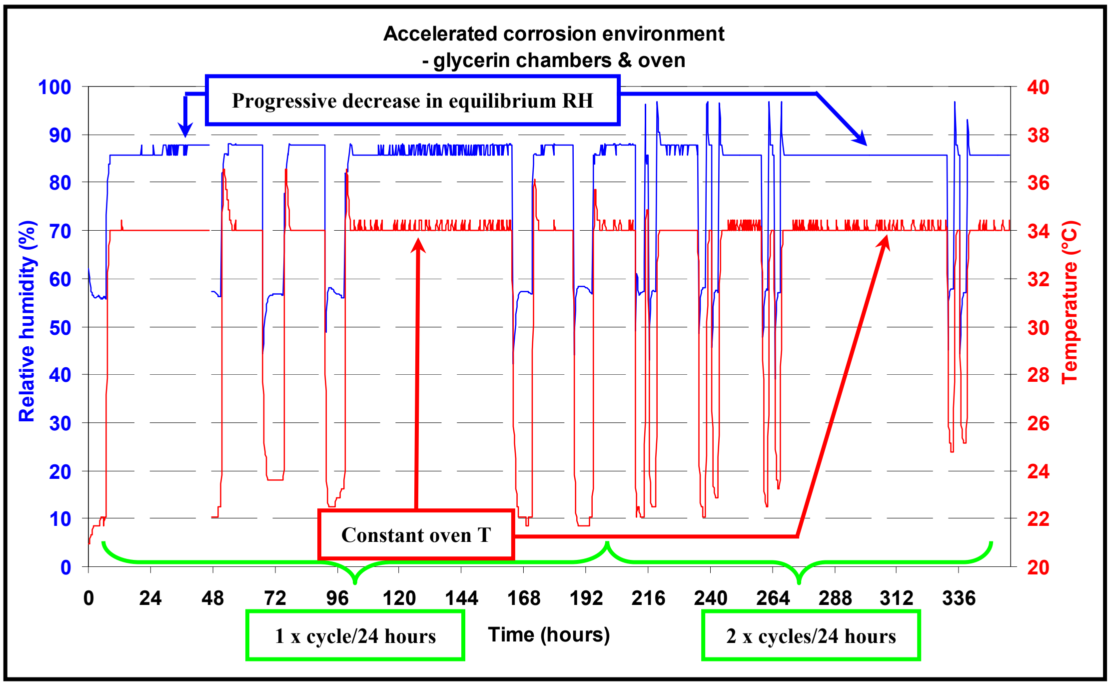
[961] Onset, 2003

from the chambers, probably particularly during opening and closing of the chambers to insert and remove the coupons. The temperature's diurnal fluctuations and longer-term net changes are attributable to the uncontrolled ambient laboratory environment (Graph 3-1).



Graph 3-1 Temperature and relative humidity recorded during the accelerated corrosion regime of the armour analogues over 4 months

For the two-week corrosion regime, a similar discrepancy (circa -2%RH) between the targeted and recorded RH was observed. It was also noticed that the temperature recorded by the logger (circa 34°C) was consistently below the oven thermostat (35°C). Like the four-month corrosion regime, a slight decline in the overall equilibrium RH was noticed for the two-week regime. The upper temperature during the two-week regime is constant overall, and is attributable to the oven's thermostat (with minor heat-loss and heating fluctuations). Greater temperature variation outside the oven is due to the uncontrolled ambient laboratory environment (Graph 3-2).



Graph 3-2 Temperature and relative humidity recorded during the accelerated corrosion regime of the armour analogues over 2 weeks

3.3.1.2 Armour analogue selection

After accelerated laboratory corrosion, the armour analogues were inspected for selection for continued investigation. The criterion for selection was the development of sufficient corrosion products formed in morphologies representative of the armour.

Coupon Series 2, 3, 5 and 7 (Figure 3-18) did not meet the selection criterion. Coupon Series 2 and 3 (each without corrosion accelerant) both failed to corrode sufficiently. The application of sodium chloride was therefore essential for accelerating the corrosion processes in the required timeframe. Series 3 demonstrated the complementary value the coating provided by retaining in place the otherwise loose white pigment applied superior limitos markers. The armour analogues designed to propagate filiform corrosion, Coupon Series 5 & 7, were only successful in creating this morphology in several localised places. Instead it appears the defect in the film coating, that was intentionally created to provide an initiation site with sodium chloride, had instead provided a defect in the metal for pitting corrosion to initiate and propagate. The scarcity of filiform corrosion propagating from the initiation sites meant this morphology could not be investigated appropriately on these coupons as anticipated.

The discontinuation of Coupon Series 2 (barium sulphate with coating) & 3 (barium sulphate without coating) meant that it would no longer be possible to investigate the effects the coating might have had on the position of the applied superior limitos marker and the limitos (between these otherwise identically prepared coupons)[962].

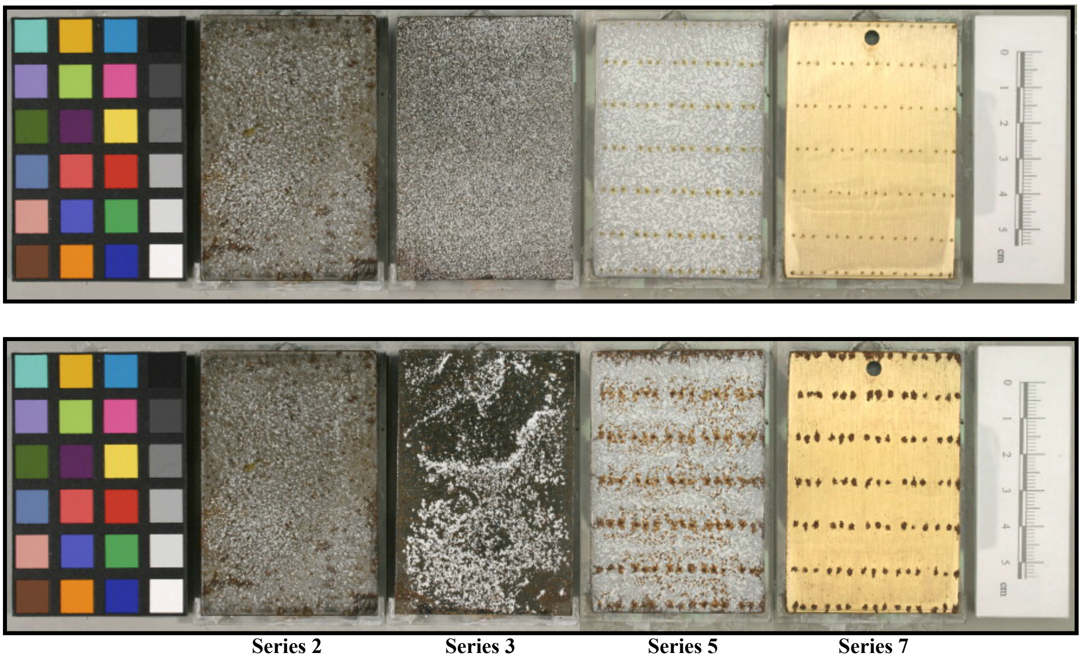


Figure 3-18 Representative armour analogues from the four Coupon Series *not* selected for continued investigation Top row: Before accelerated corrosion regime Bottom row: After accelerated corrosion regime

Coupons Series 1, 4 & 6 were all selected for continued investigation of their original surface limits. They had all corroded in such a manner to be considered under the classification *local to general corrosion* morphology and corroded to a *primary extent* (Figure 3-19).

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[962] 3.3.1.1.5 Protective coating

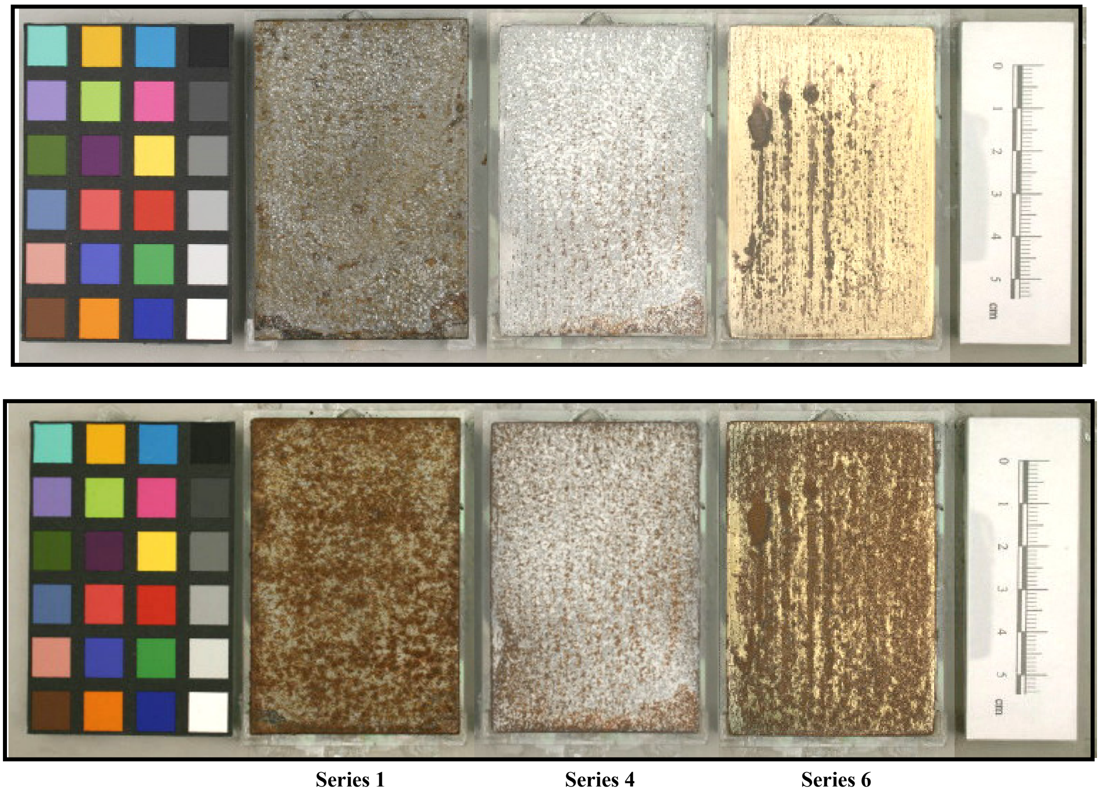

Figure 3-19 Representative armour analogues from the three Coupon Series selected for continued investigation. Top: Before accelerated corrosion regime Bottom: After accelerated corrosion regime

The presence of corrosion products indicates, superficially at least, that Coupon Series 6 (with the gold marker) had corroded significantly more than the zinc oxide/barium sulphate covered analogues (Coupon Series 4), which were prepared and exposed to otherwise identical conditions. It is probable then that the respective behaviours of the applied superior limitos markers are responsible for this discrepancy in CP evolution. Also notable was the presence of filiform corrosion, of varying shapes, heights, lengths and widths, on all coupons, but more prevalent on Coupon Series 1. The simultaneous presence of filiform and pitting corrosion was a similarity shared with the authentic armour corrosion product morphologies[963].

To limit recorrosion between preparation and investigation procedures, coupons were contained in desiccated storage boxes.

3.3.2 ARMOUR ANALOGUES: OBJECTIVES & DESTRUCTIVE INVESTIGATIONS

The major advantage of studying contemporarily manufactured analogues is the ability to unhesitatingly destructively investigate them. Importantly and equal to this advantage is that the surfaces represent a known history, which make it possible

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[963] 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy: Table 4-2 & Table 4-3

to infer with much greater confidence their fabrication and present-day condition after a purposely induced degradation, such as an accelerated corrosion regime in a laboratory. As previously outlined[964], so-called historical artefacts exposed to unknown atmospheric environments and human interventions, such as pollution and corrosion product removal procedures, introduce attributes that cannot usually be confidently explained, or at best, ambiguously explained. The uncontrolled environment of the Palace Armoury and the lack of documentation concerning restoration interventions on the munition armour exacerbate this fundamental situation, which makes it difficult to know exactly how CPs have evolved in this polluted environment and how interventions have affected this process.

The armour analogues were destructively used for a series of three principal objectives; building the experimental framework briefly presented here, and elaborated later[965]:

1. Armour analogue objective 1, Limitos determination: Characterisation of corrosion product stratigraphy and metal leading to limitos determination
   The first objective pursued understanding the corrosion products' properties and their relation to the uncorroded metal. These investigations sought clues in the complicated CP stratigraphies that could indicate any presence of the limit of the original surface in these CPs;

2. Armour analogue objective 2, Palace Armoury technique: Documentation & investigation of the current Palace Armoury cleaning procedure and results
   The second objective was carried out to understand the corrosion product removal procedures currently performed at the Palace Armoury. The performance and documentation of the level of CP removal procedures practiced at the PA would provide a reference point to the limitos anticipated to be determined from the previous objective. Indeed it might have been possible that the Palace Armoury is already empirically practicing CP removal to a level comparative to a diagnostically determined limitos; and

3. Armour analogue objective 3, Limitos application: Removal of corrosion products according to limitos determination
   The third and final objective provided space to demonstrate the practical application of corrosion product removal techniques that remove non-limitos materials and reveal the CPs anticipated to have previously been determined to represent the limit of the original surface. This objective would provide ultimate samples for collaborative curatorial discussion.

The individual coupons had an area of sufficient size that was equally divisible into the *sub-coupons* (25 x 50 x 2-3mm) required for the three objectives (Figure 3-20).

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[964] 2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour
[965] 3.3.2.3 Analogues: destructive investigations

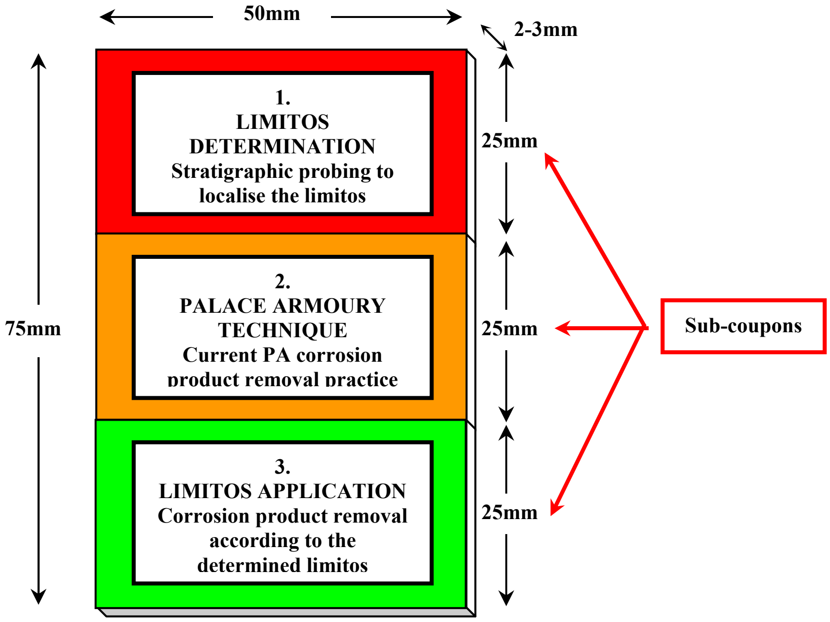
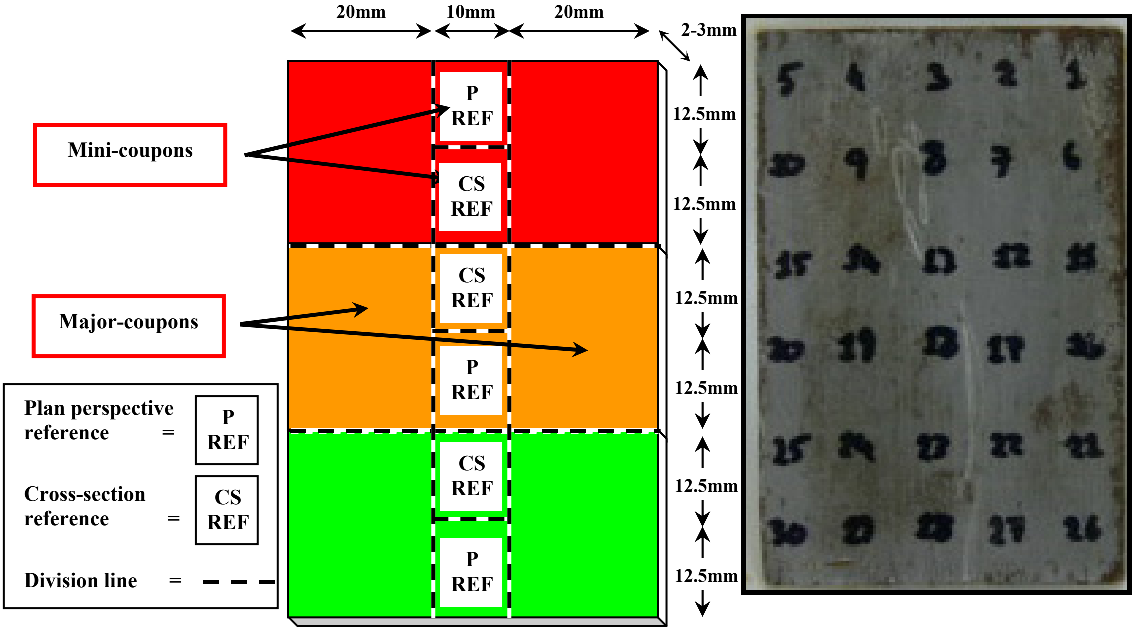


Figure 3-20 Schematic summary of armour analogue coupon with sequential objectives

Achieving each series of objectives on divisible components originating from an initially united substrate was performed to increase reliable comparability of results between the three identically prepared areas. The three *sub-coupons* (each representing one of the three objectives, Figure 3-20) were then further subdivided into four coupons that included two *mini-coupons* for plan (P) and cross-section (CS) observations and analyses (Figure 3-21: left). These mini-coupons (12.5 x 10 x 2-3mm) were anticipated for use as unaltered references. The central location of the unaltered references was decided for greater representativeness of the corrosion products on the adjacent major-coupons, thereby minimising unrepresentative edge effects. Two *major-coupons* (25 x 20 x 2-3mm) for each objective were produced per coupon (i.e. 6 major coupons per Coupon Series per Armour analogue objective) (Figure 3-21: left). Prior to cutting and their subsequent investigation, the analogue reverses were marked by pen with identification numbers (Figure 3-21: right) to track the numerous coupons.



Schematic division of armour analogues

Numbered reverse of coupon

Figure 3-21 Overview of the armour analogues' division (left) and numbering (right)

Separation of coupons was achieved using a hydraulic sheet metal guillotine (Figure 3-22: centre). Such a cutting technique was appropriate since it involved no heating, no generation of metal filings and no coolant liquids, which could all potentially interfere with the coupon materials. Before cutting the coupons, carbon paper was wrapped around them (Figure 3-22: left). The carbon paper served two purposes:

1. To protect surfaces from grease contamination during the guillotine cutting procedure; and
2. To mark the cutting edge with black carbon to assist highlighting the edges compressed by the guillotine cutting action. Compressed areas and adjacent zones would thus later be identifiable and be discounted from further examination.

Figure 3-22 Left: Armour analogues being wrapped (bottom: unwrapped, top: wrapped) in carbon paper before cutting. Centre: Industrial sheet metal cutting guillotine used to divide armour analogues. Right: Assembly of cut major-coupons (Armour analogue objective 1, Limitos determination only) from Coupon Series 1, 4 & 6

3.3.2.1 Analogues: plan surface preparation

Besides removing the carbon paper from the analogue samples, no specific preparation was required for the coupons to be observed by plan perspective by optical microscopy. For SEM-EDS investigations in plan perspective, coupons were carbon coated as later outlined[966], while Coupons Series 6 did not require a further conductive coating since they were already covered in gold. This series did however require removal of the Paraloid B-72™ coating with acetone on cotton swabs to enable observation of the surface topography with the secondary detector. The coatings were removed from the underside of all mini-coupons with acetone for electrical contact with the aluminium stub SEM-EDS stage sample holder.

3.3.2.2 Analogues: cross-section preparation

To prevent the surfaces of the cross-section samples from disintegrating during grinding and polishing, they were embedded in epoxy resin for consolidation.

Unlike with uniform corrosion and corrosion product morphologies, the localised nature of the morphologies on the armour analogues meant that cross sections could not simply be taken at random through a sample: doing so would not guarantee localising a significant pit, or any pit, for investigation. Before embedding these samples in preparation for cross-section examination, the likely zones of interest were documented and their distances from the edges of the coupons were measured with a screw gauge micrometer.

Custom-designed silicone rubber trays consisting of 20 cubic moulds (20 x 20 x 20mm) were fabricated to accommodate the numerous coupon cross-section samples (Figure 3-23: left). To avoid introducing adhesives, samples were physically held in place by polycarbonate inserts during the embedding procedure (Figure 3-23: centre & right).

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[966] 3.5.2.1 SEM-EDS sample preparation

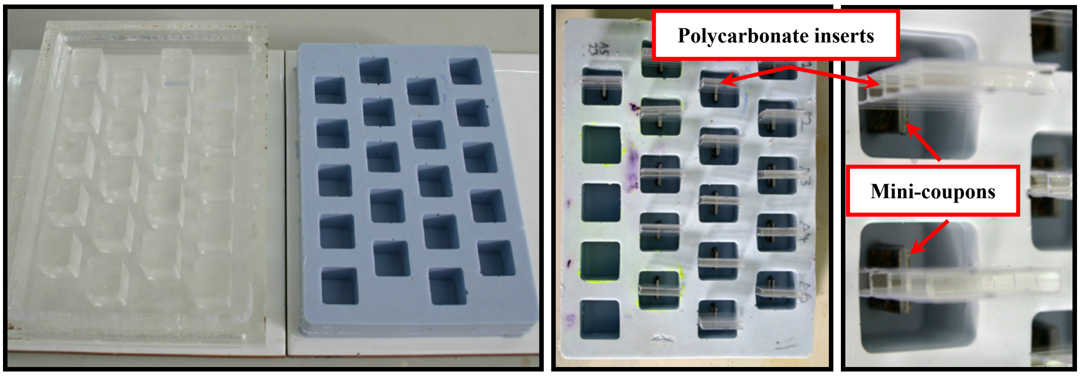

Figure 3-23 Left: Computer Numerical Control (CNC) machined acrylic positive mould and cast silicone negative mould custom-designed for dimensions of armour analogue sections Centre & right: Overview and detail of mini-coupons (i.e. cross-section samples) in embedding tray before resin application

Previous experiences with preparing metal samples with corrosion products prompted the necessity to optimise retention of the CP layers that are susceptible to being *pulled-out* during grinding and polishing. An embedding procedure that was consolidating and a gentle, progressive grinding and polishing regime were deemed to be of high priority since preserving the CP layers meant retaining the prime areas of interest for investigation. Struers Epofix™, a low viscosity epoxy resin was ordered for the cross-section sample embedding.

Embedding was performed under partial vacuum to remove air in the porous CPs and the applied superior limitos markers and to improve consolidation of these materials with embedding resin. Partial vacuum-embedding was achieved using an electric rotary vacuum pump and glass bell jar (Figure 3-24). A commercial partial vacuum-embedding unit was not available at the laboratories. Such units offer the considerable advantage of evacuating air from the samples *before* introducing the embedding resin.

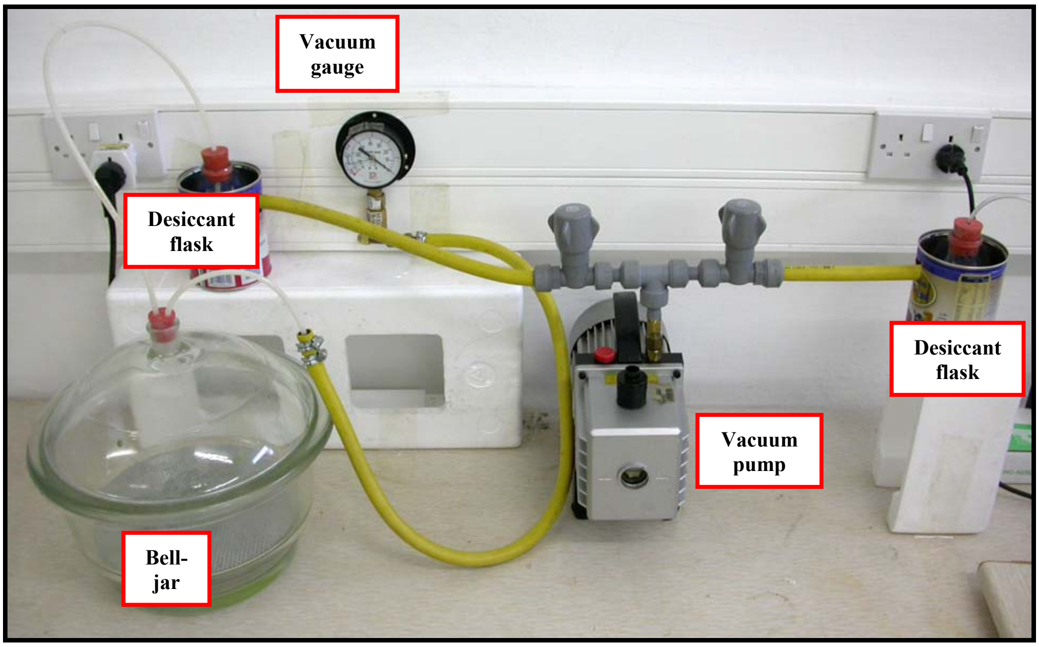

Figure 3-24 Laboratory constructed vacuum resin embedding system

Samples with their freshly mixed resin were introduced into the bell jar, which was pumped from ambient atmosphere, circa 1bar, to a partial vacuum of 0.1-0.2bar as advised by the manufacturer[967]. A partial vacuum around 0.0533bar (40mm Hg) was avoided as this is the boiling point of epoxies and would have overheated the resin and introduced air-bubbles into the embedding resin[968]. The partial vacuum was released and pumped for a second time "to force air out and epoxy into blind-ending cavities"[969]. The resin was allowed to cure at ambient pressure for 12 hours.

Cured embedded samples were ground and polished on a specimen preparation wheel, initially with aluminium oxide grit paper, and later silicon carbide grit paper. Tap water was used as a lubricant until the last two grit sizes. To avoid flash rusting, white spirit (Paraloid B-72™ insoluble[970]) was used to perform the last two polishing stages and to dewater the samples quickly after completing polishing. To limit contamination across layers the samples were polished with the surface orientated parallel to the polishing wheel direction (Figure 3-25).

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[967] Jensen, 18/6/2007, pers. comm.

[968] Nielsen & Maiboe, 2000, p. 3

[969] Ibid., p. 1

[970] Insolubility in white spirits (or Stoddard's solvent, a mixture of 85% nonane and 15% trimethyl benzene (Lewis, 2002, p. 1126)) was suspected due to B-72™'s insolubility in heptane (Horie, 1987, p. 205). Insolubility was then confirmed by a solubility test involving immersion of the granulated resin in white spirits and agitation with a magnetic stirrer for 48 hours.

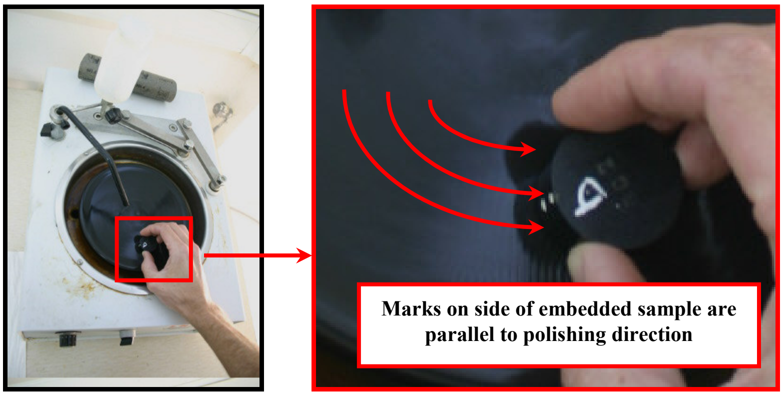

Figure 3-25 Sample polishing table and example detail of sample orientation and abrasive wheel direction

A grinding/polishing regime previously established by trial and error on the methodology pilot coupons was followed to retain an acceptable proportion (>90%) of the corrosion product layers. A Microsoft Excel™ spreadsheet automatically calculated the amount of sample to be ground/polished away before progressing to the subsequently finer grit paper (Table 3-7). This computation was especially of use for the numerous samples that each presented zones of interest at different distances from the coupon edges. To maximise CP retention, 1.5mm from each sample had to be slowly removed using 1000 grit paper to approach the zone of interest before the last much shorter polishes were performed.

		ANALOGUE IDENTIFICATION	**1-2**	**1-2**	**1-2**
		CROSS-SECTION NUMBER	**8**	**13**	**23**
		CROSS-SECTION DIMENSION	**(mm)**	**(mm)**	**(mm)**
DIMENSION REMOVED PER GRIT SIZE		**START DIMENSION**	13.60	13.30	13.20
		DIMENSION TO ZONE OF INTEREST	9.500	8.100	6.900
Grit	**(mm)**	**TOTAL DIMENSION TO REMOVE**	4.10	5.20	6.30
80	≥2.000	Dimension remaining after 80 grit	11.575	10.175	8.975
320	0.500	Dimension remaining after 320 grit	11.075	9.675	8.475
1000	1.500	Dimension remaining after 1000 grit	9.575	8.175	6.975
2400	0.050	Dimension remaining after 2400 grit	9.525	8.125	6.925
4000	0.025	DIMENSION AFTER 4000 grit	9.500	8.100	6.900

Table 3-7 Summary example of three cross-sections in the sample grinding dimension calculator (Microsoft Excel™)

During grinding with the 1000 grit, the sections were repeatedly inspected via binocular microscope until the zone of interest became exposed (i.e. the corrosion pit and corrosion products). Care was taken not to grind too far past the corrosion pit, while at the same time aiming to maximise the cross-section that exposed the deepest pit possible.

3.3.2.3 Analogues: destructive investigations

The rationales and subsequent methodologies followed for each of the three objectives pursued with the destructive investigations on the armour analogues are described next.

3.3.2.3.1 Armour analogues, limitos determination: corrosion/corrosion product morphology & limitos investigations

For Armour analogue objective 1, Limitos determination, characterisation of the armour analogues' corrosion product strata in terms of their composition, distribution, aspect and physical properties such as fragility and tenacity formed the basis of achieving this prime objective.

The characterisation of the CP stratigraphies and determination of the limitos of each of the three Coupons Series was performed via two perspectives:

1. Cross-section investigations of the stratigraphies of uncleaned mini-coupons (Figure 3-21). Three mini-coupons from each coupon were observed in cross-section; and
2. Plan/vertical physical probing investigations of the stratigraphies of uncleaned major-coupons (Figure 3-21). Two major-coupons from each coupon were vertically probed.

Each perspective presented its advantages for the methodology and was complementary to the other. Before completing the vertical probing, cross-sections of the uncleaned mini-coupons were observed and analysed[971] to determine the general layout of the exogenous material (i.e. coating, applied superior limitos marker) and the metal/corrosion product stratigraphy[972]. This cross-section perspective aimed to permit locating superior, inferior and corresponding limitos markers and provide a guiding *map* to the subsequent vertical stratigraphic probing performed on the major-coupons. The principal potential benefit of the vertical stratigraphic probing was that observation via the surfaces was the same perspective that an armour surface would be approached during a conservation-restoration intervention. Any limitos markers found from this perspective could be invaluable to a conservator responsible for corrosion product removal from armour. Vertical probing also permitted rapid investigation of numerous zones of interest. Cross-section samples embedded in resin were anticipated to limit the number of rapidly investigated zones of interest due to the necessary grinding/polishing to new zones of

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[971] 3.5.1.3 Laboratory photomicroscopy & 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[972] Raman micro-spectroscopy was unavailable for the armour analogue investigations.

interest. Moreover, the correlation of many zones of interest with the previously observed non-embedded surface morphologies would have been an excessively time-consuming process for the numerous samples.

CROSS-SECTION ZONES OF INTEREST SELECTION & INVESTIGATION

Investigation of the armour analogues' reference mini-coupons via cross-section perspective was performed to better understand the composition and orientation of the sample's stratigraphy and more particularly to witness the subsequent position of the applied superior limitos marker after the corrosion regime. The position of the applied superior limitos marker was anticipated to indicate (with comparison to the uncorroded control coupons and/or adjacent uncorroded areas), how the features and position of the corrosion products had been modified from the metal state.

The cross-section zones of interest ideal selection criteria were:

1. One or more zones of interest composed of corrosion pits with superimposed corrosion products; and
2. Significant amounts of corrosion products with sufficiently distributed superimposed applied superior limitos marker.

Evidently, to understand the interactions between the two criteria above, these components must have been simultaneously present. For example, there would have been less purpose in examining a cross-section featuring CPs that was devoid of corrosion pits and/or the applied superior limitos marker.

As mentioned[973], prior to cross-section investigation and vertical stratigraphic probing, potential zones of interest were selected via the plan perspective. To establish representiveness, an initial overview and assessment of all the coupons in each Coupon Series was made with the naked eye to ensure there were not any significantly varying CP morphologies and varying extents of development perceptible on a macro scale. Areas near the outer edges (circa 1-2mm) of the coupons were deemed unrepresentative of the larger inner areas available for investigation and would not be investigated since they had corroded differently (more or less, depending on the particular Coupon Series. i.e. an *edge-effect* occurred). Preliminary surveys of individual coupons under binocular microscope (mag. 20-50x) were made to determine the prevalent morphologies present and their constituent components. As planned for these three Coupon Series (1, 4 & 6) the

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[973] 3.3.2.2 Analogues: cross-section preparation

corrosion product morphology chosen for these cross-section zones of interest was *local to general corrosion*. Although also present, filiform CP morphologies were both too few in number for practical use in cross-section. To achieve transversal-cross-sectioning of filaments and base metal, recording the location and orientation, embedding and grinding/polishing to the filiform filament would have been necessary. Transversally-sectioning a filiform filament and also distinguishing it from all the other CPs on these coupons would not have been efficient or reproducibly achievable on mass. This is where the role of the anticipated Coupon Series 5 & 7 was intended to be advantageous. Filiform CP morphologies were nonetheless investigated by stratigraphic probing on the coupons from Coupon Series 1, 4 & 6. After selection of the zones of interest was made on the mini cross-section reference coupons (Figure 3-21) they were embedded and polished as previously detailed[974].

Preliminary observation of the cross-sections was first undertaken via optical microscopy and metallographic microscopes[975]. The coupons coated with zinc oxide were observed both under visible light and under ultra-violet light for fluorescence and to possibly indicate its location within corrosion products. For greater magnification, phase contrast and elemental analyses during observation, prioritised cross-sections were investigated under SEM-EDS[976] following the standard sample conductivity preparation procedure[977].

Considering that determination of the limitos is ideally made by simultaneous alignment of superior, corresponding and inferior limitos markers[978], it was decided to check if there was a determinable inferior marker for the corroded contemporary steel. Very minor amounts of fine (5µm), short (100-150µm) and isolated slag inclusions had previously been observed by others during metallographic observation of the polished uncorroded metal[979, 980] used in the armour analogues (Figure 3-26); so it was not expected to easily find, if at all, such an inferior limitos marker in the metal's corrosion products. Modern steel, such as that used for the armour analogues,

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[974] 3.3.2.2 Analogues: cross-section preparation

[975] 3.5.1.3 Laboratory photomicroscopy

[976] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry

[977] 3.5.2.1 SEM-EDS sample preparation

[978] 2.3.1.2.1 Localisation of the limitos

[979] Before microstructure modifications (3.3.1.1 Metal selection & substrate preparation)

[980] Vella & Degrigny, 2005a, p. 3

is generally of a relatively high purity with few inclusions, especially when compared with pre-contemporary wrought ferrous metals that are heterogeneous[981].

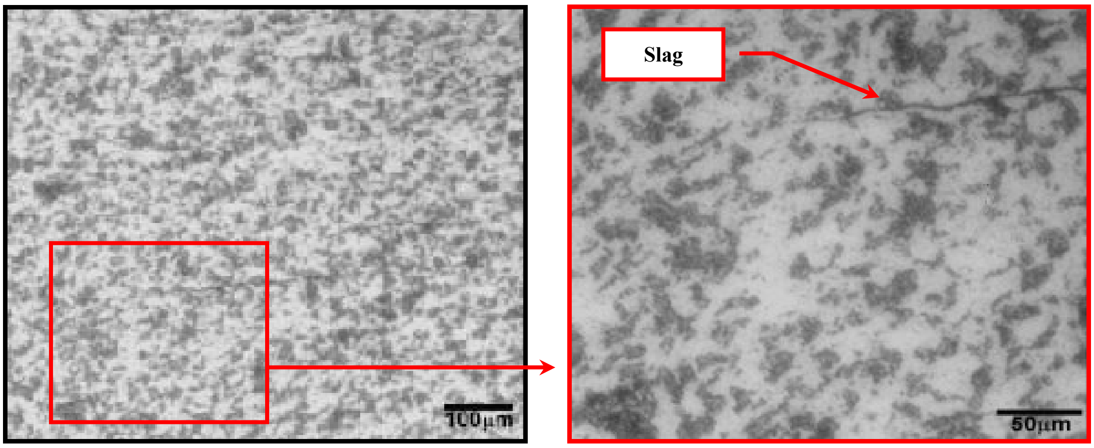

Figure 3-26 Slag in metallographic cross-section of armour analogue[982]

The method for checking inferior markers was trialled with EDS and was expected to be based on elemental compositional differences between the various CP phases and the metal. Similar examples of corrosion phenomena where variations in elemental composition of the corrosion products and the metal can indicate the limitos include dealloying of bronze by decuprification[983] or graphitisation of grey cast iron[984]. Iron was excluded from being considered as a discriminating element (at least in concentration) since the extreme heterogeneity of mixed phases of the common atmospheric ferrous corrosion products and their relative closeness in iron composition (e.g. Fe_3O_4 = 72%at.wt. Fe, while FeOOH = 50%at.wt. Fe) was thought to be too unreliable to account for gradients in iron concentration and too demanding for EDS's capabilities. The two most abundant minor alloying elements in the low-carbon steel had previously been determined to be: manganese (Mn: 0.5130-0.5190%wt or 0.5058-0.5119%rel.at.wt.) and silicon (Si: 0.1959-0.2012%wt or 0.0987-0.1014%rel.at.wt.)[985]. Their concentrations were at the limit or below the detection range of the EDS in optimum conditions[986]. The third most abundant alloying component in the armour analogues was carbon (C: 0.1250-0.1572%wt or 0.0269-0.0339%rel.at.wt.)[987]. Like manganese and silicon, the carbon concentration was also under the optimum detection range for the EDS, however EDS is not ideal

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[981] 2.1.2.1 Metal extraction & processing
[982] Vella et al., 2006a, p. 3
[983] Robbiola et al. 1998, p. 2094
[984] 2.3.1 What is the original surface & why determine its presence?
[985] 3.3.1.1 Metal selection & substrate preparation
[986] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry
[987] 3.3.1.1 Metal selection & substrate preparation

for accurately detecting such a low atomic weight element[988]. Carbon was thus excluded as a potential candidate for marking the inferior limitos, but it could still be trialled if prepared with a gold sputter coat (rather than graphite[989]) or with more appropriate analyses techniques. The use of silicon as a marker was excluded since its faint presence on the polished samples was omnipresent: most probably due to the silicon carbide polishing papers used in sample preparation[990]. Similarly to carbon, silicon could be trialled if the samples were prepared with non-ambiguous materials (e.g. alumina/diamond-based abrasive). Manganese thus remained as the only likely candidate for elemental concentration discrimination by EDS.

Visually different (i.e. varying morphologies and greyscales of corrosion products) phases of CPs and metal were surveyed variously by point and area analyses with EDS for manganese at varying magnification in areas of the CP stratigraphy. Small area analyses (circa 1-9μm^2) were applied to restricted areas of specific morphologies to limit the background effect of potential non-manganese containing zones: it was thought that if a non-homogenous presence of manganese exists, any zones poor in manganese concentration could potentially mask a small signal for manganese. The survey initially started on the metal as a reference point and then on CPs in the bottom of the corrosion pit and progressed upwards to the outer surface that interfaced with the applied superior limitos marker. To relate the concentrations of any determined manganese, a conversion from the atomic emission arc induced spectroscopy's units of measurement (% weight) to EDS's units of measurement (% relative atomic weight) was made, and included EDS's 20% accuracy tolerance range when in optimum conditions[991].

PLAN PERSPECTIVE ZONES OF INTEREST SELECTION & INVESTIGATION

The major corrosion product forms were micro-photographed[992] in plan perspective on the major-coupons available for plan observation and subsequent stratigraphic probing under Armour analogue objective 1[993]. The corrosion product nomenclature system established by Bertholon[994] was employed to describe the characteristics of the various features present. The position of these various corrosion

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[988] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry
[989] 3.5.2.1 SEM-EDS sample preparation
[990] 3.5.2.1 SEM-EDS sample preparation
[991] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry
[992] 3.5.1.3 Laboratory photomicroscopy
[993] Figure 3-21
[994] 2.3.1.2.1 Localisation of the limitos, Corrosion/corrosion product stratigraphy terminology

products and materials relative to the proposed limitos were annotated accordingly: s = superior limitos marker or i = inferior limitos marker. For example, in the documentation of Coupon Series 1[995], the Paraloid B-72™ coating was annotated as D2s: meaning a deposit (D) that is superior (s) to the limitos and is layered second (2) to the outer interface with the atmosphere.

To better characterise the nature of each of these labelled and localised features they were then described in terms of their composition (e.g. heterogeneity), distribution (e.g. continuousness), appearance (e.g. colour, shine), profile (e.g. irregularity), texture (e.g. roughness) and physical properties (e.g. hardness, cleavage).

According to the nature of the materials present, physical or solvent-chemical means were used for manual probing. *Physical probing* involved using a scalpel, cotton swab (moistened with white spirit for lubrication) or fibreglass pen, for example, to remove corrosion products from corrosion pits. *Solvent-chemical probing* involved cotton swabs moistened with acetone, for example, to remove the Paraloid B-72™ coating. To assist the plan perception during stratigraphic probing, observations previously made with the embedded cross-sections of uncleaned references were used to complement (confirm or supplement) the stratigraphies observed. During such probing, determination of the presence or absence of the limitos in the stratigraphy of various CP and materials was achieved as later detailed[996].

3.3.2.3.2 Armour analogues, Palace Armoury technique: current armour corrosion product removal practice

To satisfy Armour analogue objective 2, Palace Armoury technique major coupons from each Coupon Series were given to the Palace Armoury staff member currently performing corrosion product removal on the armour. These armour analogues facilitated a diagnostic assessment of the current corrosion product removal practice applied on the Palace Armoury munition armour. A real-time comparison of the surfaces and stratigraphies between the PA’s cleaned major-coupons and their uncleaned reference mini-coupons was enabled. Furthermore, an evaluation could be made between these major-coupons cleaned by the PA and the

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[995] Figure 4-47

[996] 4.2.1.1 Plan perspective investigations

major-coupons[997] that were cleaned by the research author according to the results from the diagnostically determined limitos[998, 999].

These coupons from <u>Armour analogue objective 2, Palace Armoury technique</u> were cleaned of their coating and CPs according to the materials and procedures followed at the Palace Armoury (Figure 3-27):

1. Armour analogues (major coupons: 20 x 25 x 2-3mm) inserted into cardboard holder to facilitate manipulation.
2. <u>Coating (i.e. Paraloid B-72™) removal</u>
    a. Acetone on cotton swab (bamboo skewer wrapped with cotton wool) used to dissolve and remove most of Paraloid B-72™ coating.
    b. Perspex acrylic scraper and metal scraper used to remove tacky masses of coating.
    c. Acetone on tissue paper used to remove coating remnants.
3. <u>Upper (i.e. positioned above adjacent metal profile) corrosion product removal</u>
    a. Scalpel used to remove, as much as possible, CPs superior to adjacent metal surfaces.
    b. Acetone on tissue paper used to wipe surface of loose CPs from previous step.
4. <u>Lower (i.e. positioned in pits below adjacent metal profile) corrosion product diminution</u>
    a. Machine oil (3-in-1™) added directly to coupon and added to 0000 grade steel wool that was then dipped in rottenstone powder (silica-limestone abrasive) and applied in a circular motion to remove most of remaining corrosion products on coupon. Emphasis made to help remove some of those CPs remaining in pits.
    b. Acetone on tissue paper used to wipe off CPs and oil slurry.
5. <u>Surface polishing</u>
    a. Small wad/ball of 0000 grade steel wool dipped into Pre-Lim™ abrasive polishing paste and applied in a circular motion to clean and polish metal surface.
    b. Acetone on tissue paper used to wipe surface of Pre-Lim™ paste and particles from previous step.

Armour analogue inside holder

From left and top: Acrylic scraper, scalpels, cotton swab, paper tissue, steel wool and rottenstone powder

From left: Acetone, 3-in-1™ machine oil and Pre-Lim™ polishing paste

Figure 3-27 Equipment and materials used to clean armour analogues

In accordance with corrosion product removal from munition armour at the Palace Armoury[1000] all work was undertaken without magnification. The same CP

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[997] 3.3.2.3.3 Armour analogues, limitos application: corrosion product removal to the limitos

[998] 3.3.2.3.1 Armour analogues, limitos determination: corrosion/corrosion product morphology & limitos investigations

[999] Figure 3-20 & Figure 3-21

removal procedure was applied to each of the three Coupon Series. These coupons were not waxed in order to avoid impeding subsequent metal and CP surface observations and photography.

For comparative purposes, the surfaces of the cleaned Armour analogue objective 2 major coupons were macrophotographed before and after PA CP removal[1001]. The cleaned surfaces were then documented by photomicroscopy[1002]. The examination of the extent of corrosion product removal undertaken by the Palace Armoury on the armour analogues was made on Coupon Series 4 and 6 only, not Coupon Series 1.

3.3.2.3.3 Armour analogues, limitos application: corrosion product removal to the limitos

Providing evidence of any limitos would actually be determinable via the first objective of the armour analogues, the third and final objective, Armour analogue objective 3, Limitos application, was performed to ascertain if the present research author could practically reveal the limitos via commonly applied and available conservation procedures. Subsequent to this, any revealed limitos would need to be critiqued in terms of the implications of leaving the limitos corrosion products on the armour surface in a museum context.

The method of coating and CP removal varied according to the Coupon Series. The Paraloid B-72™ coating was removed from Coupon Series 1 & 4 by repeatedly rolling a cotton swab moistened with acetone over the surface, while full immersion in acetone and agitation with a magnetic stirrer was used for Coupon Series 6. Corrosion product removal was performed either by scalpel or cotton swab moistened with white spirits for lubrication. Identification of limitos corrosion products and controlled selective cleaning was performed with binocular microscope magnification (20-50x).

The surfaces of the Armour analogue objective 3 major coupons[1003] were macrophotographed before and after CP removal according to the determined

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[1000] 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique
[1001] 3.5.1.2 Laboratory macrophotography
[1002] 3.5.1.3 Laboratory photomicroscopy
[1003] Figure 3-21 Overview of the armour analogues' division (left) and numbering (right)

limitos. Also, surfaces before and after attempted cleaning to the limitos were documented by optical microscopy[1004].

3.4 PRELIMINARY NON-INVASIVE OBSERVATION OF THE DETERMINED LIMITOS ON AUTHENTIC MUNITION ARMOUR

Following the determination of the limitos on the armour analogues[1005], selected areas of armour previously documented according to 3.2.3.1.2 Armour surface macrophotography & photomicroscopy, were non-invasively examined for evidence of the limitos. This exercise was necessary to validate or not, albeit in a non-interventionist manner, the potential comparability of the armour analogues with the authentic armour. Under binocular microscope, areas were observed where the protective coatings had already been removed during prior studies of their coating systems[1006].

With the curators' permissions, various interventive approaches on the munition armour (including treatment of a backplate via partial corrosion product removal to this research's diagnostically determined limitos) were initially planned for this stage of the research. These treatments were withdrawn due to the large scope required to comprehensively advance the research question to this point.

3.5 INVESTIGATION METHODS & INSTRUMENTATION

A series of observation and analytical methods was employed during the investigations of the authentic armour and armour analogues. To benefit from complementarities between investigation techniques, the same zones of interest were examined, particularly with the cross-sections.

3.5.1 MACROPHOTOGRAPHY & PHOTOMICROSCOPY

Photography at macro- and microscopic scales was used throughout the investigations as a form of material surface documentation on which observations were recorded.

[1004] 3.5.1.3 Laboratory photomicroscopy

[1005] 3.3.2.3.1 Armour analogues, limitos determination: corrosion/corrosion product morphology & limitos investigations

[1006] Lemasson et al. 2004, pp. 40-41

3.5.1.1 *In-situ* macrophotography

Macrophotography of the wall-displayed armour in the museum environment of the Palace Armoury was performed. Documentation was made by digital photography (Canon 300D with 18-52mm lens) with diffused flash while and observations were recorded on a proforma (Figure 3-28).

Figure 3-28 *In-situ* photographic and written documentation process of armour wall displays in the Palace Armoury Armour Hall

The ability to immediately review images via digital photography permitted performing the photography in on-site conditions much more efficiently than when compared with analogue photographic image processing.

3.5.1.2 Laboratory macrophotography

Laboratory macrophotographic documentation was made with digital cameras tethered to a personal computer. A Canon 300D was used for wider shots of the armour, while a Nikon Coolpix 4500 was used for close-ups. The Canon was used for the macrophotography of the armour analogues. Both cameras were tripod- or copy stand-mounted and illumination was provided by tungsten lamps (Figure 3-29).

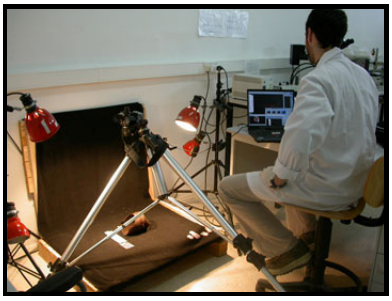

Figure 3-29 Macrophotography of overall armour

3.5.1.3 Laboratory photomicroscopy

Optical photomicroscopy of the armour surfaces was performed with a tripod-mounted digital camera (Nikon Coolpix 4500) set onto the ocular of an

Olympus SZ11 binocular microscope mounted on a counterbalanced arm to accommodate the armour's size. A fibre-optic tungsten light source was used with a 10-60° angle of incidence. Images were taken either at 20x or 80x magnification.

Photomicroscopy provided the most useful means to observe and record the surface features, corrosion product morphologies and their interrelationships, before and/or after the various investigative interventions on the armour analogue's surfaces.

Photomicroscopy of the armour cross-section samples and armour analogue plan and cross-sections was performed with the following microscopes:

- Olympus BX-50 optical microscope (plan observations and cross-sections) at 40x, 100x, & 200x; and
- Leitz MM5 inverted metallographic microscope (cross-sections[1007]) at 64x, 128x & 256x.

The Canon 300D digital camera was mounted, without its lens, directly onto the Olympus BX-50 optical microscope. Again a fibre-optic tungsten light source was used with a 10-60° angle of incidence. To lessen glare from metal surfaces, therefore increasing contrast, light was polarised with a cassette filter in the microscope objective. The armour analogues prepared with zinc oxide[1008] were observed under polarised visible light and also under non-polarised ultra-violet light (Olympus U-ULH mercury burner & U-RFL-T UV adaptor connected to the Olympus BX-50 microscope) with a 90° angle of incidence for fluorescence observation. The Nikon Coolpix 4500 was tripod mounted onto the ocular of the metallographic microscope (Figure 3-30). A reflected non-polarised tungsten light source via the objective (i.e. 90° angle of incidence) was used.

[1007] The Leitz metallographic microscope is ideally suitable for flat and highly polished surfaces as for cross-sections, thus it was not used for plan perspective observations.

[1008] 3.3.1.1.4 Applied superior limitos

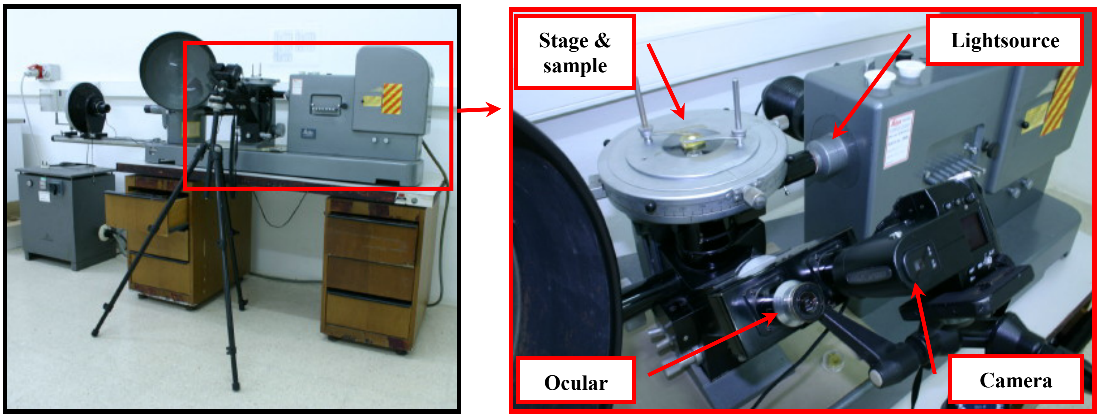

Figure 3-30 Photomicroscopy configuration: Leitz MM5 inverted metallographic microscope and tripod mounted Nikon Coolpix 4500 digital camera

Dimension scaling for the Olympus BX-50 and the Olympus SZ11 binocular photomicroscopy was performed using a glass slide (Olympus AX 0001 OB-M) with a 1mm graticule featuring 100 intervals. Scaling for the Leitz MM5 metallographic microscope was performed via the eyepiece graticule. Faint scales were embedded into photographs with imaging software (Adobe Photoshop CS2™) for subsequent annotation in MS Word™.

Both optical/binocular and metallographic microscopy served as useful observation methods for becoming familiar with the various predominant features on each sample size, shape, corrosion product presence, characteristics and distribution, coating thickness etc. Specific capabilities of the microscopes were used to differentiate between colours of the stratigraphies and surfaces (optical/binocular microscopes) and between the porosity and the metallic/non-metallic components (metallographic microscope). The Leitz MM5 (metallographic) microscope was beneficial in determining phase differences between the various corrosion strata by observing reflectance variations, but mostly in greyscale. The high reflectivity and contrast observable with the metallographic microscope was particularly useful for locating porosities (highlighted by black zones) and small areas of uncorroded metal nodules (white zones) amongst CPs that were otherwise unseen by the standard optical microscope. Since corrosion product organisation and distribution were of principal interest, not metallographic structure, etching was not performed when using the metallographic microscope.

The low magnification familiarisation of the samples also served for short-listing zones of interest for subsequent higher magnification observations and analyses using scanning electron microscopy-energy dispersive spectrometry.

3.5.2 SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY

A scanning electron microscope (Oxford LEO 1430) coupled with an energy dispersive spectrometer with an ATW2 window powered by Inca software (version 11A) was used to investigate the armour cross-sections. In essence, the SEM can characterise morphologies, while the EDS can associate the elemental composition of these particular features.

Scanning electron microscopy was anticipated to not only provide greater observation magnification of morphologies, but also increased phase contrast of the various mixtures of the predominant iron corrosion products and/or phase mixtures. The SEM using the BSE detector represents those materials of relatively higher average atomic number (Z) in the image with relatively whiter greyscale levels: the higher the average atomic number, the greater the backscattering and the more radio-opaque (i.e. whiter)[1009].

When SEM is coupled with energy dispersive spectrometry, the system can also provide elemental analyses of materials from carbon ($Z = 6$) upwards, if sufficiently present. In practice, with conditions of high background and broad peaks, the detection limit of EDS on mixtures of elements ($Z > 10$) is circa 0.5±0.1% atomic weight, but can be reduced to 1-2% atomic weight. Although Heritage Malta's EDS is not used for full quantitative analyses (requiring real/non-virtual standards) the EDS is used to provide relative concentrations (% relative atomic weight) thereby providing a semi-quantitative relative measure. The EDS is calibrated by using a real cobalt standard. In optimum conditions, the energy dispersive spectrometer has a 20% accuracy tolerance range[1010].

The relative concentrations (% relative atomic weight) from the EDS analyses were generally classified according to a semi-quantitative measure of major (>5%), minor (1-5%), and trace (<1%). These figures were not exactly relied upon, but provided a relative indication of the concentrations of the elements detected in each spectrum.

The application of SEM-EDS was prioritised to zones of interest on the short-listed samples from the optical microscopy observations. For these normally flat cross-sections the secondary electron (SE) detector (topographical contrast) was useful to determine if the section was truly flat, and subsequently the backscatter

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[1009] Rochow & Tucker, 1994, p. 302

[1010] Sbaraglia 24/11/07, pers. comm. (Assing, SEM-EDS Service Engineer) electron detector was applied. Inherent porosity or losses from the corrosion product strata during sample preparation were probable causes of voids in cross-section surfaces.

The main operating conditions of the SEM-EDS used were EHT = 20.00kV, filament current = 2.797A & beam current = 80µA.

Three spatial formats of EDS analyses were used on the cross-sections:

1. Points analysis;
2. Area analysis; and
3. Mapping analysis.

Points analysis restricts the incident beam and detection to a localised zone fixed around one point on the zone of interest, while area analysis covers a rectangular field area adjustable according to the size of the zone of interest[1011]. For both of these formats separate spectra with accompanying data (% rel.at.wt. of elements detected) were generated. Mapping analysis produces data with a sum numerical total of the relative percentages of the elements detected, as well producing pictorial representations of the elemental distribution with separate images assigned for each element[1012].

3.5.2.1 SEM-EDS sample preparation

Prior to SEM-EDS investigations, samples were carbon coated (Agar SEM Carbon Coater – B7367) and locally coupled with removable double-sided copper tape to form the conductive circuit required on the aluminium stub, which was then attached to the SEM-EDS stage. The addition of the non-conductive epoxy embedding resin to the otherwise conductive metal necessitated this sample preparation stage to avoid *charging* that prevents observation. The addition of the copper tape was locally applied under binocular microscope to avoid masking zones of interest previously determined via optical microscopy.

3.5.3 RAMAN MICRO-SPECTROSCOPY

Raman micro-spectroscopy was performed abroad on the three cross-section armour samples by Ms Judith Monnier, Laboratoire Pierre Süe, CEA (Commissariat Energie Atomique) Saclay, France. Micro-Raman measurements of the corrosion product layers[1013] were performed at the Laboratoire de Dynamique, Interaction et

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[1011] Figure 4-20

[1012] Figure 2-43

[1013] Monnier, 2005a-c

Réactivité (LADIR, CNRS and Paris6 laboratory, Thiais, France) with a micro-Raman notch-based spectrometer LabRam Infinity (Jobin Yvon-Horiba)[1014].

Raman spectroscopy is a useful tool for corrosion product characterisation since, unlike x-ray diffractometry, non-crystalline (or poorly crystalline) as well as crystalline species can be identified[1015]. It was thought that Raman micro-spectroscopy might provide information regarding the complicated ferrous CP strata.

Limitations to Raman spectroscopy however, include the inability (due to peak overlap) of it to discriminate between low concentrations of magnetite in goethite[1016] and low concentrations of magnetite in maghemite[1017]. This is where a complementary technique such as XRD[1018] might be required for differentiation *if necessary* for the research objectives[1019]. Contrarily, discriminating between magnetite and maghemite by XRD spectra has proven to be very difficult especially if they are mixed and this is where Raman spectroscopy proves complementary and successful[1020].

Regarding the methodology for the Raman micro-spectroscopy, radiation (green, 532 nm) was produced by a frequency-doubled Nd:YAG laser. Samples were observed under an Olympus microscope and objectives with 100x magnification, giving a beam waist diameter of about 3µm. The spectrometer setting offers a spectral resolution of about 2cm^{-1}. As some iron oxides are highly sensitive to laser irradiation, measurements were always performed with a power at the sample surface kept below 100µW in order to avoid any phase transformations[1021].

A pre-selection of potential zones of interest were previously determined by scanning electron microscopy and accompanied the samples for their analysis abroad. Multiple individual point analysis sites with the Raman micro-spectrometer were first selected manually on the cross-sections to identify visually differing phases. Later, linear and mapping profiles (with hyperspectral imaging) over the

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[1014] Monnier, 06/10/2007, pers. comm.

[1015] Neff et al., 2006 p. 1229

[1016] Figure 3-31

[1017] Neff et al., 2004. p. 743

[1018] The results from synchrotron radiation micro-XRD of samples extracted from the Palace Armoury munition armour already been presented in Chapter 1. It is not presented here since although the characterisation is of interest the method of sampling did not preserve the stratigraphic orientation that might be useful for these studies.

[1019] For this case, i.e. during the determination of the limitos such complementary analyses were not required.

[1020] Neff et al., 2006, p. 1229

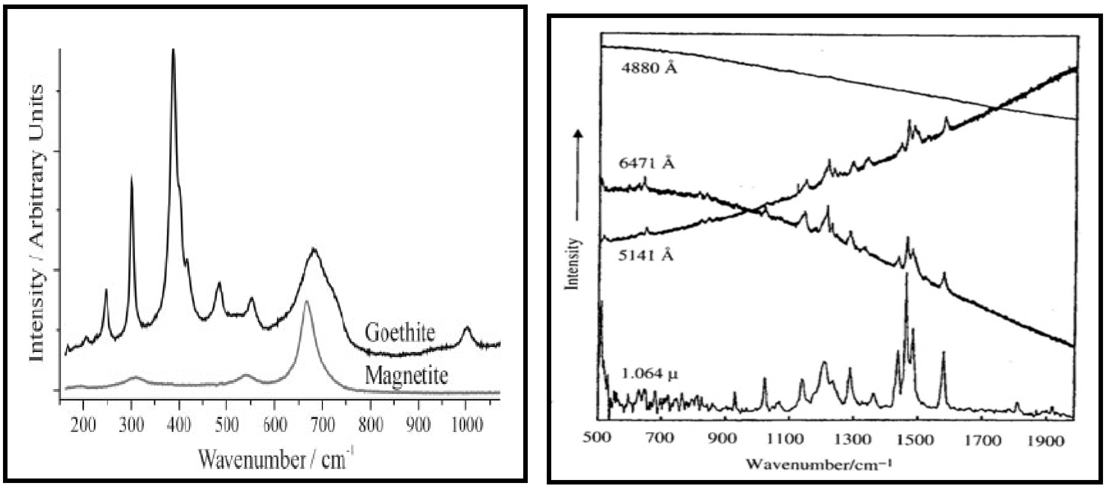
[1021] Monnier, 06/10/2007, pers. comm.

thickness of CP layers were performed. While taking longer, the use of hyperspectral imaging with the Raman micro-spectrometer "increases the statistic on the results by describing the phase organisation in the corrosion scale and ensures a better reliability of the conclusions brought up"[1022]. LabSpec™ (Jobin Yvon-Horiba) software was used to acquire and manipulate hyperspectral maps and the established methodology has been published[1023]. The analyst performed phase identification by comparison with reference spectra[1024].

A brief summary of the Raman micro-spectroscopy analysis principles is provided since it explains non-Raman signals, particularly *fluorescence*, later observed in the results[1025]. "Raman scattering and fluorescence emission are two competing phenomena, which have similar origins"[1026]. Raman spectra are obtained from the electromagnetic radiation scattered by the molecules subjected to the excitation source[1027], typically a laser. The scattered photons are less energetic and demonstrate a frequency shift due to the absorption of energy by the molecules under investigation. The particular shift in frequency depends on molecular vibrations that are characteristic of defined compounds[1028]. If the excitation source provides enough energy to cause an electronic transition from the sample's molecules, then direct absorption of photons can occur at the excited electronic state; this is then followed by a return to the electronic ground state. If the process is relatively slow (10^{-9} seconds) then fluorescence occurs[1029].

The change in frequency of the laser for Raman signals is represented by Raman shift peaks versus an arbitrary scale (Figure 3-31 left). However, fluorescence signals can reduce or eliminate the ability to match a signal pattern to reference spectra since they obscure the peaks that make identification possible (Figure 3-31 right).

[1022] Neff et al., 2006, p. 1229
[1023] Ibid, 2006, pp. 1231-1232
[1024] Monnier, 06/10/2007, pers. comm.
[1025] 4.1.3.2.4 Armour cross-section Raman micro-spectroscopy
[1026] Horiba Jobin Yvon, n.d., p. 1
[1027] Cornell & Schwertmann 2003, p. 146
[1028] Horiba Jobin Yvon, n.d., p. 1
[1029] Ibid.



Separate Raman spectra for goethite and magnetite

Raman spectra of cyanine dye using different laser wavelengths 488. 647, 514 and 1064nm. Fluorescence signals increase with shorter wavelengths until identifying peaks are unobservable: 488nm)

Figure 3-31 Example spectra exhibiting Left: Raman signals[1030] & Right: mainly fluorescence signals (right)[1031]

Fluorescence is cited to be caused by a variety of factors commonly occurring on heritage artefacts, including:

- Surface roughness (asperity)[1032];
- Organic materials (e.g. varnishes, resins such as coatings)[1033]; and
- Impurities from the exposure environment[1034].

[1030] Neff et al. 2004, p. 743
[1031] Edwards & Chalmers, 2005, p. 43
[1032] Monnier, 2005a, p. 3
[1033] Edwards & Chalmers, 2005, p. 42 & Monnier, 2005a, p. 3
[1034] Ibid.

4 RESULTS

The results from the series of experimental investigations on the mid 16th-mid 17th century northern Italian-style wrought plate munition armour of the Palace Armoury, and the contemporary analogues of this armour, are presented in this chapter. Preliminary interpretations of the results in reference to the limit of the original surface's determination are made, while major findings of this study's determination and practical exposure of the limitos in these ferrous materials' corrosion products are summarised.

4.1 PALACE ARMOURY ENVIRONMENT, MUNITION ARMOUR & CORROSION PRODUCT CASE STUDIES: NON-INVASIVE & NON-DESTRUCTIVE INVESTIGATIONS

The results from the various *in-situ* Palace Armoury and laboratory investigations performed on the Palace Armoury pollution, and surfaces and cross-sections of the authentic armour are presented next.

4.1.1 ARMOUR HALL WALL DISPLAY: *IN-SITU* CORROSION SURVEY

The *in-situ* wall display armour characteristically featured metal surfaces juxtaposed with corrosion product-covered surfaces. Usually, the same sheets of ferrous metal shared this contrast. A large bias of particulate matter was present on the CP-covered surfaces, which were non-inverted. In comparison, the greater majority of the metal surfaces were inverted and relatively particle-free (Figure 4-1). In the few cases where corrosion products did occur on inverted surfaces, they occurred very locally.

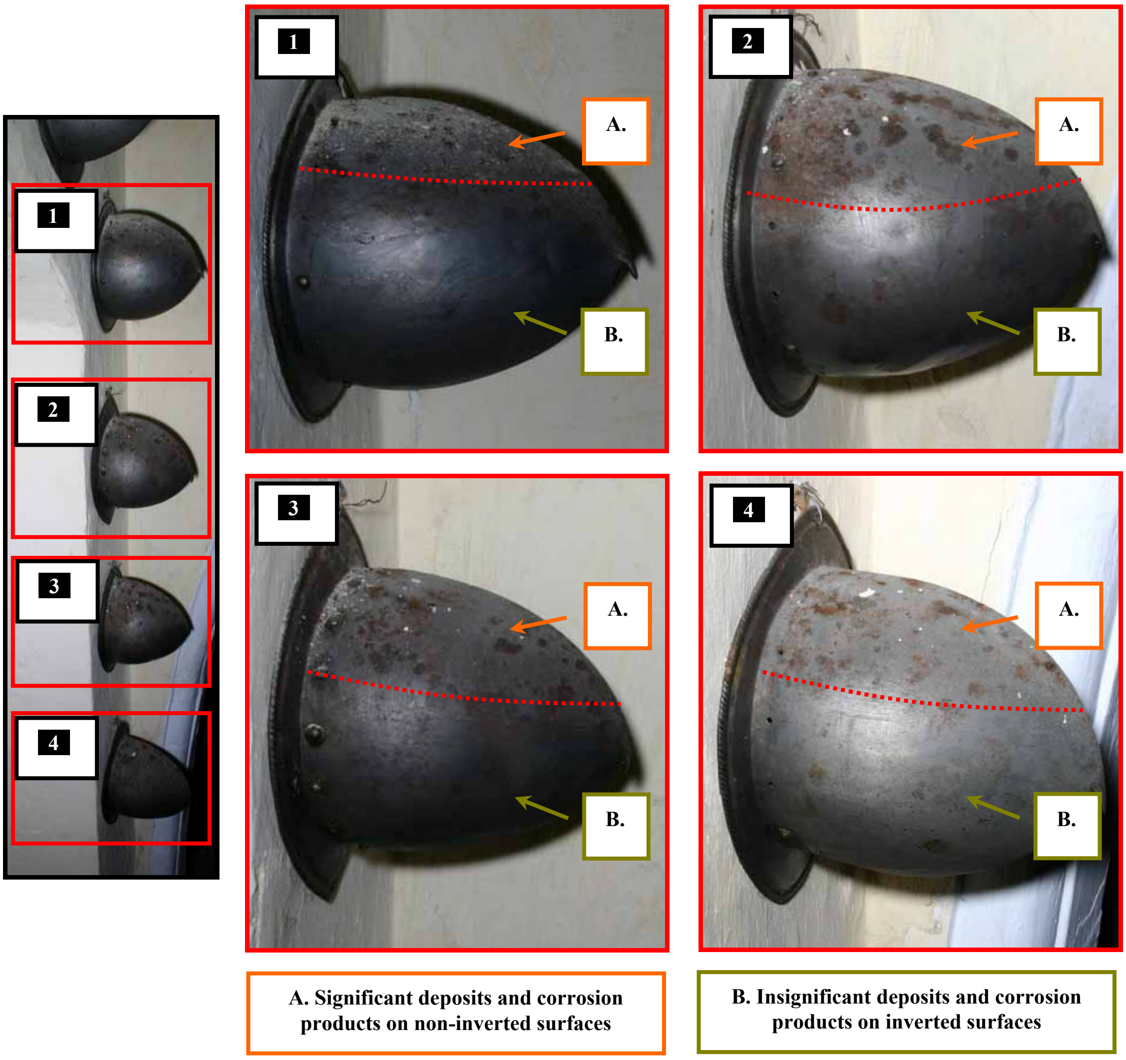


Figure 4-1 Left: Context of wall-displayed coated *cabasset* type helmets at the Palace Armoury. Centre & right: Details of helmets reproducibly exhibiting corrosion products on surfaces with particulate deposits.

From the observable surfaces several CP morphologies were visible: filiform; localised surface coverage; and more generalised coverage; all outlined in further detail in 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy.

Armour typically (circa 90%) featured a yellow-green transparent varnish, while the minority of armour (circa 10%) appeared to have been recently intervened since they had very few particles and CPs on the surfaces, and had differing coatings (wax and oil) known to be used in the more recent times of the present PA curator[1035].

[1035] Stroud, 2006-2007, pers. comm.

4.1.2 ARMOUR HALL AEROSOL POLLUTANTS: SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY

The SEM-EDS of the aerosol samplers collected from the Palace Armoury was made in an attempt to better understand how parts of the PA environment could be present in the armour's corrosion products, and to help determine if there were any environmental elements that could be used as superior limitos markers in these CP layers. The various elements detected by SEM-EDS are presented here.

4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

From the EDS performed on the adhesive samplers (Figure 4-2) a range of elements was detected, most notable was the high abundance of materials containing, or contaminated with, calcium-based species (100%) (Table 4-1). Oxygen, sulphur, carbon, chlorine, silicon and aluminium were all detected in the majority of sites investigated, while nine other elements were detected in the minority of sites. Detected copper was disregarded from the obtained spectra since it was attributable to the copper substrate of the adhesive tape used to collect the particles[1036].

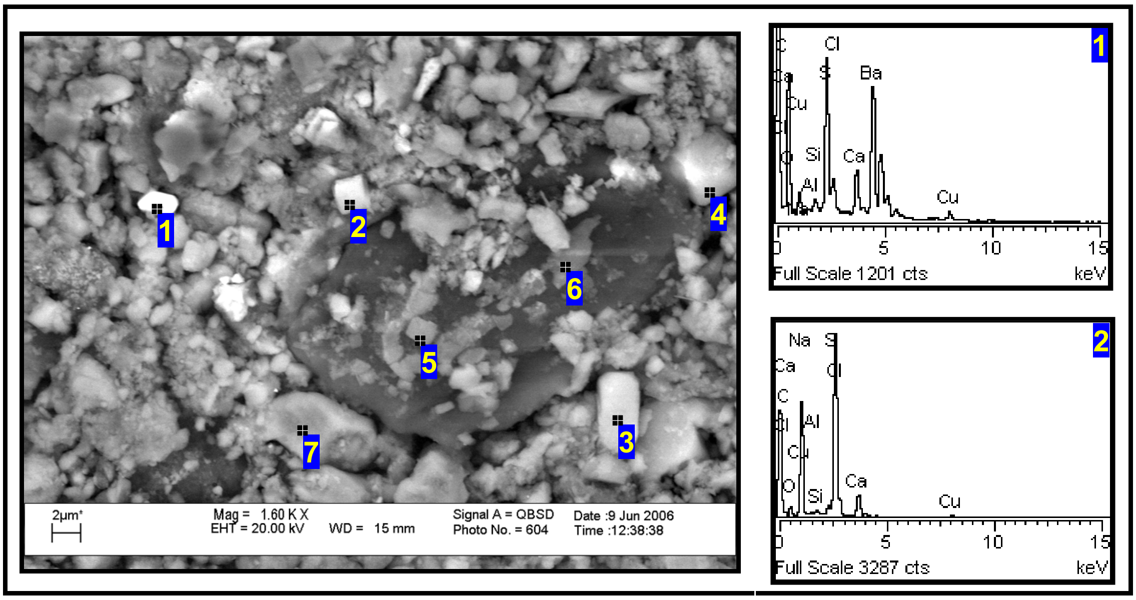


Figure 4-2 Example of a high magnification SEM BSE image (x1600) of collected Palace Armoury particulates and example spectra from the EDS sites of analyses (1 & 2)[1037].

[1036] 3.2.2 Armour Hall aerosol pollutants: scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

[1037] Vella, 2006

Results	
Element detected	**Frequency (n = 18)**
Calcium	100%
Oxygen	88.9%
Sulphur	88.9%
Carbon	83.3%
Chlorine	83.3%
Silicon	77.8%
Aluminium	61.1%
Sodium	44.4%
Potassium	33.3%
Magnesium	27.8%
Barium	16.7%
Lead	11.1%
Iron	11.1%
Phosphorus	5.6%
Chromium	5.6%

Table 4-1 Summary of raw data[1038] of Palace Armoury particulate deposits analyses by SEM-EDS.

4.1.3 AUTHENTIC MUNITION ARMOUR CORROSION/CORROSION PRODUCT MORPHOLOGIES: LABORATORY INVESTIGATIONS OF SURFACES & STRUCTURES

The results from the various laboratory investigations performed on the surfaces and cross-sections of the authentic munition armour are subsequently presented.

4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

In accordance with the results from the Armour Hall *in-situ* corrosion survey, areas of the armour studied in the laboratory proved to feature contrasting surfaces: i.e. metallic surfaces mostly without corrosion products and surfaces mostly with corrosion products. The remnant hanging wires testified the armour's former display orientation (Figure 4-3). On the laboratory-studied armour a correlation was again made between corrosion products and those formerly non-inverted surfaces, which had collected particulate matter. Also similar with the *in-situ* studied armour, the presence of CPs on inverted surfaces was a very occasional and limited exception to the trend.

[1038] Ibid.

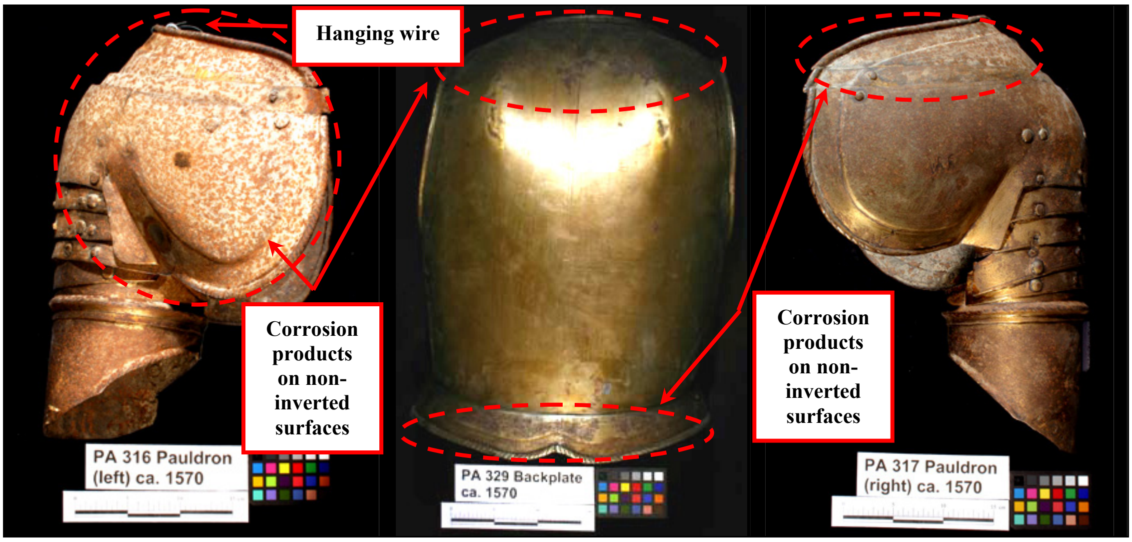


Figure 4-3 Former wall-displayed munition armour with corrosion products on non-inverted surfaces (15cm scales).

*

The types of corrosion product morphologies and their extent of development from macro perspectives are given in Table 4-2. These classifications of *extent of corrosion product development* are a simple relative scale (primary, secondary, tertiary) depicting the most representative range of corrosion phenomena on the Palace Armoury munition armour. The listed corrosion morphology of *local to general corrosion* did not attempt to indicate the profile or extent (i.e. even/uneven, shallow/deep) of the corrosion's vertical penetration since for the vast majority of armour and their respective surfaces, cross-sections required to provide this information were non-existent. No single, individual armour component featured all of the described corrosion product morphologies and extents of corrosion development, so a selection from several armour is presented to demonstrate this classification system. The inclusion of an image from the inner side of an armour element (PA RC 166) has been used to exemplify the tertiary local to general corrosion classification since none of the six armour selected for further laboratory-based surface studies featured the tertiary classification of local to general corrosion. This was despite many cases of other PA munition armour with this type and extent of corrosion[1039].

The corrosion product morphologies of local to general corrosion and filiform corrosion occurred independently of each other or simultaneously. As the degree of

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[1039] Refer to image 3 of Figure 3-2 (Three backplate armour selected to be representative of the corrosion extent on the wall displays) for a munition armour with an outer surface area featuring corrosion products comparable to the classification: tertiary local to general corrosion.

filiform development increased, a greater correlation with the local to general corrosion prevailed (refer to blue arrows in Table 4-2).

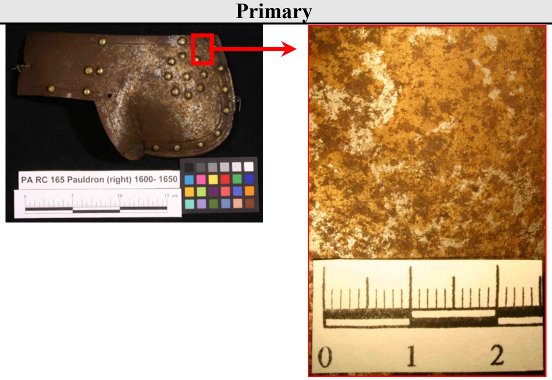
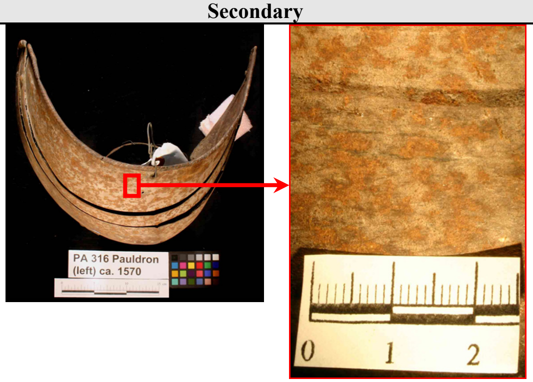
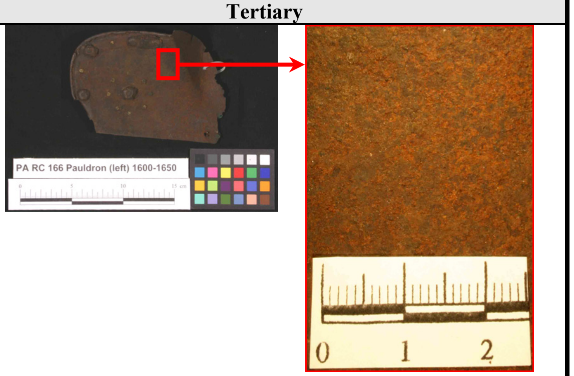
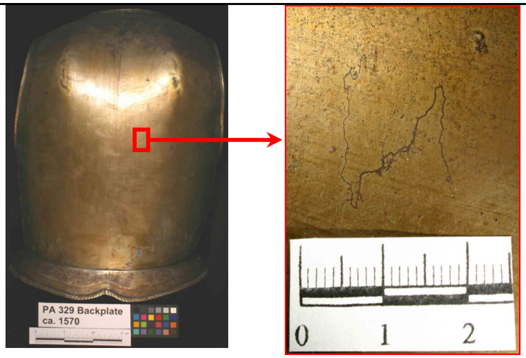
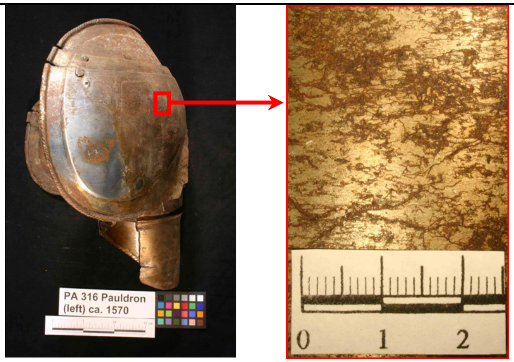
Corrosion product morphology		Degree of corrosion product development		
		Primary	**Secondary**	**Tertiary**
	Local to general	 **Left : Outer surface of PA RC 165 – Pauldron** **Right : corrosion product detail**	 **Left : Outer surface top of PA 316 – Pauldron** **Right : corrosion product detail**	 **Left : Inner surface of PA RC 166 – Pauldron part** **Right : corrosion product detail**
		Isolated areas of apparently thin surface CPs partly masked the metal surface. Yellow-green appearance resulted from a surface coating.	United areas of apparently thin localised surface CPs predominantly/totally masked the metal surface below and above the coating.	Evenly distributed and apparently thick areas of surface CPs totally masked the metal surface.
			↑	← ← ↰
	Filiform	 **Left : Outer surface of PA 329 – Backplate** **Right : corrosion product detail**	 **Left : Outer surface front of PA 316 – Pauldron** **Right : corrosion product detail**	 **Left : Outer surface side of PA 316 – Pauldron** **Right : corrosion product detail**
		Localised area of surface CPs restricted to the filament morphology positioned underneath protective coatings. The filiform might have diverged or terminated. Yellow-green appearance resulted from a surface coating.	Filiform density has increased and CPs have dispersed outwards from the filament threads forming a CP film over the metal. The filiform was still visible, but the film of CPs predominated and began to locally deposit CPs above the coating.	The dispersion of the CP film continued and was heavily present above the coating. The filiform was almost obscured. Yellow-green appearance resulted from a surface coating.

Table 4-2 Summary classification of proposed evolution of corrosion product morphologies and degrees of development on laboratory studied munition armour.

*

Table 4-3 provides microscopic details of the same surfaces presented in Table 4-2. The influence of the topography of the originating metal on the corrosion products became apparent, especially for the filiform corrosion morphology. In the case where parallel surface corrugations in the metal were present, the filiform filaments propagated along these micro-grooves (Table 4-3: secondary development of filiform corrosion morphology). Meanwhile, when local to general CPs evolved on these corrugated surfaces, the influence on their propagation and morphology was less apparent or non-existent (Table 4-3: primary development of local to general corrosion morphology). Although micro-grooves were noted on some metal surfaces during this microscopic examination, no such evidence of this corresponding limitos marker was observed in the corrosion products. When metal surfaces were more *randomly* flawed (e.g. metal surface depressions/pits), filiform corrosion accordingly followed this irregular arrangement (Table 4-3: primary development of filiform corrosion morphology). Eventually, as for both tertiary cases of corrosion development, deposition of corrosion products over the coating became more prevalent.

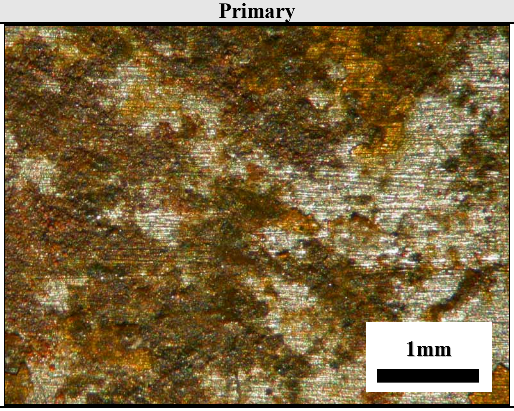
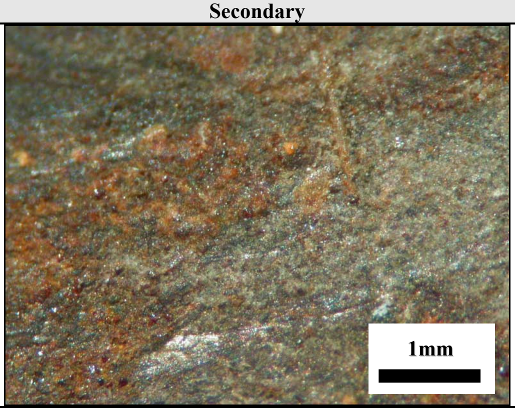
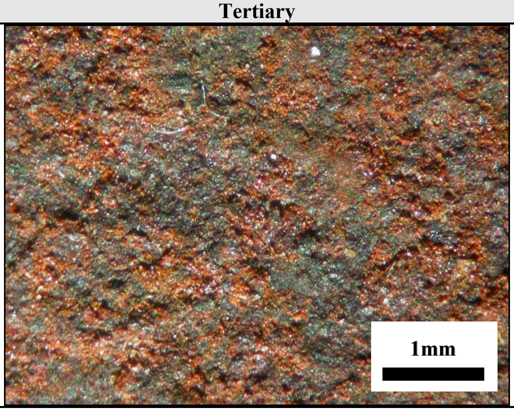
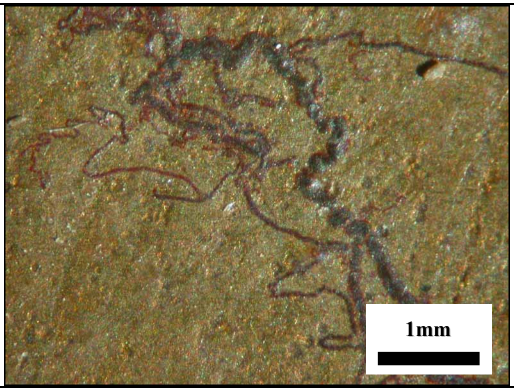
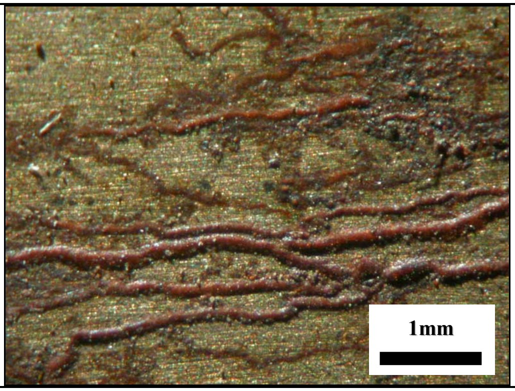
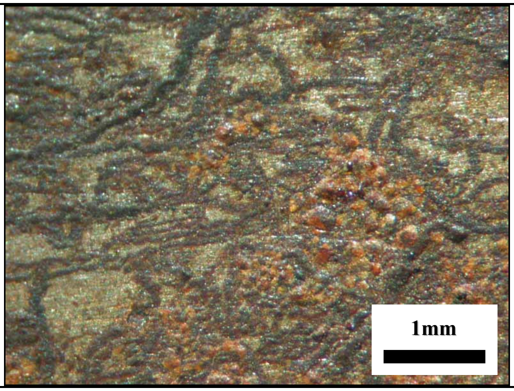
		Degree of corrosion product development		
		Primary	**Secondary**	**Tertiary**
Corrosion product morphology	**Local to general**			
		Isolated areas of apparently thin surface corrosion products partly masked the metal surface. The orientation of the local to general CPs did not appear to correspond with the parallel corrugations in the metal surface.	United areas of apparently thin localised surface corrosion products predominantly/totally masked the metal surface below and above the coating (orange-brown CPs).	Evenly distributed and apparently thick areas of surface corrosion products totally masked the metal surface.
			↑ ←	← ↰
	Filiform			
		Localised area of surface corrosion products restricted to the filament morphology positioned underneath protective coatings. The filiform might have diverged or terminated. The *random* orientation of the filiform CPs corresponded with irregularly positioned indentations (past corrosion pits formerly emptied of CPs?) in the metal surface. Yellow-green appearance resulted from a surface coating.	Filiform density has increased and corrosion products have dispersed outwards from the filament threads forming a CP film over the metal. The filiform was still visible but the film of CPs predominated and began to locally deposit CPs above the coating. The predominantly parallel orientation of the filiform corrosion corresponded with the parallel corrugations in the metal surface.	The dispersion of the corrosion product film continued and was heavily present above the coating (orange-brown). The filiform was almost obscured. Yellow-green appearance resulted from a surface coating.

Table 4-3 Corresponding photomicroscopy of the summary classification of proposed evolution of corrosion product morphologies and degrees of development given in Table 4-2.

*

Although these macro- and microscopic surface observations did not determine the possible location of the limitos in the corrosion products, an indication of where the limitos is *not* likely to be found was given. It is supposed that the limitos would not exist in any CP formations positioned superior to a coating layer. The basis of this notion is that it seems highly improbable that CPs, in a form still retaining a morphology or interface that represents the former metal surface, could *migrate* intact through an organic coating layer. In this way, it is then proposed the coating can act as a form of superior limitos marker. A coating is a common constituent on historical artefacts, but much less so on archaeological artefacts (at the time of excavation), where the concept of the limitos has its origins[1040]. Contemporary coatings are therefore a useful, if not obvious, addition to the possible array of superior limitos markers for historical artefacts such as armour.

4.1.3.2 Armour corrosion cross-section observations & analyses

It is demonstrated next via the results obtained from the various observational and analytical techniques used on the cross-sections that the Palace Armoury munition armour and their constituent metal and corrosion products were determined to be heterogeneously composed, and the first indications of a proposed limitos are made.

4.1.3.2.1 Armour cross-section sampling site surface macrophotography & photomicroscopy

Photography of the armour surfaces corresponding to the area immediately adjacent to each cross-section sampling site is presented here on macro- and microscopic scales.

PAULDRON (PART) PA RC 166

Like the rest of this armour, the surface adjacent to the sampling site on the incomplete pauldron, PA RC 166, appeared to have been left in an unpolished condition (both outer and inner surfaces) for many years or even decades (Figure 4-4). Significantly, these undisturbed areas could possibly hold remnants of the limitos in CP layers that have developed considerably over time. No coatings were

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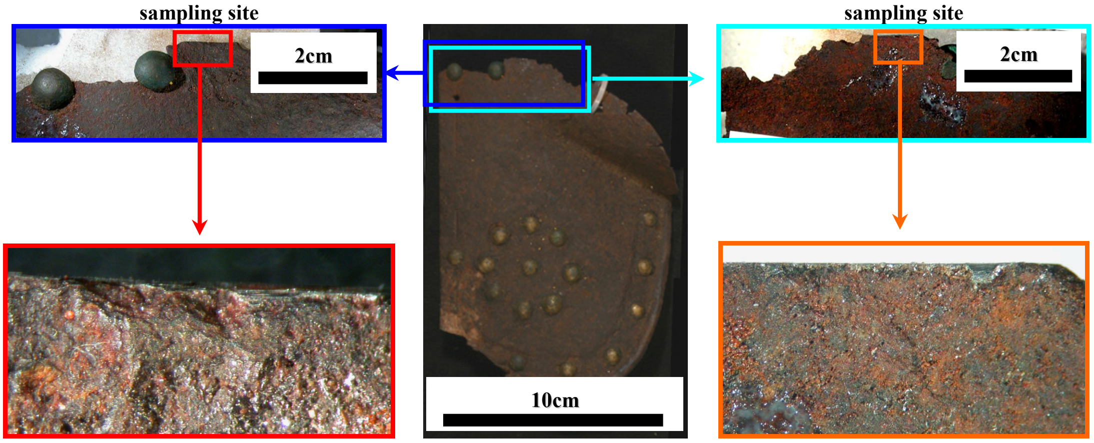
[1040] 2.3 Metal heritage artefact conservation & corrosion products: philosophy & practice observable on the outer or inner surfaces. The sampling site was at the broken edge of the armour and was therefore made at the former centre of the armour plate.



Local context of *outer* surface and sampling site

Local context of *inner* surface and sampling site

***Outer* surface and edge adjacent to sampling site**

Macro context of armour *outer* surface and sampling site

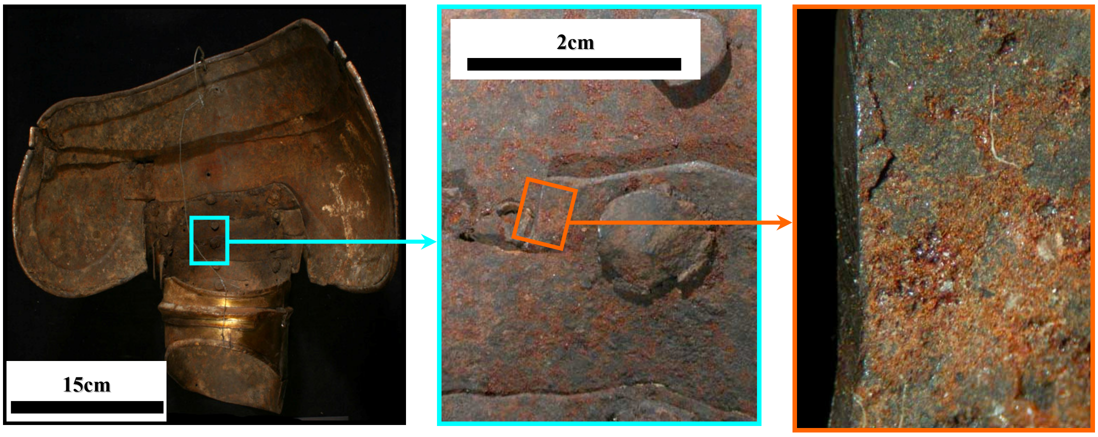
***Inner* surface and edge adjacent to sampling site**

Figure 4-4 Sampling location and surface documentation of Pauldron (part) PA RC 166.

Overall, Pauldron (part) PA RC 166 was unlike the wall-displayed armour since it did not feature the contrast between surfaces with and without corrosion products.

Pauldron PA 316

The inner surfaces of Pauldron PA 316 (Figure 4-5) were unpolished and supported layers of corrosion products: typical of the PA munition armour's inner surfaces. The outer surfaces immediately adjacent to the sampling site of Pauldron PA 316 could not be documented since the sample was extracted from the edge of a lame with a visually inaccessible outer surface (i.e. between lames). Nonetheless, it was noted from the visible outer surfaces that a coating was present in the area adjacent to the inaccessible outer surface. It could not be determined from the armour if this coating extended to the sampling site.



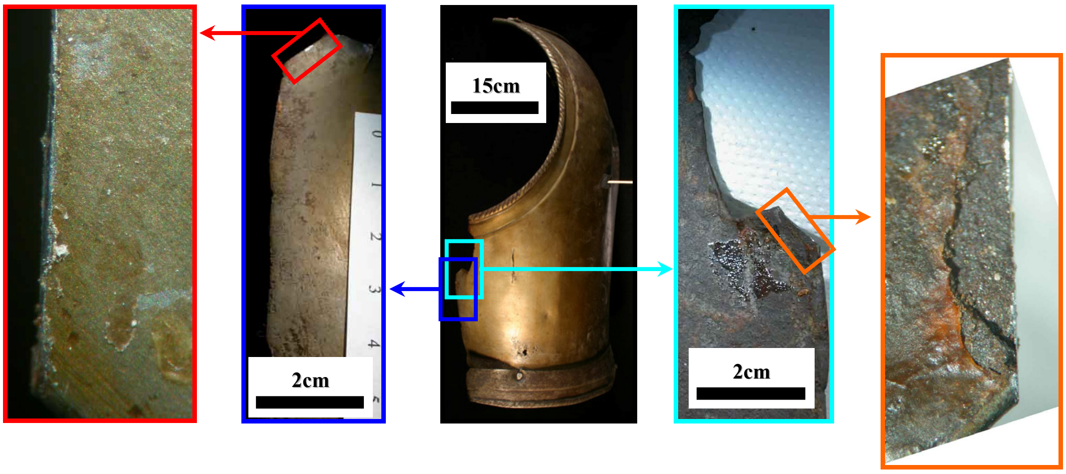
Macro context of armour *inner* surfaces and sampling site **Local context of *inner* surfaces and sampling site** ***Inner* surface and edge adjacent to sampling site**

Figure 4-5 Sampling location and surface documentation of Pauldron PA 316.

Overall, Pauldron PA 316 represented typical wall-displayed armour since it had a bias of corrosion products on the non-inverted outer surfaces.

Backplate PA 329

Lastly, most of the outer surfaces of Backplate PA 329 were not obscured with corrosion products and permitted observation of minutely pitted surfaces largely devoid of CPs (similar to Table 4-3: primary filiform). The inner surfaces were covered with thick deposits of coating materials and unidentified dark materials (Figure 4-6); making the inner surface relatively uniform when compared with the inner surfaces of the two previously described armour. The sampling site was on the side edge of the backplate.



***Outer* surface and edge adjacent to sampling site** **Local context of *outer* surface and sampling site** **Macro context of armour *outer* surfaces and sampling site** **Local context of *inner* surface and sampling site** ***Inner* surface and edge adjacent to sampling site**

Figure 4-6 Sampling location and surface documentation of Backplate PA 329.

Similar to Pauldron PA 316, overall, Backplate PA 329 represented the typical corrosion condition of armour displayed on the walls (i.e. corrosion and CPs on non-inverted surfaces). The outer surface of Backplate PA 329 at the sampling site represented the other extreme of munition armour, which have subsequently had most of their corrosion products removed.

4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy

PAULDRON (PART) PA RC 166

The maximum metal core thickness[1041] of sample PA RC 166 was circa 1.10mm: a remarkably thicker sample than the subsequent samples. The internal structure was marked by corrosion parallel with the surfaces (Figure 4-7). Uneven local corrosion fronts with shallow pits featured. Notably, one area featured a possible site where a slag stringer prevented corrosion from passing through into the underlying metal: an example of the corrosion protection offered by slag, a trait more typical of wrought structural iron/steel[1042]. On one area of corrosion products along the inner armour side (ZOI 3), a relatively thick and even general CP layer was parallel to the metal surface and parallel to the internal corrosion. Meanwhile, adjacent to this thickest CP layer, there appeared to be a loss of CPs that might have been provoked during the sampling process[1043]. A protective coating was not apparent from this perspective either.

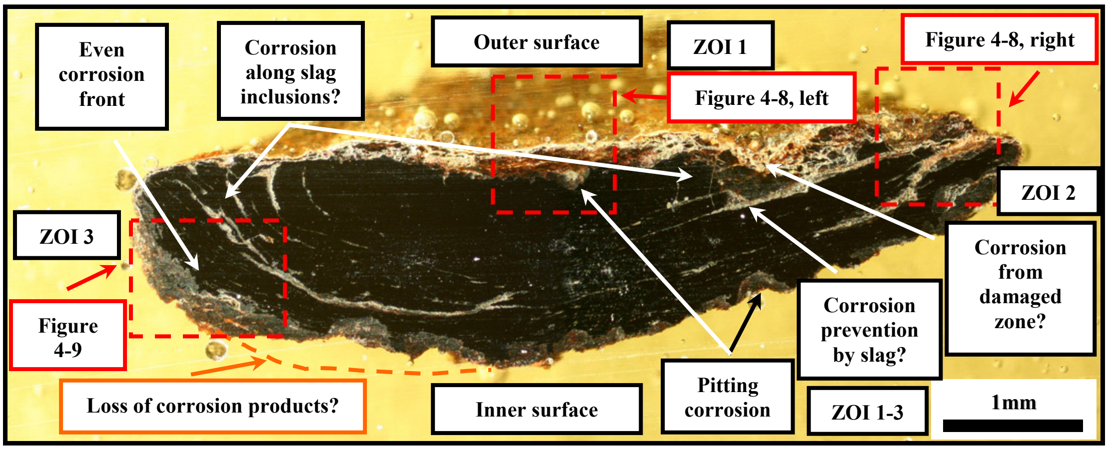


Figure 4-7 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Overall context photograph using the Olympus BX-50 optical microscope.

*

[1041] Allowing for the non-perpendicular embedding angle (Figure 4-7)

[1042] 2.2.3.3 Uneven local to uneven general corrosion/corrosion product morphology

[1043] Vella et al., 2005b, p. 319

Easily differentiating between features of any varying corrosion product phases was not possible at the preliminary magnification (40x) of the standard optical microscope. Higher magnification (200x) revealed there were observable layers of orange-brown corrosion products and dark brown-black areas (Figure 4-8). The areas of CPs that *appeared* dark brown-black were generally located next to the remaining metal core, while the areas of CPs that *appeared* orange-brown were located in a layer further away from the metal and closer to the atmosphere. The dark brown-black corrosion products were more polished than the orange-brown corrosion products.

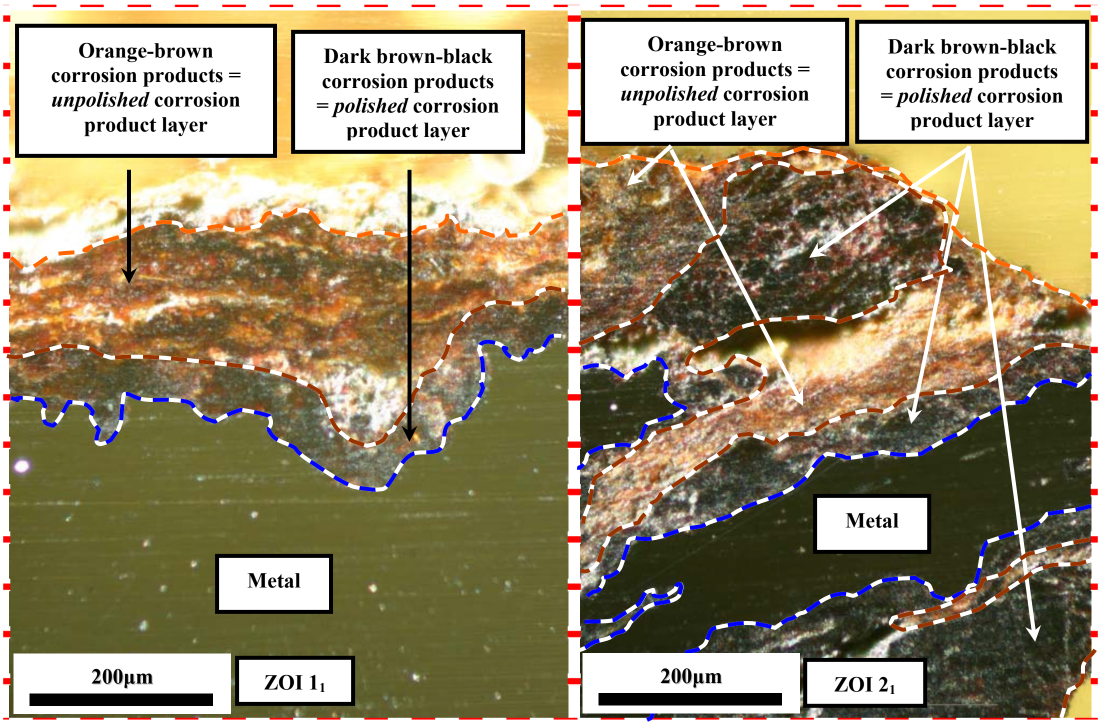


Figure 4-8 Palace Armoury armour cross-sections, Pauldron (part) PA RC 166: *Apparent* corrosion product colours in corrosion product stratigraphies (ZOIs 1_1 & 2_1) as observed by optical microscopy. Context image in Figure 4-7.

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To limit and help identify uncertainties regarding the *appearance* of CP colouration (possibly introduced by unpolished sections), a corrosion product stratigraphy that was predominantly polished flat was selected for further examination (Figure 4-9). The previously apparent stratigraphic separation of variably coloured layers (i.e. orange-brown in contrast to brown-black) became almost non-existent in this ZOI, which scarcely featured unpolished zones. Again it was observed that the relatively few unpolished (i.e. recessed) areas exhibited orange-brown colouration, while most of the remaining flat zones were dark brown-black. Remarkably, the lines of dark brown-black CPs along the interior were unpolished, yet still exhibited this dark brown-black colour. Meanwhile, an area of the outermost CP edge that bordered the embedding resin had an orange appearance.

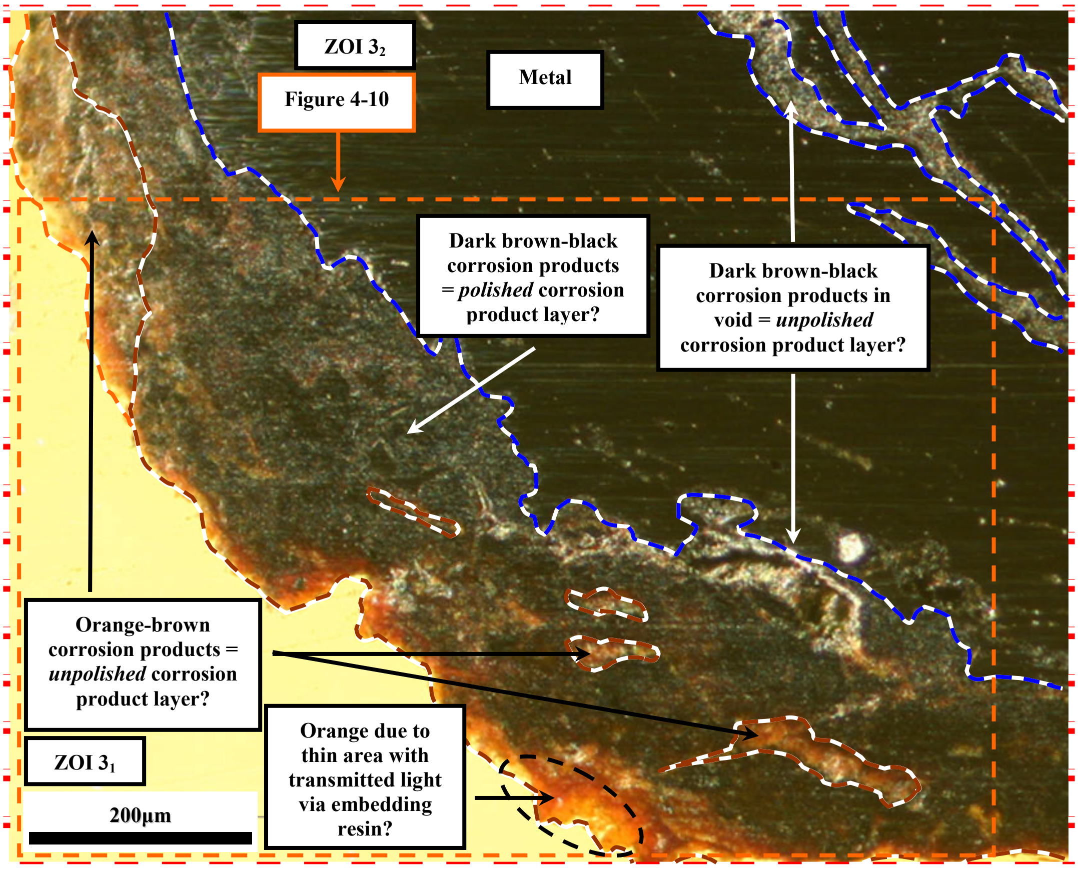

Figure 4-9 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: *Apparent* corrosion product colours in corrosion product stratigraphies as observed by optical microscopy of ZOI 3$_1$. Context image in Figure 4-7.

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To benefit from the complementarity of the two selected optical microscopy techniques, the same zone was examined via the metallographic microscope (128x) (Figure 4-10). Thanks to the high reflectivity provided by the metallographic microscope and its largely greyscale imaging, contrast between phases of differing reflectivity made them more distinguishable and without the potential ambiguities introduced by colouring.

Losses/porosity (i.e. voids) of the CPs in the cross-section surface became much more apparent. Sandwiched between the metal and the outermost corrosion products was a layer of CPs characterised by small pores and large voids (the latter being marked with black dashed lines, Figure 4-10). This inner corrosion product layer was 250µm at its maximum thickness. Between this inner CP layer and the embedding resin was another CP layer that had a seemingly higher porosity (indicated by slightly larger, dark and apparently recessed areas) than the layer below

(Figure 4-10). The marked relative differences in apparent porosity between these two corrosion product layers is accordingly distinguishable with two terms used in the literature describing corroded terrestrially buried wrought iron: the dense product layer (DPL); and transformed medium (TM) (Figure 4-10)[1044]. Here the less porous inner layer is also termed the DPL, while the more highly porous outer layer is termed the TM. The appellation, TM & DPL, of these different CP layers according to their observed relative properties, is important for communicating their anatomy during the results presentation and subsequent interpretation and discussion[1045].

Also via the application of the metallographic microscope, the metal's bright white reflectance raised awareness of a nodule of metal in the DPL's corrosion products (Figure 4-10).

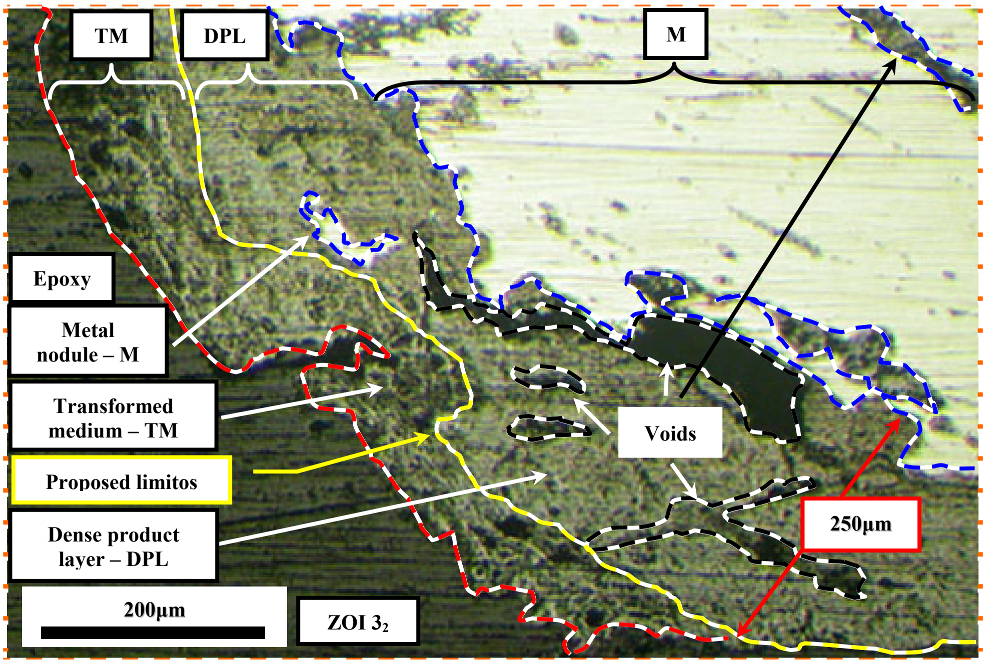

Figure 4-10 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Metallographic microscope image of ZOI 3_2. Equivalent area represented by Figure 4-9. Context image in Figure 4-7.

The uncorroded metal nodule, an inferior limitos marker[1046], was the first indication that this layer (or at least the area of this layer) could also be an inferior limitos marker. It is thought that the metal nodule was created by corrosion of the metal in the surrounding volume. The larger voids in the DPL could perhaps have been formed from losses of corrosion products from inclusion-associated corrosion similar to that previously observed in the metal core (Figure 4-7 & Figure 4-9).

[1044] 2.3.1.2.1 Localisation of the limitos

[1045] For both the authentic armour, and the armour analogues.

[1046] Table 2-3

While the presence of the metal nodule within the DPL suggests this layer might be below the limitos, superior and corresponding limitos markers are still required to indicate the location of the TM relative to the limitos. With these early indications, a tentative notion is that the limitos on atmospherically corroded wrought iron could feature in the same stratigraphic location as already established in the literature for terrestrially interred and corroded iron: i.e. between the transformed medium and the dense product layer[1047]. The noted relative differences in compactness/porosity between the DPL and TM layers on atmospherically corroded wrought iron might provide indications of the limitos. Indeed, *providing* this sample of atmospherically corroded wrought iron is in agreement with the location of the limitos on wrought iron from a terrestrial burial environment, then the DPL/TM interface could form a corresponding limitos marker[1048]. In summary, further limitos markers, as determined by subsequent instruments, are required to definitively support this preliminary supposition that the limitos is located between the DPL and the TM, as indicated by the yellow-dashed line in Figure 4-10.

PAULDRON PA 316

The maximum metal core thickness of the sample from PA 316 measured circa 0.25mm: a remarkably thin armour sample (Figure 4-11). At low magnification (40x) the sample was characterised by a thin metal strip encased on both sides with voluminous masses of orange-brown corrosion products.

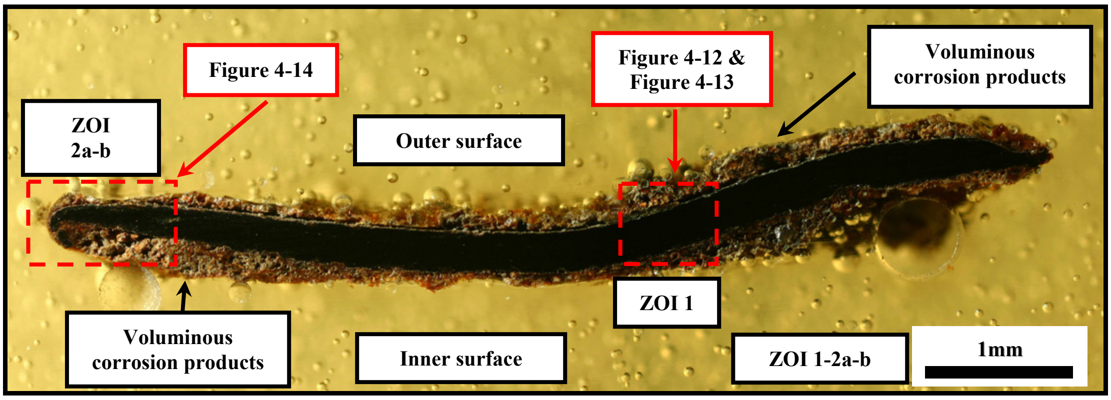

Figure 4-11 Palace Armoury armour cross-section, Pauldron PA 316: Overall context photograph using the Olympus BX-50 optical microscope.

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At higher magnifications, remnants of a transparent protective coating (C) and the void it once occupied (probably lost during grinding/polishing) were evident

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[1047] 2.3.1.2.1 Localisation of the limitos
[1048] 2.3.1.2.1 Localisation of the limitos

on the outer surface (Figure 4-12). Above this coating, masses of red-brown and orange-brown corrosion products were present. The red-brown CPs appeared almost continuous and compact and were positioned discreetly and immediately along the coating interface. The orange-brown CPs positioned above the red-brown CP layer appeared porous and fragmented (akin to the transformed medium) and were topped by the embedding resin. Meanwhile, below the coating, several shallow corrosion pits in the metal were filled with relatively compact dark brown-black corrosion products (hence being referred to as the dense product layer). Similarly appearing dark brown-black CPs featured in the metal core; distributed in lines corresponding with the forging direction.

A similar presence and distribution of CPs was visible on the inner side of the sample from Pauldron PA 316 when compared to the outer side, however, a coating was not visible (Figure 4-12). This observed absence of a coating corresponded to the appearance of the sampling site's inner surface[1049] and is discussed later[1050].

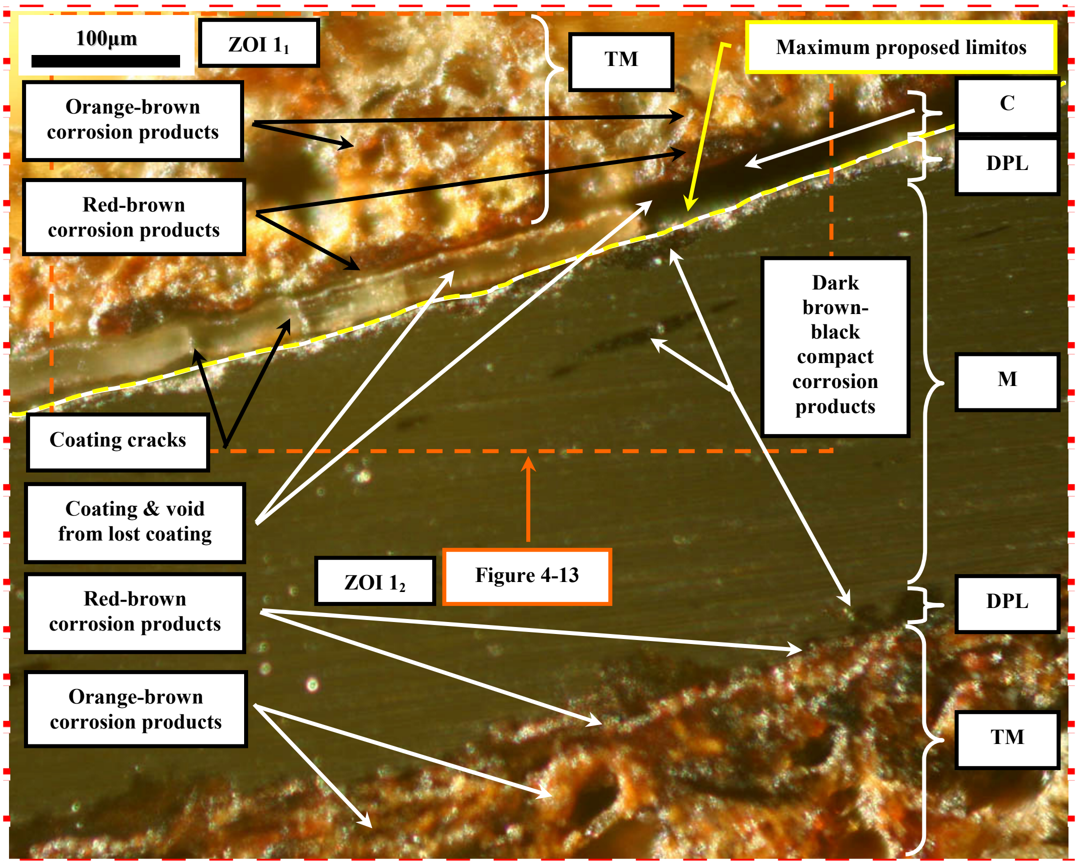

Figure 4-12 Palace Armoury armour cross-section, Pauldron PA 316, Corrosion product stratigraphy of ZOI 1$_1$, observed by optical microscopy. Context image in Figure 4-11.

[1049] Figure 4-5

[1050] 5.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron PA 316

The presence of the coating on Pauldron PA 316 warrants further mentioning since it was not noted on the previous sample (PA RC 166) and is more representative of the Palace Armoury munition armour. As previously introduced[1051], a coating, being an applied exogenous material, and being intimately coupled to the metal could itself, in certain conditions, form a type of superior limitos marker. Looking at Figure 4-12, it appears at first observation that the coating failed and permitted metal corrosion and propagation of the DPL directly underneath. Meanwhile CPs managed to permeate the defective coating (via the cracks evident in the coating[1052] and possibly elsewhere unobservable in the third dimension) and deposited on top, thereby forming the TM. The sequence of these events, however, or any others proposed cannot be proven since the histories of the surfaces are unknown. This issue is later reinvestigated at higher magnification with the scanning electron microscope[1053]. For now, the maximum location of the limitos on this sample is proposed to be at the interface below the coating (Figure 4-12).

*

Using the metallographic microscope on the same zone of interest, greater contrast was achievable between the two previously cited corrosion product phases of the transformed medium. The orange-brown CPs observed under the standard optical microscope still showed this coloured aspect through the metallographic microscope, while the red-brown CPs appeared different: a white aspect (Figure 4-13). This high reflectivity might have indicated the non-porous surface of this corrosion product phase and make it an atypical component of the relatively porous TM observed thus far.

[1051] 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

[1052] Figure 4-12

[1053] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron PA 316

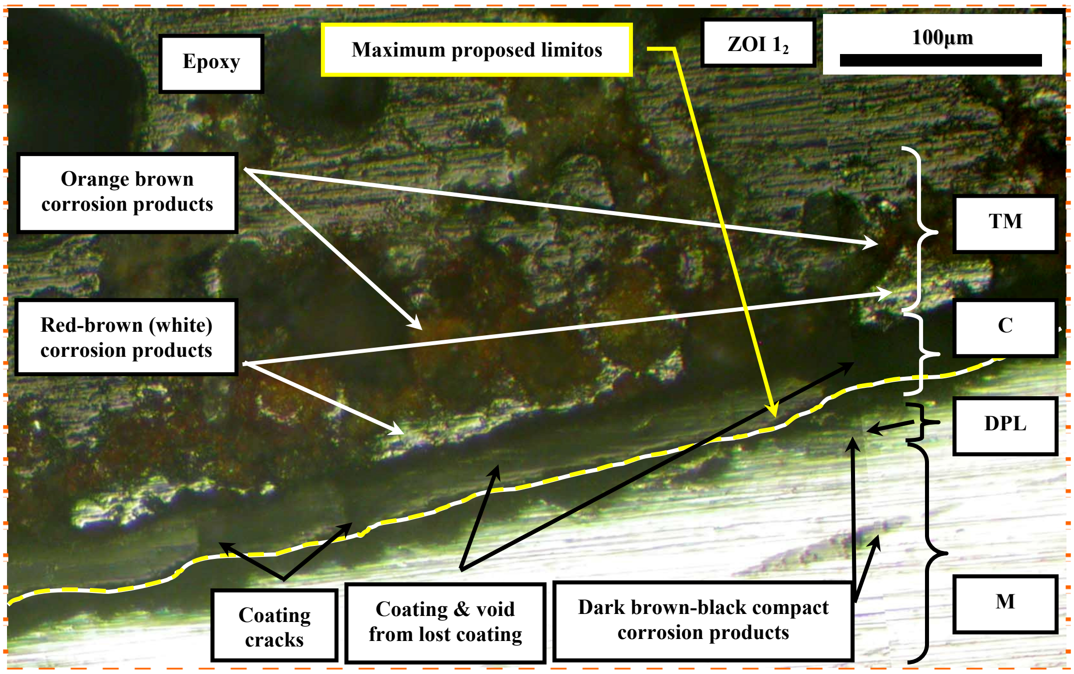

Figure 4-13 Palace Armoury armour cross-section, Pauldron PA 316: Metallographic microscope image of ZOI 1_2 on corresponding area represented in Figure 4-12. Context image in Figure 4-11.

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The previously summarised stratigraphy of PA 316[1054] was reflected elsewhere on the sample, although greater voids in the areas of the coating and red-brown and orange-brown corrosion products were noticed (Figure 4-14). The voids in the red-brown and orange-brown corrosion products could either be attributable to losses during sample preparation or inherent porosity. Due to the large size of the voids relative to the CP layer, the former scenario is more likely.

[1054] Figure 4-12 & Figure 4-13

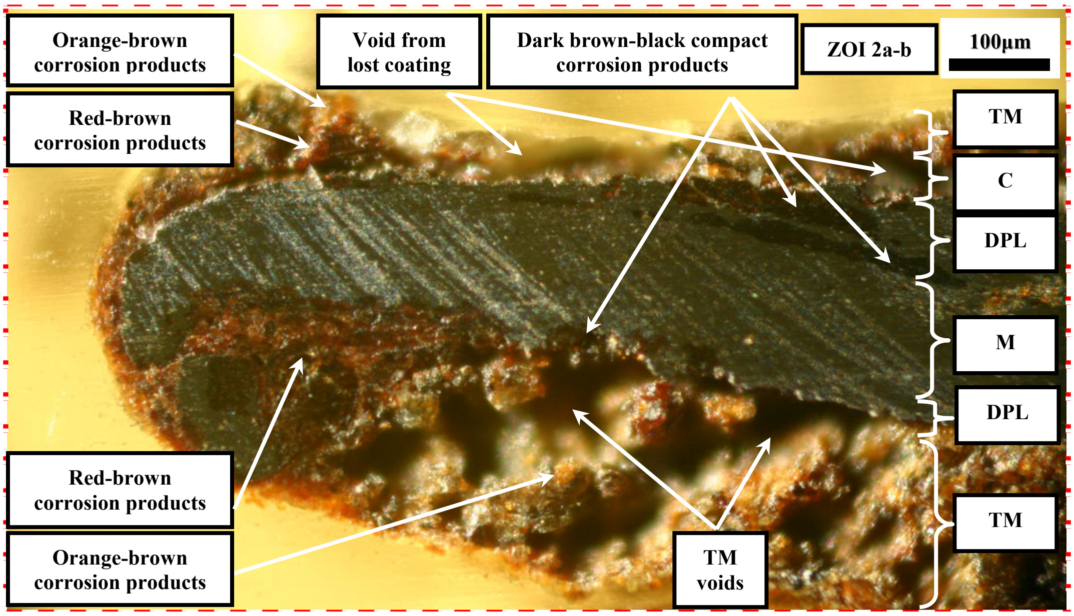

Figure 4-14 Palace Armoury armour cross-section: Pauldron PA 316, Stratigraphy of ZOI 2a-b, as observed by optical microscopy. Context image in Figure 4-11.

BACKPLATE PA 329

The maximum metal core thickness of the sample from PA 329 measured circa 0.40mm: another thin armour sample. This sample was characterised by the distinct differences between the respective absence and presence of corrosion products on the outer and inner surfaces, which were clearly observable at low magnification (40x) (Figure 4-15). Each side of the armour was coated and there was a virtual absence of corrosion and CPs in the internal metal core. The surface of the sampling site[1055] confirmed the coating's presence and difference in the corrosion product's presence.

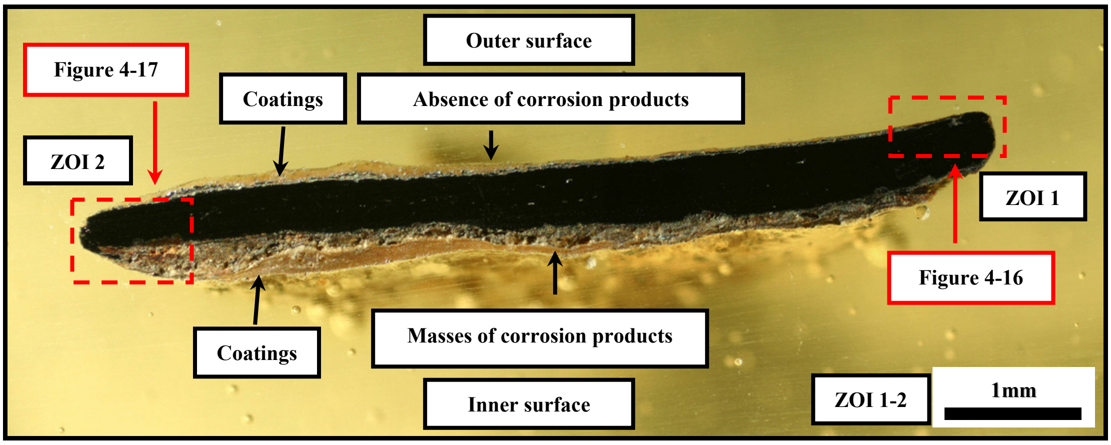

Figure 4-15 Palace Armoury armour cross-section, Backplate PA 329: Overall context photograph using the Olympus BX-50 optical microscope.

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[1055] Figure 4-6

Greater magnification of the outer surface reconfirmed this near absence of corrosion and corrosion products. The outer surface was metallic and corrugated with pits. Only one zone on the outer surface was found to contain CPs, which were of a dark and compact nature (i.e. DPL) (Figure 4-16).

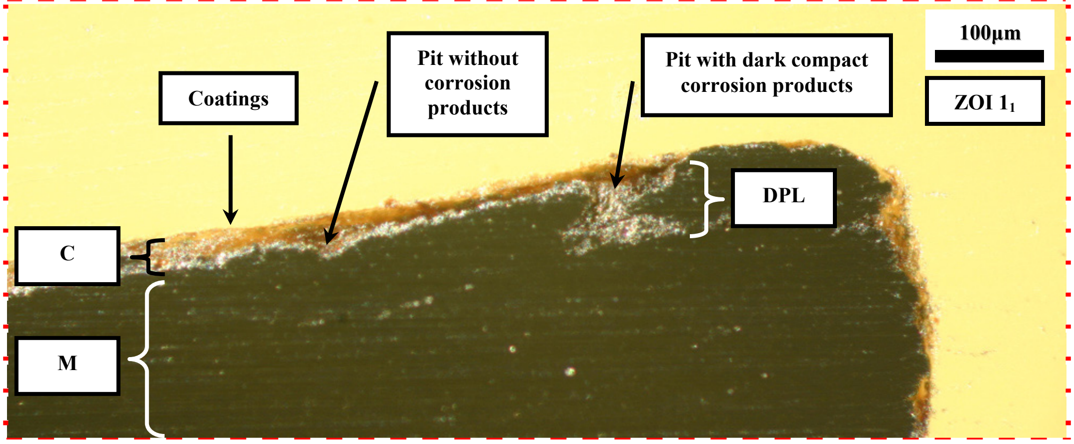

Figure 4-16 Palace Armoury armour cross-section, Backplate PA 329: Corrosion product stratigraphy of ZOI 1_1 as observed by optical microscopy. Context image in Figure 4-15.

*

To facilitate the research, a second zone of interest (Figure 4-17) containing more corrosion products than the first was also selected for investigation, despite its location on the armour's inner surface. Here the basic stratigraphy was the same as for the inner sub-surface of the sample from Pauldron PA 316 (Figure 4-14), although in the present case there was the additional presence of the coating layer on top of the transformed medium. The CP layers were composed of the dark brown-black more compact phases (DPL) in the metal's corrosion pits, while more porous red-brown and orange-brown CPs (TM) were above these. The red-brown CPs of PA 329's stratigraphy were porous, unlike the red-brown CPs of PA 316. Two layers of protective coatings of variable thickness were present on both the outer (evident in Figure 4-17) and inner surfaces. Corrosion corresponding with possible slag inclusions was also evident elsewhere on this sample, but very slight when compared with the preceding two sample cross-sections.

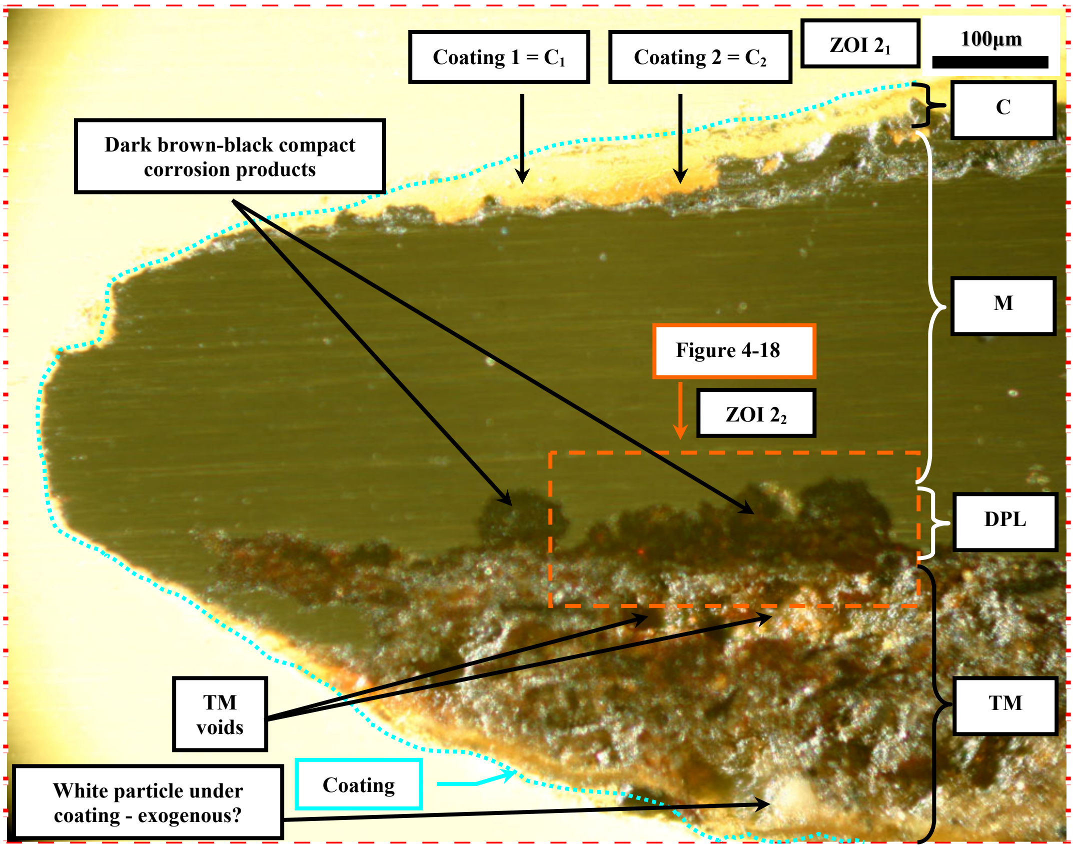

Figure 4-17 Palace Armoury armour cross-section, Backplate PA 329: Stratigraphy of ZOI 2_1 as observed by optical microscopy. Context image in Figure 4-15.

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Increased magnification with the metallographic microscope of the same zone of interest as in Figure 4-17, resolved probable remnants of uncorroded metal present inside the dense product layer (Figure 4-18).

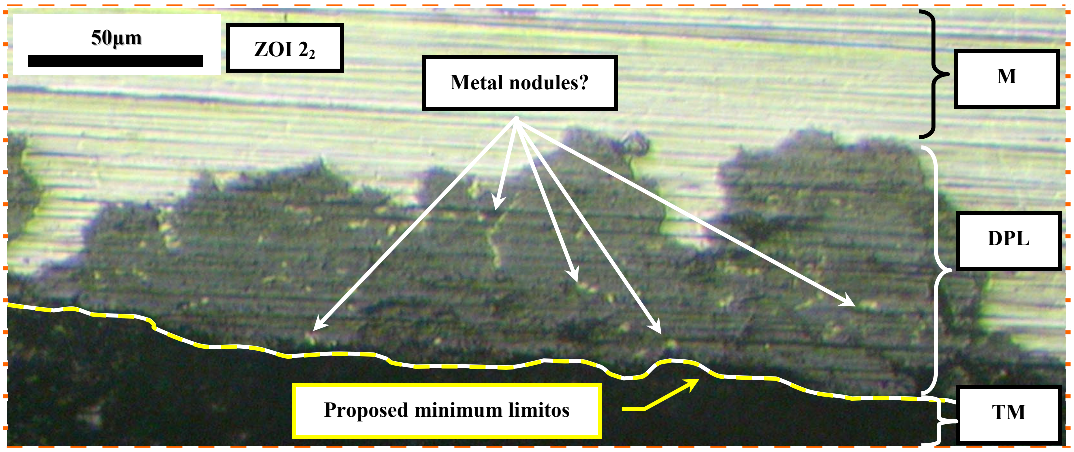

Figure 4-18 Palace Armoury armour cross-section, Backplate PA 329: Metallographic microscope image of ZOI 2_2 on area represented in Figure 4-17. Context image in Figure 4-15.

The occurrence of uncorroded metal in the DPL, coupled with the fact it is located below the adjacent uncorroded metal, suggests the DPL corrosion products are indeed below the limitos. The maximum possible location of the limitos cannot be suggested, yet associating these inferior limitos markers of uncorroded metal could suggest again that the dense product layer is a corrosion product stratum that indicates a position corresponding to, or at least below, the limitos.

SUMMARY OF ARMOUR CROSS-SECTION OPTICAL & METALLOGRAPHIC PHOTOMICROSCOPY

On these three samples a dual layering of corrosion product colours (upper red-orange ochres and lower brown-black) was noted for the CPs positioned between the metal and the atmosphere. Supposed metal nodules were located in the dense product layer, identifying this layer as inferior to the limitos.

4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

An introductory remark regarding the SEM-EDS investigations on the armour cross sections is required. The cross-section from Pauldron (part) PA RC 166 and the presence of seemingly undisturbed and thick layers of corrosion products gave it the greatest investigative potential. The proportion of results, interpretation and subsequent discussion[1056] from this sample reflects its value.

To facilitate tracking the context of the subsequent ZOIs at higher SEM magnification (and later for the Raman micro-spectroscopy [1057]) a preliminary low magnification SEM image features for each sample.

PAULDRON (PART) PA RC 166

The improved phase contrast of BSE SEM (Figure 4-19) compared with optical microscopy[1058] already demonstrated superior legibility of the materials, even at comparable magnifications. The area that featured a possible site where a slag stringer had prevented corrosion from passing through into the underlying metal was more observable. As a whole, the profusion of corrosion/corrosion products at the metal surface/atmosphere interface and internally along elongated slag predominated the cross-section.

[1056] 5.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

[1057] 4.1.3.2.4 Armour cross-section Raman micro-spectroscopy

[1058] Figure 4-7

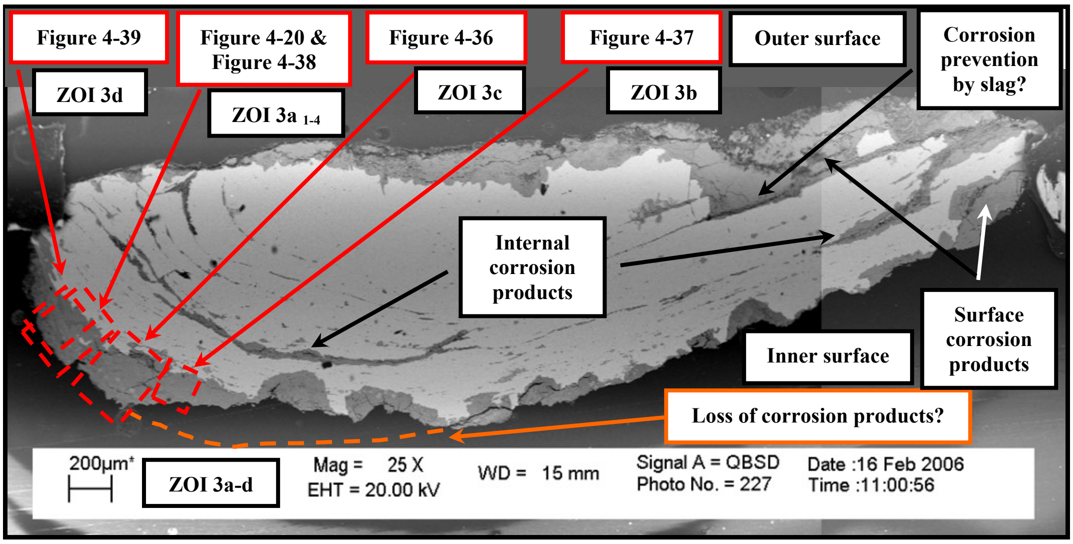

Figure 4-19 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Overall context SEM BSE image with contexts for ZOIs 3a-d presented in Figure 4-20, Figure 4-36, Figure 4-37, Figure 4-38 & Figure 4-39.

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At zone of interest $3a_1$ (presented in Figure 4-20 and corresponding to ZOIs 3_1 & 3_2 in Figure 4-9, Figure 4-10 & ZOI $3a_{1\text{-}4}$ in Figure 4-19), a preliminary survey by SEM observation and EDS point and area analyses at low magnification indicated that the area of metal and CPs is best summarised as being heterogeneous in morphology and composition (Figure 4-20 & Table 4-4).

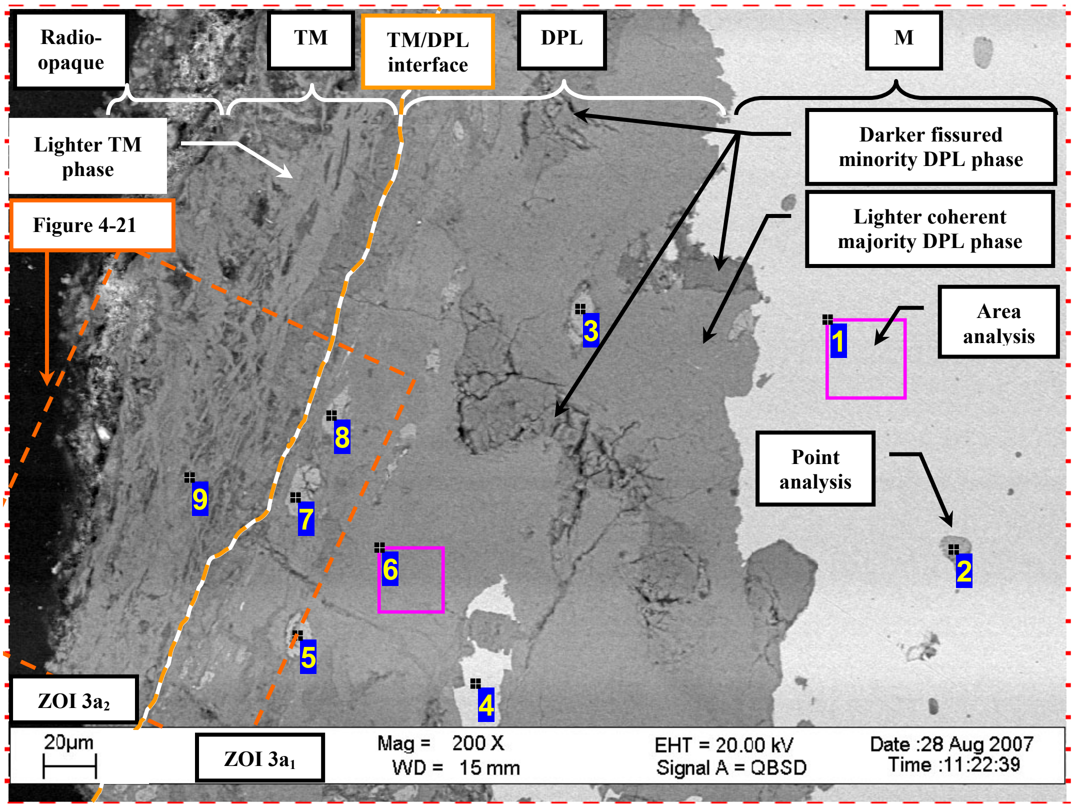

Figure 4-20 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: SEM BSE image (200x) of inner armour subsurface stratigraphy at ZOI $3a_1$ and sites of EDS analyses (1-9). Context image in Figure 4-19.

Results				Interpretation
Spectra	Elements detected (%rel.at.wt.)			Probable/possible (?) materials
	Major (>5%)	Minor (1-5%)	Trace (<1%)	
1.	Fe	-	-	metal
2.	Fe, O	V	-	slag
3.	Fe, O	-	V	slag
4.	Fe	-	-	metal
5.	Fe, O	V	Si, Al, Mn	slag
6.	Fe, O	-	Ca, K, Cl	Corrosion products, pollution (?)
7.	Fe, O	V	Cr, Al	slag
8.	Fe, O	V	-	slag
9.	Fe, O	Ca, Cl	K, P, S	Corrosion products, pollution (?)

Table 4-4 Pauldron (part) PA RC 166: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-20.

Beginning from the uncorroded metal core (denoted by Spectra 1: iron without oxygen), globules (probably slag inclusions as indicated by the vanadium[1059]: Spectrum 2) were randomly present and the metal's interface with the corrosion product layers above was uneven. According to the varying shades of grey (representing average atomic number while using BSE detector[1060]), ferrous CPs (as

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[1059] Vanadium, as well as magnesium, manganese sodium, aluminium, silicon, phosphorous, sulphur, potassium, calcium, barium, titanium are all known to occur in ferrous metals made from pre-contemporary smelting processes as outlined in 2.1.2.1.1 Direct process: bloomery furnace

[1060] 3.5.2 Scanning electron microscopy-energy dispersive spectrometry indicated by expanses of iron and oxygen, without vanadium: Spectrum 6) of possibly two or more phases or phase mixtures, were present at the CP layer closest to the metal. Both CP phases at this innermost layer appeared relatively compact and the majority phase was lighter and largely coherent, while regions of the minority phase it contained were darker and fissured. Together, these compact phases corresponded with the overall layer identified with the metallographic microscope[1061] and is here continued to be referred to as the dense product layer. Inside the DPL, a nodule of uncorroded metal (as previously suggested[1062] and now confirmed by the detection of iron without oxygen: Spectrum 4) remained. Also in the DPL, large globules of proposed slag (as indicated by the vanadium, chromium, aluminium, manganese and silicon: variously in Spectra 3, 5 & 7-8) were present in distribution comparable to the proposed slag inclusions detected in the metal core (Spectrum 2). The association of metal and slag within this layer further indicated the DPL as being an inferior limitos marker.

Above the DPL, layers of corrosion products (as indicated by iron and oxygen without vanadium: Spectrum 9) appeared porous, and striated with lines running parallel with the DPL interface (dashed orange line in Figure 4-20). This layer's porosity was again noted since the cross-section surface was void in places (indicated by dark shadows of recessed areas inaccessible to the electron microscope). This CP layer will continue to be referred to as the transformed medium, as earlier[1063]. The TM appeared to be composed of at least one material that had a greyscale comparable to the majority phase in the DPL. Notably, the TM did not contain the proposed slag globules and metal, which were in the DPL and metal core; again indicating the possibility that the TM layer was superior to the limitos.

The two layers of the DPL and TM both shared calcium, chlorine and potassium as common elements (Spectra 6 & 9). Greater quantities of these elements were detected in the TM than in the DPL, while extra elements of phosphorus and sulphur featured in the TM as well. At this stage, these elements could be attributable to exogenous sources since they were not yet detected in the metal (Spectra 1 & 4) or proposed slag (Spectra 2-3, 5, 7-8) and since they were all detected in the prior

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[1061] Figure 4-10

[1062] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron (part) PA RC 166

[1063] Figure 4-10

Palace Armoury environmental analyses[1064]. Increased presence and quantity in the TM corrosion products, which were closer to the former atmosphere is another indication of their likely exogenous provenance.

Above the TM, material featured with a seemingly high atomic number as the whiteness of this image area indicated that radio-opaque materials were present. The possibility of an *artefact*[1065] with the SEM imaging in this area is not discounted from occurring, as the area was not analysed by EDS at this magnification.

From the interpretation of the results from the preliminary SEM-EDS survey at 200x magnification (Figure 4-20 & Table 4-4) it can now generally be summarised:

> It is apparent that a possible location for the limit of the original surface should be above the uppermost of these vanadium-based slag inclusions (particularly Spectra 7-8). The presence of slag and an uncorroded metal nodule in the dense product layer, combined with their apparent absence in the transformed medium, indicate the interface of the TM and DPL could be the location for the original surface limit. Markers definitively attributable to the superior limitos and corresponding limitos are still required though.

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Further elemental analyses performed at higher magnification (500x) on an area of the TM/DPL interface are presented (Figure 4-21 & Table 4-5) and correspond with the context image given in Figure 4-20.

[1064] 4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

[1065] *Artefact* = in this context, an unreal feature created by the investigative technique and can therefore mislead accurate interpretation of observed phenomena.

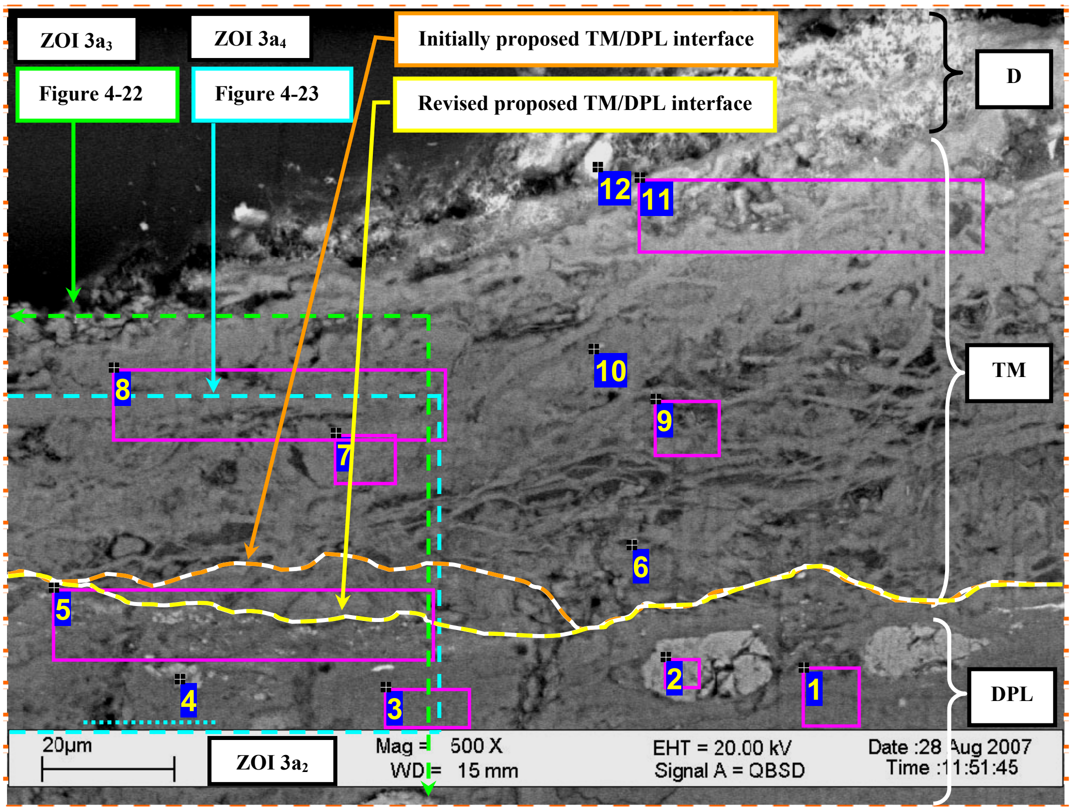

Figure 4-21 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: SEM BSE image (500x) of inner armour subsurface stratigraphy at ZOI 3a$_2$ and sites of EDS analyses (1-12). Context image in Figure 4-20.

Results				Interpretation
Spectra	Elements detected (%rel.at.wt.)			Probable/possible (?) materials
	Major (>5%)	Minor (1-5%)	Trace (<1%)	
1.	Fe, O	Ca	K	corrosion products, pollution (?)
2.	Fe, O	V	Al	slag
3.	Fe, O	Ca	S	corrosion products, pollution (?)
4.	Fe, O	V	Si	slag
5.	Fe, O	Ca	P, S, Al	corrosion products, pollution (?), slag (?)
6.	Fe, O	-	Ca, S	corrosion products, pollution (?)
7.	Fe, O	-	S, Ca	corrosion products, pollution (?)
8.	Fe, O	Ca	Cl	corrosion products, pollution (?)
9.	Fe, O	Ca	Mg, Cl, S	corrosion products, pollution (?)
10.	Fe, O	-	Ca, Cl	corrosion products, pollution (?)
11.	Fe, O	Ca, S	K	corrosion products, pollution (?)
12.	O	Ba, S, Fe	-	corrosion products, pollution

Table 4-5 Pauldron (part) PA RC 166: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-21.

The outer layer of material between the transformed medium and the sample's embedding resin (representing the most recent interface with the atmosphere) is referred to as the deposit layer (D) due to the assembly of fine particles of contrasting shape and intensity. While still containing ferrous corrosion products, there appeared to be a greater proportion of exogenous materials as indicated by various particle morphologies. Analysis of one of the seemingly radio-opaque particles (previously observed[1066] in the upper stratigraphy) revealed oxygen, barium, sulphur and iron (Spectrum 12), and is thought to be present as barium sulphate (with iron corrosion products) attributable to deposited paint pigment[1067]. Whatever the exact source, the important point is that it appears the barium materials are exogenous to this armour since barium was not detected in the metal core or contained slags (Figure 4-20, Table 4-4: Spectra 1-2, 4).

Emphasis on analyses was made on features in the transformed medium by performing area scans on morphologically varying areas (Spectra 7-9 & 11), while point analyses were made on particles in the TM (Spectra 6 & 10). The area analyses demonstrated that these ferrous corrosion product areas normally contained minor amounts of calcium, sometimes with trace metals, and often sulphur and sometimes chlorine. The point analyses gave similar results although they showed only trace amounts of calcium, sulphur and chlorine in the ferrous corrosion product matrix. All of the elements denoted by Spectra 6-12 were also detected in the PA environment[1068], but not yet in the EDS point analyses of the metal or slag, again indicating exogenous provenances.

Particles containing vanadium (Spectrum 4), which were much smaller than other vanadium containing globules (Spectrum 2), became observable in areas of the DPL immediately (10μm) below the proposed TM/DPL interface (orange dashed line in Figure 4-21, corresponding with Figure 4-20). The area analyses denoted by Spectrum 5 appeared to contain material of similar morphology to the particles further below denoted by Spectrum 4, but the resulting spectrum showed that no vanadium was detected (with trace amounts of aluminium). The trace amounts of aluminium detected in Spectrum 5 could indicate slag, but normally in this sample aluminium's presence in the supposed slag has been correlated with a presence, and a more concentrated one, of vanadium. Energy dispersive spectrometry point analyses, locally at higher magnification on these particles, would better confirm vanadium's presence or absence.[1069].

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[1066] Figure 4-20

[1067] Table 4-1 & Table 5-1

[1068] Table 4-1

[1069] Figure 4-20, Table 4-4: Spectra 5 & 7 and Figure 4-21, Table 4-5: Spectrum 2

At even higher magnification (1000x: context image in Figure 4-21) further EDS analyses of these small particles were made to help identify these materials close to the TM/DPL interface (Figure 4-22 & Table 4-6).

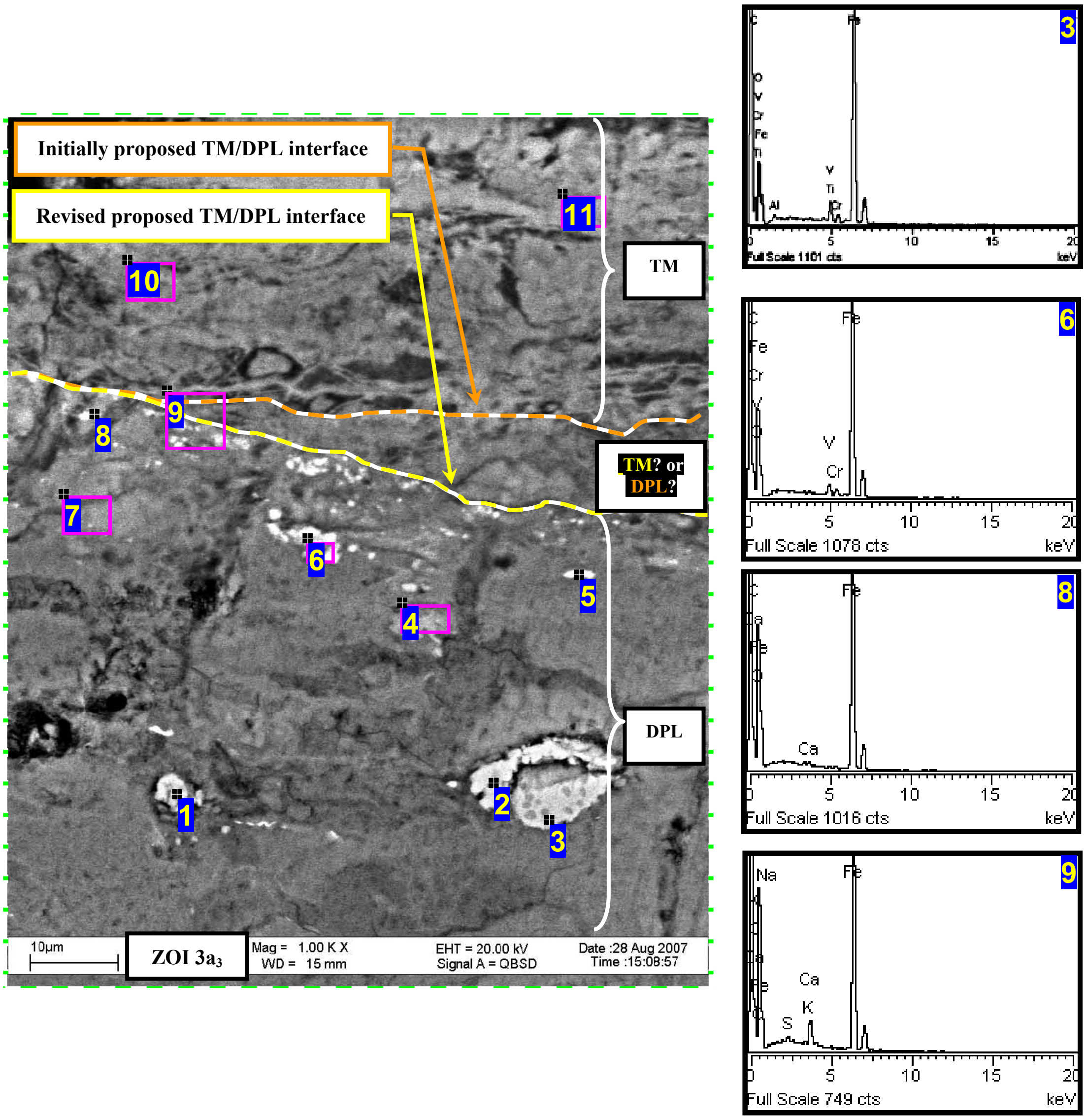

Figure 4-22 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: High magnification (1000x) SEM BSE image of inner armour subsurface stratigraphy at ZOI 3a$_3$ of the *globules* in the dense product layer & example spectra from the sites of EDS analyses (3, 6, 8-9). Context image in Figure 4-21.

Results				**Interpretation**
Spectra	**Elements detected (%rel.at.wt.)**			**Probable/possible (?) materials**
	Major (>5%)	**Minor (1-5%)**	**Trace (<1%)**	
1.	Fe, O	V	Cr, Al, P, Ca	slag
2.	Fe, O	V	Cr, Si	slag
3.	Fe, O	V, Cr, Al	Ti	slag
4.	Fe, O	-	Ca, Mg, K	corrosion products, pollution
5.	Fe, O	-	-	slag
6.	Fe, O	V, Cr	-	corrosion products, slag
7.	Fe, O	Ca, Pb, Na	K, Mg, P	corrosion products, pollution
8.	Fe, O	-	Ca	slag, pollution
9.	Fe, O	Ca	S, Na, K	slag, corrosion products, pollution
10.	Fe, O	-	Na, Ca, Cl, S, Mg	corrosion products, pollution
11.	Fe, O	-	Ca, P, S	corrosion products, pollution

Table 4-6 Pauldron (part) PA RC 166: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-22

Elemental analyses of some of the observed particles in the DPL area near the TM indicated that these particles were not slags of the previously determined chromium and vanadium type: Spectra 5, 8 & 9 revealed that these areas were free of vanadium, chromium and titanium, yet contained major amounts of iron and oxygen. The point and area analyses respectively represented by Spectra 8 & 9 additionally featured minor and trace amounts of calcium, sulphur, sodium and potassium. Since the particle morphology within this area suggests slag inclusions, it could be that they are in fact slags simply consisting of iron and oxygen with some exogenous elements. Since wüstite[1070]-based slags prevail in ferritic iron[1071] it is supposed that these smaller[1072] particles in the DPL area nearest to the interface with the TM are slags of wüstite: more inferior limitos markers. The proposed position of the limitos can be considered somewhere superior to this endogenous material. The detected elements of calcium, sulphur, sodium and potassium in Spectra 8 and 9 can also generally be found as oxides in slags[1073], but since no other slags with these elements were found in this particular sample, and since these elements have been detected elsewhere in the DPL and TM corrosion product layers, it is supposed that they derive from exogenous sources. These alleged exogenous elements might have migrated into the corrosion layer as dissolved species[1074].

The consistent morphological differences between the transformed medium and the dense product layer might provide a continuity to assist as a corresponding

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[1070] Elementally iron and oxygen (FeO); 2.2.3.3.2 Galvanic corrosion mechanism

[1071] 2.2.3.3.2 Galvanic corrosion mechanism

[1072] When compared to the large globules of vanadium slag in Figure 4-20 & Figure 4-21

[1073] 2.2.3.3.2 Galvanic corrosion mechanism

[1074] As discussed in terms of *transcorrosion product layer mobility* in sub-section 5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties limitos marker. The orange dashed-lines in Figure 4-21 & Figure 4-22 represent such a possible interface demarcated by the optically apparent differences in compactness and porosity between the two layers of the DPL and TM. The orange dashed-line is referred to as the "Initially proposed TM/DPL interface?". The latter was a partially incorrect initial proposition of the TM/DPL interface that was made on the visual assessment of the CP layers' porosity (denoted by black zones under SEM BSE).

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In a detail from Figure 4-22, SEM-EDS area mapping presented in Figure 4-23 provided a clearer indication of the distribution of the detected elements over field areas in a localised area exhibiting this disputed interface between the transformed medium and the dense product layer. The mapped zone also corresponds with the context area outlined in Figure 4-21.

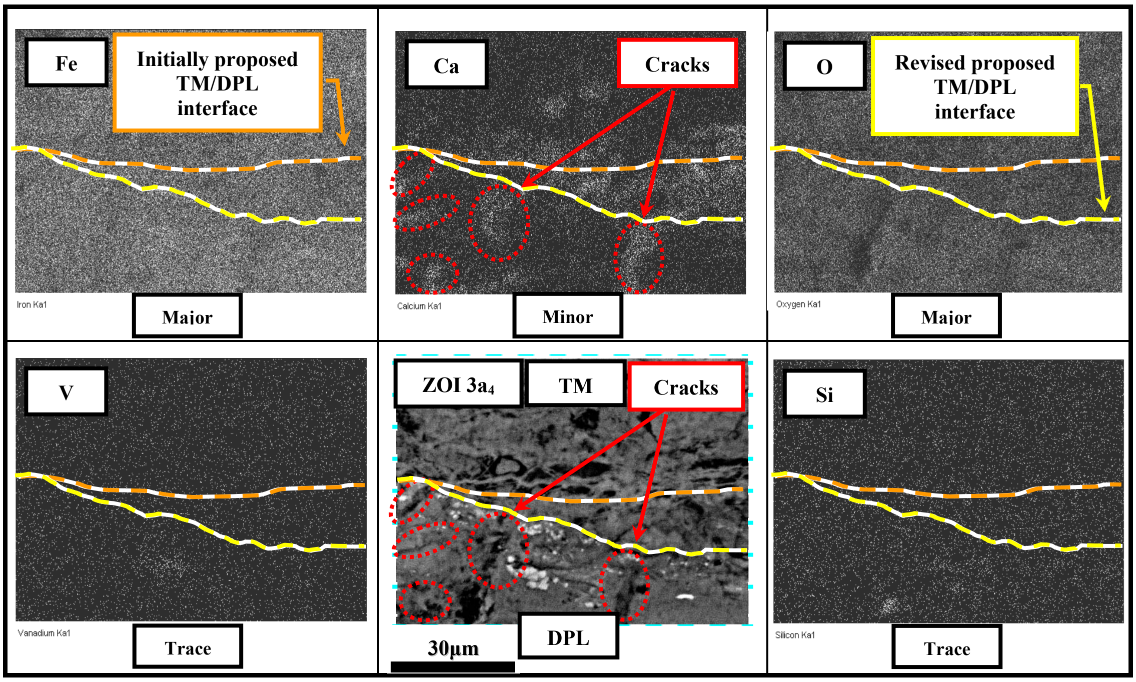

Figure 4-23 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Normalised (%rel.at.wt.) EDS elemental mapping of areas above and below the initially & revised proposed TM/DPL interfaces (as respectively marked by the orange & yellow dashed lines) on inner armour subsurface stratigraphy at ZOI 3a$_4$. Context image in Figure 4-21.

Iron and oxygen predominated the normalised EDS mapping[1075], while the distribution of relative concentrations of calcium in this ferrous corrosion product matrix did not reflect the initially proposed entire boundary between the TM and the DPL (as per orange dashed line, Figure 4-20, Figure 4-21, Figure 4-22 & Figure 4-23). Below the initially proposed TM/DPL interface, an increased concentration of

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[1075] Trace amounts of chlorine and magnesium and minor amounts of sodium were detected with no apparent concentration gradients over the area and have therefore not been presented.

calcium consistently featured until the yellow dashed line (the revised TM/DPL interface, Figure 4-23), and also occasionally in specific areas further below this yellow line. The locally significant calcium quantities, which were below this revised TM/DPL interface, correlated with cracks that extended from the lower limit of the transformed medium and into the dense product layer (Figure 4-23, centre SEM image and EDS calcium map). It seems from that diffusion of calcium into the dense product layer CPs was particularly facilitated by any cracks and interconnected pores. The concentrations of calcium denoted by the EDS mapping calcium signal in Figure 4-23 indicated variations in *transcorrosion product layer mobility*, discussed later[1076].

The revised interface of the transformed medium with the dense product layer's and its contained slag indicates a lower probable location of the limitos for this area on the sample. The dense product layer's discernibly increased compactness (this time differentiated by the calcium concentration gradient, rather than by visually apparent pores) marks the interface. If the limitos truly correlates with the DPL/TM interface, then it appears calcium can provide indications of a corresponding limitos marker; providing concentration gradients between areas are used.

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Notably, during the SEM investigations, the grain boundaries of the former ferritic metal[1077] were neither observed in the corrosion products, nor (more specifically) in the dense product layer: the approximate area where the grain boundaries are expected to have once existed forming the predominant matrix containing the determined various slags.

PAULDRON PA 316

Globally, at low magnification (25x), it already became evident that this cross-section demonstrated few corrosion zones both in the metal surface and internally around slag inclusions (Figure 4-24), especially when compared with Pauldron (part) PA RC 166. In contrast to this relatively small amount of metal corrosion, disproportionate masses of heterogeneous material, initially perceived

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[1076] 5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties & 5.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

[1077] Table 3-1 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations (according to their ochre colouring) to simply be corrosion products, were observed on each surface of the cross-section, but particularly on the inner surface.

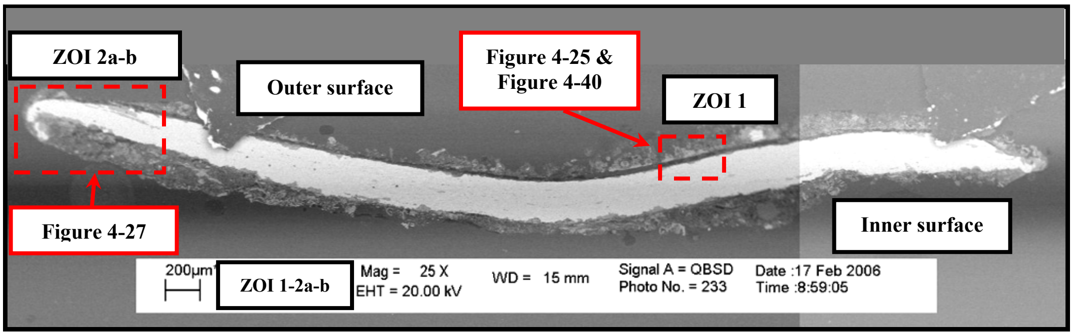

Figure 4-24 Palace Armoury armour cross-section, Pauldron PA 316: Overall context SEM BSE image with contexts for ZOIs 1-2 presented in Figure 4-25, Figure 4-27 & Figure 4-40.

Zone of interest 1_{1-2} (Figure 4-25 & Figure 4-26), with its coating and accumulation of materials on top, is mainly presented to demonstrate the various superior limitos marker features. While for ZOI $2a_{1-3}$ (Figure 4-27, Figure 4-28 & Figure 4-29), greater corrosion of the metal presented a better opportunity to highlight the materials later deemed to provide inferior limitos markers.

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At the low SEM magnification (300x) of ZOI 1_1 (Figure 4-25) the coating already presented via optical microscopy[1078] was evident. The designated DPL on ZOI 1_1 was located from the coating interface downward where compact CPs filled the pits, while numerous and various particles, featured largely above the coating and CPs of the TM. Each side of the coating appeared detached from these corrosion product layers. Judging by several matching positive and negative forms in the coating and the CP layers below and above it, this separation probably occurred after corrosion product formation ceased: they were probably disrupted during sample preparation.

[1078] Figure 4-12 & Figure 4-13

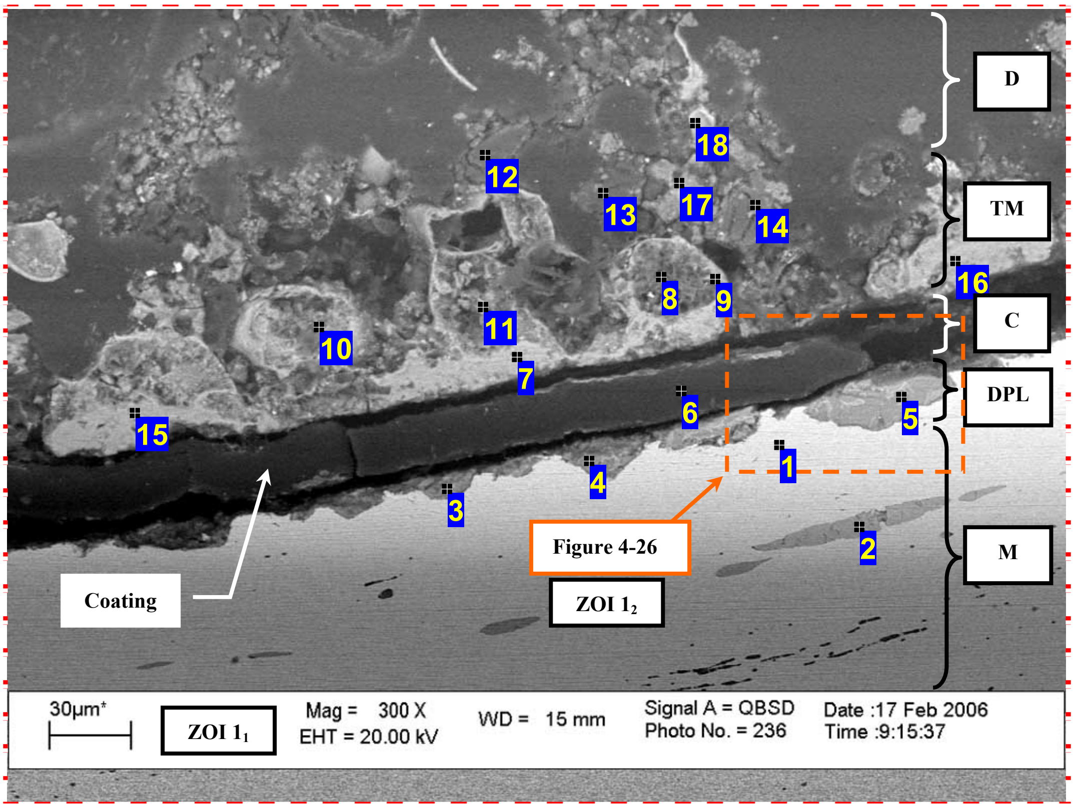

Figure 4-25 Palace Armoury armour cross-section, Pauldron PA 316: SEM BSE image (300x) of outer armour subsurface stratigraphy at ZOI 1_1 and sites of EDS analyses (1-18). Context image in Figure 4-24.

Energy dispersive spectrometry point analyses were performed throughout ZOI 1_1 to gain an overview of the elemental constituents of the observed morphologies. In summary, Spectrum 1 (iron) denoted the metal core and Spectrum 2 (iron, oxygen, manganese and magnesium) from the elongated inclusion in the metal indicated the elemental constituents of slag[1079]. Spectra 3-5 (iron, oxygen with trace amounts of calcium, chlorine, sulphur) on the DPL indicated ferrous corrosion products with exogenous sources since they were not found in the metal or slag, and they are in agreement with the Palace Armoury environmental analyses[1080]. The signal for carbon and oxygen (Spectrum 6) on the film corresponded with the coating. The area above the coating (Spectra 7-18) was largely characterised by iron coinciding with oxygen (indicating ferrous CPs that have possibly perforated and deposited on top of the coating[1081]) and minor to trace amounts of calcium, chlorine, sulphur, silicon and aluminium (indicating exogenous sources, by the same reasoning as for Spectra 3-5). Trends in the elements detected in the particles on this sample

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[1079] 2.1.2.1.1 Direct process: bloomery furnace

[1080] Table 4-1

[1081] The corrosion products of the TM could have also been deposited there from other areas during a corrosion product removal intervention.

were close to the previous analyses of the transformed medium on the sample from Pauldron (part) PA RC 166[1082].

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An increased magnification (750x) of ZOI 1_1 (Figure 4-25) is presented as ZOI 1_2 (Figure 4-26).

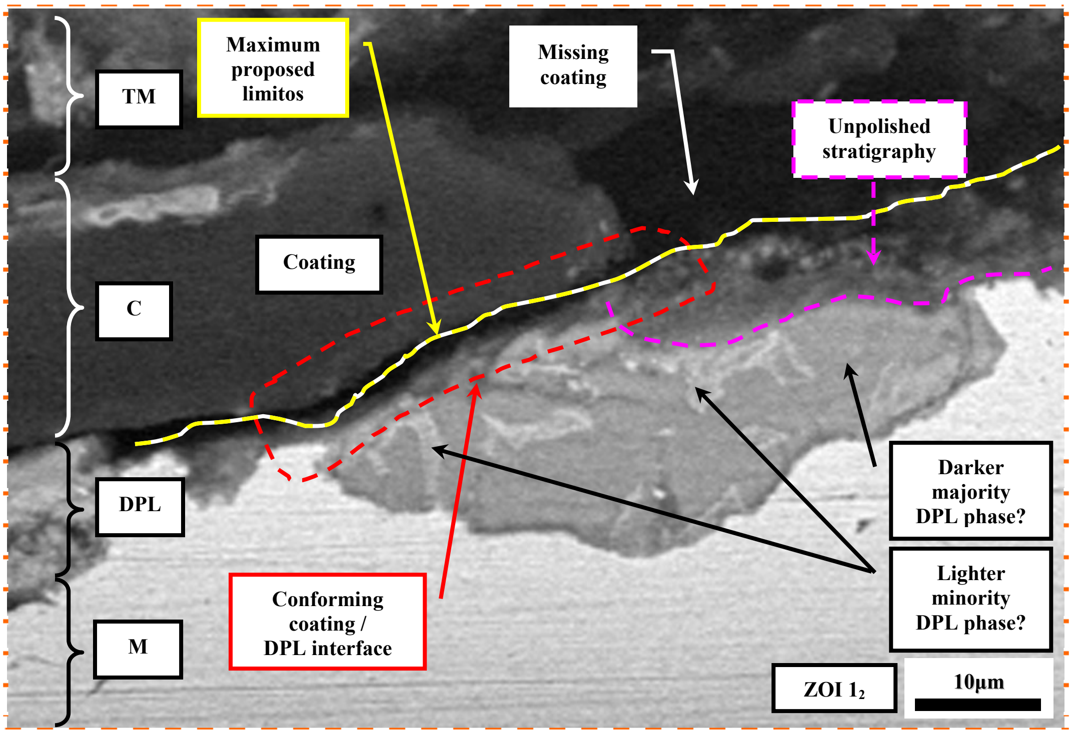

Figure 4-26 Palace Armoury armour cross-section, Pauldron PA 316: SEM BSE mid-range magnification (750x) image of the coating and dense product layer interface at ZOI 1_2. Context image presented in Figure 4-25.

At the magnification presented in Figure 4-26 there appeared to be two atomically contrasting CP phases in the DPL of the corrosion pits: a lighter one inside a darker one. Contrasting CP phases in the DPL was a similarity shared with Pauldron (part) PA RC 166, but in this case the darker CP phase was the majority.

Compared with the optical microscopy of ZOI $1_{1\text{-}2}$ on the sample from Pauldron PA 316[1083], the higher magnification under SEM determined that the shape/thickness of the underside of the coating conformed to the corrosion products of the DPL (Figure 4-26). During the optical microscopy results interpretation on the sample from Pauldron PA 316[1084], the coating was mentioned during a hypothesis regarding the propagation of corrosion products in this area *after* the application of the coating. The coating's conforming shape suggests the CPs of the DPL were

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[1082] Figure 4-21 & Table 4-5: Spectra 6-12

[1083] Figure 4-12 & Figure 4-13

[1084] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron PA 316 possibly already present at the time of coating application. Since it appears the coating was applied onto a surface already supporting corrosion products, the *maximum* position of the limitos can only be proposed. This position is proposed to coincide with the interface immediately below the coating. When the sample was still attached to the armour, this surface was located in a relatively inaccessible and hidden part of the armour[1085]; an area between the lames and having a clearance from the lame above. It would therefore seem reasonable that the surface might have been isolated from any preparatory physical corrosion product removal techniques; possibly explaining why the coating was applied to a surface bearing corrosion products. However (as testified by the coating's presence), the surface was accessible enough for liquid application of the coating, suggesting that this area was also accessible to solutions of chemical CP stripping agents[1086]. Perhaps the CPs remained since they were simply unobservable in the position between lames. Such speculative interpretation is not without doubts due to the long uncertain history of the armour, and is another example why the authentic armour and its surface materials (in this case, the coating) are flawed for categorically determining the limitos.

*

While the presence of the coating and the various deposits on zone of interest $1_{1\text{-}2}$ made it suitable for investigation of these characteristics, this zone under-represented other important features found elsewhere. As mentioned, a comparative absence of DPL corrosion products necessitated the examination of another zone of interest. Still on the outer surface, but with more DPL corrosion products, ZOI $2a_1$ was selected (Figure 4-27) and like some areas of ZOI $1_{1\text{-}2}$, it appeared by the black void that the coating was removed during sample preparation. Meanwhile, a thicker layer of heterogeneously shaped materials on the inner surface of the armour sample (ZOI $2b_1$ in Figure 4-27) was accordingly heterogeneously composed: iron, oxygen, calcium, manganese, chlorine, silicon, sulphur, lead and barium were detected by EDS point and area analyses (not presented).

[1085] Figure 4-5

[1086] 2.1.3.4.1 Restoration

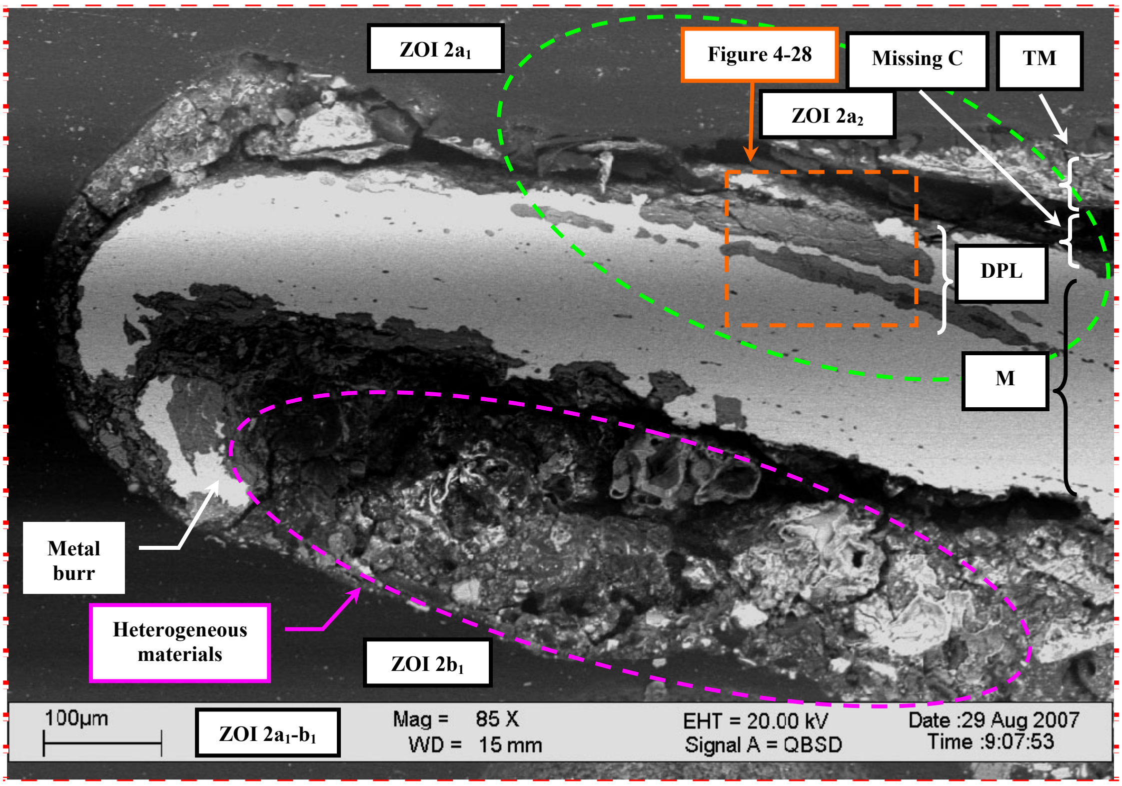

Figure 4-27 Palace Armoury armour cross-section, Pauldron PA 316: Low magnification (85x) SEM BSE image of stratigraphy at ZOI 2a$_1$-b$_1$. Context image in Figure 4-24.

The bias for an accumulation of various materials on the armour inner surface (ZOI 2b$_1$) is typical of the munition armour, and in this ZOI their retention was probably facilitated by the curved metal burr on the sample edge. The detected iron and oxygen are attributable to corrosion products, while the remaining elements, with the exception of the manganese, are most probably solely exogenous since they were not yet detected in this sample's metal or slag[1087] and they correlate with the Palace Armoury's environmental analyses[1088]. Since manganese was previously not detected in the PA's environmental analyses and detected in the slag[1089], then following the same previous rationale, manganese's attribution ought to be slag. However, it is questioned if the manganese detected in the upper layers of ZOI 2a$_1$ and in the heterogeneous materials of ZOI 2b$_1$ could have provenanced the slag or an exogenous source not determined in the environmental analyses[1090]. The locations for the manganese detected in ZOI 2a$_1$ and ZOI 2b$_1$, respectively above the coating and within a matrix of heterogeneous exogenous particles (especially barium that is

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[1087] Figure 4-25: Spectra 1-2
[1088] Table 4-1
[1089] Figure 4-25: Spectrum 2
[1090] Table 4-1

probably present in the form of the highly insoluble barium sulphate[1091]), suggest that even if manganese might have once provenanced the metal's slag, it no longer formed a part of the limitos.

*

Looking closer now at a higher magnification (500x) overview of zone of interest $2a_2$, preliminary EDS point and area analyses (Figure 4-28 & Table 4-7) were performed over the stratigraphy to establish a comparison with ZOI 1.

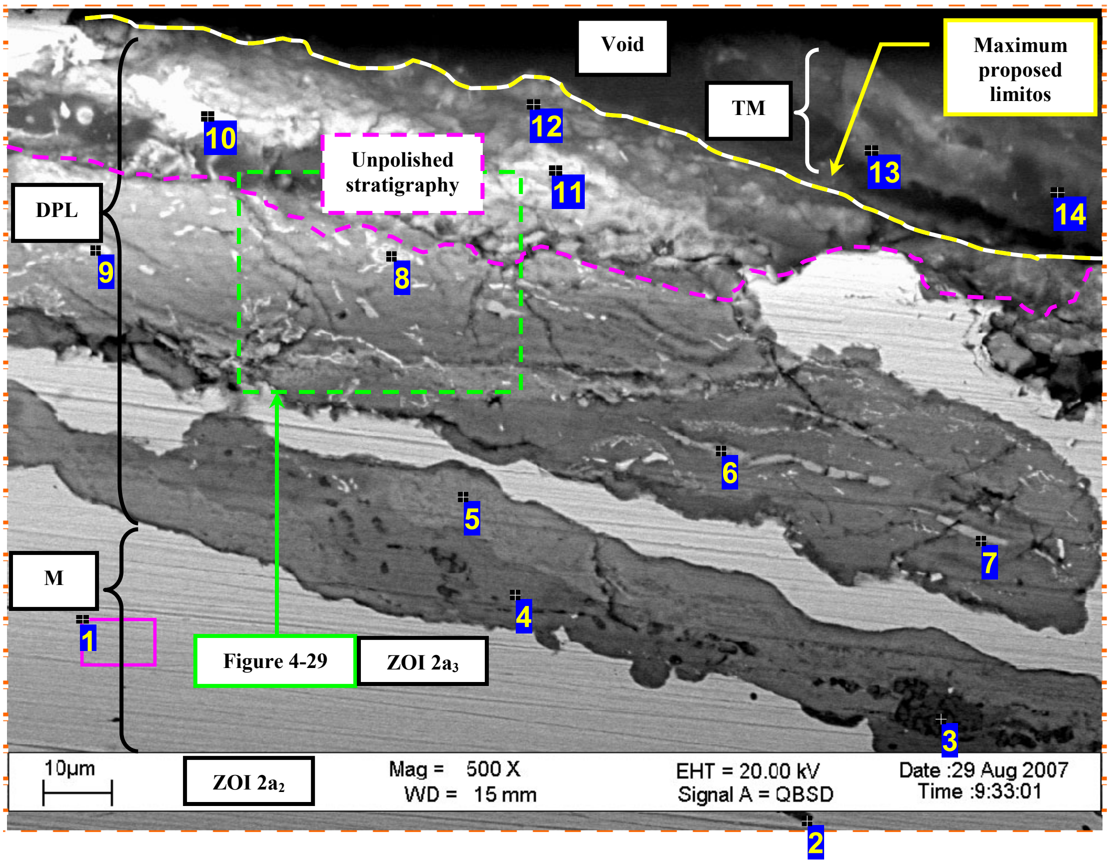

Figure 4-28 Palace Armoury armour cross-section, Pauldron 316: SEM BSE image (500x) of outer armour subsurface stratigraphy at ZOI $2a_2$ and sites of EDS analyses (1-14). Context image in Figure 4-27.

[1091] 5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties

Results				**Interpretation**
Spectra	**Elements detected (%rel.at.wt.)**			**Probable/possible (?) materials**
	Major (>5%)	**Minor (1-5%)**	**Trace (<1%)**	
1.	Fe	-	-	Metal
2.	Fe, O, Si	Mn, Ca, Al, K	Mg	Slag
3.	O, Fe, Si, Mn, Ca	Al, Mg, K	-	Slag
4.	Fe, O	-	-	Corrosion products
5.	Fe, O	-	-	Corrosion products
6.	Fe, O	Mn	-	Corrosion products, slag
7.	Fe, O	Mn	Mg, Ca	Corrosion products, slag
8.	Fe, O	-	Mn	Corrosion products, slag?, pollution?
9.	Fe, O	-	Mn	Corrosion products, slag?, pollution?
10.	Fe	-	-	Metal
11.	Fe, O	Ca	Cl	Corrosion products, pollution
12.	Fe	Ca, O, Cl	S	Corrosion products, pollution
13.	O, Fe, Si, Ca	S	-	Corrosion products, pollution
14.	O, Fe, Si, Ca	S	-	Corrosion products, pollution

Table 4-7 Pauldron 316: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-28

In partial agreement with zone of interest 1_1 (Figure 4-25), the iron-based metal (Spectrum 1) contained a material (Spectrum 2) rich in iron, oxygen and silicon, with minor amounts of manganese, calcium, aluminium and potassium and traces of magnesium (probably slag). Spectrum 3 exhibited exactly the same qualitative elemental composition as Spectrum 2, but on an area surrounded by corrosion product zones (Spectra 4-5: iron and oxygen). This corrosion product zone appeared compact and will be referred to as the dense product layer. In the DPL's corrosion products, thin and elongated bands of a middle-grey material displayed minor amounts of manganese with major amounts of iron and oxygen (Spectra 6-7). Meanwhile smaller areas of much whiter material also contained manganese, but at trace concentrations (Spectra 8-9). These traces of manganese in the DPL's upper areas of the armour outer could have provenanced the slag inclusions or from an exogenous source. Spectrum 10, iron only, denoted a nodule of uncorroded metal near the interface with the void above. The loss of the coating during sample preparation appears to have provoked a collapse of the adjacent CP areas: both in the TM and the upper region of the DPL. Compared with the composition of the lower features in ZOI $2a_2$, Spectra 11-12 detected markedly increased amounts of calcium, chlorine and sulphur, while Spectra 13-14 detected major amounts of silicon and calcium together with major amounts of iron and oxygen, and minor amounts of sulphur. The secondary electron detector confirmed that the topography of the area above the pink dashed line in Figure 4-28 & Figure 4-29 featured large voids, and was therefore not polished flat, and made it inappropriate for confident stratigraphic cross-section observation and analyses.

The proposed identification of the slag materials in the CPs by Spectra 2-3 & 6-7 and their inherent locations below or inside the uncorroded metal confirmed that they are indeed below the limitos. The identification of the white ferrous materials (without high concentrations of the slag-associated non-ferrous metals) detected by Spectra 8-9 is not immediately apparent. The fragment of uncorroded metal (Spectrum 10: iron only) indicated that this upper area is also inferior to the limitos. The markedly increased amounts of chlorine and sulphur (Spectra 11-12) in ZOI $2a_2$ indicated contamination from superior layers, since unlike calcium, they did not feature in the metal or slag. This increase in typical exogenous elements[1092] could be attributable to the area's inherent closeness to the atmosphere before sampling and/or as a result of the coating loss and subsequent disintegration of the stratigraphy. Meanwhile, the materials from which Spectra 13-14 were acquired appear to have originated from these collapsing layers. The minor amounts of sulphur (Spectra 13-14), unattributable to the metal, slag or lowermost corrosion products, indicate that these collapsing layers came from the TM above. Following the rationale of the determined various inferior limitos markers and the uncertainty introduced by the unpolished stratigraphy, the limitos for this area of the sample is proposed to fall between the lines marked "Unpolished stratigraphy" and "Maximum proposed limitos" in Figure 4-28.

*

Given the unsuitability for continued investigation of the dense product layer/coating interface, focus was drawn on further identifying examples of inferior limitos markers at high magnification (2000x), ZOI $2a_3$ (Figure 4-29 & Table 4-8).

[1092] Table 4-1

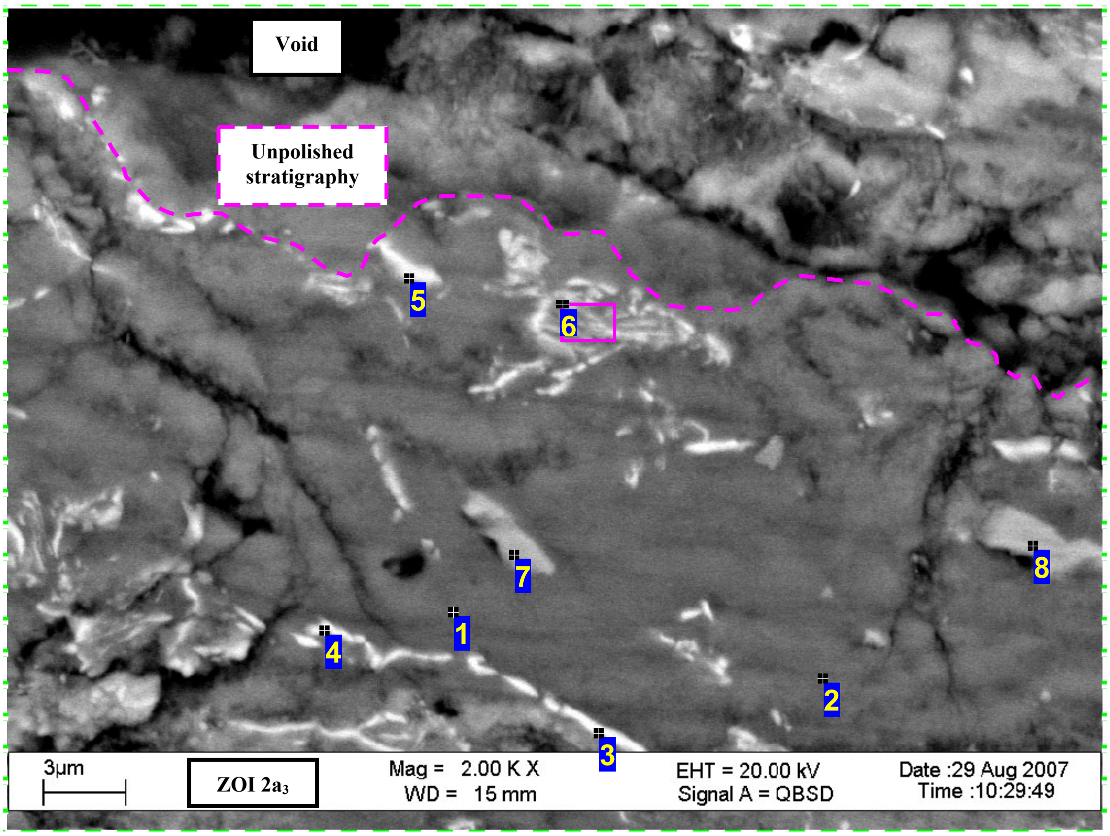

Figure 4-29 Palace Armoury armour cross-section, Pauldron PA 316: SEM BSE high magnification detail (2000x) of outer armour subsurface stratigraphy at ZOI 2a$_3$ and sites of EDS analyses (1-8). Context image in Figure 4-28

Results				Interpretation
Spectra	Elements detected (%rel.at.wt.)			Probable/possible (?) materials
	Major (>5%)	Minor (1-5%)	Trace (<1%)	
1.	Fe, O	-	Ca, Cl	Corrosion products, pollution
2.	Fe, O	-	-	Corrosion products
3.	Fe, O	-	-	Carbides, Corrosion products
4.	Fe, O	-	-	Carbides, Corrosion products
5.	Fe, O	-	Ca	Carbides, slag?, pollution
6.	Fe, O	-	Ca	Carbides, slag?, pollution
7.	Fe, O	Mn	Mg, Si	Slag
8.	Fe, O	Mn	Mg, Si	Slag

Table 4-8 Pauldron PA 316: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-29

The higher magnification permitted more localised EDS analyses of the various morphologies present inside the DPL corrosion products (Spectra 1-2: iron and oxygen) already outlined at lower magnification[1093]. The white phase of various thin morphologies, either single- (Spectra 3-5) or multiple-streaked lines (Spectrum 6), all contained iron and oxygen (a potential form of carbide as explained further below, in reference to Figure 4-30). The analysis sites closest to the outer surface (Spectra 5-6) also contained traces of calcium: perhaps slag or an influence of the

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[1093] Figure 4-28 & Table 4-7

proximity of an environmental pollution source. The thin and elongated bands of the middle-grey phase material (proposed slag) noted at the previous magnification (ZOI 2a$_2$, Figure 4-28) were not seen at ZOI 2a$_3$, but shorter particles also containing minor amounts of manganese became evident here (Spectra 7-8). These shorter pieces are perceived to be of the same origins as the thin and elongated bands in ZOI 2a$_2$ and are thus also considered to be slag.

*

Morphology similarities between various materials in the dense product layer noted during these latter SEM-EDS investigations were also previously noted via cross-section photomicroscopy of the uncorroded metal of the same armour sample. Vella et al. first observed these structures during metallographic examinations of the polished and etched metal[1094]. To compare morphology and size of these identified materials. Figure 4-30 provides a detail of a photograph at the equivalent magnification given in the SEM image presented in Figure 4-29. Both the thin single- or multiple-streaked lines, and also the shorter or elongated inclusions, can be seen. The thin streaked structures previously observed via metallography were perceived to be “irregularly shaped carbides” possibly having transformed from pearlite[1095, 1096].

[1094] Vella et al, 2004, p. 227

[1095] Ibid.

[1096] These features were first indicated and referred to as “white flakes” in the preliminary studies of Vella et al., 2005b, p. 324. Vella et al. proposed that the whiter intensity, while under observation with the SEM backscatter detector, could be attributable to an iron-rich phase such as iron carbide.

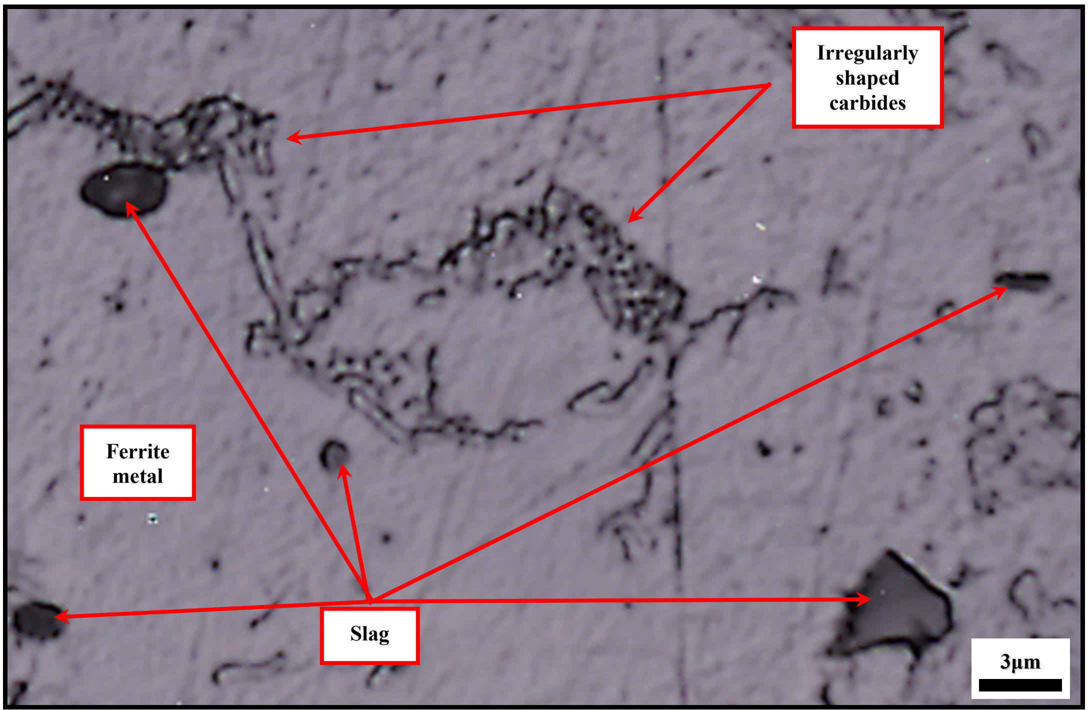

Figure 4-30 Palace Armoury armour cross-section, Pauldron PA 316: Metallographic image[1097].

The correlation of these morphologically identical phases existing in the corrosion products (Figure 4-29) and in the uncorroded metal (Figure 4-30), further proves that the structures within the dense product layer are indeed residual from the uncorroded metal: further confirming their and the DPL's validity as inferior limitos markers. The relative apparentness and permanence (and therefore usefulness as inferior limitos markers) of these supposed carbides was contrasted by the non-observation[1098] of any *ghost* structures of grain boundaries of ferrite[1099] in the corrosion products[1100].

BACKPLATE PA 329

At low magnification (25x) of the whole cross-section sample, Backplate PA 329 again distinguished itself from the previous two cross-sections due to its relative freedom of corrosion and corrosion products; both through the interior and near the surfaces (Figure 4-31). Relative to the sample itself, the cross-section represented surfaces marked by a distinct dichotomy: an outer surface that was irregularly pitted

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[1097] Enlargement of image published by Vella et al, 2004, p. 227

[1098] Via SEM in BSE and SE detector modes.

[1099] Table 3-1 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[1100] Previous studies by Vella et al. (2004, p. 227) determined that the uncorroded metal is composed of ferrite with a pearlite that had been converted into irregularly shaped carbides.

and almost devoid of CPs, and an inner surface that was intermittently corroded and filled with CPs while being covered by multitudes of irregularly distributed particles.

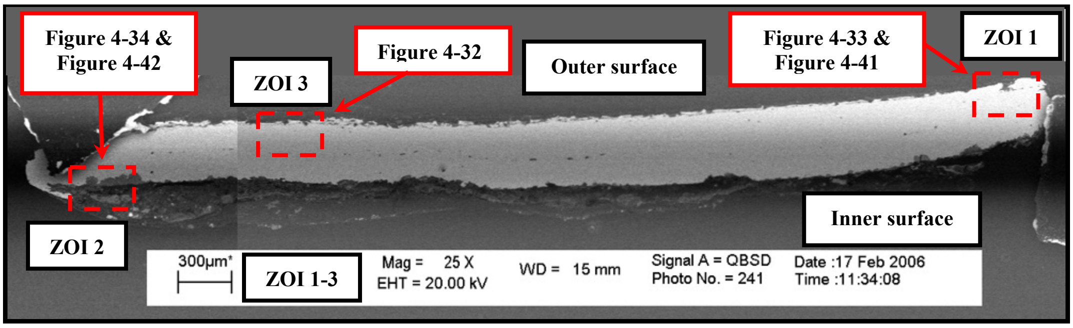

Figure 4-31 Palace Armoury armour cross-section, Backplate PA 329: Overall context SEM BSE image (25x) with contexts for ZOIs 1-3 presented in Figure 4-32, Figure 4-33, Figure 4-34, Figure 4-41 & Figure 4-42.

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Zone of interest 3_1 (Figure 4-32) provides an indication of the metal surface roughness and almost complete absence of corrosion products along the outer surface.

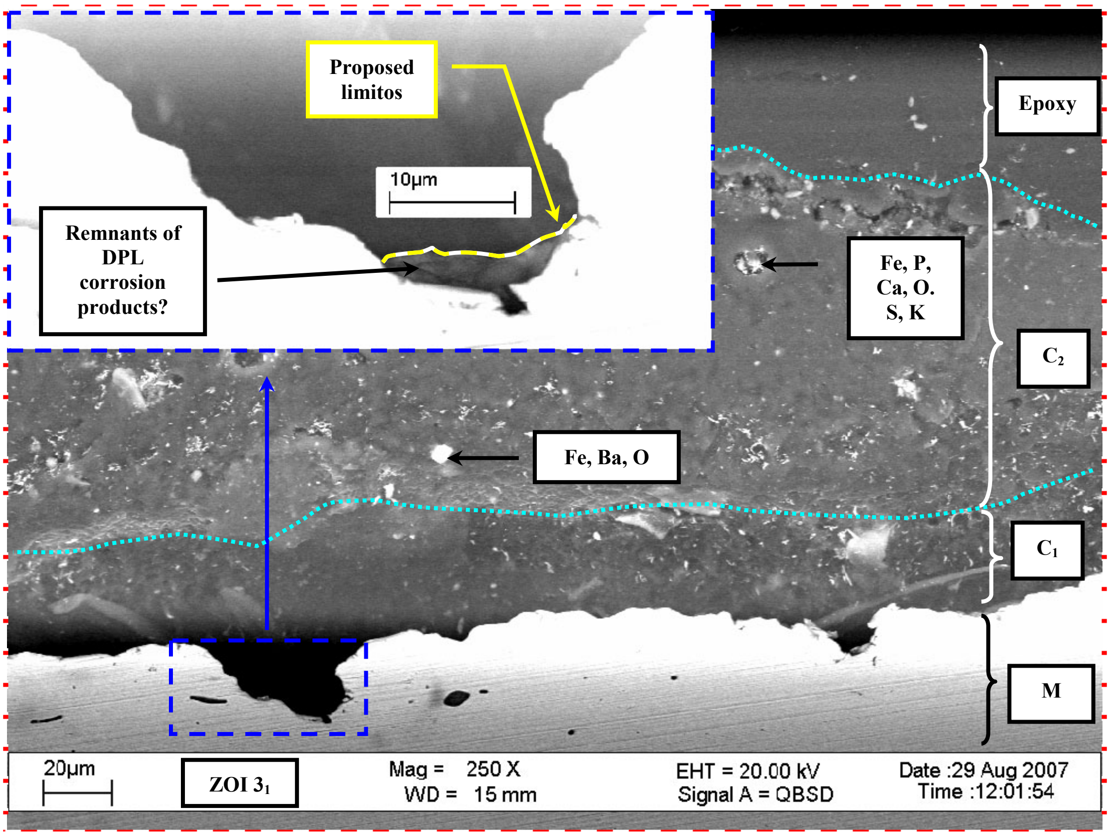

Figure 4-32 Palace Armoury armour cross-section, Backplate PA 329: Main: Low magnification (250x) SEM BSE image of outer armour subsurface stratigraphy at ZOI 3_1. Context image in Figure 4-31. Inset: Corrosion pit with trace amounts of corrosion products.

Only a small amount of (compact) corrosion products remained in the bottom of a pit (Figure 4-32: inset) (DPL). The prevalence of particles in the two coating layers was also apparent. Point energy dispersive spectrometry was performed on these particles, but the counts were either low or non-existent: it is thought that the particles were difficult to detect since they were inside the third dimension of the coating, i.e. below the cross-section surface[1101]. It would appear that these particles contaminated the coating either via a polluted surface prior to coating or a polluted coating brush or coating formula.

It would seem that the corrosion products located at the bottom of the pit in ZOI 3_1 (Figure 4-32: Inset) are remnants surviving from a previous cleaning intervention, and this perspective correlates with the pitted armour surface seemingly devoid of CPs[1102]. Since the corrosion products have mostly been removed, the limitos, or rather its remnant substrate, can now only be represented by the surface of the CPs in the pit, as discussed later[1103].

*

Zone of interest 1_1 was selected since it featured the corrosion pit on the outer surface with the most significant amount of corrosion products. Energy dispersive spectrometry point analyses (not presented) and mapping (Figure 4-33) of ZOI 1_1 determined a prevalence of silicon and calcium-based inclusions in this CP layer and inside the metal. Some material containing phosphorus, iron and oxygen near the coating interface also featured.

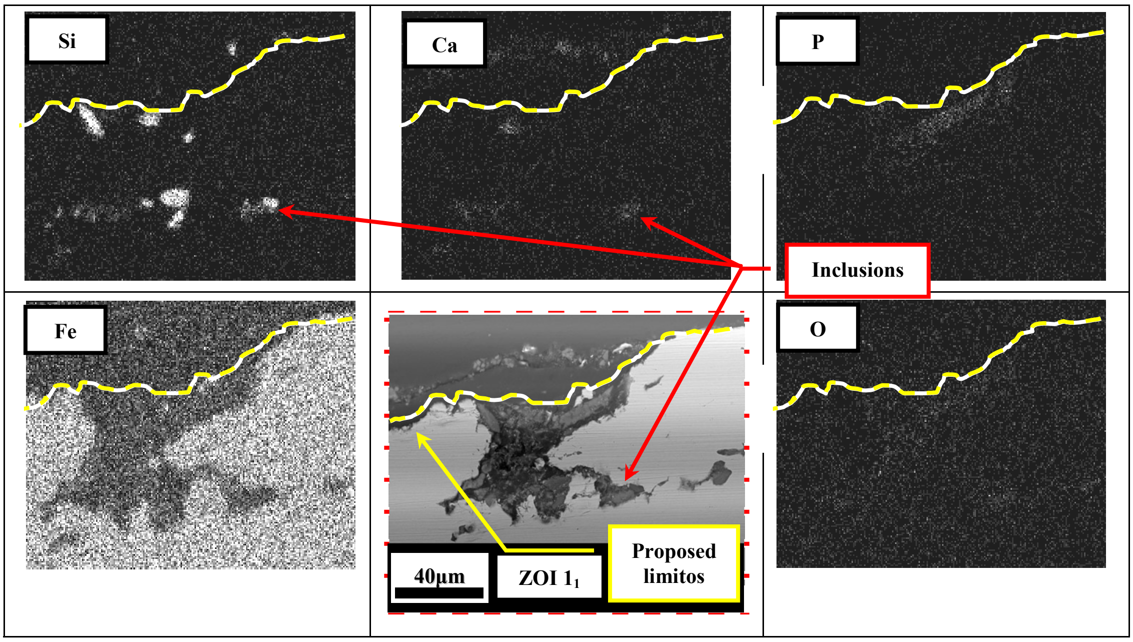

Figure 4-33 Palace Armoury armour cross-section, Backplate PA 329: Energy dispersive spectrometry mapping at ZOI 1_1. Context image in Figure 4-31.

[1101] The elements detected in the coating are presented, but without relative quantities.

[1102] Figure 4-6

[1103] 5.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Backplate PA 329

Since inclusions and corrosion on the cross-section only appeared very occasionally, it appears that the inclusions detected by EDS point analyses and mapping[1104] have been influential in contributing to this localised corrosion (galvanic?/crevice corrosion?[1105]). It is however difficult to conclude whether the inclusions contributed to the corrosion, or indeed if inclusions were only made obvious due to surrounding corrosion products.

The location of the CPs in ZOI 1_1 was evidently below a possible limitos since they were positioned in a pit below the adjacent metal. This area could be considered another[1106] part of a remnant dense product layer. The limitos (rather its remnant substrate) for this cross-section is proposed to be below the coating, but above the metal, DPL corrosion products and silicon-based inclusions present in the corrosion product pit (Figure 4-33).

*

Although ZOIs 1 & 3 were informative about the metal condition of the outer surface of this part of the armour (possibly documenting the extent of a former corrosion product removal treatment), the necessity for a cross-section area with CPs on more developed and less intervened stratigraphies was required to advance the research.

Low magnification (250x) SEM on zone of interest $2a_1$ (Figure 4-34), located on the inner side of the armour, resolved the coating layer above a very thick and heterogeneous layer of materials[1107]. Energy dispersive spectrometry mapping and point analyses (not presented) on the heterogeneous materials identified a predominant matrix of iron, oxygen and phosphorus. A random particle distribution of calcium, chlorine, sulphur, lead, potassium, silicon, and aluminium occurred through this matrix. This layer of heterogeneous materials was in turn located above some pits in the metal that contained a relatively uniformly-phased and compactly packed material (dense product layer).

[1104] Figure 4-33

[1105] 2.2.3.3.1 Pitting corrosion mechanism & 2.2.3.3.2 Galvanic corrosion mechanism

[1106] As per ZOI 3_1, Figure 4-32

[1107] As per Figure 4-17

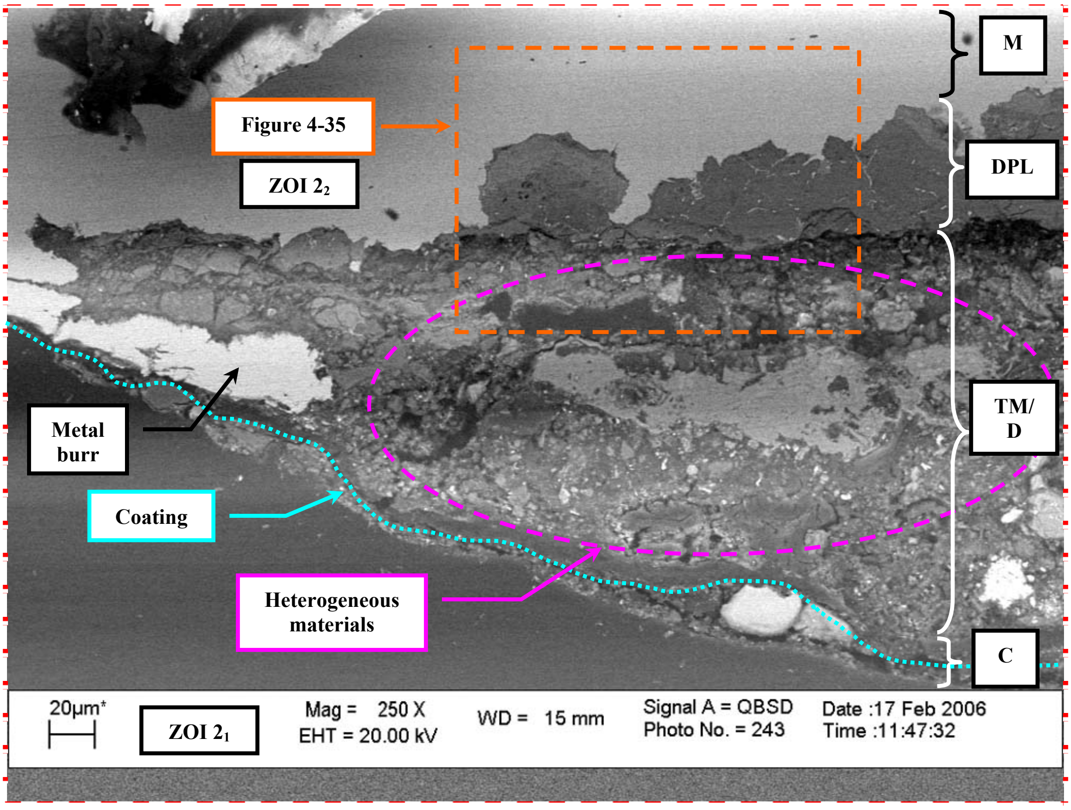

Figure 4-34 Palace Armoury armour cross-section, Backplate PA 329: SEM BSE image (250x) of inner armour subsurface stratigraphy at ZOI 2_1. Context image in Figure 4-31.

The heterogeneous matrix containing iron, oxygen and phosphorus, near the coating interface was probably ferrous CPs, with exogenous phosphorous since the latter was not detected in the metal or slag[1108]. Phosphoric acid a former CP removal agent[1109] is a possible candidate for attribution of phosphorous. The co-occurrence of silicon and calcium[1110] and aluminium and potassium[1111] in the slag with their presence in this layer of heterogeneous materials puts an assessment of these elements as only representing exogenous sources in question. However, the co-presence in the area marked "Heterogeneous materials" of the other elements (chlorine, sulphur and lead) not found in the inclusions, makes silicon, calcium, aluminium and potassium as pollution a more credible explanation, or indeed a second source. Considering the wide composition of these materials and their location on the inner side of the armour at the edge of the curved metal burr[1112], the materials in the heterogeneous layer are perceived to be superior to the limitos.

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[1108] Figure 4-33 and later in Figure 4-35 & Table 4-9

[1109] 2.1.3.4.1 Restoration

[1110] Figure 4-33

[1111] Aluminium and potassium were detected subsequently, as presented in Figure 4-35 & Table 4-9

[1112] Resembling a similar aspect to the sample from Pauldron PA 316, Figure 4-27

At higher magnification (400x) of ZOI 2_1 EDS was performed on the metal, inclusions and dense product layer, where phases of two greyscales became apparent: ZOI 2_2 (Figure 4-35 & Table 4-9).

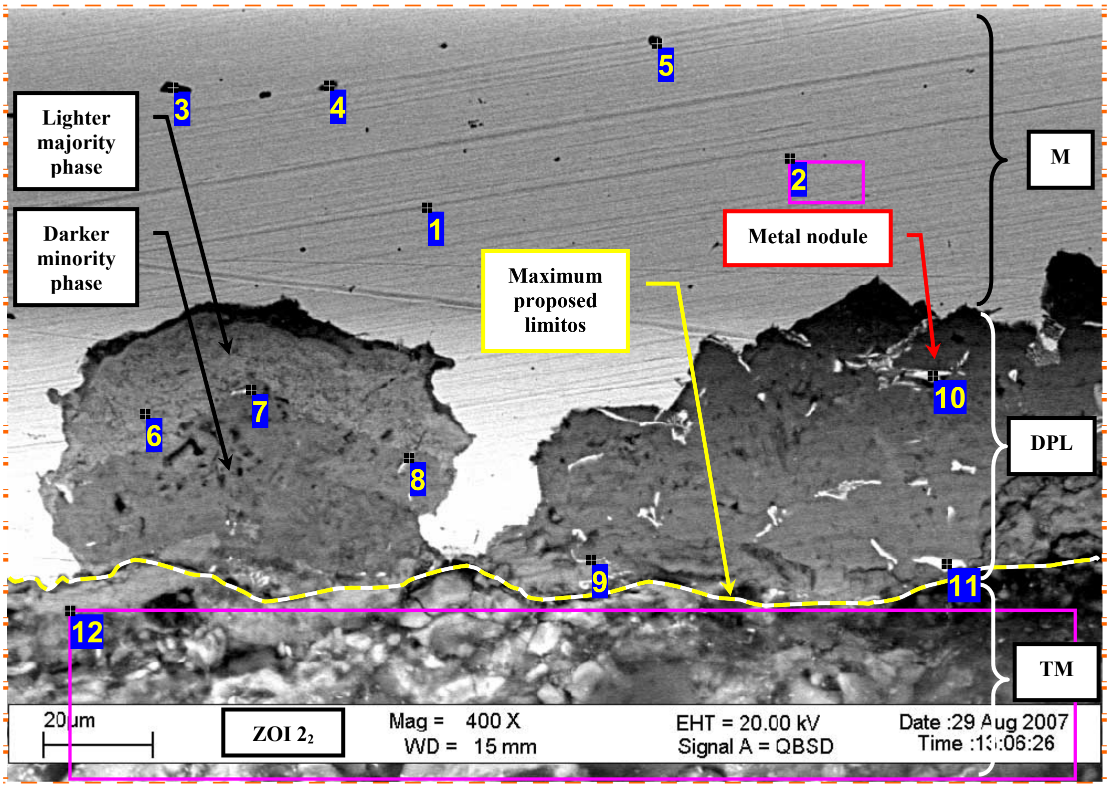

Figure 4-35 Palace Armoury armour cross-section, Pauldron PA 329: SEM BSE detail (400x) of inner armour subsurface stratigraphy at ZOI 2_2 and sites of EDS analyses (1-12). Context image in Figure 4-34.

Results				Interpretation
Spectra	Elements detected (%rel.at.wt.)			Probable/possible (?) materials
	Major (>5%)	Minor (1-5%)	Trace (<1%)	
1.	Fe	-	-	Metal
2.	Fe	-	-	Metal
3.	Fe, O, Si, Ca	Al, Mn, Mg, K	-	Slag
4.	Fe, O, Si, Ca	Al, Mg, Mn, K	-	Slag
5.	Fe, O, Si, Ca	Mn, Al, Mg, K	-	Slag
6.	Fe, O	Cl	-	Corrosion products, pollution
7.	Fe, O	-	Cl	Corrosion products, pollution
8.	Fe, O	-	Ca	Corrosion products, pollution
9.	Fe, O	-	Cl, Ca	Corrosion products, pollution
10.	Fe	-	-	Metal
11.	Fe	-	-	Metal
12.	Fe, O, P	Ca, Cl	-	Corrosion products, pollution

Table 4-9 Pauldron PA 329: Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-35.

Spectra 1-2 (iron only) denoted the presence of the metal, while Spectra 3-5 on the inclusions in the metal consistently proved to be composed of iron, oxygen, silicon, calcium, aluminium, manganese, magnesium and potassium (probably slag). Spectra 6-9 mainly revealed iron and oxygen (indicating ferrous CPs) with minor and trace amounts of chlorine (exogenous, source since not found in metal or slag) and trace amounts of calcium (exogenous and/or endogenous inclusion source). Spectra 10 & 11 (iron without oxygen) determined the presence of uncorroded metal nodules inside the dense product layer: again evidencing the presence of inferior limitos markers inside the DPL. Voids were present in some of the heterogeneous stratigraphy adjacent to the DPL. Area analyses (Spectrum 12) were made on this area to provide a summary of its constituent materials: mainly iron, oxygen and phosphorus, while minor amounts of calcium and chlorine also featured. Of these elements phosphorus and chlorine indicate this area's probable exogenous attribution, but it is only the overall morphology of heterogeneous particles that indicates this area is unrelated to the limitos. The maximum proposed limitos on ZOI 2_2 possibly falls between the layer of heterogeneous materials and the dense product layer with its contained metal nodules.

*

Higher magnifications (1500-2000x) with the SEM in BSE and SE detector modes on the dense product layer were used to see if there were any remnants of the Widmanstätten ferrite-pearlite microstructures previously established from the metal[1113], but none were identified.

SUMMARY OF ARMOUR CROSS-SECTION SEM-EDS RESULTS

Variously according to the samples, SEM-EDS identified the presence of metal nodules[1114], slag inclusions[1115] and a type of carbide microstructure[1116] in the dense product layer; evidence that inferior limitos markers are associated with the DPL layer.

The SEM-EDS of the corrosion product layers (transformed medium and dense product layer) identified many of the elements detected in the PA environment[1117], with prevalence in the layers closest to the atmosphere and above any coatings[1118]. Exclusive attribution of some elements (detected via EDS in corrosion products) with exogenous sources was not always possible due to their co-

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[1113] Vella 2004, p. 224 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[1114] PA RC 166: Figure 4-20 ; & PA 329: Figure 4-35

[1115] PA RC 166: Figure 4-20, Figure 4-21, Figure 4-22; PA 316: Figure 4-28, Figure 4-29; & PA 329: Figure 4-33

[1116] PA 316: Figure 4-29

[1117] 4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

[1118] PA RC 166: Figure 4-21, Figure 4-23; PA 316: Figure 4-28; & PA 329: Figure 4-35 presence in the slag inclusions[1119]. Compared with the DPL, the absence of inferior limitos markers and greater quantities of non-endogenous elements and heterogeneously distributed particles in the TM provided evidence to (at least) suggest that this layer might not be inferior to the limitos. Although inconclusive, the most probable location determined thus far for the limitos is at the transformed medium/dense product layer interface.

Observation by SEM BSE of all CP cross-sections also revealed that the corrosion products of the TM & DPL were constituted of various compounds/mixtures, since differing greyscales[1120] were clearly visible with backscattered electrons.

4.1.3.2.4 Armour cross-section Raman micro-spectroscopy

Raman micro-spectroscopy was performed on the cross-sections to analyse the composition of the different corrosion product phases previously investigated with SEM-EDS. A sample of the Raman micro-spectroscopy results produced by Ms Judith Monnier[1121] for the main zones of interest is presented. An emphasis on the zones of interest presented elsewhere in the methodology was made to provide complementarity of techniques. A representative sample of the various Raman spectra obtained is given in Appendix G[1122]. The thick corrosion product layers on the cross-section from Pauldron (part) PA RC 166 concentrated the Raman micro-spectroscopy analyses on this sample.

PAULDRON (PART) PA RC 166

Following from the previous SEM-EDS investigations, the focussed zones of interest for the Raman micro-spectroscopy on PA RC 166 were along the left inner side (ZOI $3a_1$-d_1) where the corrosion products were thickest and most retained[1123].

Zone of interest $3c_1$ (analysed by scattered point analyses and regrouped from 6 images for presentation at a lower magnification in Figure 4-36), predominantly featured ferrihydrite (Spectra 1-2, 5, 10, 12-14) and goethite (Spectra 3-4, 11) throughout the corrosion product layers, while akaganéite (6-8) slightly predominated ferrihydrite in the outer layers close to the CP/atmosphere (embedding

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[1119] PA 316: Figure 4-25 & Figure 4-27, PA 329: Figure 4-35, Figure 4-33, Figure 4-34

[1120] PA RC 166: Figure 4-20; PA 316: Figure 4-26; & PA 329 Figure 4-35

[1121] 3.5.3 Raman micro-spectroscopy

[1122] Appendix G – Raman micro-spectroscopy spectra: representative selection from zones of interest on armour cross-sections PA 316 & PA RC 166

[1123] Figure 4-19

resin) interface. A goethite-lepidocrocite mixture (Spectrum 9) also featured in this area. Notably, fluorescence[1124] signals were also obtained and only from the outermost layers (Spectra 6-9, 13)[1125].

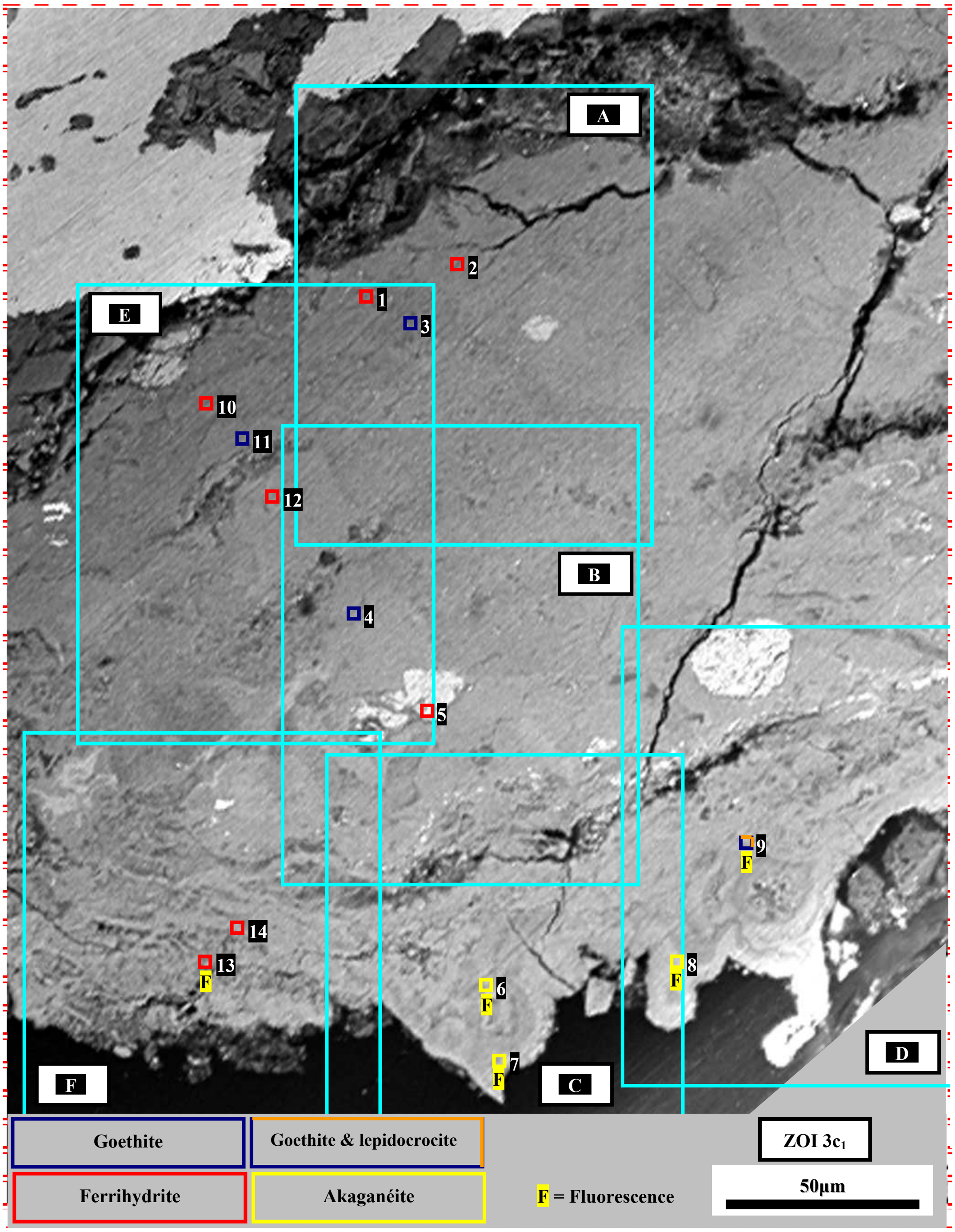

Figure 4-36 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: SEM BSE image representing six (A-F) areas of Raman micro-spectroscopy analyses of inner armour subsurface stratigraphy for ZOI 3c$_1$ and the results for the respective analysis points (1-14)[1126]. Context image in Figure 4-19.

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[1124] 3.5.3 Raman micro-spectroscopy & Figure 3-31

[1125] Monnier, 2005a, pp. 1-3

[1126] Ibid.

Zone of interest 3b$_1$, also examined by scattered point analyses, proved to be predominantly composed of goethite (Spectra 31-41, 43-46, 48-50) and ferrihydrite (Spectra 31-39, 41-42, 45-50) and also with some lepidocrocite (Spectra 32-33, 35, 39-40, 45-46) near and far from the metal (Figure 4-37). No akaganéite was detected[1127]. Exceptionally, weak fluorescence occurred on two occasions: close to a crack; and at the corrosion product/metal interface. There was no apparent bias in CP composition distribution.

Although mixtures of corrosion product phases were often indicated by the Raman spectra, the analyst was able to suppose which phases were the majority according to the relative size of the peaks. In ZOI 3b$_1$, the three spectra (31-33) closest to the metal were deemed to clearly be a majority phase of goethite over ferrihydrite, while beyond the crack, ferrihydrite featured as a light marbling[1128, 1129] (Spectra 34-38) in the darkest area. In the darkest zone[1130, 1131] that followed (Spectra 39-40), goethite featured as the majority over ferrihydrite. From the middle area until the embedding resin, spectra indicated ferrihydrite-goethite mixtures, but with majority phases of goethite (Spectra 49-50) and ferrihydrite (Spectra 41, 45-46, 48)[1132].

[1127] Ibid., pp. 4-5

[1128] "marbrures claires" (Ibid., p. 7)

[1129] Based on OM image and corresponding to the lighter appearance on the same feature observed by SEM BSE.

[1130] "la zone plus sombre" (Monnier, 2005a, p. 7)

[1131] Based on OM image and corresponding to the darker appearance on the same area observed by SEM BSE.

[1132] Monnier, 2005a, p. 7

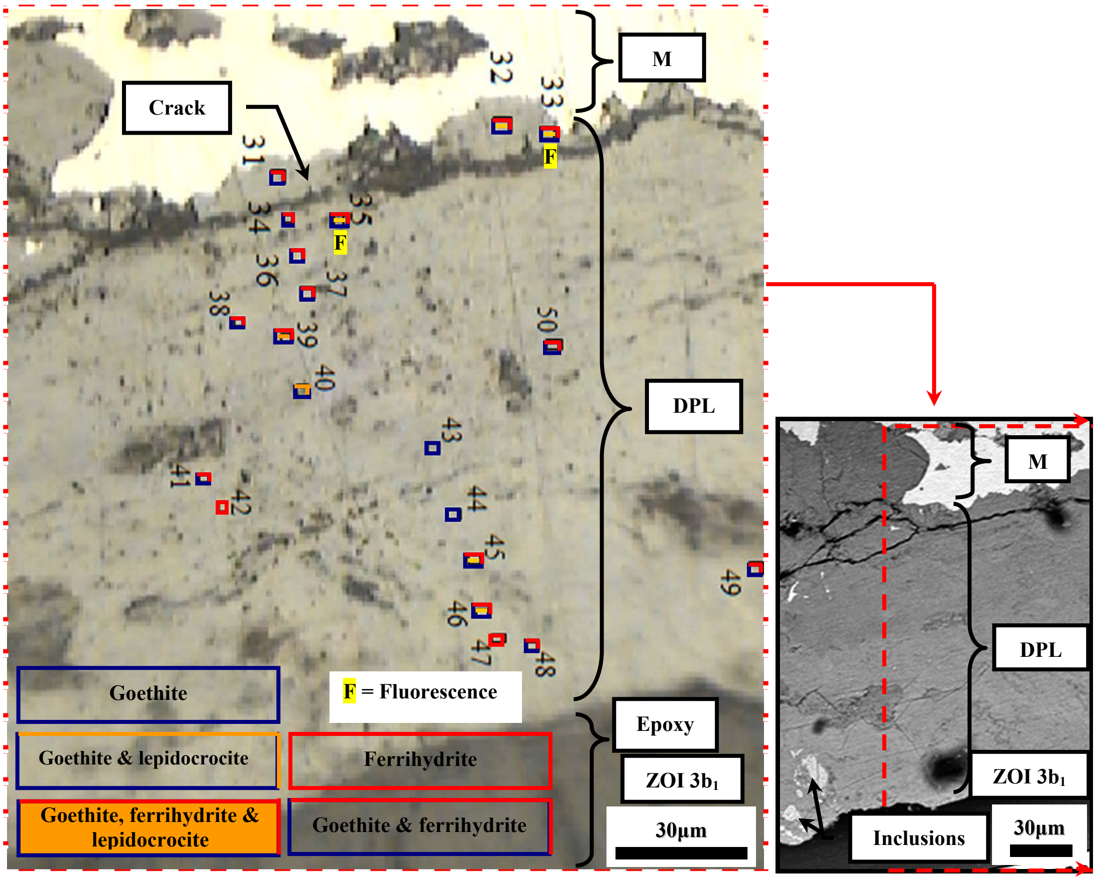

Figure 4-37 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Left: Optical microscope image representing areas of Raman micro-spectroscopy analyses of inner armour subsurface CP stratigraphy for ZOI 3b$_1$ and the results for the respective analysis points (31-50)[1133]. Context image in Figure 4-19. Right: SEM BSE image of same area and adjacent inclusions inside the dense product layer.

The absence of akaganéite and fluorescence in the outer layer of ZOI 3b$_1$ (when compared with the previous ZOI, 3c$_1$) is possibly attributable to the real outer layer having been lost during sampling[1134]. The current outer layer is proposed to actually be the remnants of an inner layer, which is perceived to be the dense product layer. As viewed by BSE SEM, the presence of inclusions at the boundary of this area supports this perception (Figure 4-37: right)

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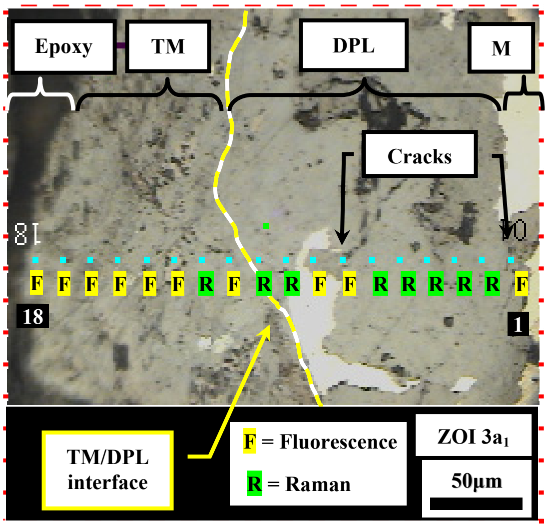
The results from zone of interest 3a$_1$, obtained via linear profiling (Figure 4-38), again demonstrated a predominance of ferrihydrite and goethite throughout the corrosion product layers, with lepidocrocite at a lesser frequency. No akaganéite was detected[1135]. Like ZOI 3c$_1$, fluorescence signals dominated the outer layers (TM)

[1133] Ibid, pp. 4-5

[1134] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron (part) PA RC 166, Figure 4-7 & 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166, Figure 4-19

[1135] Monnier, 2005a, p. 6

while the majority of the fluorescence in the inner areas (DPL) is possibly explained by cracks recorded in the optical microscopy image (Figure 4-38).



Spectra number	Signal	Corrosion product phase detected
1.	Fluorescence	Ferrihydrite
2.	Raman	Goethite, lepidocrocite, (ferrihydrite)
3.	Raman	Goethite, ferrihydrite
4.	Raman	Goethite, ferrihydrite
5.	Raman	Goethite, ferrihydrite
6.	Raman	Goethite, lepidocrocite, (ferrihydrite)
7.	Fluorescence	Ferrihydrite
8.	Fluorescence	Goethite, ferrihydrite
9.	Raman	Ferrihydrite
10.	Raman	Lepidocrocite, (goethite), ferrihydrite
11.	Fluorescence	Goethite
12.	Raman	Lepidocrocite, ferrihydrite
13.	Fluorescence	Inclusion
14.	Fluorescence	Goethite, ferrihydrite
15.	Fluorescence	?
16.	Fluorescence	?
17.	Fluorescence	Goethite, ferrihydrite
18.	Fluorescence	Goethite?

Figure 4-38 Palace Armoury armour cross-section and composition, Pauldron (part) PA RC 166: Left: Optical microscope image representing Raman micro-spectroscopy linear profiling of inner armour subsurface corrosion product stratigraphy for ZOI 3a$_1$. Context image in Figure 4-19. Right: Results for the respective Raman micro-spectroscopy analysis points (1-18)[1136].

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The results from zone of interest 3d$_1$ reconfirmed the prevalence of goethite and ferrihydrite through all layers that could be analysed without fluorescence interference[1137]. This time the field area of the profiling was increased to make a map (Figure 4-39). The map was more helpful in determining distribution of fluorescence and possible reasons for its cause. Again the fluorescence had predominantly occurred in the outer corrosion product layers (TM) and also in an area at the metal CP interface. The surfaces that appeared evenly reflective emitted Raman signals without fluorescence. Meanwhile the surfaces that appeared to feature greater asperity (or roughness and porosity, as exhibited by the dark stippled surfaces) seem to have been less uniformly reflective and emitted fluorescence signals. The area of fluorescence at the metal/CP interface demonstrates that this phenomenon does not necessarily exclusively occur in the outer corrosion product layers, although it was apparent that fluorescence was significantly more prevalent in the outer layers previously referred to as the transformed medium[1138].

[1136] Ibid.

[1137] Ibid., p. 7

[1138] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

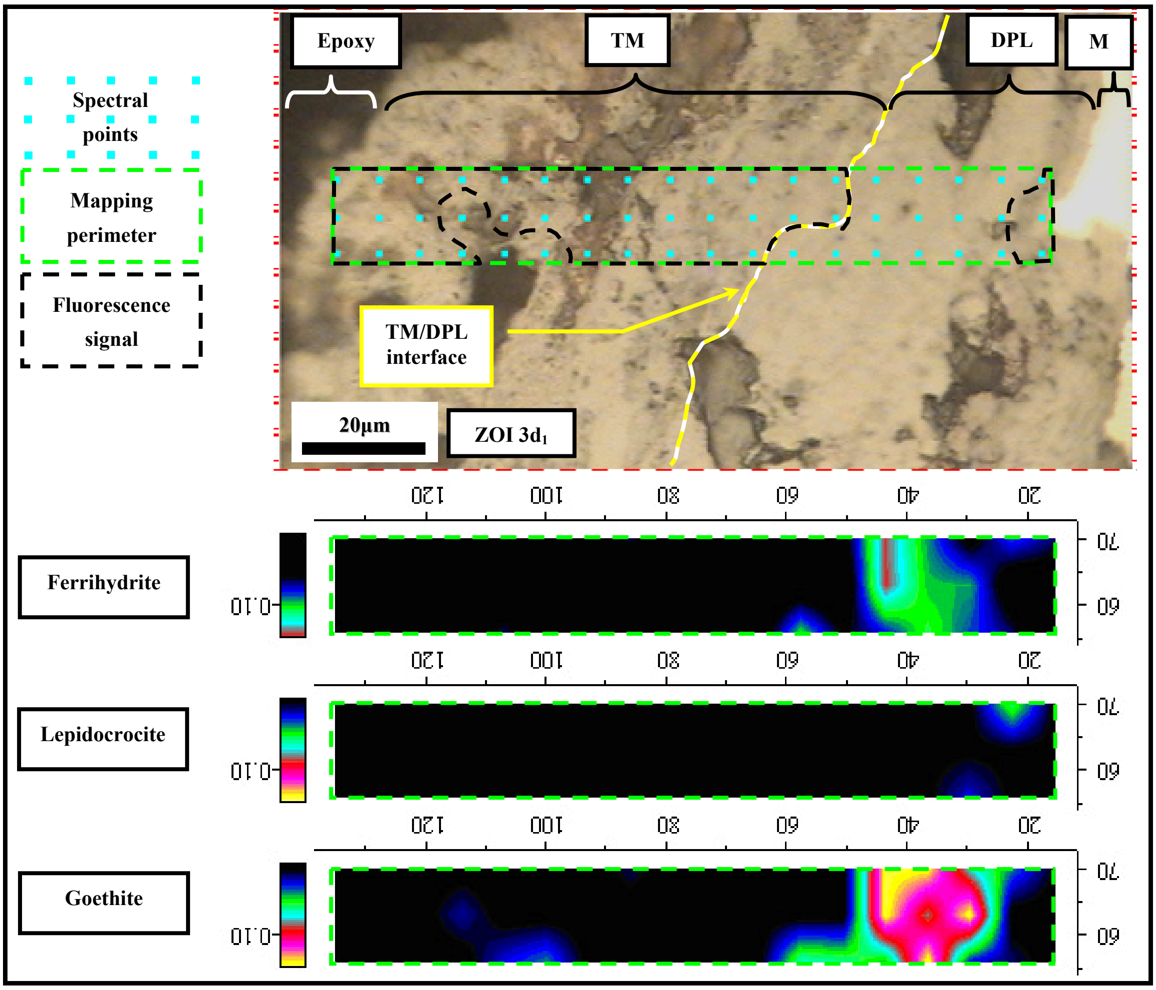

Figure 4-39 Palace Armoury armour cross-section, Pauldron (part) PA RC 166: Top: Optical microscope image with Raman micro-spectroscopy mapping at ZOI $3d_1$. Context image in Figure 4-19. Bottom: Hyperspectral mapping results by intensity of corrosion product phases. Black denotes areas of strong fluorescence[1139].

*

Summarising the Raman micro-spectroscopy results from the several zones of interest on Pauldron (part) PA RC 166, it was apparent that goethite and ferrihydrite were the major phases occurring both in the DPL and the TM. Goethite and ferrihydrite were often intimately mixed (i.e. non-stratified). There was no distinctive position for the CP phases in the layers with the exception of akaganéite, which was located in the outer layers closer to the former atmosphere.

PAULDRON PA 316

Results from a number of Raman micro-spectroscopy analyses performed on the only zone of interest (1_2) investigated on this cross-section reconfirmed the majority presence of ferrihydrite and goethite[1140] and the non-linear stratification of

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[1139] Ibid.

[1140] Monnier, 2005b, pp. 1-3

the dense product layer (Figure 4-40). For this sample, the transformed medium (the area that typically exhibited fluorescence on cross-section PA RC 166) was not analysed by Raman micro-spectroscopy since it was not immediately present above the DPL and was separated by the remnants of the transparent protective coating[1141]. The lighter contrasting phase in the DPL (Figure 4-26 & Figure 4-40), perceived to be “irregularly shaped carbides”[1142], appeared to correlate more with the zones that the Raman micro-spectroscopy determined to be unmixed ferrihydrite (Spectra 3, 5, 8) with one exception (Spectrum 9). Meanwhile, the darker majority phase in the DPL appeared to correlate with unmixed goethite (Spectra 4, 10, 15) and elsewhere the spectra demonstrated mixtures of ferrihydrite and goethite (Spectra 1, 2, 6, 7, 11)[1143]. Notably only one (Spectrum 8) of the thirteen analysis sites emitted a fluorescence signal and this is thought to be explainable since it was “…on the edge of a crack”[1144].

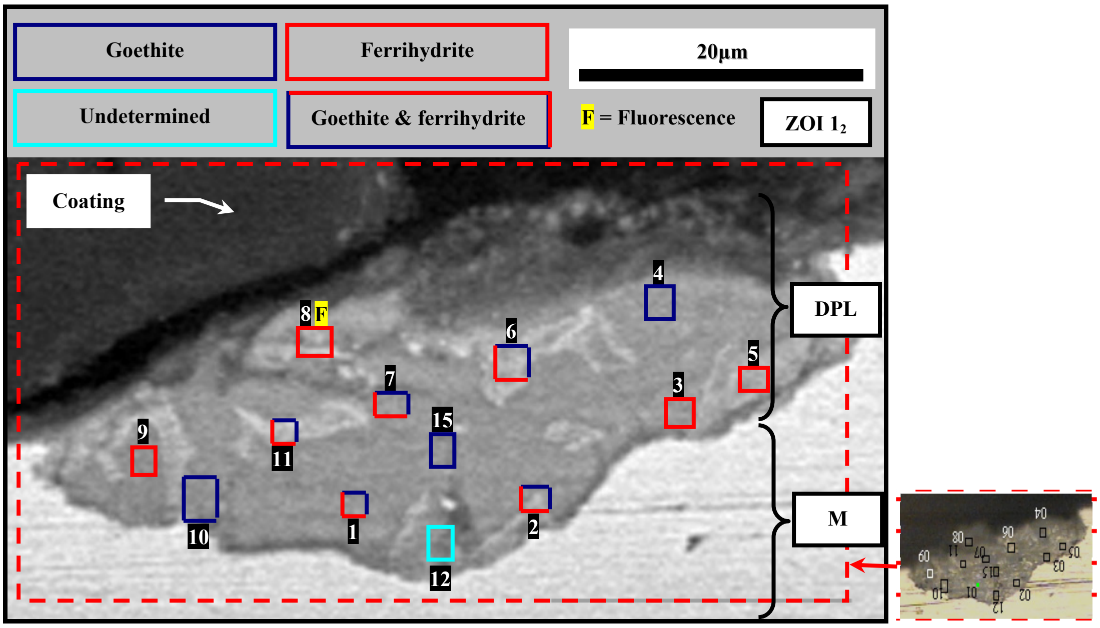


Figure 4-40 Palace Armoury armour cross-section, Pauldron PA 316: Left: SEM BSE image representing Raman micro-spectroscopy point analyses of cross-section inner armour subsurface stratigraphy at ZOI 1_2 and the results for the respective analysis points (1-12, 15). Context image in Figure 4-24 Right: Optical microscope image with original Raman analyses points[1145].

[1141] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron PA 316

[1142] Vella et al, 2004, p. 227

[1143] Monnier, 2005b., pp. 1-3

[1144] Translated from “08: présente de la fluorescence; logique car en bord de la fissure” (Monnier, 2005b, p. 3).

[1145] Monnier, 2005b, p. 1

BACKPLATE PA 329

The occurrence of fluorescence limited the number of spectra taken from this sample. Fluorescence signals throughout the corrosion product layer required longer acquisition times[1146]. Zone of interest 1_1[1147], containing a pit on the outer surface partly filled with CPs, exhibited fluorescence and therefore could not be characterised at all even after long acquisition times[1148]. When observing, with secondary emission SEM, the topography of the constituents in the pit it was seen that they were not flat (Figure 4-41): this could account for the fluorescence.

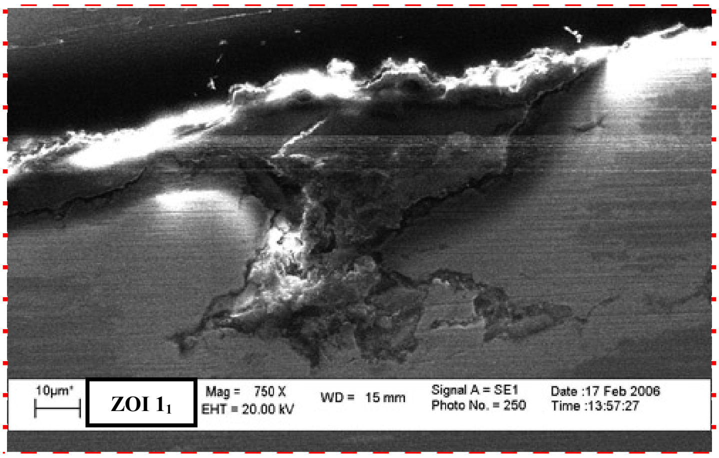


Figure 4-41 Palace Armoury armour cross-section, Backplate PA 329: SEM SE image of ZOI 1_1. Context image in Figure 4-31.

Fluorescence also occurred in ZOI 2_2[1149] and it was only with longer acquisition times that characterisation was possible[1150]. The relatively few characterised points are given in Figure 4-42 and their low number statistically limited reliable interpretation of the results. The limited results, however, are indicative of the previously determined trends where goethite (mostly) and ferrihydrite were the predominating ferrous corrosion products in the dense product layer. They also highlighted that fluorescence also occurred in the dense product layer, perhaps due to the interfaces of the CPs with the numerous metal nodules.

[1146] Monnier, 2005c, p. 1
[1147] Figure 4-31
[1148] Monnier, 2005c, pp. 2-3
[1149] Context in Figure 4-31, Figure 4-34 & Figure 4-35
[1150] Monnier, 2005c, p. 1

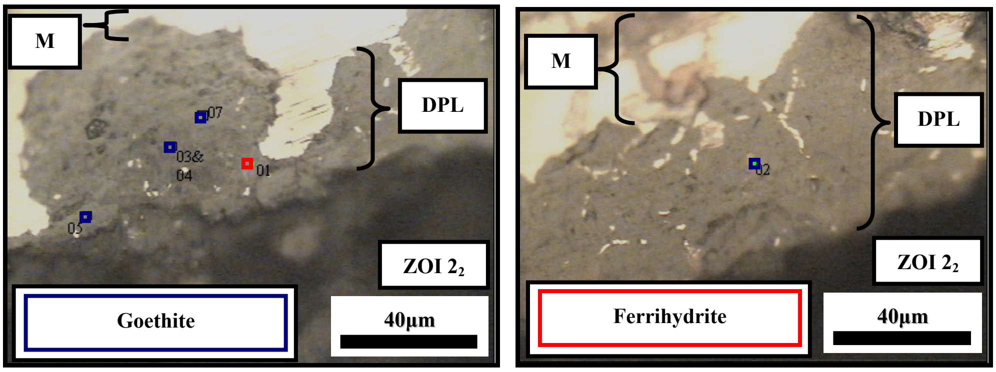


Figure 4-42 Palace Armoury armour cross-sections, Backplate PA 329: Optical microscope images representing Raman micro-spectroscopy analyses at ZOI 2_2 on the cross-section and the results for the respective analysis points (1-5, 7)[1151]. Context image in Figure 4-31.

Summary of armour cross-section Raman micro-spectroscopy results

Raman micro-spectroscopy confirmed the non-stratigraphic and complex mixture of mineralised iron as products of wrought ferrous (iron and steel) atmospheric corrosion processes. Of those corrosion products detected, it was clear that the predominant species present in the three samples' various zones of interest were ferrihydrite and goethite. Like the dense product layer[1152], the composition of the transformed medium[1153] featured goethite and ferrihydrite as the main phases. Notably, fluorescence signals detected by the Raman spectrometer appeared to inadvertently mark the interface between the DPL and the TM; the previously[1154] proposed most probable corresponding limitos marker.

4.1.3.2.5 Summary of armour corrosion cross-section observations & analyses results

The investigations of the armour cross-sections demonstrated that the local to general corrosion morphologies evident at the surface proved to have further impact on the metal core; mostly by means of an uneven corrosion front led by pits. It was not possible to isolate a filiform corrosion filament in a cross-section, but since this corrosion typology is a surface corrosion with minor pitting depth[1155], then deep pits would not be expected to occur. The cross-sections determined a third possible type of corrosion: crevice and/or galvanic corrosion. This corrosion type appears to have an association with the local to general corrosion morphologies.

[1151] Ibid.

[1152] PA RC 166: Figure 4-36, Figure 4-37, Figure 4-38 & Figure 4-39; PA 316: Figure 4-40 & PA 329: Figure 4-42

[1153] PA RC 166: Figure 4-36, Figure 4-38 & Figure 4-39

[1154] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Summary of armour cross-section SEM-EDS results

[1155] 2.2.3.2 Filiform corrosion/corrosion product morphology

As for the CPs, they were typically distributed between two physically dissimilar, but chemically similar layers: the lower and compact DPL and the upper porous TM; both mainly containing ferrihydrite and goethite. The presence of inferior limitos markers (i.e. metal nodules, slag inclusions, a type of carbide) in the DPL suggests this layer is below the limitos. Corresponding markers were not determined on the armour cross-sections, although the interface between the transformed medium and the dense product layer appears to be a likely candidate since the TM did not feature the inferior limitos markers.

Notably, *ghost* grain microstructures[1156] remnant from the former metals (i.e. metal microstructures previously documented in the literature[1157]) were not observed in any of the samples via any of the investigation techniques applied on the cross-sections.

4.1.4 AUTHENTIC MUNITION ARMOUR CORROSION PRODUCT REMOVAL: THE PALACE ARMOURY TECHNIQUE

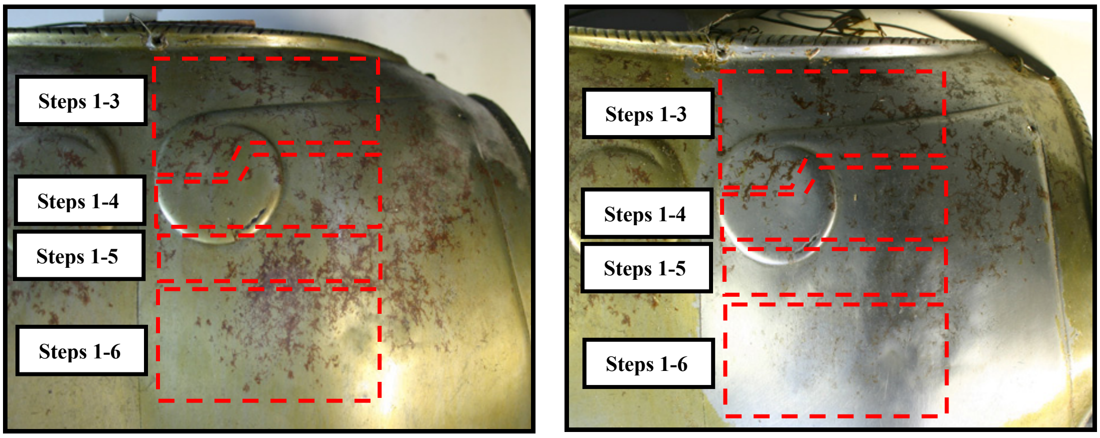
In preparation for the second phase of investigations, the armour analogues[1158], the method of corrosion product removal taken at the Palace Armoury was documented. Documentation of the current Palace Armoury munition armour cleaning practice was performed before and after cleaning, but prior to the wax coating step so as not to impede surface observation. The cleaning[1159] was initially undertaken in a stepped manner so as to temporarily leave examples of the surfaces achieved after each of the major intervention steps (Figure 4-43).

[1156] 2.3.1.2.1 Localisation of the limitos & Figure 2-51

[1157] Table 3-1 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[1158] 4.2 Munition armour analogues: laboratory corrosion case studies & destructive investigations

[1159] 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique



Before

After

Figure 4-43 Palace Armoury armour backplate: Comparison of effects before and after consecutive steps of corrosion product removal and associated interventions.

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It was observed that after steps 1-3 (removal of particulate deposits and coating), well defined filiform with tangentially branched filaments remained on the surface, while after step 4 (the first intentional corrosion product removal step), the CPs were greatly diminished. During this step the various corrosion product removal techniques applied to remove superficial CPs had the most influential effect yet on the CPs. Filiform filament tracks remained, if only much more faint (Figure 4-44).

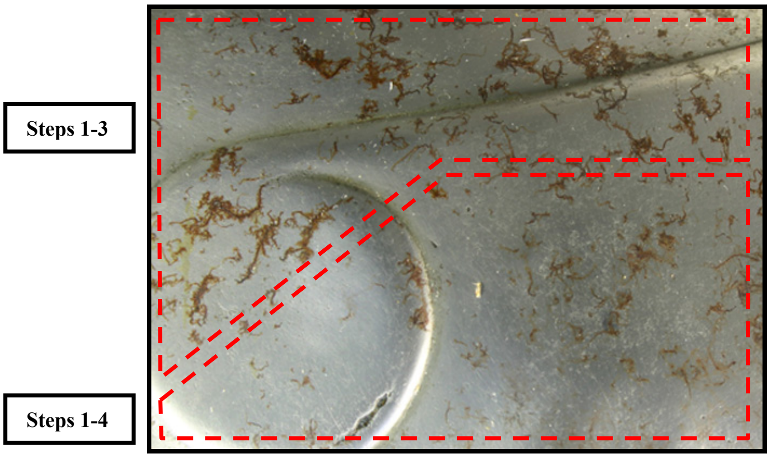

Figure 4-44 Palace Armoury armour backplate: Detail of effects from corrosion product removal and associated interventions after steps 1-3 and 1-4 of the Palace Armoury technique.

*

After approaches to remove corrosion products in the pits were applied (Step 5) it was apparent that a further lessening of CPs was achieved, but was noticeably incomplete. The surface finishing (step 6) did not appear to reduce the CP presence, but instead increased the lustre of the metallic surfaces (Figure 4-45).

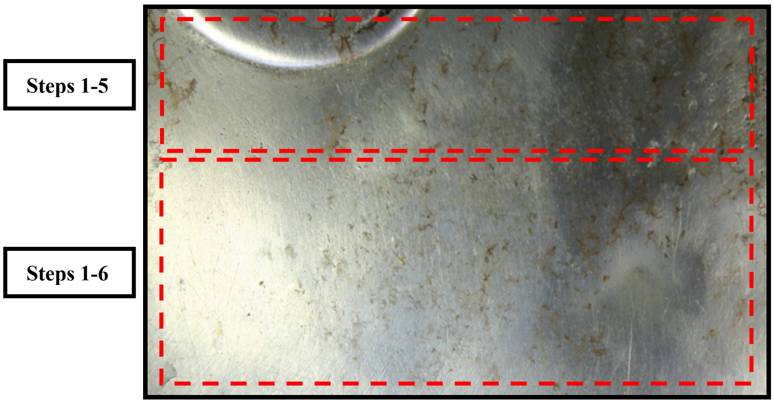

Figure 4-45 Palace Armoury armour backplate: Detail of effects from corrosion product removal and associated interventions after steps 1-5 and 1-6 of the Palace Armoury technique.

4.2 MUNITION ARMOUR ANALOGUES: LABORATORY CORROSION CASE STUDIES & DESTRUCTIVE INVESTIGATIONS

The results obtained from following the methodologies for pursuing the various interventions and levels of investigation on the munition armour analogues are presented here. Firstly, a summary reminder of the series of three consecutive experimental objectives for the armour analogues follows[1160]:

1. Armour analogue objective 1, Limitos determination: Characterisation of corrosion product stratigraphy and metal leading to limitos determination;
2. Armour analogue objective 2, Palace Armoury technique: Documentation & investigation of the current Palace Armoury cleaning procedure and results; and
3. Armour analogue objective 3, Limitos application: Removal of corrosion products according to limitos determination.

To avoid repetition a selection of results from each of the Coupon Series is presented.

4.2.1 ARMOUR ANALOGUES, LIMITOS DETERMINATION: CORROSION/CORROSION PRODUCT MORPHOLOGIES & LIMITOS INVESTIGATIONS

The main corpus of results presented for Armour analogue objective 1, Limitos determination[1161] come from Coupon Series 1 (i.e. pre-corroded, applied barium sulphate superior limitos marker and subsequently corroded for 4.5 months total). Meanwhile specific contributing highlights from Coupon Series 4 and 6 are also presented. Coupon Series 1 featured varying extents of limitos preservation (unlike Coupon Series 4) and experimental triplicates were available for statistical confirmation and validity (unlike Coupon Series 6).

[1160] For objective details refer to 3.3.2 Armour analogues: objectives & destructive investigations

[1161] 3.3.2 Armour analogues: objectives & destructive investigations

4.2.1.1 Plan perspective investigations

A representative site selected from a major coupon (Figure 4-46) that contained all major corrosion product forms and other features present on the surface of Coupon Series 1 before stratigraphic probing is presented in Figure 4-47.

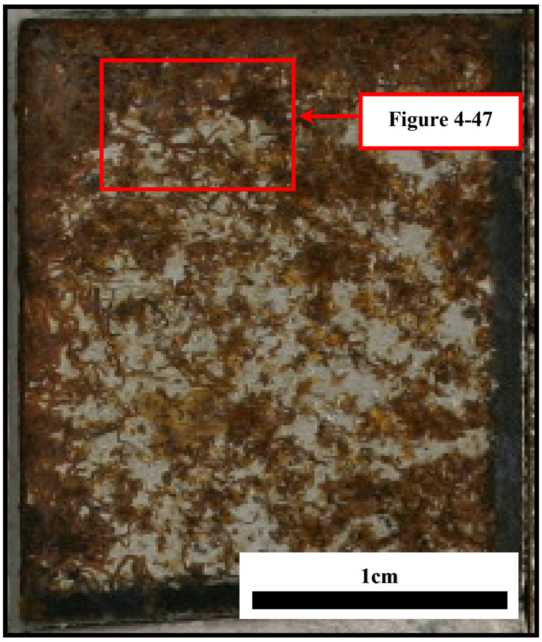

Figure 4-46 Armour analogue plan perspective, Coupon Series 1: Major coupon used to demonstrate surface features and context frame for Figure 4-47.

*

Annotation of the various surface features in the following figures (Figure 4-47 & Figure 4-48) and summary tables (Table 4-10 & Table 4-11) are presented for easier communication of the results, their interpretation and subsequent discussion[1162]. The colour coding system is presented to help convey to the reader which materials and corrosion products were proposed to belong and not belong to the limitos. Materials and CPs coded in green could be removed since they were deemed to be superior to the limitos. Those corrosion products coded yellow exhibited evidence of the limitos and those coded red were below these limitos CPs, and thus both were to be retained.

[1162] 5.2.1.1 Plan perspective investigations

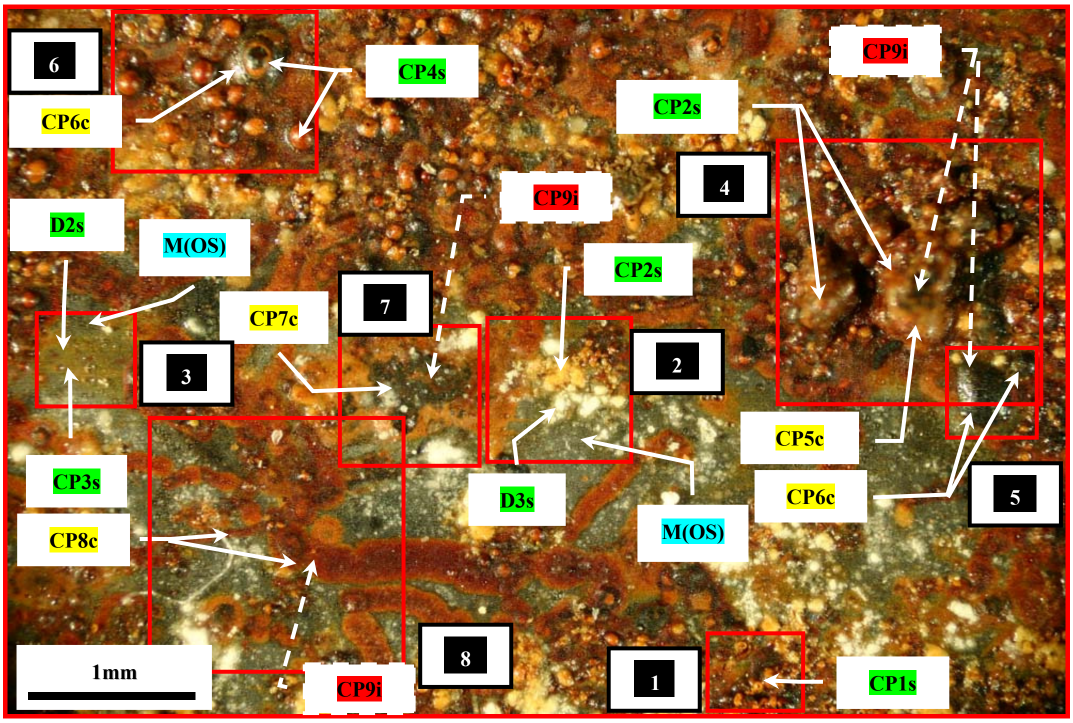

Figure 4-47 Armour analogue plan perspective, Coupon Series 1: Overview of area containing representative corrosion product morphologies and context frames for Figure 4-48 (before coating removal and CP probing).

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Greater magnifications of respective details in Figure 4-47 are given in Figure 4-48.

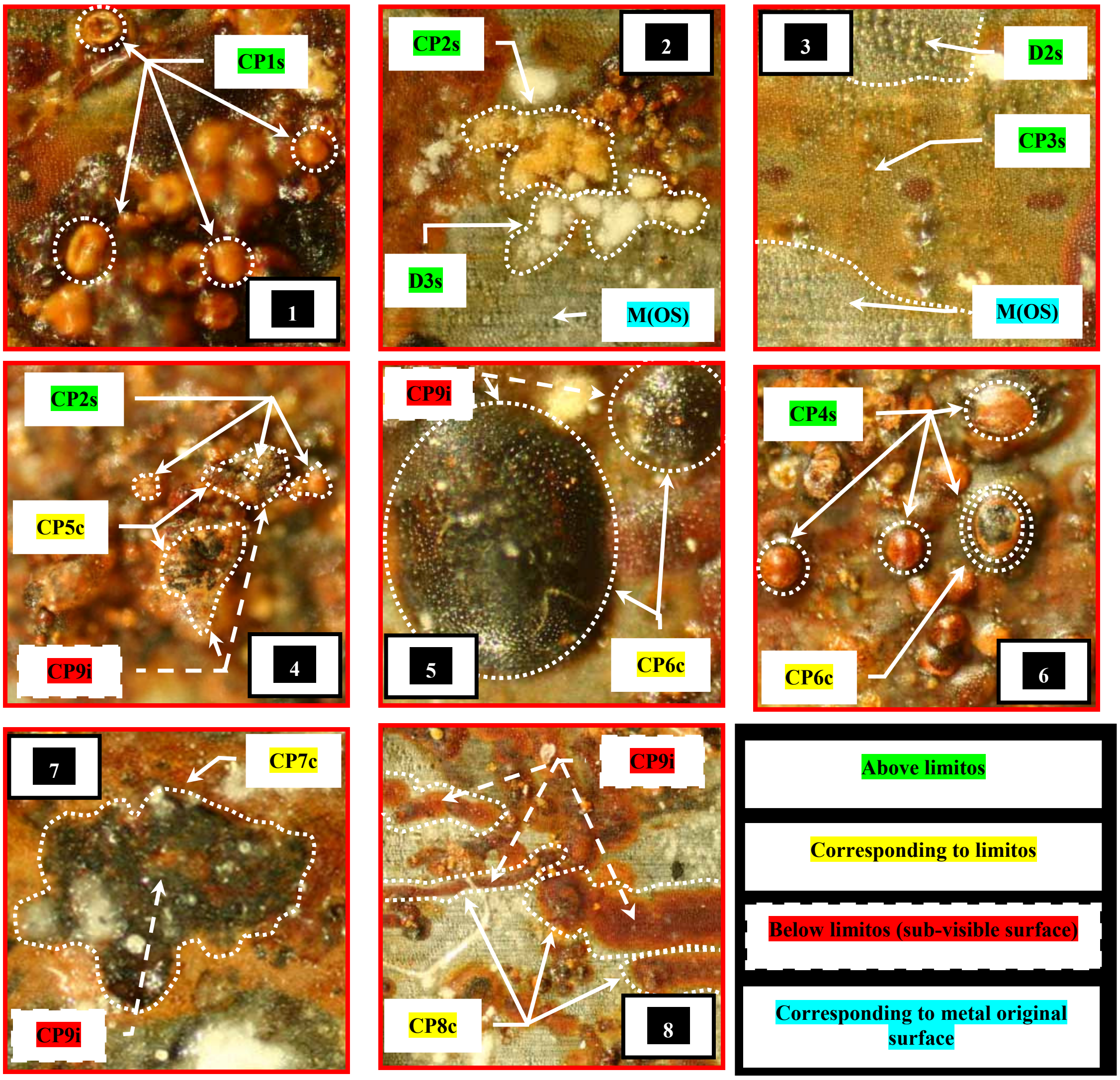

Figure 4-48 Armour analogue plan perspectives, Coupon Series 1: Details of areas from Figure 4-47 containing representative materials and corrosion product morphologies (before coating removal and CP probing).

*

Detailed descriptions of each of the major materials and CPs, their location in the stratigraphy and subsequent justifications for their determination relative to the limitos are given in Table 4-10. These descriptions, in terms of appearance, distribution and physical properties, were made before and during stratigraphic probing. Physical stratigraphic probing revealed the otherwise unobservable subsurface CPs (indicated as being sub-surface in Figure 4-48 by white dashed boxes and arrows) and underlying pitted metal. An important point to emphasise for these partly corroded surfaces is that the metal's original surface (M(OS): unmodified surface) could still locally be found uncorroded: either visible or masked underneath the barium sulphate applied superior limitos marker (D3s) and corrosion products (notably CP3s). The determination of the unmodified metal surface was relatively obvious compared to the determination of the limit of the original surface in corrosion product structures, and was obviously also subject to conservation considerations.

Morphological feature classification & position relative to the limitos	Appearance	Distribution	Physical properties	Certain/possible (?) materials
D1s = Deposit 1, superior	Black film. Not pictured.	Very rare, occasionally on high points of topography.	Loosely adhered.	Carbon paper from overlay used during sectioning/cutting
D2s = Deposit 2, superior	Transparent and glossy film.	Mostly laterally complete, exceptionally where CP1s & CP2s have perforated it. Below D1s and above all CPs excepting CP1s & CP2s.	Plastic.	Acrylic resin - Paraloid B-72™
D3s = Deposit 3, superior	White, opaque powder granular shape of varying sizes differing to over an order of magnitude.	Incomplete plan coverage.	Moderately cohesive and moderately adhered to surfaces due to consolidation by D2s.	Barium sulphate.
CP1s = Corrosion Product 1, superior	Complete and collapsed bright orange and brown spheres.	Clusters over low forms of CP5c, CP6c and other lower CPs. Spheres are empty and are positioned above D2s.	Brittle, non-cohesive, only slightly adherent to surface due to B-72™.	Iron corrosion products - beta iron oxyhydroxides (?)
CP2s = Corrosion Product 2, superior	Bright orange ultra-fine particles.	Intimately mixed throughout some, but not all clusters of D3s and positioned on top of CP5c.	Poorly cohesive and very poorly adhered to surfaces.	Iron corrosion products - iron oxyhydroxides (?)
CP3s = Corrosion Product 3, superior	Thin transparent orange film of variable thin thicknesses.	Isolated patches on metal.	Brittle, non-coherent, non-adhesive to metal.	Iron corrosion products - iron oxyhydroxides (?)
CP4s = Corrosion Product 4, superior	Bright orange domed caps.	Isolated. On some, but not all peaks of CP6c.	Poorly cohesive and very poorly adhered to surfaces.	Iron corrosion products - iron oxyhydroxides (?)
CP5c = Corrosion Product 5, corresponding	Black-brown globular and sometimes vertical tubercules of varying sizes, sometimes complete. Larger ones are sometimes exploded open exposing the contents: a void and CP9i. Translucent fibres (probably D2s) stretched across the open globules.	Isolated. Contains CP9i; mainly of black-brown type rather than orange.	Coherent and poorly adhered to the metal.	Iron corrosion products – alpha iron oxyhydroxides, magnetite (?)
CP6c = Corrosion Product 6, corresponding	Black domed and smooth blisters featuring manufacturing-micro-grooves on the outer surface. Manufacture-micro-grooves are not apparent on blisters with orange caps.	Discontinuous, positioned above the metallic horizontal surface. Contains CP9i; mainly of orange type rather than black-brown.	Hard, coherent and not brittle. Adherent to the metal.	Iron corrosion products – alpha iron oxyhydroxides, magnetite (?)
CP7c = Corrosion Product 7, corresponding	Black rough and irregular film forming blisters sometimes featuring manufacture-micro-grooves, or broken remnants of, on the outer surface.	Discontinuous, positioned above the metallic horizontal surface. Contains CP9i; mainly of orange type rather than black-brown.	Hard and brittle. Adherent to the metal. Coherent or incoherent	Iron corrosion products – alpha iron oxyhydroxides, magnetite (?)
CP8c = Corrosion Product 8, corresponding	Filiform of varying profiles (low & domed) and thicknesses (mostly thicker, than thin) and colour (red-brown and occasionally black). Filiform always feature manufacture-micro-grooves on the outer surface.	Discontinuous, positioned slightly above the metallic horizontal surface. Predominantly oriented in direction of surface grinding, but often also in other directions. Domed and low profile filiforms contain CP9i of orange type rather than black-brown.	Low profile filiforms are very fragile and very brittle. Hemispherical filiforms are hard and less brittle.	Iron corrosion products Tail ferric iron oxyhydroxides (?), head ferrous chloride (?)
M(OS) = Metal original surface	Reflective, metallic lustre with laterally orientated micro-grooves and corrosion pits from preparation stage.	Uncorroded surfaces.	Hard. Coherent.	Low-carbon steel.
CP9i = Corrosion Product 9, inferior	Mixture of granulated porous black-brown and/or bright orange material.	Porously packed and situated inside CP5c (as black-brown type), CP6c (as bright orange type), CP7c (as bright orange type) and CP8c (as bright orange type).	Pulverulent. Slightly cohesive and poorly adhered to surfaces.	Iron corrosion products - iron oxyhydroxides (?)
MC = Metal core, inferior	Reflective, metallic lustre with corrosion pits from laboratory accelerated corrosion regime and without/with lessened laterally orientated micro-grooves from preparation stage.	Corroded substrate under CP9i, which is in turn under CP5c, CP6c, CP7c & CP8c.	Hard. Coherent.	Low-carbon steel.

Table 4-10 Summary of classifications and characteristics of corrosion products, applied materials and metal on Coupon Series 1

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After Bertholon[1163], a completed summary table, of the complicated limitos stratigraphies, in terms of the relative positioning of the superior, corresponding and inferior limitos markers, is given in Table 4-11. The labelled features (e.g. CP1s etc) can be cross-referenced with the higher magnification images given in Figure 4-48 and the descriptions presented in Table 4-10. Notably, the type of markers more easily determinable were *layers* and not *layer interfaces* (Table 4-11).

Two corresponding limitos markers were identified: the micro-grooves from the former metal's fabrication; and a CP layer interface marked by poor adhesion of certain CP morphologies. Due to the many and heterogeneously distributed corrosion product structures for Coupon Series 1, the limitos was therefore located between a range of the possible combinations of CP structures. In terms of the CP layer and interface classification, the limitos was determined to be located between the layers CP3s/CP4s and the layers CP5c/CP6c/CP7c/CP8c i.e. at interface 3/4 (Table 4-11).

Layers of corrosion products	**Limitos marker**		
	Superior	**Corresponding**	**Inferior**
Layer 1	CP1s	Absent	Absent
Interface 1/2	Absent	Absent	Absent
Layer 2	D1s, D2s, D3s, CP2s	Absent	Absent
Interface 2/3	Absent	Absent	Absent
Layer 3	CP3s, CP4s	Absent	Absent
Interface 3/4	Absent	Generally poor adherence of Layer 3 with Layer 4	Absent
Layer 4	Absent	CP5c, CP6c, CP7c, CP8c	Absent
Interface 4/5	Absent	Absent	Absent
Layer 5	Absent	Absent	CP9i
Interface 4/M	Absent	Absent	Hardness/aspect differences
Metal	Absent	Absent	CM

Table 4-11 Coupon Series 1: Summary of corrosion product stratigraphy and limitos determination

To follow the subsequent justification for the determination of the limitos between the various materials present on Coupon Series 1, it is necessary to refer simultaneously to Figure 4-48 and for the synthesis of the observations, Table 4-10. Additional complementary examples after stratigraphic probing[1164] and cross-sectioning[1165] are presented later.

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The removal of the coating permitted better surface observation since light reflected variously from the differently oriented surfaces of the micro-grooves in the

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[1163] Bertholon, 2000, p. 223, Table 5.2 & Figure 2-53

[1164] Figure 4-49, Figure 4-50, Figure 4-51, Figure 4-52, Figure 4-53, Figure 4-54 & Figure 4-55

[1165] 4.2.1.2 Cross-section perspective investigations

metal (a reference point) and in its corrosion products. Those CP morphologies that retained micro-grooves as *direct* evidence of the limit of the original surface included: CP6c, CP7c and CP8c (Figure 4-48: images 5, 6, 7 & 8). The evidence that substantiated the assertion that CP6c, CP7c and CP8c were corresponding limitos CPs is presented next.

Corrosion products of the filiform morphology (CP8c) consistently preserved the micro-grooves from the former metal surface. Filiform CPs featured arched filaments or consecutive domed blisters (Figure 4-49).

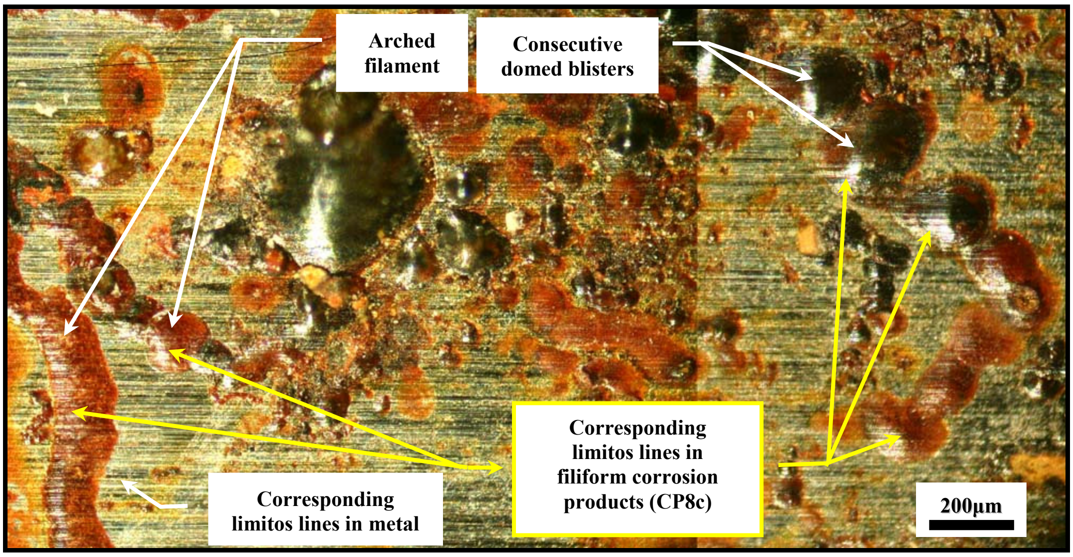

Figure 4-49 Armour analogue plan perspective, Coupon Series 1: Various filiform corrosion filaments (CP8c) exhibiting micro-grooves from the metal (after coating removal and before CP probing).

*

Corrosion products (CP6c) resulting from local to general corrosion that contributed to local and/or general CP morphologies also featured these micro-grooves that provided direct evidence of the former metal surface. However, the continuity of the limitos micro-grooves was typically more distorted (Figure 4-50) than for those of the filiform morphology. The local to general corrosion product morphology sometimes did and sometimes did not exhibit this limitos evidence; depending on the crust shape (domed or rough), and its diameter-height ratio. The CPs with highly fragmented limitos micro-grooves were very fragile.

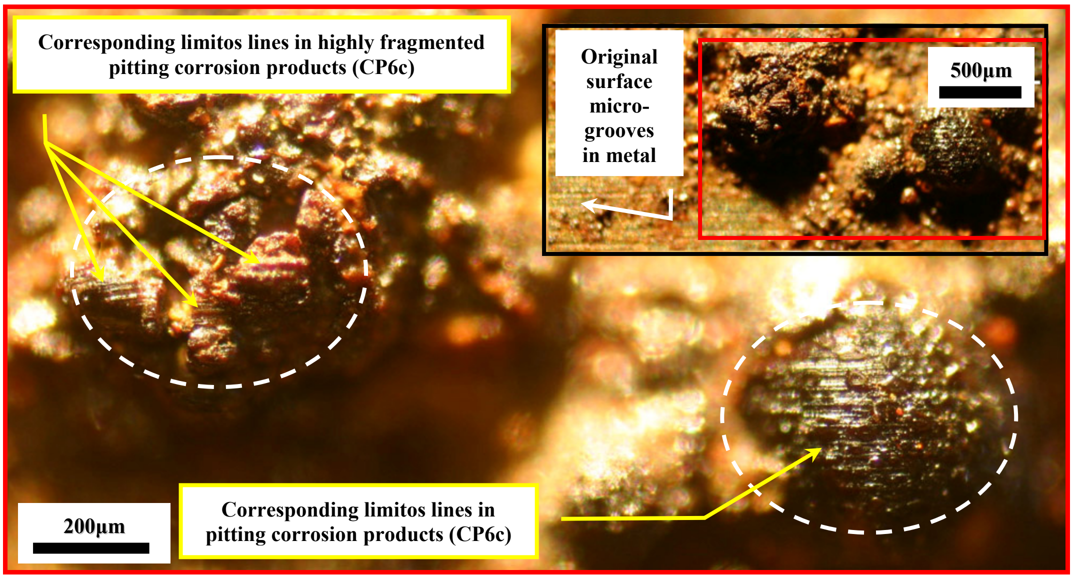

Figure 4-50 Armour analogue plan perspective, Coupon Series 1: Main: Two corrosion blisters (CP6c) in varying states of preservation that exhibit micro-grooves from the metal. Inset: Context of blisters with metal and micro-grooves (after coating removal and before CP probing).

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Conversely, while some corrosion products appeared to retain very distorted and localised evidence of the micro-grooves, they were still very coherent and adherent to the surface due to their unfragmented state (Figure 4-51).

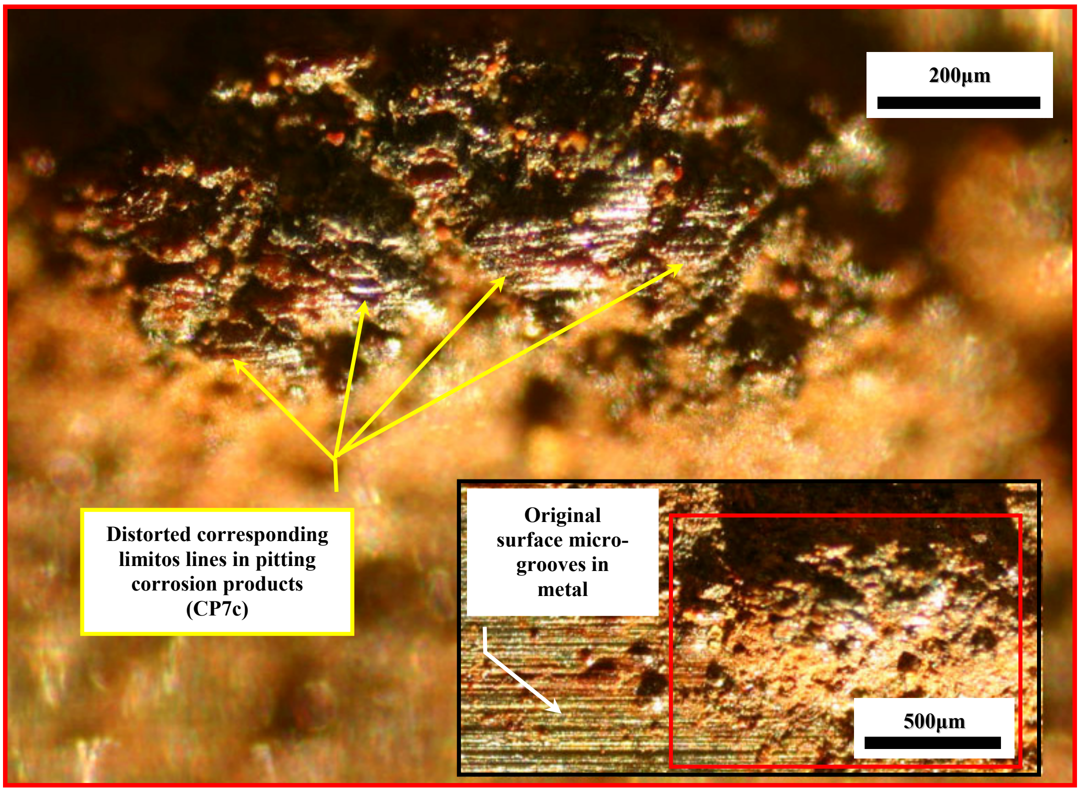

Figure 4-51 Armour analogue plan perspective, Coupon Series 1: Main: Corrosion blister (CP7c) exhibiting micro-grooves from the metal. Inset: Context of blister with metal and micro-grooves (after coating removal and before CP probing).

*

Corrosion Product 5c (Figure 4-48: image 4) was *indirectly* assigned the classification of a limitos corrosion product by association with its similar characteristics and position shared with CP6c, CP7c and CP8c (Table 4-10). Any micro-grooves on CP5c were not observable, supposedly due to their highly distorted or fragmented (and subsequently fragile) state.

At corrosion product interface 3/4 (as per Table 4-11) of Coupon Series 1, the consistent tactile non-adherence or relatively very poor adherence of the orange corrosion products (i.e. CP1s, CP2s, CP3s & CP4s) to the layers underneath (CP5c, CP6c, CP7c, CP8c) suggested the use of this interface property as a marker between layers. This interface coincided with the interface defined by the micro-grooves: making it a complementary form of corresponding limitos marker.

The interface of the coating with the corrosion products below did not appear to indicate an interface with the limit of the original surface. Corrosion products that remained under the coating, and were deemed to not hold morphologies potentially characteristic of the limitos, included the bright orange particle or film CPs (Figure 4-48, image 2: CP2s and image 3: CP3s). It was presumed that CP2s and CP3s were indeed similar or the same corrosion product phase; the difference lay in their distribution. It appeared from numerous examples that CP2s was the result of staining particles of the white barium sulphate superior limitos marker (Figure 4-48, image 2: D3s). The bright orange corrosion products (Figure 4-48, image 6: CP4s) on the top of domed black corrosion product blisters (Figure 4-48, images 5 & 6: CP6c) were often also below the coating and did not retain observable evidence of the limitos. After the removal of caps of orange corrosion products (CP4s) from many of the black domed and smooth blisters (CP6c) the usual micro-grooves were not observed. This absence of surface micro-grooves on the upper limits of CP4s suggests they might have been above the limitos. However the simple absence of a corresponding limitos marker does not provide conclusive evidence that this corrosion product was actually a superior limitos corrosion product. The bright orange caps corrosion products are presented later with a cross-section perspective[1166] since their small size, and the relative position of the transparent

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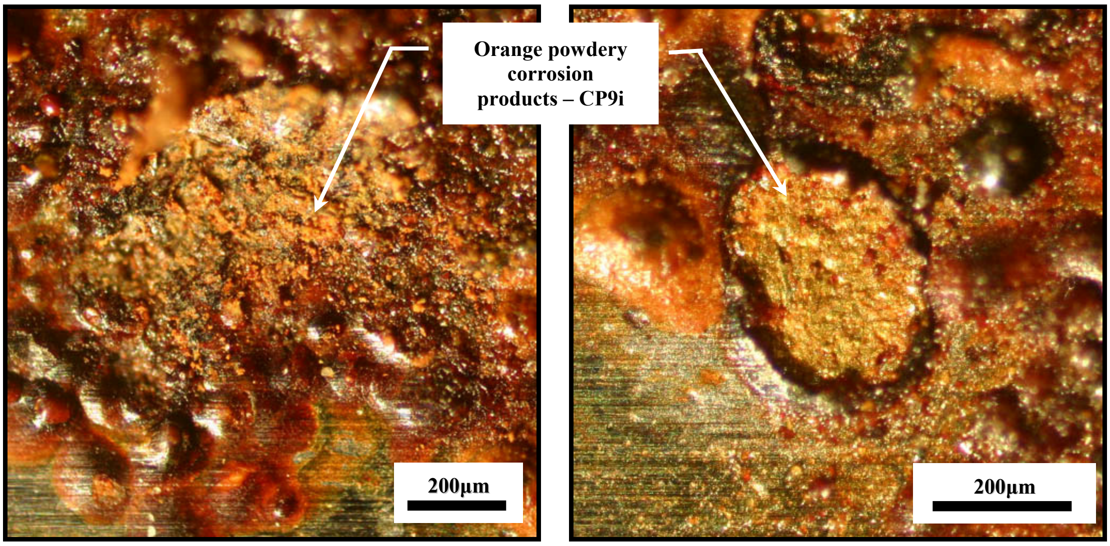
[1166] 4.2.1.2 Cross-section perspective investigations

coating (D2s) and the applied superior limitos marker (D3s) to these features in Figure 4-48, were difficult to isolate in plan perspective.

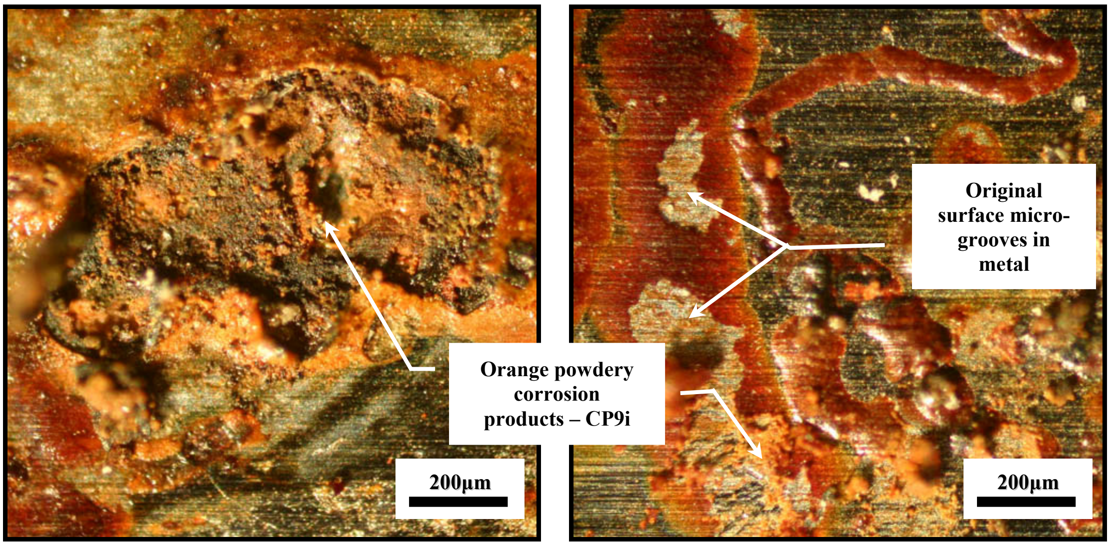
*

All the corresponding limitos corrosion products (i.e. CP5c, CP6c, CP7c and CP8c) were physically probed and were determined to contain orange to brown powdery corrosion products (CP9i) (Figure 4-52). Only the thickest filaments of the filiform corrosion morphology were found to exhibit strong traces of the micro-grooves in the metal surface remaining beneath CP9i (Figure 4-52: bottom right).



Subsurface of CP5c in image 4 of Figure 4-48

Subsurface of CP6c in image 5 of Figure 4-48



Subsurface of CP7c in image 7 of Figure 4-48

Subsurface of CP8c (no context image)

Figure 4-52 Armour analogue plan perspectives, Coupon Series 1: Exposure of CP9i (orange powdery corrosion products) under various corrosion product morphologies holding the limitos (after coating removal and during CP probing).

*

Similar corrosion product structures on Coupon Series 1 also featured on Coupon Series 4 and 6 and are described next. The thick and almost complete surface coverage of the zinc oxide/barium sulphate marker on Coupon Series 4 made it impractical to examine the CP structures without extensive probing of the marker. The corrosion products that had stained this white pigment mixture were considered above the limitos and indicative of an appropriate minimum level for CP removal. After removal of the zinc oxide/barium sulphate marker, adherent and coherent crusts of corrosion products were found. The prevalent local to general corrosion had produced corrosion products that became incorporated in the superior limitos marker and occupied pits with hard dark brown CPs (Figure 4-53). Traces of the limitos present as micro-grooves in the local to general CP surfaces were very rarely found and were only very faint and localised. Very occasionally filiform corrosion filaments had formed, but predominantly on the metal not covered with superior limitos marker. Here the filiform CPs also featured the micro-grooves as a corresponding limitos marker.

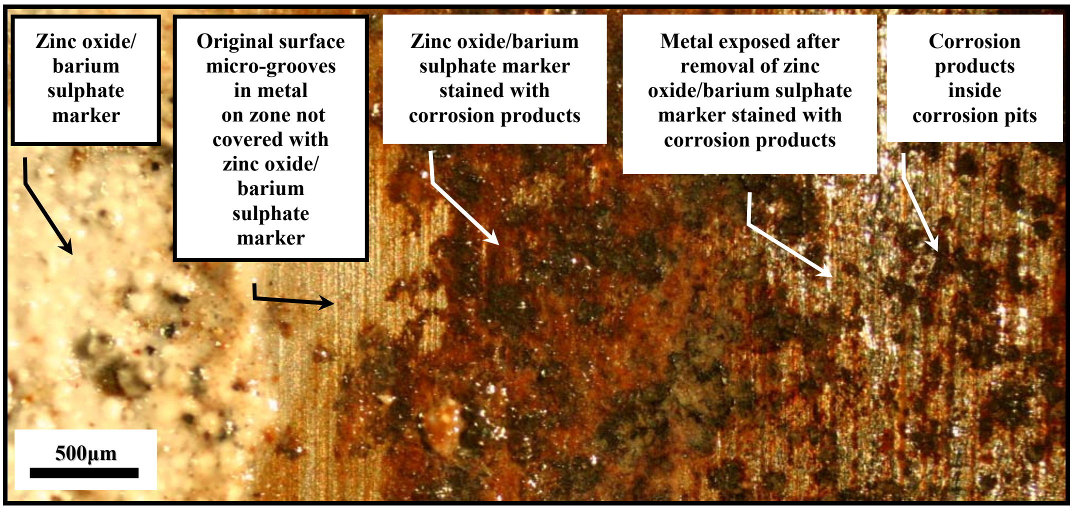


Figure 4-53 Armour analogue plan perspective, Coupon Series 4: Stepped stratigraphy during stratigraphic probing.

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The gold superior limitos marker used on Coupon Series 6 was determined to be a more appropriate superior limitos marker in plan perspective than the zinc oxide/barium sulphate superior limitos markers used on Coupon Series 1 and 4. An example of a filiform corrosion filament from Coupon Series 6, which is comparable to those largely found on Coupon Series 1, is given in Figure 4-54. The manufacture micro-grooves marking the corresponding limitos were seen after coating removal. Unlike Coupon Series 1 & 4, micro-grooves were observed even before the removal of the respective applied superior limitos marker. The very fine particles and thin layer of gold were considered to have the high *clarity* required for surface observation, even if not transparent. The pictured filiform filament (Figure 4-54) was dissected and featured a similar inferior limitos CP phase (orange powdery particles) to those (CP9i) inside filiform (CP8c) from Coupon Series 1 (Table 4-10).

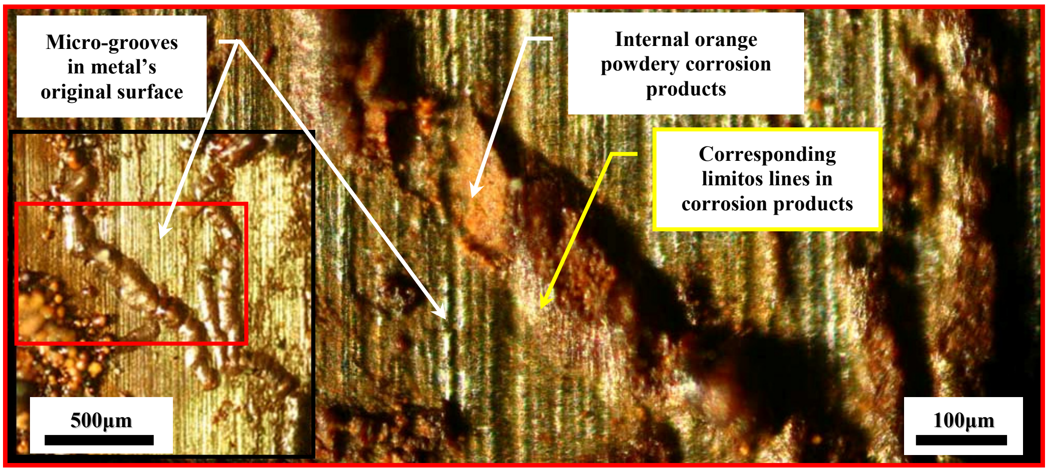


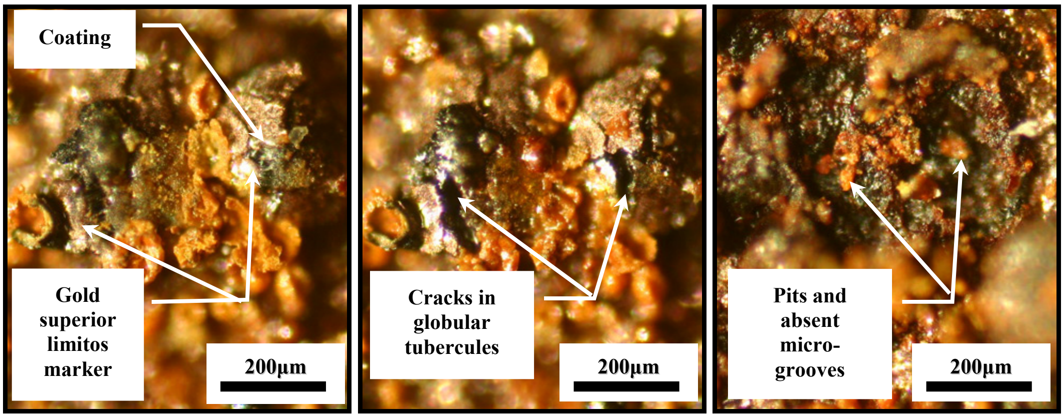
Figure 4-54 Armour analogue plan perspective, Coupon Series 6: Inset: Context of main image, of surface from (before coating removal and before CP probing). Main: Micro-grooves on filiform filament surface and internal orange CPs inside the same filament (after removal of coating and gold marker and during CP probing).

*

The globular tubercle corrosion product morphologies[1167] on Coupon Series 6 (Figure 4-55) were similar in morphology to CP5c in Coupon Series 1 (Figure 4-48: image 4). The coating was observed traversing the opened cracks in the gold-coated globular tubercles. When these hollow globular tubercles were removed, a pitted metal surface, absent of micro-grooves was revealed (including small particles of orange CPs) (Figure 4-55). It was supposed that the limitos corresponded with the interface below the gold superior limitos marker. However, it will be later discussed with reference to cross-sections that the limitos can also be one CP layer lower and not necessarily always correspond with the interface of the gold superior limitos marker[1168].

[1167] Suggesting that perhaps biological organisms (bacteria) are coinciding with electrochemical corrosion and resulting in *tuberculation*, as reported for aerobic corrosion of iron and steel (Dexter, 1998, pp. 116-117, 119).

[1168] 4.2.1.2 Cross-section perspective investigations, Figure 4-58 & 5.2.1.3 Applied superior limitos markers review, Figure 4-59



Before probing: gold covered globular tubercles with cracks tenuously held together by bands of coating

After application of acetone: gold covered globular tubercles open slightly due to released compression by coating dissolution

After physical removal of gold covered globular tubercles: gold superior limitos marker is removed with tubercles thereby exposing a void, orange corrosion products & pitted surface without micro-grooves

Figure 4-55 Armour analogue plan perspective, Coupon Series 6: Globular tubercle corrosion products with gold marker before and during probing.

4.2.1.1.1 Summary of armour analogue corrosion plan perspective investigations results

Micro-grooves *emanating* from the topography of the uncorroded metal were observed in certain corrosion product features on the armour analogues, providing a corresponding limitos marker: the definitive evidence that the limitos can exist on these rolled low-carbon steel materials. Micro-grooves were identified in filiform corrosion products and to a lesser frequency in local to general CPs. Micro-grooves were always perceptible on filiform corrosion morphologies, while the preservation of the micro-grooves in corrosion products of local to general CP morphologies varied considerably; depending on the shape and proportions of the resulting CPs. The interiors of each limitos CP morphology were filled with powdery orange to dark brown CPs.

The most prominent cases of the micro-groove evidence of limitos were respectively on Coupon Series 1 & 6, while very little evidence was found on Coupon Series 4 where the ZnO/$BaSO_4$ was expected to have interacted with the corrosion processes and influenced the production of largely incoherent surfaces[1169].

4.2.1.2 Cross-section perspective investigations

By cross-section, the standard optical microscope and the scanning electron microscope proved to be the most useful observation instruments, especially when

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[1169] 5.2.1.3 Applied superior limitos markers review used complementarily. The low magnification and colours observable under the optical microscope built the necessary bridge for the human eye to take advantage of the higher resolution offered by the SEM and its elemental characterisation capacities when combined with the EDS[1170]. The most useful results and those presented are thus those obtained via OM and SEM-EDS. Metal's high reflectivity observable with the metallographic microscope contributed to the preliminary observation of the armour analogues and the heterogeneity of their dense corrosion product layers. However this main virtue of the metallographic microscope could not be exploited due to the apparent absence of nodules of metal in the CPs on the armour analogues. The absence of uncorroded nodules deemed presentation of the metallographic microscope's images unnecessary.

From Coupon Series 1, Figure 4-56 demonstrates SEM and OM images of a cross-section of a corrosion pit in the metal, which was filled with corrosion products and had further CPs above the level of the adjacent uncorroded metal. A crack was present and this related quite closely to the former metal's original surface.

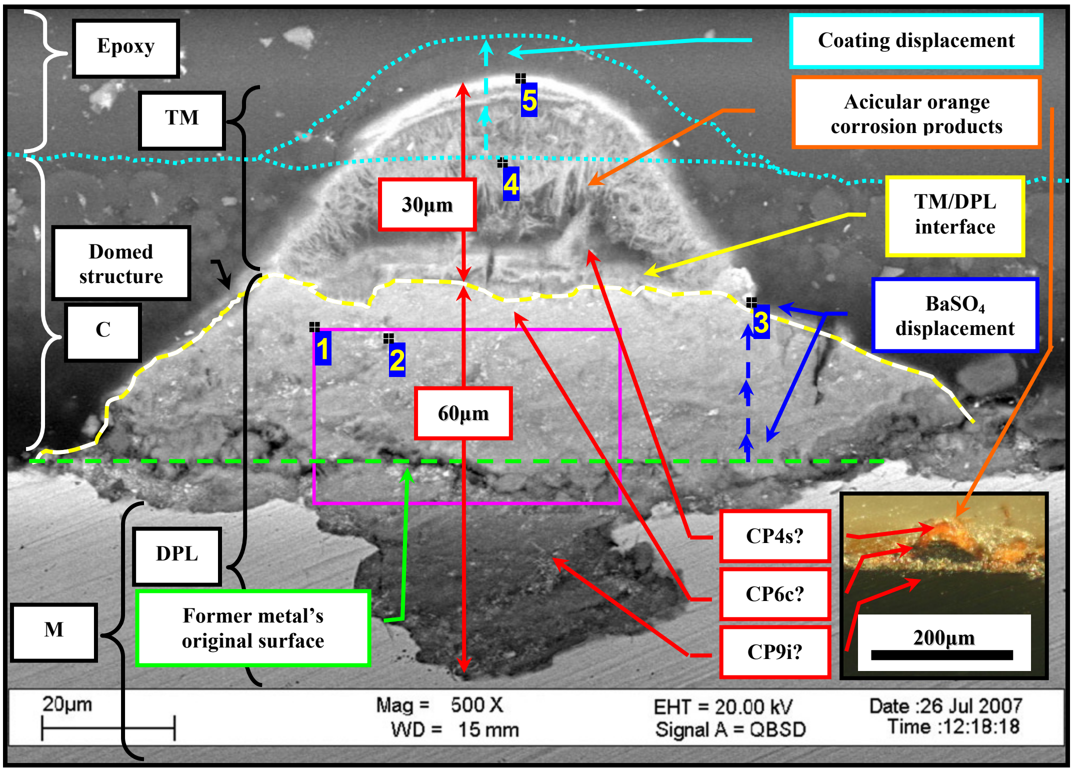

Figure 4-56 Armour analogue cross-section, Coupon Series 1: Main: SEM BSE image (500x) of stratigraphy and sites of EDS analyses (1-5). Inset: Optical microscope image of corresponding site depicting indicative corrosion product colours.

[1170] 3.2.3.2.5 Armour cross-section scanning electron microscopy-energy dispersive spectrometry

Results				Interpretation
Spectra	**Elements detected (%rel.at.wt.)**			**Probable/possible (?) materials**
	Major (>5%)	**Minor (1-5%)**	**Trace (<1%)**	
1.	Fe, O	-	Si	corrosion products
2.	Fe, O	Si	Na, Cl	corrosion products, corrosion accelerant
3.	O, Fe, Ba, S	Na	Al	barium sulphate, corrosion products, corrosion accelerant
4.	Fe, O	Cl	-	corrosion products, corrosion accelerant
5.	Fe, O	Ca	Cl	corrosion products, corrosion accelerant, pollution

Table 4-12 Semi-quantitative summary of elements found on EDS analyses sites depicted in Figure 4-56.

It is probable that the CPs above this crack were more able to freely expand when compared to their counterparts, which were retained and compressed by the surrounding metal of the pit. The thicker (circa 60μm) corrosion product areas in and immediately above the pit appeared similar and compact in cross-section and are designated as the dense product layer, while above, the seemingly porous and acicular orange corrosion products are referred to as the transformed medium. This orange capped and domed corrosion product structure appears similar to those observed in plan perspective[1171].

Energy dispersive spectrometry determined that chlorine was in greater concentrations in the orange acicular corrosion product phase than the DPL below. The orange acicular corrosion product phase contained chlorine in minor and trace quantities, respectively in its interior and upper limits (Figure 4-56, Table 4-12: Spectra 4-5). Further analyses (Spectra 3) of the cross-section confirmed that an isolated particle of barium sulphate was present at the edge of the interface between the coating and the dense corrosion product layer. It appears that the DPL developed and rose above the former metal's topography, and caused displacement of the coating and barium sulphate.

*

Coupon Series 6 provided results potentially complementary to Coupon Series 1, where similar CP morphologies were represented and where the gold applied superior limitos marker featured instead of barium sulphate (Figure 4-57).

[1171] Figure 4-48: CP6c capped with CP4s

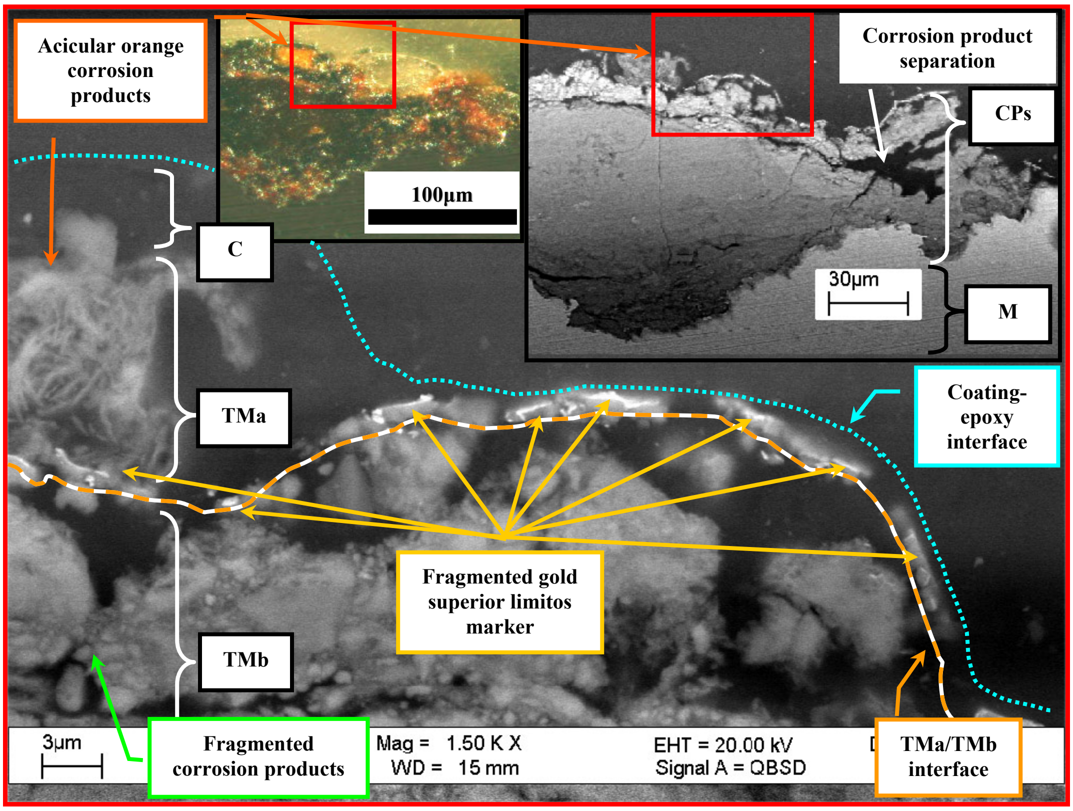

Figure 4-57 Armour analogue cross-section, Coupon Series 6: Inset: Optical microscope and scanning electron microscope context images for main image. Main: High magnification (1500x) SEM BSE image of stratigraphy and initially proposed limitos area between transformed medium and dense product layer.

The beneficial continuous distribution of the gold marker was again drawn into diagnostic application, but this time here in cross-section. The fragmented white line, representing gold (observed in Figure 4-57 Main, and confirmed by EDS point analyses), marked the interface between the porous acicular orange corrosion products (TMa) and the fragmented CP layer (TMb) immediately below. This cracked, fragmented and delaminated appearance of the CPs immediately below the gold superior limitos marker appeared too porous to be attributable to the usual classification of the dense product layer and appeared more akin to the classification of the transformed medium, hence its appellation TMb (Figure 4-57, Main).

Gold's fragmented coverage is attributable to the expansion of the underlying metal when it was transformed into corrosion products. It would appear that this fragmentation permitted the orange acicular CPs to pass through, and any of the coating's adhesive effect was insufficient to retain the latter corrosion products. The proposed limitos on this sample was therefore considered at this stage, to be no higher than the gold superior limitos marker (orange-dashed line in Figure 4-57). Since the orange CPs (TMa) proved to be superior to the limitos, their removal would be justifiable in terms of respecting the limitos. However, it still remained undetermined as to whether the limitos was really located further below, since the extent of the coating’s adhesive effect on the applied superior limitos marker (in this case, gold), and how CP layers below were affected, remained unknown.

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To further concentrate on the CP layers below the applied superior limitos marker, other details from the same cross-section as in Figure 4-57 are presented in Figure 4-58.

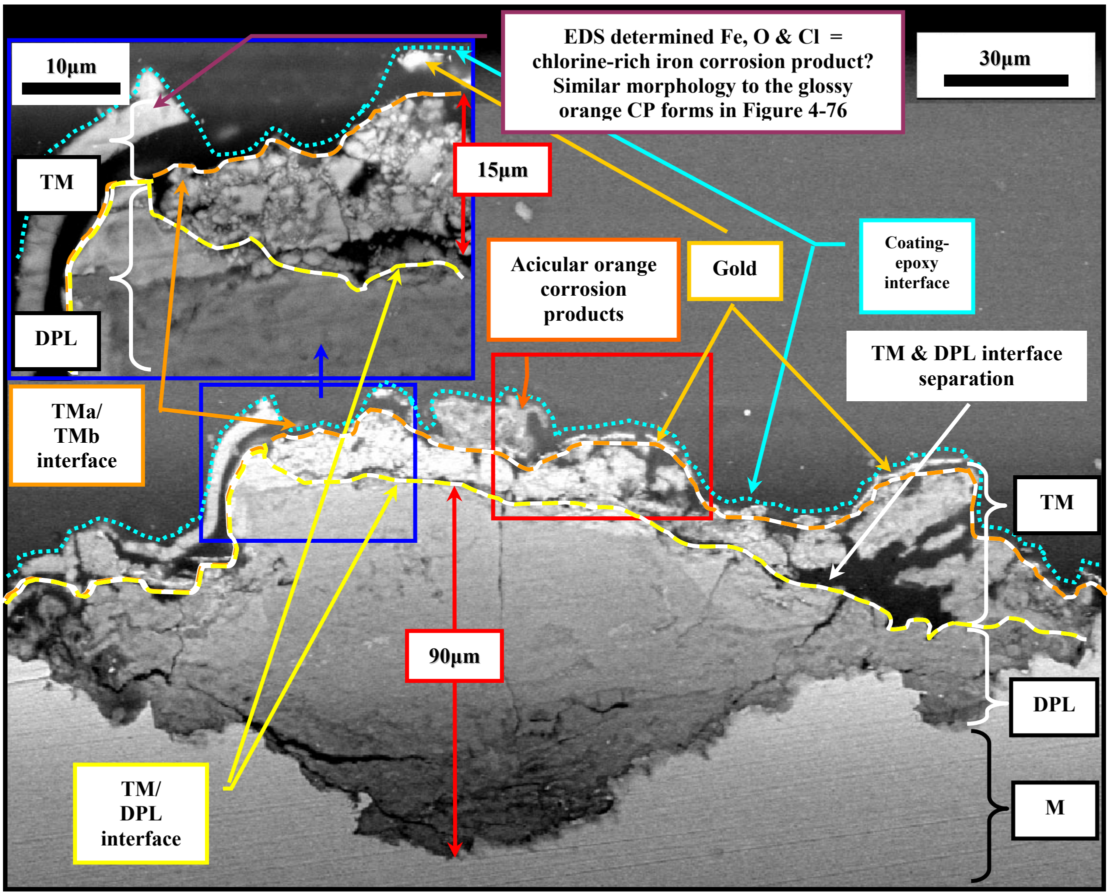

Figure 4-58 Armour analogue cross-section, Coupon Series 6: Main: Low magnification (250x) SEM BSE context image for inset. Inset: High magnification (1500x) SEM BSE image of stratigraphy and revised proposed limitos area between transformed medium and dense product layer

Here (particularly Figure 4-58: Inset) the morphological differences of the corrosion product layers were more noticeable: the compact thicker (circa 90µm) CP layer (DPL) was below the porous fragmented thinner (circa 15µm) CP layer, TMb). This porous fragmented layer was a CP phase not represented by the stratigraphy present in Figure 4-56.

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The above-described dual corrosion product layer morphology i.e. the dense product layer positioned above the metal pit, and the transformed medium located above the DPL, also features in Figure 4-59.

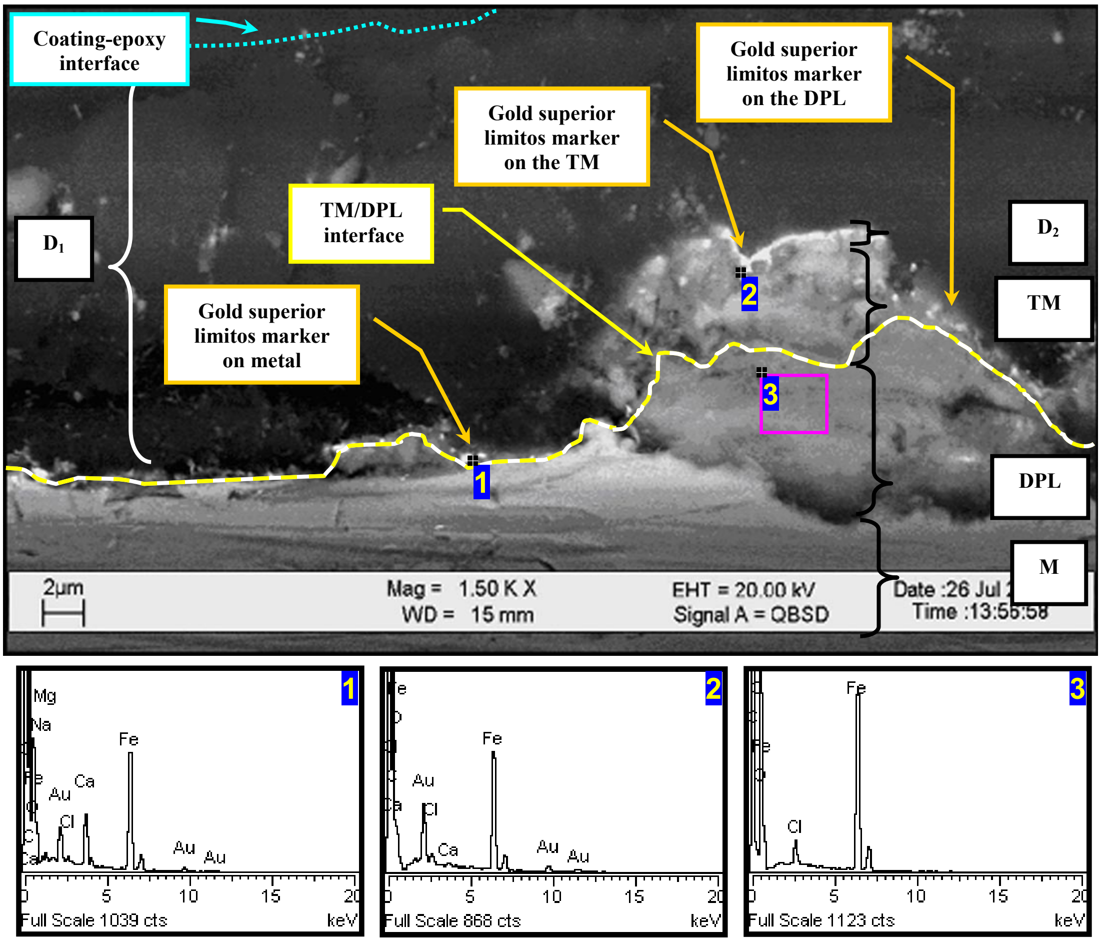


Figure 4-59 Armour analogue cross-section, Coupon Series 6: Discrimination between ferrous corrosion products and gold superior limitos marker by SEM-EDS. Top: High magnification (1500x) SEM BSE image. Bottom: Spectra from the sites of EDS analyses (1-3).

In this particular example, the superior limitos marker was positioned in two locations relative to the TM and DPL. On the far right side, the gold superior limitos marker corresponded to the position on top of the dense product layer. Simultaneously, on the left side of the same corrosion product mass, the gold superior limitos marker was positioned on the transformed medium. Therefore, on the same cross-section the gold superior limitos marker did not exclusively remain positioned on top of the DPL.

*

To report the results obtained by ultra-violet optical microscopy on Coupon Series 4, it was established that the fluorescing property of zinc oxide, under ultra-violet light did not contribute to the *definitive* determination of the limitos in iron corrosion products. The anticipated concept was to delimit the limitos with UV light by differentiating between CPs that had precipitated into the fluorescing zinc oxide. The CPs in the zinc oxide were supposed to have indicated a position superior to the limitos. However, before it was even possible to discuss the potential effects of coatings and the diffusion of CPs through this superior limitos marker, it was observed on cross-sections from Coupon Series 4 that the ferrous corrosion products suppressed fluorescence of zinc oxide while under UV light. Fluorescence inhibition by binders and pigments was previously suspected from the paint technology literature, but it was not specified if ferrous-based pigments could do this[1172]. This negative influence of iron CPs was confirmed on separate tests only containing mixtures of zinc oxide (i.e. no barium sulphate) and iron filings that were subsequently corroded in a condensing environment and accelerated with an aqueous solution of sodium chloride.

While under visible light the brilliant white of zinc oxide and/or barium sulphate on Coupon Series 4 was sufficient for it to *assist* as an applied superior limitos marker in the determination of the limitos. A comparison of observation techniques on the same ZOI is presented in Figure 4-60.

[1172] 3.3.1.1.4 Applied superior limitos markers

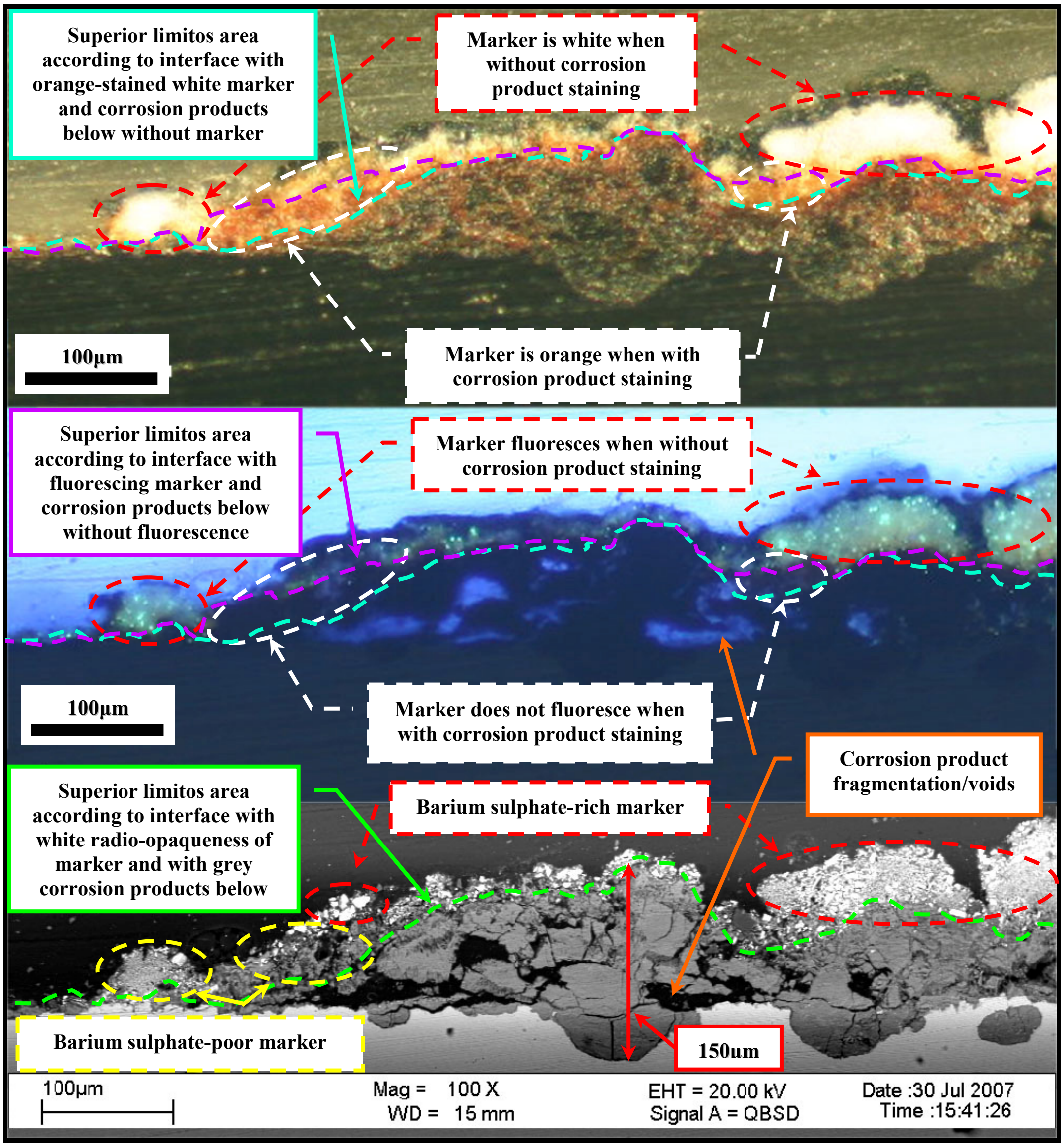


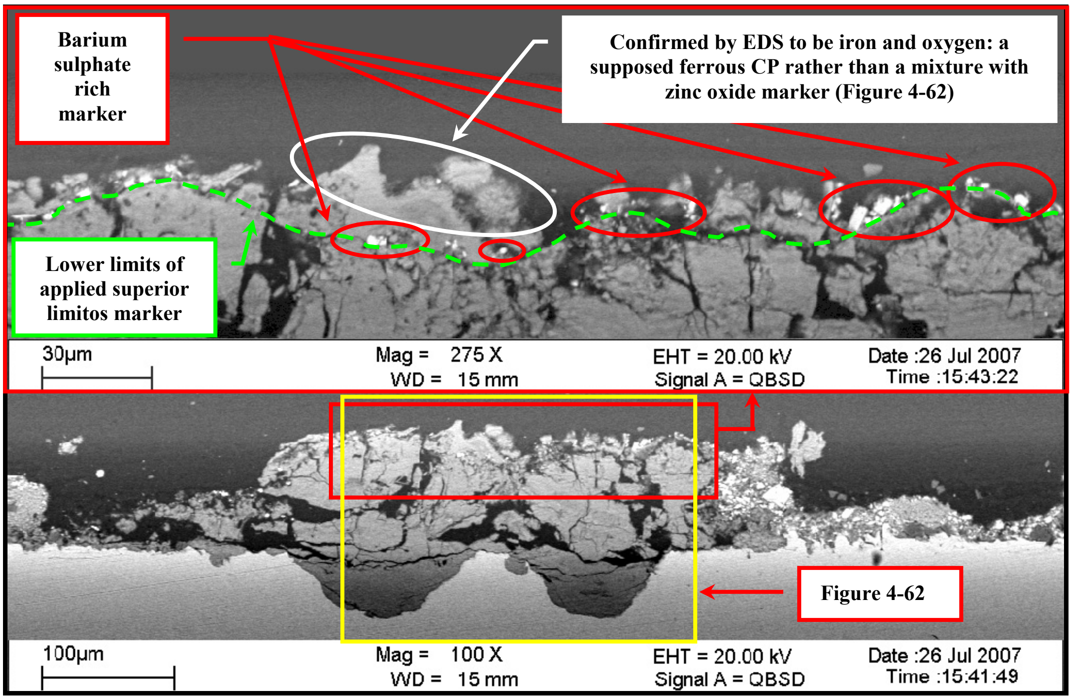
Figure 4-60 Armour analogue cross-section, Coupon Series 4: Comparison of observation techniques. Top: optical microscope visible light. Middle: optical microscope ultraviolet light. Bottom: SEM BSE image (100x) of stratigraphy.

It was seen that the same areas that appeared white under visible light (Figure 4-60 Top: “Marker is white without corrosion product staining”) exhibited strong fluorescence when under UV light (Figure 4-60 Middle: “Marker fluoresces when without corrosion product staining”). Meanwhile, areas of zinc oxide/barium sulphate marker stained with corrosion products (Figure 4-60 Top: Marker is orange when with corrosion product staining) did not fluoresce when under UV light (Figure 4-60 Middle: Marker does not fluoresce when with corrosion product staining). As a consequence, if the zinc oxide observed under UV light was the only superior limitos marker used to assist determination of the limitos then the limitos would have been incorrectly determined to be too high (Figure 4-60 Top: Superior limitos area according to interface with orange-stained white marker and corrosion products below without marker & Middle: Superior limitos area according to interface with fluorescing marker and corrosion products below without fluorescence).

The fragmentation of the iron corrosion products was particularly noticeable with the 90° angle of incidence used while under UV examination and also with the SEM BSE detector (Figure 4-60 Middle & Bottom). Also notable from Figure 4-60 was the heterogeneity of the zinc oxide/barium sulphate mixture. Some applied superior limitos marker areas appear richer in barium sulphate: as appears from the relatively more radio-opaque (white) zones (Figure 4-60 Bottom: Barium sulphate rich-marker versus barium sulphate poor-marker).

*

During SEM observation of Coupon Series 4 in cross-section, the greater lateral distribution of the applied superior limitos marker (when compared to the poor coverage on Coupon Series 1) was useful in determining a possible site for the areas superior to the limitos that were between similarly appearing corrosion products (Figure 4-61).



Confirmed by EDS to be iron and oxygen: a supposed ferrous CP rather than a mixture with zinc oxide marker (Figure 4-62)

Figure 4-61 Armour analogue cross-section, Coupon Series 4: Top: Detail of area in corrosion products stratigraphy with the lower limits of applied superior limitos marker (green line) Bottom: SEM BSE context image of top detail.

Observation and immediate recognition of some areas proposed to be superior to the limitos was possible through the radio opaqueness of barium in the barium sulphate. Compared with zinc oxide the latter quality made barium sulphate's SEM BSE observation advantageous especially since the ferrous CPs and zinc oxide appeared to have a similar level of radio-opacity. The particle morphology of zinc oxide aided its visual identification, but routine confirmation by EDS (typically points analyses), or complementary UV (if unstained by CPs) or visible light microscopy was necessary to discriminate between the zinc oxide and the ferrous corrosion products (Figure 4-61).

*

Since the use of zinc oxide as a superior limitos marker necessitated the use of energy dispersive spectrometry analyses (preferably mapping for complete ZOI area characterisation (Figure 4-62)), it was therefore deemed less efficient for discrimination purposes than with exclusive use of barium sulphate and the SEM BSE detector.

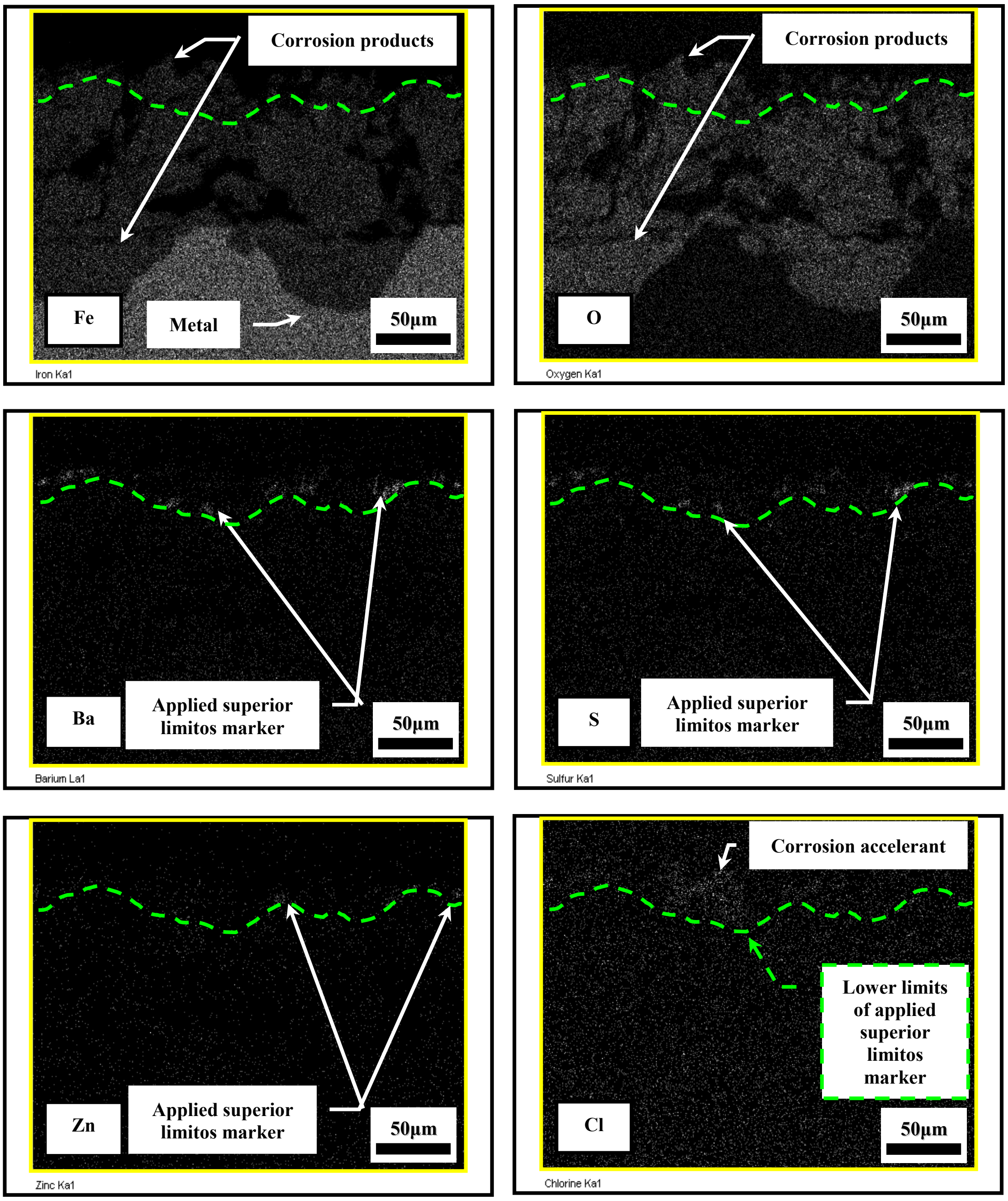


Figure 4-62 Armour analogue cross-section, Coupon Series 4: Normalised EDS mapping and lower limits of superior limitos marker (green dashed line) of context image in Figure 4-61: Bottom.

*

The plan perspective of the armour analogues had permitted observation of the significant contribution made by the manufactured micro-grooves as a corresponding limitos marker for determination of the limitos, whereas, in cross-section no useful corresponding limitos markers could be established. None of the three inferior limitos markers (slag inclusions, nodules of uncorroded metal or the carbide microstructure) that were previously identified in the authentic wrought iron and steel armour cross-sections were identified in the armour analogues made from contemporary rolled steel. They were not identified via the applied techniques[1173] since they were either unobservable or non-existent. The preliminary attempt to find a complementary inferior limitos marker by elemental discrimination was made in a cross-section from Coupon Series 4 (Figure 4-63).

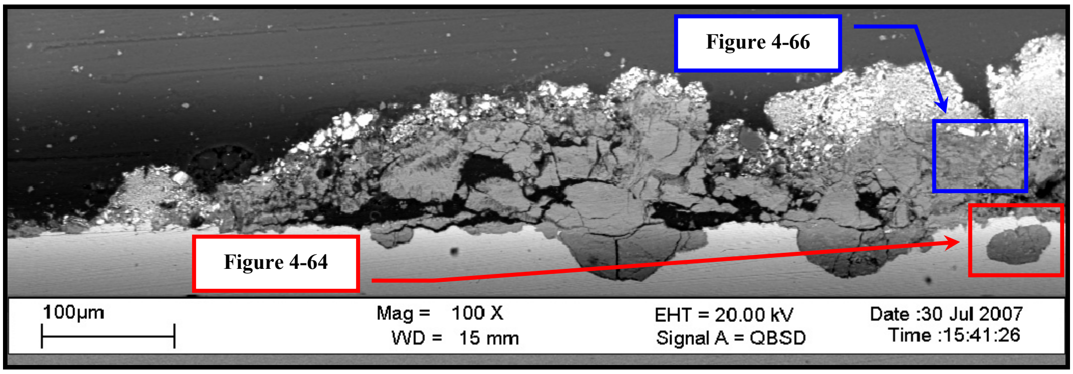


Figure 4-63 Armour analogue cross-section, Coupon Series 4: Low magnification (100x) SEM BSE image with contexts for zones of interest in Figure 4-64 & Figure 4-66.

The selected areas featured a deep pit with CPs that was relatively isolated from CP layers above the metal surface (Figure 4-64) and a relatively coherent corrosion product stratigraphy (Figure 4-66). It is supposed that this isolated pit was indeed connected to the surface via the third dimension not represented in the cross-section.

The local context of the EDS survey of the metal and bottom of the corrosion pit are shown in Figure 4-64, while the results are given in Figure 4-65.

[1173] Optical microscopy (standard with visible and UV light, and metallographic microscopes) and SEM with BSE or SE detectors and coupled with EDS

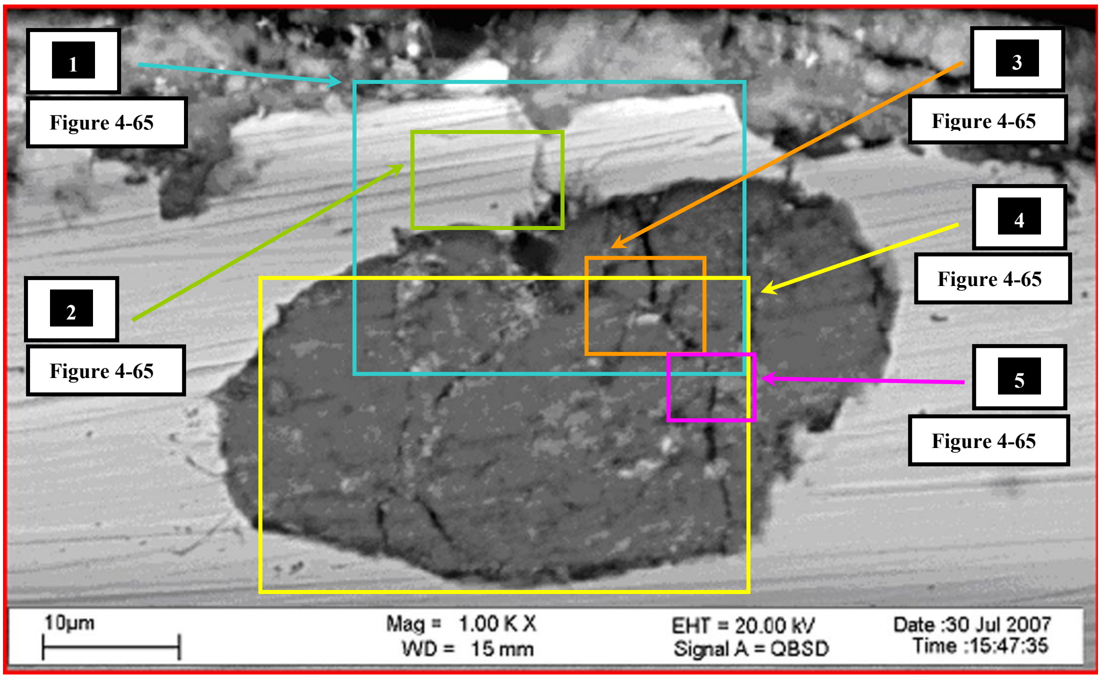


Figure 4-64 Armour analogue cross-section, Coupon Series 4: High magnification (1000x) SEM BSE image of a cross-section with contexts for zones of interest in Figure 4-65. Context image in Figure 4-63.

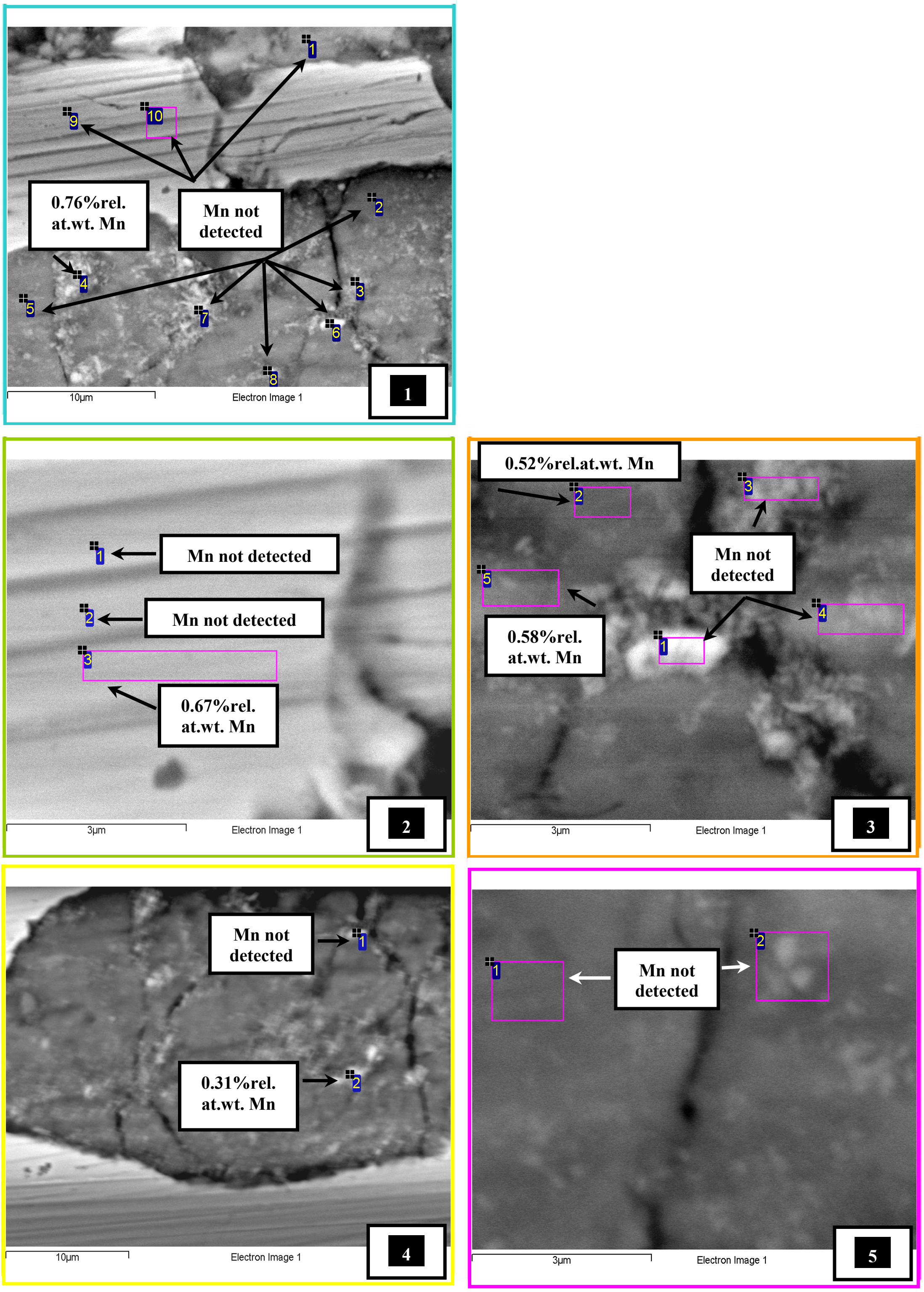


Figure 4-65 Armour analogue cross-section, Coupon Series 4: SEM BSE images and results of manganese EDS analyses (%rel.at.wt.) of the metal and corrosion products in a corrosion pit. Context image in Figure 4-64.

From the five sites of point and area analyses (Figure 4-65) performed on the metal only one (or 20%) detected manganese (Image 2: 0.67%rel.at.wt.) and the quantity corresponded marginally above (circa 10%) the upper tolerance range of that expected from the prior metal analyses by atomic emission arc induced spectroscopy (Mn: 0.5130-0.5190%wt = 0.5058-0.5119%rel.at.wt.[1174]). It appeared then, that when detectable, the EDS analyses for manganese in the metal were close to agreement with those made by atomic emission arc induced spectroscopy. If such a trend was repeatable via a statistically improved survey quantity (preferably by EDS area analyses) then this outcome would have increased the reliability of the subsequently acquired results.

From the sixteen analyses carried out on the corrosion products below the former metal surface (Figure 4-65), only four (or 25%) registered manganese (Image 1: 0.76%rel.at.wt., Image 3: 0.520.76 & 0.580.76%rel.at.wt., Image 4: 0.310.76%rel.at.wt.). These detected quantities were slightly more (circa 24% above) to less (circa 23% below) than that expected from the maximum (0.6143%rel.at.wt.) and minimum (0.4046%rel.at.wt.) quantities[1175] previously detected by the prior metal analyses; and possibly demonstrated that manganese levels (when detectable) remained the same in the corrosion pit's corrosion products. No particular CP morphologies in the pit were considered attributable or not to manganese's detected presence.

Figure 4-66 & Figure 4-67 depict the context and results from the outer surface CPs that were above the corrosion pit and below the applied superior limitos marker.

[1174] 3.3.1.1 Metal selection & substrate preparation

[1175] Calculated from Table 3-2 by including EDS's 20% accuracy tolerance range when in optimum conditions (3.5.2 Scanning electron microscopy-energy dispersive spectrometry).

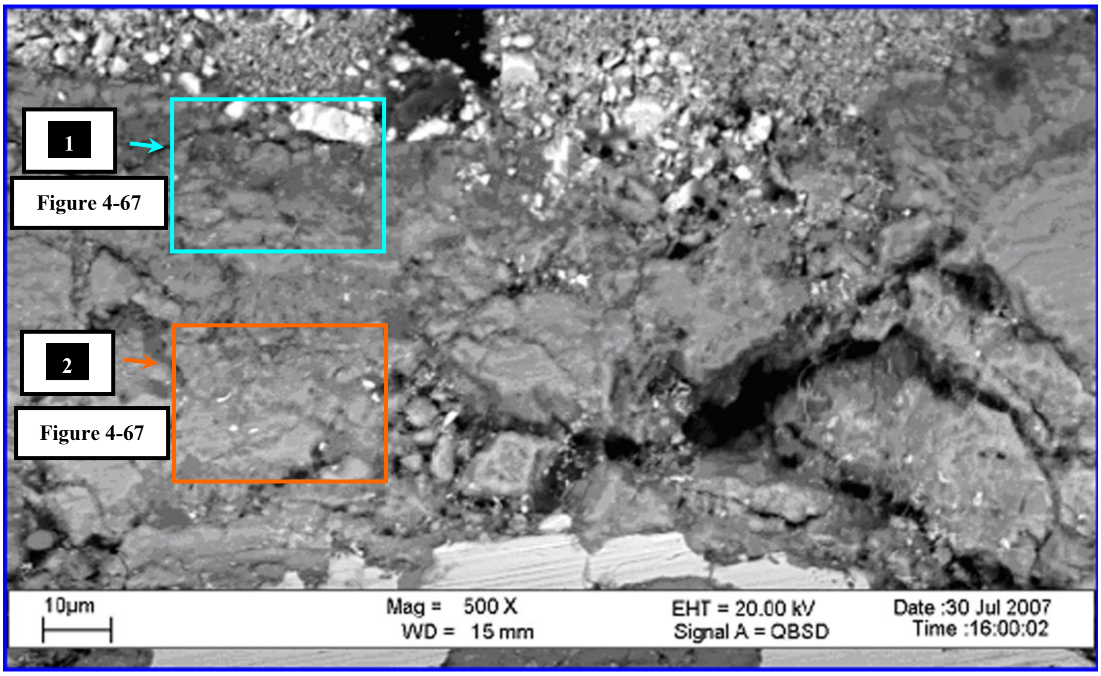


Figure 4-66 Armour analogue cross-section, Coupon Series 4: Low magnification (500x) context SEM BSE context image zones of interest in Figure 4-67. Context image in Figure 4-63.

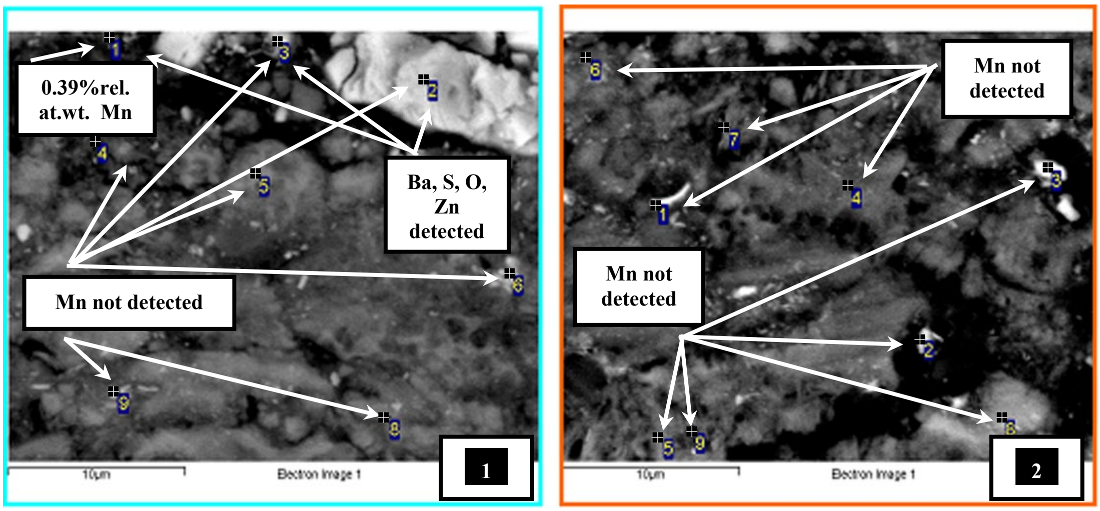


Figure 4-67 Armour analogue cross-section, Coupon Series 4: SEM BSE images and results of manganese EDS analyses (%rel.at.wt.) of corrosion products above a corrosion pit. Context image in Figure 4-64.

From the fifteen sites of analyses performed on these corrosion products below the superior limitos marker, yet still above the corrosion pit (Figure 4-67), only one (or 7%) registered the presence of manganese (Image 1: 0.39%rel.at.wt.); a concentration marginally less (circa 4%) than that expected from the metal's minimum detected amount of manganese.

An area mapped by EDS at 2000x is also represented by Figure 4-67: Image 1; a very faint signal for manganese was given all over the corrosion products and limitos marker. The feint signal for manganese from the EDS mapping at 2000x, on the one hand, suggests manganese did not perform as an inferior limitos marker due to its penetration into the applied superior marker. While on the other hand the faint signal might also be attributable to cross-stratigraphy contamination from the sample polishing process.

When comparing the three data sets acquired from the metal (Mn detection frequency = 20%), corrosion pit (Mn detection frequency = 25%) and above the corrosion pit (Mn detection frequency = 7%) it can be seen a trend might have emerged: the frequency of the detected manganese between the metal and corrosion pit's CPs is similar, while it was circa 3-4 times less when it was above the level of the uncorroded former original surface.

In summary, when detected, the quantities of manganese in the metal and the CPs were close to that expected from the atomic emission arc induced spectroscopy analyses. However, manganese was infrequently detected in the metal and corrosion products. As a result it was not possible to evaluate manganese as a potential inferior limitos marker.

4.2.1.2.1 Summary of armour analogue corrosion cross-section investigations results

Cross-section observations of the armour analogue stratigraphies permitted a better perspective to judge the relative positions of the metal surface level/corrosion depth and corrosion products. The elevating influence of the corrosion process on the position of the coating and applied superior limitos markers was ascertained. The dual layer morphology of a porous and fragmented upper layer (TM) on a more compact lower layer (DPL) in contact with the pitted metal was exemplified[1176].

The distribution of the various applied superior limitos markers within these layers varied considerably. Depending on the particular instances, it was demonstrated the applied superior limitos marker could feature at any of the following interfaces:

- DPL/coating[1177];
- TMa/TMb[1178]; or
- TM/coating[1179].

[1176] Figure 4-56, Figure 4-57, Figure 4-58 & Figure 4-59

[1177] Figure 4-56, Figure 4-59

[1178] Figure 4-57, Figure 4-58

[1179] Figure 4-57, Figure 4-58, Figure 4-59

Notably the lowest recorded location for the superior limitos markers was on the dense product layer, suggesting the DPL as a maximum possible location for the limitos in the CP stratigraphies[1180] on these rolled low-carbon steel materials.

The distorted and fragmentary nature of the ferrous corrosion products on these armour analogues was also noted, while inferior limitos markers could not be established.

4.2.1.3 Summary of armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations' results

The one *definitive* corresponding limitos marker determined from the armour analogues was the raised micro-grooves that resembled a topography from the former metal. These micro-grooves comprised the surface of the dense product layer. A *complementary* corresponding limitos marker was the tactile differences between the non-adherent CPs of the transformed medium and the comparably adherent DPL. The cross-section perspective, which suggested the maximum possible location for the limitos is on the DPL, correlates with this finding. The applied materials (coating and applied superior limitos markers) were evidently deemed to be superior to the limitos, while no inferior limitos markers could be determined from the armour analogues.

The limitos in the corrosion products for the armour analogues, made of rolled low-carbon steel, is therefore proposed to be located at the interface of the dense product layer and the transformed medium. This interface was typically below the superiorly positioned TM (e.g. porous granulated orange-brown corrosion products) or more simply at a DPL/applied limitos marker-coating interface. The main CP forms were types of localised corrosion (pitting or filiform).

4.2.2 ARMOUR ANALOGUES, PALACE ARMOURY TECHNIQUE: CURRENT ARMOUR CORROSION PRODUCT REMOVAL PRACTICE

Macro-perspectives of major coupons from Coupon Series 4 (Figure 4-68) and 6 (Figure 4-69) are provided to evidence the amount of corrosion product removal performed by the Palace Armoury technique.

[1180] Deemed to represent local to general corrosion rather than filiform corrosion morphologies.

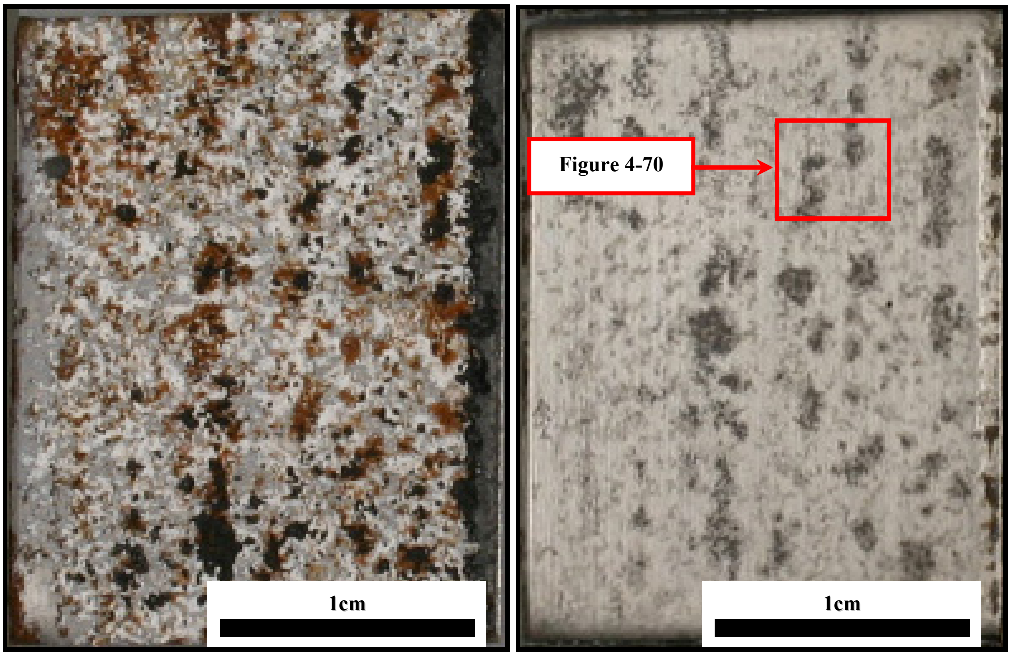


Figure 4-68 Armour analogue major coupon plan perspective, Coupon Series 4. Left: Before and Right: After partial corrosion product removal by the Palace Armoury (with red context frame for Figure 4-70).

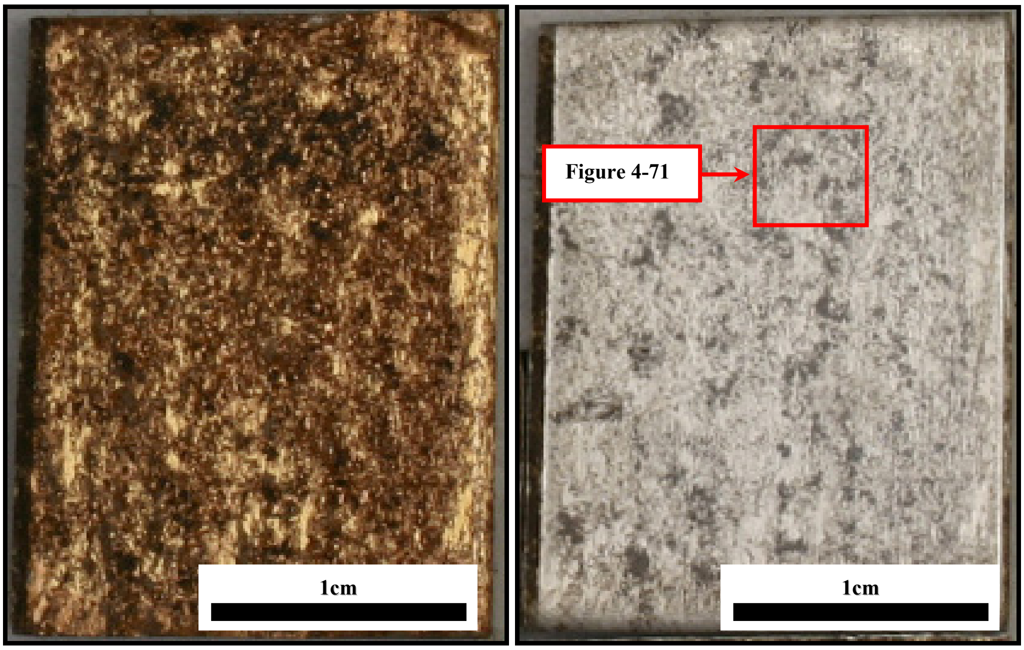


Figure 4-69 Armour analogue major coupon plan perspective, Coupon Series 6. Left: Before and Right: After partial corrosion product removal by the Palace Armoury (with red context frame for Figure 4-71).

For both Coupon Series, generally it can be said on a macroscopic level, that the surfaces were not stripped of all their corrosion products: most, but not all, CPs were removed. All the observable red-brown CPs were removed while much of the darker brown-black CPs were retained. The retention of some, but not all corrosion products, demonstrates that the Palace Armoury does not perform complete corrosion product stripping.

*

Correspondingly, on a microscopic level, the extent of corrosion product retention between Coupon Series 4 and 6 was similar overall, while it varied between areas on individual coupons (Figure 4-70 & Figure 4-71).

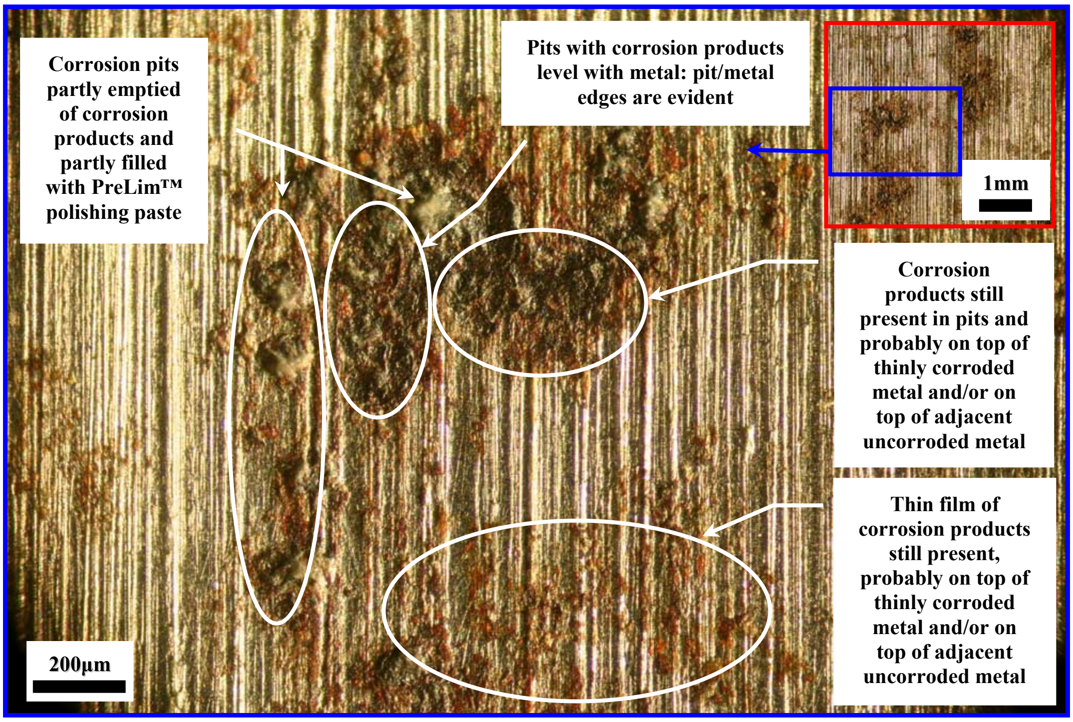


Figure 4-70 Armour analogue major coupon plan perspective, Coupon Series 4: Main: Raking light optical microscope image of cleaned armour analogue by the Palace Armoury. Inset: Context image from Figure 4-68.

The Palace Armoury's corrosion product removal technique created surfaces that were essentially more or less level with the adjacent metallic surface. Sometimes the corrosion pits were partly emptied of corrosion pits, while much less occasionally, CPs appeared to be very slightly above the adjacent metal surface level. Generally, it was observed that corrosion products were mostly retained level with their pit edge. Pre-Lim™ polishing paste was also observed in the corrosion pits, even despite the last rinsing step with acetone and toilet tissue[1181]. Some very minute scratches in circular shapes were observed on the armour analogues' metal surfaces (not pictured).

Very superficial layers of orange-brown corrosion products were left on the metal surfaces. It was not possible to reveal by observation alone if these CPs were covering areas of ultra-shallow corrosion pits and thin CPs or if it was surface staining of CPs that precipitated on the surface from adjacent corrosion activity.

[1181] 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique

Subsequent limited probing under binocular microscope (50x) of these CPs and surfaces suggested that a combination of these effects was likely.

*

Searching for traces of the limitos, or at least remnants of their potential corrosion product structures, was not feasible on Coupon Series 4 since such features were not very evident; even on the stratigraphically probed coupons from the first objective[1182]. Coupon Series 1 and 6 however provided more examples of the limitos as determined by the surface micro-grooves observed during prior stratigraphic probing[1183]. However, none of these limitos CP structures were found on the Palace Armoury's cleaned armour analogues from Coupon Series 6. Associated with this absence were consecutive corrosion pits partly filled with corrosion products as featured in areas of Coupon Series 6 (Figure 4-71) and later discussed[1184].

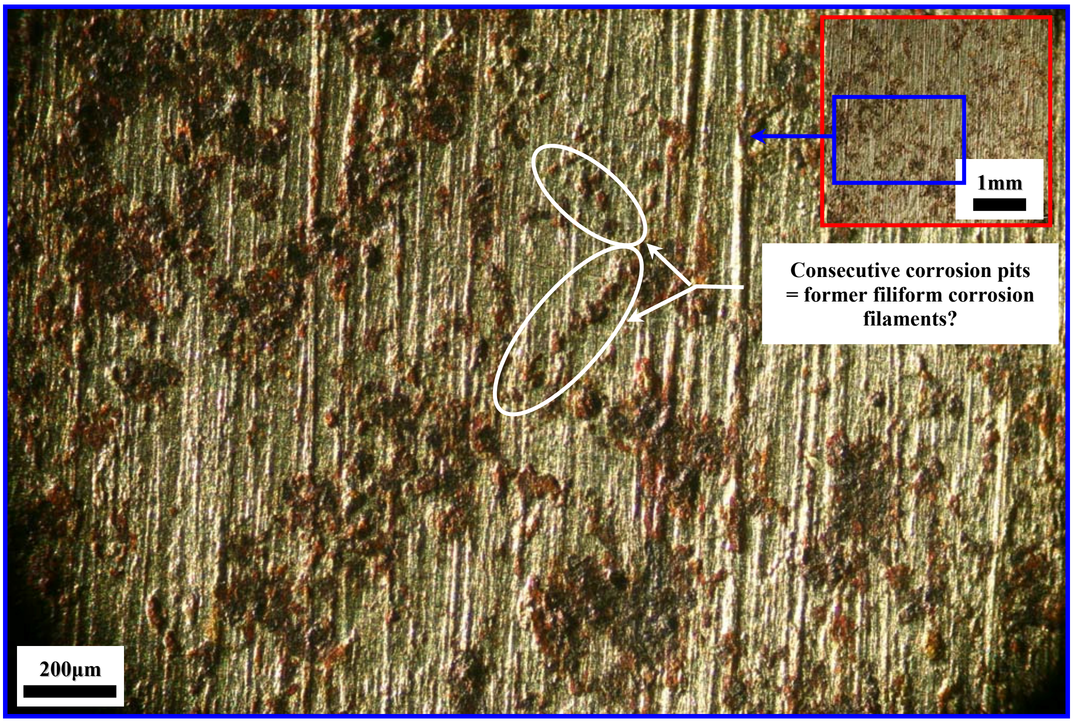


Figure 4-71 Armour analogue major coupon plan perspective, Coupon Series 6: Main: Raking light optical microscope image of Armour analogue cleaned by the Palace Armoury. Inset: Context image from Figure 4-69.

*

[1182] 4.2.1 Armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations

[1183] 4.2.1 Armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations

[1184] 5.2.2 Armour analogues, Palace Armoury technique: current armour corrosion product removal practice

Although anticipated in the experimental design[1185], it was decided to not investigate by cross-section perspective the armour analogues cleaned by the Palace Armoury. This decision was made on the basis that the loss of the limitos by the PA cleaning technique was already obvious from the plan perspective. Furthermore, since the limitos was only definitively identifiable by the corresponding micro-grooves (which were only observable in plan perspective[1186]), confirming the loss of the limitos would not have been possible in cross-section.

4.2.3 ARMOUR ANALOGUES, LIMITOS APPLICATION: CORROSION PRODUCT REMOVAL TO THE LIMITOS

The level of cleaning undertaken with these major coupons followed the determination from the first part of the armour analogue experiment, Armour analogue objective 1, Limitos determination[1187], which indicated the limitos was positioned at the upper surface of the DPL (usually indicated by the micro-grooves).

*

Macro perspective examples from each Coupon Series before and after coating removal and selective corrosion product removal cleaning according to the previously determined limitos[1188] are given in Figure 4-72, Figure 4-73 & Figure 4-74.

[1185] 3.3.2.3.2Armour analogues, Palace Armoury technique: current armour corrosion product removal practice

[1186] 4.2.1.1 Plan perspective investigations

[1187] 4.2.1 Armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations

[1188] 4.2.1 Armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations

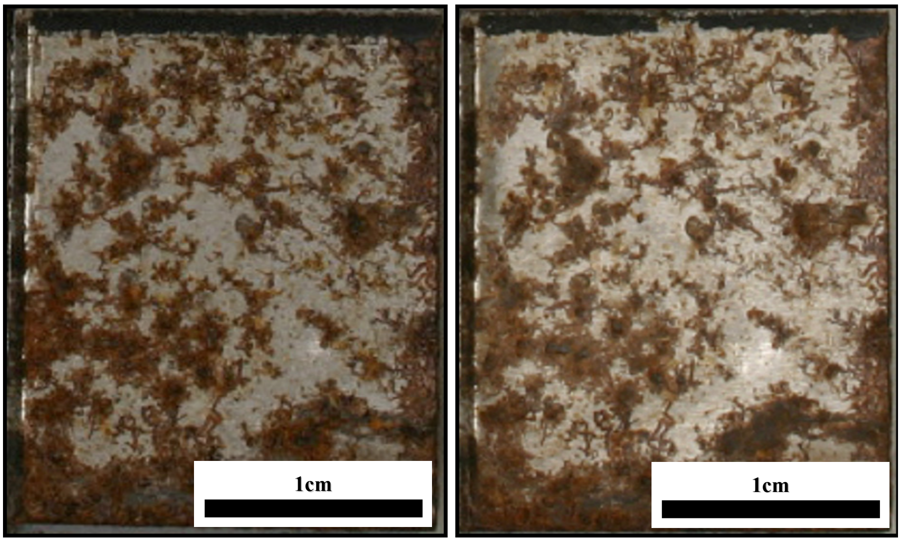


Figure 4-72 Armour analogue major coupon plan perspective, Coupon Series 1: Example of major coupon. Left: before and Right: after corrosion product removal according to the determined limitos.

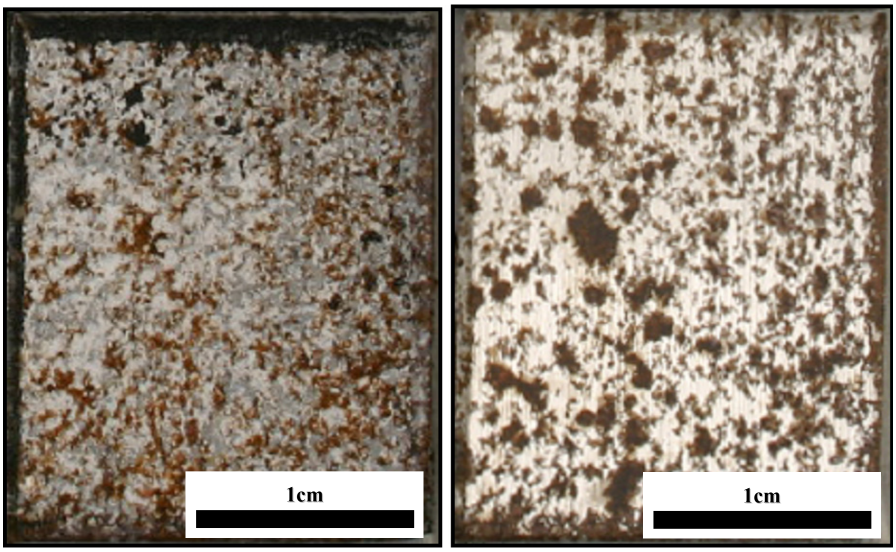


Figure 4-73 Armour analogue major coupon plan perspective, Coupon Series 4: Example of major coupon. Left: before and Right: after corrosion product removal according to the determined limitos.

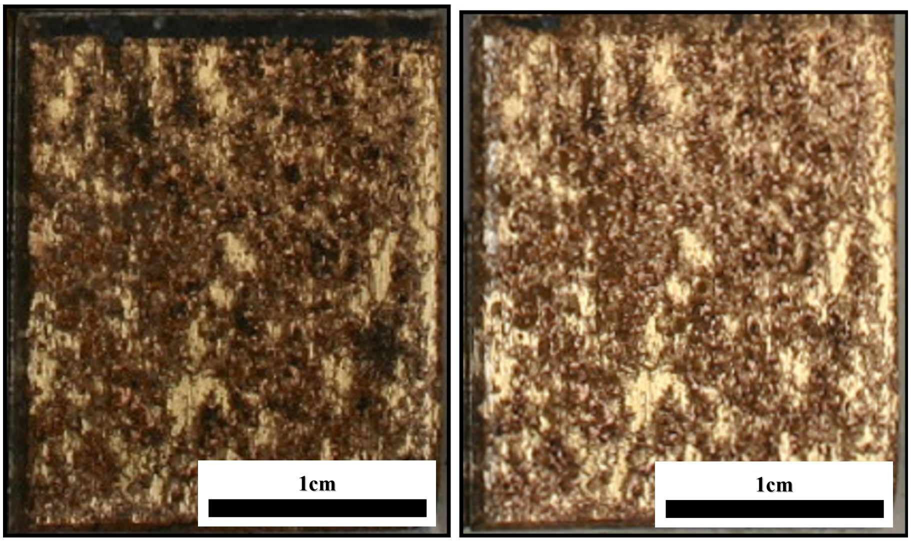


Figure 4-74 Armour analogue major coupon plan perspective, Coupon Series 6: Example of major coupon Left: before and Right: after corrosion product removal according to the determined limitos

Of particular note was the relatively small difference in CP presence, while less importantly, was the increase in metal surface reflectivity perceived to be due to the removal of the coating. The attempted removal of CPs included the bright orange or brown weeping droplets/beads (CP1s)[1189], the orange films and particles (CP2s, CP3s)[1190] and bright orange domed caps (CP4s)[1191]. As intended the red-brown corrosion products (CP6c, CP7c, CP8c)[1192], representing the limitos, largely remained after the performed cleaning, with the exception of CP5c[1193]. Those resilient corrosion product structures that were deemed by association to form the limitos, but which did not exhibit micro-grooves (i.e. the more distorted instances of CP7c), were also maintained in place.

*

Corrosion products above the coating were largely removed by the respective coating removal procedure[1194]. The white applied superior limitos markers (which mostly became orange stained) on Coupon Series 1 & 4 basically guided the extent of corrosion product removal. Attempts were also made to remove CPs below the powder marker, such as any thin films of orange CP staining on the uncorroded metal surface, and with greater difficulty the TM CPs positioned on the dense product layer that exhibited micro-grooves.

[1189] Figure 4-48, Image 1

[1190] Figure 4-48, Images 2, 3 & 4

[1191] Figure 4-48, Image 6

[1192] Figure 4-48, Images 5, 6, 7 & 8

[1193] Figure 4-48, Image 4

[1194] 3.3.2.3.3 Armour analogues, limitos application: corrosion product removal to the limitos

Immersion in solvent was required to remove the coating from Coupon Series 6 since the multitudes of orange weeping droplet CPs above the coating were too fragile for swabbing and would have resulted in powdering into minute particles; proving extremely pervasive and difficult to subsequently remove. Immersion provided solvency for the coating and a smooth carrier action to lift away most of these droplets. The gold superior limitos marker applied to Coupon Series 6 was largely left in place since its complete removal required physical abrasion that exceeded the structural strength of the minute CPs representing the limitos.

*

Importantly for practical conservation application, discrimination between limitos and non-limitos CPs was not possible by the naked eye, nor with a desk mounted magnifying lamp: the micro-grooves as evidence of the limitos were in all cases literally microscopic. The microscopic recognition of the micro-grooves as a corresponding limitos marker thus largely depended on the level of magnification. Some corrosion products' grinding line zones were so small that they were only evident at 200x magnification (Figure 4-75).

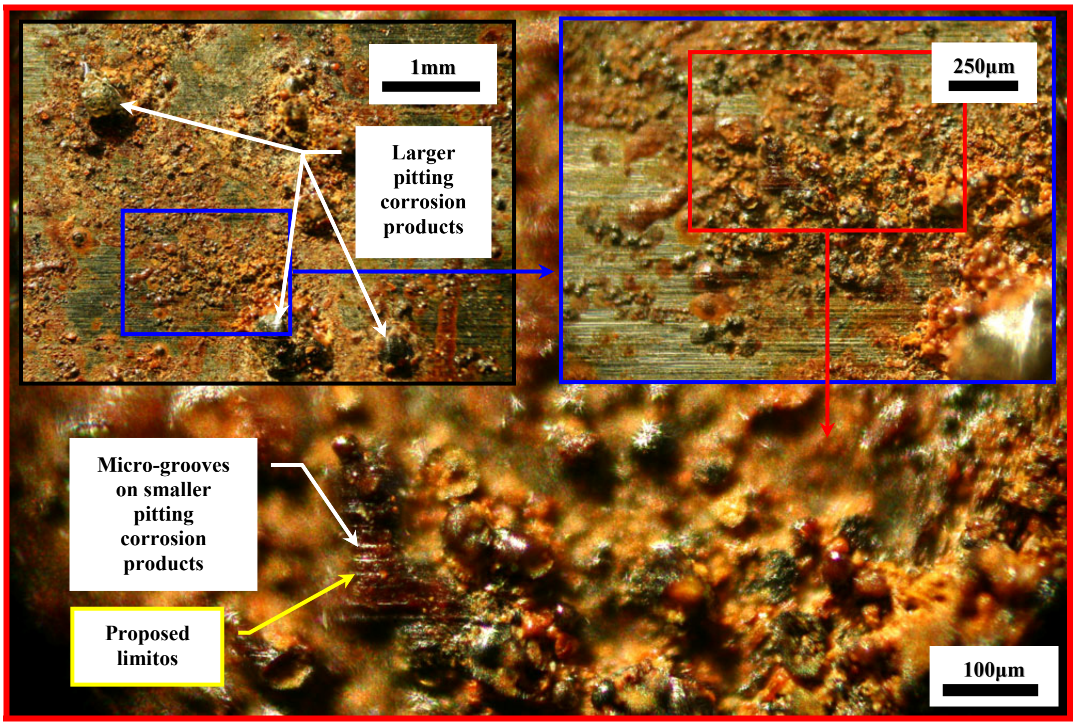


Figure 4-75 Armour analogue major coupon plan perspective, Coupon Series 1: Progressive optical microscope magnification of very thin general corrosion products exhibiting micro-grooves from the metal.

*

The durability of the pitting or filiform corrosion products varied considerably. Some corrosion products were so fragile that they disintegrated with the gentlest physical intervention, while others resisted and tenaciously remained adhered to the surface. In practice, the selective removal of certain corrosion products according to the diagnostically determined limitos was either, not fully realisable nor possible without damaging adjacent CPs bearing evidence of the limitos. Also, it was a very time-consuming or near impossible process (with current physical techniques) to remove some of the superior limitos CPs. Consequently more sensitive and conservative approaches were taken, but this still meant that some corrosion products, which were deemed to not form a part of the limitos, were in fact retained (Figure 4-76).

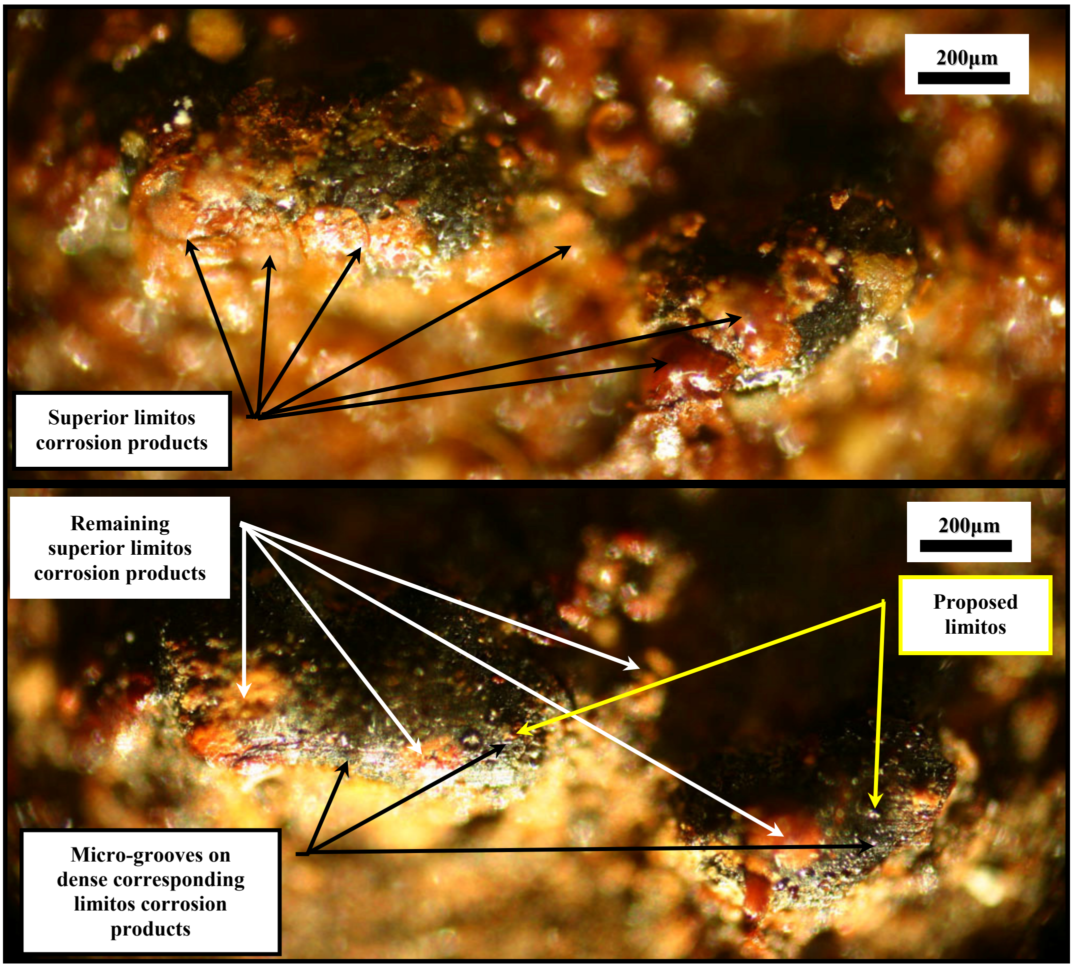


Figure 4-76 Armour analogue major coupon plan perspective, Coupon Series 1: Optical microscopy of corrosion products. Top: Before; and Bottom: After partial corrosion product removal to the determined limitos.

*

Importantly, in addition to retaining corrosion products that evidenced a limitos via the micro-grooves, some CPs were retained since they were deemed to be of the same morphology, despite not bearing direct evidence of the limitos via micro-grooves. Their similarity (e.g. brittle and hard/fragile dark brown films or blisters under the applied superior limitos marker) with CPs definitely exhibiting CP structures evidencing the limitos was used to deduce that these other CPs could have potentially formed part of the limitos, but this was inferred, not yet proven or disproven.

*

Since only thin and largely localised masses of corrosion products were removed from these coupons (which had ultimately only corroded to the primary extent[1195]) the planned investigations via cross-section were considered superfluous: the small differences before and after cleaning were already observable by the plan perspectives.

4.2.3.1 Curatorial perspectives on corrosion product removal to the limitos

Examples of the major cleaned coupons and mini reference coupons from the Armour analogue objective 2, Palace Armoury technique and Armour analogue objective 3, Limitos application experiments (Figure 4-77) were presented for collaborative discussion with the Senior Curator[1196] and Curator[1197] of the Palace Armoury.

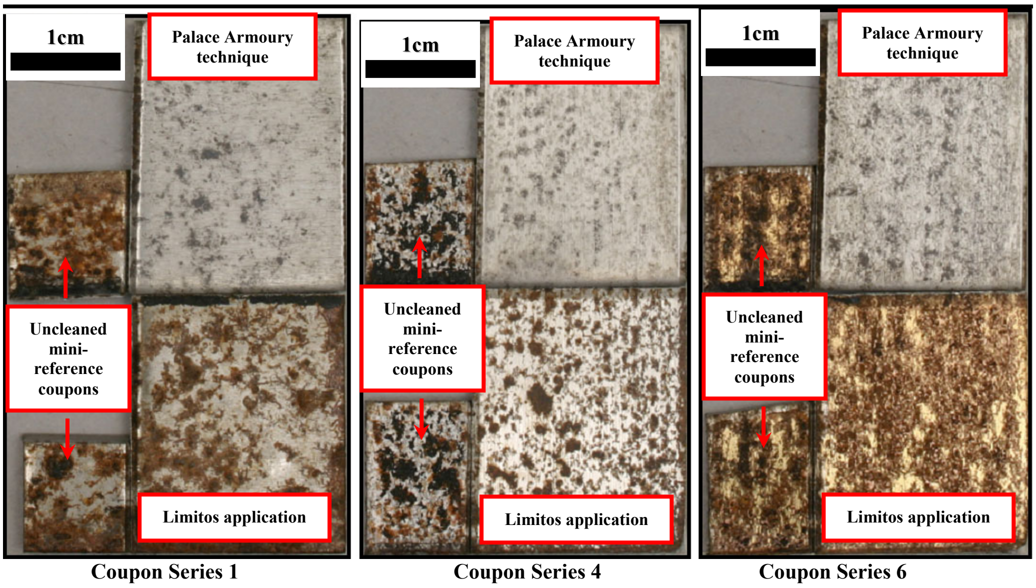


Figure 4-77 Armour analogues plan perspectives, examples of major coupons (with uncleaned mini-reference coupons). Top: Cleaned according to the current Palace Armoury technique and Bottom: Cleaned according to the diagnostically determined limitos.

The curatorial feedback, with some minor variation in opinion, was very similar. Both curators appreciated the difference, if only small, between the limitos

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[1195] 3.3.1.2 Armour analogue selection
[1196] Mr Emmanuel Magro Conti
[1197] Mr Michael Stroud

coupons and the uncleaned reference coupons, while they both preferred the result representing the current corrosion product removal procedure practiced at the Palace Armoury. This preference was formed on the basis of two principal reasons: aesthetics and stability[1198]. The Senior Curator based his aesthetic preference for the current treatment finish since he is accustomed to this appearance since childhood and from professional experience. He felt that the surfaces should have a "…clean appearance" and the finish resulting from the current Palace Armoury technique is "…nicer looking and less troublesome." He also raised the cliché image of the "knight in shining armour", although he recognised that not all armour was polished[1199]. Significantly, both curators felt that removal of corrosion products depends largely on whether the armour is on public display or in storage[1200].

The aesthetics issue evoked the related issue regarding the possible definitions of what can be considered the *original* appearance (i.e. from manufacture, from last use in warfare, last use on display etc.) and if it is indeed possible to recover this appearance or at least this modified surface, especially considering the armour has been periodically intervened over the past centuries. The value or significance of the present munition armour surfaces were not under question by the curators, despite many surfaces being created by the last corrosion product removal intervention (occurring anytime from manufacture to present; a vast period spanning up to 350-450 years, in many roles and with many custodians). It was agreed that on most areas of most munition armour the surface finishes from manufacture or early use were most probably lost forever, but it was unclear when the *use* (dynamic or static) of the armour stopped and which period of custodianship ended the historically significant lifetime of the armour[1201]. In conjunction with this temporal uncertainty, the curatorial opinion differed as regards the targeted appearance for the munition armour. The Curator perceived the appearance from manufacture to be of importance[1202], while the Senior Curator perceived the appearance evidencing its past active use to be of importance[1203]. Significantly, it was agreed that the only areas of armour where it was considered possible to find surfaces from manufacture might include inaccessible places such as under rivet heads, between lames and under coats

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[1198] Stroud, 2006-2007, pers. comm. & Magro Conti, 2007, pers. comm.

[1199] Magro Conti, 2007, pers. comm.

[1200] Stroud, 2006-2007, pers. comm. & Magro Conti, 2007, pers. comm.

[1201] Ibid.

[1202] Stroud, 2006-2007, pers. comm.

[1203] Magro Conti, 2007, pers. comm.

of old paint[1204]. The extent of any limitos preservation in the areas between lames and under rivets would not only depend on its inaccessibility, but any subsequent corrosion. If corroded, then these surfaces could potentially be represented by a CP limitos instead of the metal.

Both curators were broadly aware that corrosion products can have their deleterious effects on metal conservation. The Senior Curator felt that the CPs should be treated similarly to a gangrenous body part on a human and be removed since they risked consuming the remaining healthy (i.e. metal) parts[1205], however, he also felt that the best solution needs to be found for each piece while also considering that they normally come as components of a larger assemblage. The Senior Curator exemplified the instability of the Palace Armoury collection by citing an incident of recorrosion just three years after an armour's CP cleaning and surface protection coating[1206]. The Curator felt that the level of cleaning proposed by this study to respect the limitos (as demonstrated on the armour analogues[1207]) had "…removed a lot of the live rust, but a thick layer of corrosive material still remains and needs to be removed." He felt that less surface roughness is preferable since humidity would be encouraged to "hang on". The Curator preferred a surface finish featuring slightly emptied pits, rather than bumps, so that it is smooth to feel and has less anchorage for dust and humidity[1208].

When questioned to help delineate the issues of stability and aesthetics/supposed original appearances, the Senior Curator stated he would be willing to accept the poor aesthetic qualities of the surfaces representing the limitos providing the corrosion was truly stable[1209]. Meanwhile, for the Curator, even if the corrosion was deemed to be stable he stated that the aesthetics remained too great a problem because he is interested in returning the artefact closer to its manufactured state[1210].

[1204] Stroud, 2006-2007, pers. comm. & Magro Conti, 2007, pers. comm.

[1205] Magro Conti, 2007, pers. comm.

[1206] Ibid.

[1207] Figure 4-72, Figure 4-73 & Figure 4-74

[1208] Stroud, 2006-2007, pers. comm.

[1209] Magro Conti, 2007, pers. comm.

[1210] Stroud, 2006-2007, pers. comm.

4.2.4 SUMMARY OF ARMOUR ANALOGUE INVESTIGATIONS

Summarising the overall results obtained from the armour analogue investigations it can be stated that the limitos was often clearly determined and was characterised by an upward displacement from the original surface of the metal. This upwards displacement was attributable to the corrosion processes that produce corrosion products that are of significantly greater volume than the originating metal. Limitos markers, of corresponding and superior types, recorded this localised limitos topography displacement. The best marker to evidence the limitos in CPs via plan observation was the micro-grooves: a corresponding limitos marker originating from the physical grinding of the metal during surface preparation[1211]. The micro-grooves were only informative in plan perspective since they were not distinguishable in cross-section. Meanwhile, the applied superior limitos markers demarcated some, but not all, CPs above the determined limitos. These superior limitos markers were useful in plan observation, but were even more compelling in cross-section observation.

In summarising and synthesising the results obtained from the three experimental phases performed on the armour analogues, important principal points were raised:

- Armour analogue objective 1, Limitos determination: proved that the limitos on rolled low-carbon steel was indeed present and was either evidenced by surface micro-grooves or hypothesised to have existed based upon inferences with properties of similar corrosion product structures that actually featured the surface micro-grooves.
- Armour analogue objective 2, Palace Armoury technique: proved that with the Palace Armoury's current munition armour corrosion product removal practices the limitos was being removed, some areas of the surface were being excavated of corrosion products and the metal surfaces were being eroded.
- Armour analogue objective 3, Limitos application: proved that the level of cleaning required to preserve the limitos retained an amount of corrosion products that was much more excessive than currently accepted in the field of munition armour conservation and posed a series of significant interrelated matters for discussion and resolution concerning establishing conservation objectives and appropriate strategies for the Palace Armoury's open displayed munition armour.

4.3 PRELIMINARY NON-INVASIVE OBSERVATION OF THE DETERMINED LIMITOS ON AUTHENTIC MUNITION ARMOUR

Evidence for a displaced limitos in both pitting and filiform morphology corrosion products was found (Figure 4-78) on one of the armour

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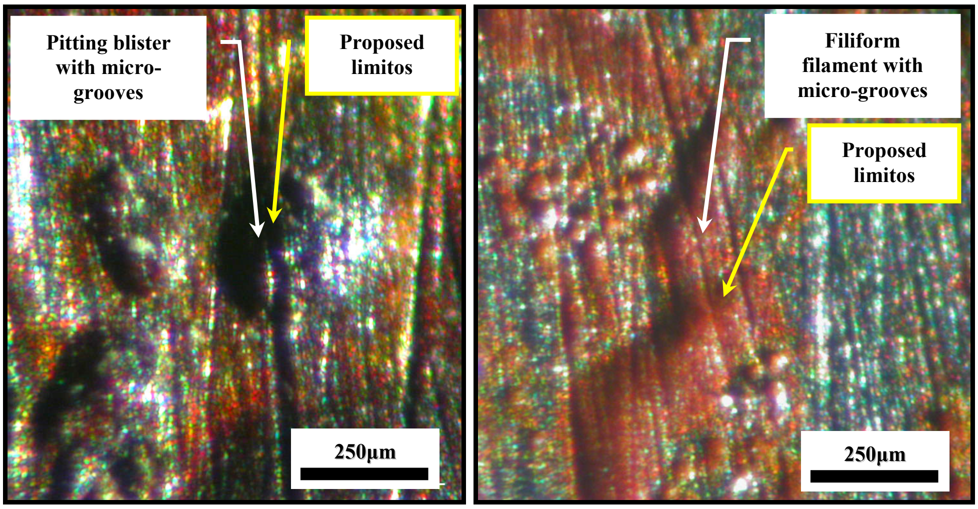
[1211] 3.3.1.1.2 Surface grinding

pauldrons (PA 316), thereby suggesting that the corrosion and CP formation mechanisms between the analogues and the armour were indeed similar.



Pitting corrosion morphology **Filiform corrosion morphology**

Figure 4-78 Palace Armoury armour plan perspectives, Pauldron PA 316: Binocular microscope images of corrosion product morphologies exhibiting a displaced limitos as evidenced by surface abrasion micro-grooves.

The absence of coatings[1212] again maximised light reflectivity from the different angles of the minutely rough surfaces. Surfaces in this uncoated area of this armour appeared relatively free of other corrosion product features (e.g. orange-brown particles or weeping droplets) that otherwise still remained in areas above and below the coating on the same armour[1213]. This absence of these other non-limitos corrosion product features on the cleaned area is therefore attributable to the previously employed coating removal procedure[1214].

In agreement with the results obtained from the steel armour analogues, more examples of the limitos displacement via the micro-grooves on the armour were found in filiform corrosion products than with pitting corrosion products. The broad type of ferrous metal (i.e. iron or steel) that exhibited these micro-grooves was unknown since the armour sample that was examined metallographically came from another lame[1215].

Invasive investigations involving the removal of coatings from a greater number of corroded munition armour are required to increase the statistic on these preliminary results.

[1212] 3.4 Preliminary non-invasive observation of the determined limitos on authentic munition armour
[1213] Table 4-3: images; Secondary local to general corrosion; and Tertiary filiform corrosion
[1214] 3.4 Preliminary non-invasive observation of the determined limitos on authentic munition armour
[1215] Figure 4-5

4.4 SUMMARY OF RESULTS

Investigations of the Palace Armoury environment and its munition armour developed the basis of how the material-environment influenced the armour's corrosion and where the limit of the original surface might have possibly been located in their ferrous corrosion products. It was established by reference to exogenous materials from the environment (i.e. solid aerosols) and protection treatments to the armour (i.e. protective coatings) and endogenous materials like metallurgical features (i.e. slag inclusions, nodules of uncorroded metal or carbide microstructures) within the armour metal and its corrosion products that the limitos most probably corresponded with an interface in the CP stratigraphy. This corrosion product interface was characterised by relative differences in its physical properties (i.e. porous-laminated aspect referred to as the transformed medium versus the relatively dense-compact aspect referred to as the dense product layer).

On the armour analogues the loosely bound, porous and fragmented CPs of the transformed medium were visually discernable in cross-section and by tactile manual means in plan perspective. Despite not being porous *and laminated* like the transformed medium on wrought iron (PA RC 166), the similarly located upper corrosion product layer of porous *and fragmented* corrosion products on top of a denser lower layer on rolled low-carbon steel was perceived to be comparable.

Significantly, the micro-grooves emanating from the grinding lines in the former metal of the armour analogues were identified as a corresponding limitos marker, thereby providing a definitive location for the limitos on the armour analogues. Without these micro-grooves and with the absence of inferior limitos markers, the determination of the limitos on the armour analogues would not have been definitively achievable. Evidence of the armour analogues' micro-groove marker was found on two types of closely related corrosion product morphologies: filiform corrosion product filaments, and local to general corrosion products (that probably formed by pitting corrosion). Filiform CPs consistently featured the displaced micro-grooves, which comprised the surfaces of filaments with arched cross-sections or consecutive domed blisters. The local to general corrosion product morphologies on the armour analogues featured the displaced micro-grooves on the surfaces of their domed blisters and also on their rough structures. Compared with filiform morphologies, the micro-grooves on local to general CP morphologies featured less often and had fragmented micro-grooves, unlike the filiform corrosion. As local to general corrosion product morphologies developed, tracing the micro-grooves as a corresponding limitos marker became far less achievable.

The concurrent observation of the Palace Armoury's present munition armour corrosion product removal technique on an authentic armour, and on the armour analogues, permitted documentation and a reliable interpretation of the effects that these contemporary interventions have had on the collection's corrosion products and metal surfaces. These techniques have not only removed the determined limitos corrosion products, but also the adjacent and underlying metal.

After practically performing CP removal to respect the determined limitos (as far as practicable by physical means) it was ascertained that many non-limitos CPs remained since very conservative techniques were necessary to minimise damage to limitos CPs. If the limitos of the more fragile and fragmented limitos structures on the analogues were to be respected physical interventions would have had to be entirely avoided. Coating removal by solvent swabbing, for example, most likely removed the fragile fragmented structures. Meanwhile some local corrosion products with distorted, yet unfragmented, micro-grooves were very resistant to physical abrasion and tolerated coating removal. Such CP fragility or tenacity needed to be determined on a case-by-case basis, and was a very difficult task to achieve unless undertaken with magnification.

When compared with the pervasive presence of corrosion products after following techniques that optimised retention of the limitos, both of the Palace Armoury Curators preferred the PA's currently employed CP removal techniques. This opinion was formed on the basis of better aesthetics and improved stability.

The non-invasive observation of areas of uncoated authentic munition armour with corrosion product morphologies (classed as filiform and local to general corrosion formed to a primary extent of development) that featured the micro-grooves confirmed that such evidence of the limitos also existed on atmospherically corroded mid-late Early Modern Period wrought ferrous metal. This association confirmed the close similarity of this particular characteristic between the contemporary experimental analogue materials and the mid 16th-mid 17th century northern Italian-style plate munition armour of the Palace Armoury.

5 DISCUSSION

Extended discussion of the results from the experimental investigations on the mid 16th-mid 17th century northern Italian-style plate munition armour of the Palace Armoury and the contemporary analogues of this armour is made in this chapter. Also, the major implications of this study's findings regarding the determination and practical exposure of the limit of the original surfaces in these ferrous materials' corrosion products and their limitations are explained.

5.1 PALACE ARMOURY ENVIRONMENT, MUNITION ARMOUR & CORROSION PRODUCT CASE STUDIES: NON-INVASIVE & NON-DESTRUCTIVE INVESTIGATIONS

The discussion from the various *in-situ* Palace Armoury and laboratory investigations performed on the PA pollution, and surfaces and cross-sections of the authentic armour is subsequently presented.

5.1.1 ARMOUR HALL WALL DISPLAY: *IN-SITU* CORROSION SURVEY

The *in-situ* wall display examination determined that permitting accumulating particles to remain on the non-inverted surfaces of the munition armour (for sufficient time) induced failure of the protective coatings and subsequent corrosion of the underlying surfaces. The *in-situ* inspection was imperative to understanding how its display orientation affected its differing susceptibility to corrosion. Applying corrosion theory, the combination of an uncontrolled environment, and no dust-removal schedule, realised the practical consequence of corrosion correlating with particulate covered surfaces[1216]. This corrosion activity was most probably intermediated by moisture locally adsorbed to these particulate covered surfaces. Without this fundamental current situation affecting the large quantities of relatively inaccessible armour on open-air display the current research question would not have been as sizeable and pressing to pursue. The extent of corrosion product development

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[1216] 2.2.2 Indoor atmospheric ferrous corrosion: definition, processes & factors probably depended more on the duration passed since each armour had been dusted of particles or cleaned of CPs, rather than other potentially influential factors such as coating type and microclimate position in the hall.

5.1.2 ARMOUR HALL AEROSOL POLLUTANTS: SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROMETRY

To aid discussion about the properties of potential exogenous species in the authentic armour cross-sections, an interpreted environmental attribution of the various elements, detected by scanning electron microscopy-energy dispersive spectrometry, in the Palace Armoury aerosol samplers is presented here.

5.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: attribution of exogenous sources

From the SEM-EDS results gained from the adhesive samplers[1217] an interpretation of the potentially attributable sources (Table 5-1) was made according to the speculated atmospheric pollution sources at the Palace Armoury[1218].

Results	Interpretation
Element detected	**Probable / possible (?) pollution source/s**
Calcium	limewash, limestone construction stone
Oxygen	limewash, limestone construction stone, limewash pigment (?)
Sulphur	limewash pigment (?), pollution (?)
Carbon	limewash, limestone construction stone
Chlorine	sea-spray, limewash, limestone construction stone
Silicon	limewash, limestone construction stone, soil (?)
Aluminium	limewash, limestone construction stone, soil (?)
Sodium	sea-spray, limewash, limestone construction stone
Potassium	sea-spray, limewash, limestone construction stone
Magnesium	sea-spray, limewash, limestone construction stone
Barium	limewash pigment (?)
Lead	limewash pigment (?)
Iron	limewash, limestone construction stone, limewash pigment (?)
Phosphorus	limewash, limestone construction stone
Chromium	limewash pigment (?)

Table 5-1 Summary of the interpreted exogenous materials attributable to the SEM-EDS-detected elements of the Palace Armoury particulate deposits.

From the small sample of 18 EDS point-analysed sites taken from three separate aerosol samplers all the elements (i.e. Ca, C, O) of the predominant calcium carbonate (calcite, $CaCO_3$) fraction of limestone were well represented in frequency

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[1217] Table 4-1

[1218] 2.2.2.3.3 Atmospheric pollutants

(83.3-100%[1219]). From previous studies, EDS area mapping of similarly exposed surfaces also confirmed the relative abundance of surfaces at the Palace Armoury covered with calcium-based materials[1220]. The limestone constructed buildings of Valletta, and moreover the limewashed interior walls of the PA[1221] make these highly probable attributable sources for these three elements. The limewash and limestone, both of calcareous sedimentary rock origins mined in Malta, feature the predominant calcite species together with many minor and trace compounds. The essential differences between Coralline Limestone[1222] (used to make wall limewash[1223]) and the Globigerina Limestone (used to make construction blocks[1224]) is respectively a comparable or greater percentage of calcite (>95% versus 92-96%) and lesser percentages of quartz, potassium feldspars ($KAlSi_3O_8$), and clay minerals[1225]. With the exception of apatite[1226] and glauconite[1227] present in the Globigerina[1228], the compositional differences appear more by quantity than quality[1229]. Many oxides are found in Lower Globigerina; principally being of calcium (46-53%), silicon (2-9%), aluminium (≤1.8%) while traces (≤0.99-0.01%) of oxides of other elements are also present (in order of decreasing quantities: magnesium, iron, phosphorus, potassium, sodium, titanium and manganese)[1230]. Table 5-2 summarises the elements found in the compounds typically present in Globigerina.

[1219] Table 4-1

[1220] EDS of steel coupons (47 & 50) exposed at Palace Armoury for 6 and 11 months: raw data (Vella & Crawford, 2006)

[1221] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1222] Upper or Lower Limestone is not specified. Data simply referred to as Coralline Limestone is presented.

[1223] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1224] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1225] Cassar & Vannucci, 2001, pp. 40-41

[1226] Apatite = a phosphate mineral: $Ca_5(PO_4)_3(F,Cl,OH)$

[1227] Glauconite = $KMg(Fe,Al)(SiO_3)_6.3H_2O$ (Tucker, 2001, p. 8)

[1228] Cassar & Vannucci, 2001, p. 40

[1229] Cassar, 01/11/2007, pers. comm.

[1230] Cassar, 2004, p. 17

Compound	Elements (excluding oxygen & hydrogen)
$CaCO_3$	Calcium, carbon
SiO_2	Silicon
$KAlSi_3O_8$	Potassium, aluminium, silicon
$Ca_5(PO_4)_3(F,Cl,OH)$	Calcium, phosphorous, fluorine, chlorine
$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2)$	Potassium, sodium, iron, aluminium, magnesium, silicon
CaO	Calcium
Al_2O_3	Aluminium
MgO	Magnesium
Fe_2O_3	Iron
P_2O_5	Phosphorous
K_2O	Potassium
Na_2O	Sodium
TiO_2	Titanium
MnO	Manganese

Table 5-2 Compound sources and elements typically present in Lower Globigerina[1231].

A possible reason behind the high prevalence of EDS-detected sulphur (88.9%) could be attributable to conversion by sulphur dioxide in the atmosphere (i.e. the *sulphation process*) of the limestone-derived calcite to gypsum ($CaSO_4$)[1232]. Also, sulphur-containing water-soluble salts of sulphates have been recorded in Globigerina exposed to indoor architectural conditions in Malta and were supposed to come from sources including marine aerosols and air pollution[1233].

The high EDS detection rate of chlorine (83.3%) and the SEM observed cubic structures of some particles, which coincided with EDS spectra revealing sodium and chlorine[1234], indicates the presence of sodium chloride. Mediterranean sea-water with its 3.86% salinity contains chlorides of sodium (sodium 0.05310-0.05528% to chlorine ratio), potassium (potassium 0.002008% to chlorine ratio)[1235] and magnesium (magnesium 0.006785% to chlorine ratio)[1236]. Sea-spray is therefore a likely local source of the detected chlorine and these other seawater associated cations, which were also elementally detected on the particle samplers (respectively, Na = 44.4%, K = 33.3% & Mg = 27.8%). Soluble salts of chlorides have also previously been recorded in Globigerina exposed to indoor architectural conditions in Malta and were supposed to come from aerosol sources[1237].

The high detection rate of silicon (77.8%) and aluminium (61.1%) could be attributable to their presence in potassium feldspars of Globigerina and Coralline Limestones, although in response to this supposition it has been remarked, "…the

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[1231] Ibid., pp. 14, 17
[1232] Van Grieken, 2006, pp. 44-50 & Trench, 2000, pp. 282-283
[1233] Cassar, 2002, p. 45
[1234] Figure 4-2 (EDS points analyses 2 & 4 and Spectrum 2)
[1235] Florian 1987, p. 4
[1236] Ibid.
[1237] Cassar, 2002, p. 45

concentration of Si & Al in Globerigina Limestone is far too small, especially when compared to the abundance of Ca, to be attributed to this source…"[1238]. It was advised that non-local sources be considered for attribution[1239]. A potential non-local source could come from alumino-silicates from Maltese soil-derived aerosols, or indeed, from the renowned Sirocco sandstorms coming from the Sahara and blowing over to Italy and Greece[1240].

The above cited relative order of abundances of the minor (Si, Al) and trace (Mg, Fe, P) metal oxides typically occurring in Globigerina are in accordance with the relative abundances of the metal elements of these oxides detected here by the EDS. Two exceptions to this trend were the higher amounts of detected potassium and sodium. The increased prevalence of potassium and sodium could be attributable to the additional pollutant source of sea-spray. Sea-spray could also explain the high frequency of magnesium in the EDS results, since as already presented above, magnesium in Globigerina is only found in trace quantities[1241].

The detection of barium (16.7%) and lead (11.1%) are proposed to possibly be attributable to pigments used to colour the limewash. The source of a white pigment might be contained in commercially available tints (*kulur tal presepju*) commonly available in Malta for colouring limewash[1242]. The barium spectra consistently and simultaneously exhibited peaks for sulphur and oxygen: indicating the presence of barium sulphate. The use of white pigments (such as barium sulphate and lead white[1243]) in an already inherently white formulation such as calcium carbonate limewash at first appears futile; making their role as a white paint pigment a doubtful explanation. However, the limewashed interior surfaces of the Palace Armoury have been coated numerous times[1244] and tinted with many colours through history (Figure 5-1). The heavy metal whites, like barium sulphate and lead oxide, have a superior hiding power over calcium carbonate whites[1245] and could have been applied within a proprietary blend of pigments. The lead traces could provenance an

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[1238] Cassar, 01/11/2007, pers. comm.

[1239] Ibid.

[1240] Blair, 1951, p. 438

[1241] 4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

[1242] Chetcuti, 30/10/2007, pers. comm.

[1243] Barium sulphate has been used as a paint pigment since 1782 (Feller, 1986, p. 49), while lead white (basic lead carbonate, $2PbCO_3.Pb(OH_2)$) (Gettens et al, 1997, p. 67) dates back over 2000 years (Gettens et al, 1997, p. 68)

[1244] 2.2.2.3.3,Atmospheric pollutants, Solid aerosols

[1245] Gettens, et al, 1992, p. 208

older paint layer, since lead white as a white paint pigment has (at least officially) been discontinued for some years. Direct analyses of the limewash at the Palace Armoury are required to verify these suppositions.

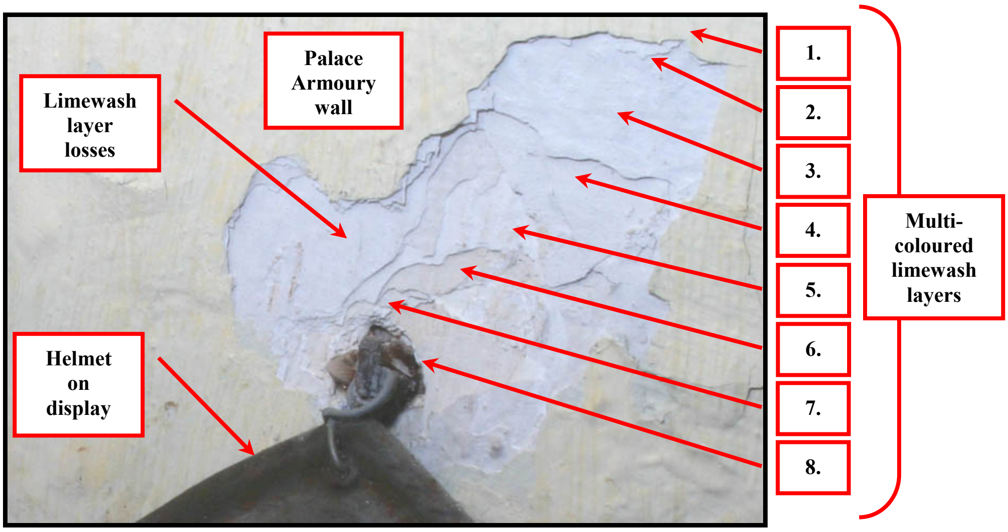

Figure 5-1 Detail of the Palace Armoury armour wall display with numerous evident layers of white and coloured limewash.

5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties

It was thought some of the various constituents of aerosol pollutants at the Palace Armoury could provide superior limitos markers in the cross-sections of the armour's CPs[1246]. These materials, which were indeed partly responsible for the ensuing corrosion, could provide indications of the limitos. The causal concurrence of these materials with the prevailing areas of corrosion products on the armour[1247] makes this possible. An evaluation of general superior limitos marker properties, and the potential contribution of some of the attributed exogenous sources[1248], is made next.

Solid phase pollutants as superior limitos markers were deemed necessarily preferable to liquid (or indeed gaseous) phase pollutants, not least due to their relative physical immobility and the applied characterisation technique of SEM-EDS. In principle, materials from the environment capable of migrating/diffusing through all corrosion product layers (i.e. the transformed medium and the dense product layer) are not considered to be as useful as those that are completely immobile. It is

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[1246] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1247] 4.1.1 Armour Hall wall display: *in-situ* corrosion survey & 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy

[1248] Table 5-1

here proposed that materials with so-called transcorrosion product layer mobility are unable to *definitively* contribute to determining the limits of the original surface that possibly exist in CP layers.

Notably, *initially* possessing a solid-state does not necessarily preclude the possibility of phase or material transformations, which subsequently increase mobility of exogenous species. For example, the potential dissolution of exogenous solid species by atmospheric water could greatly facilitate their mobility. Transport in water evidently increases the mobility of dissolved species since they can then be carried through capillaries of micropores otherwise inaccessible to the previously derived solid and/or larger constituent materials. The sodium chloride crystal (with its high solubility in water[1249]) is a good example of an exogenous/atmospheric material (i.e. in sea-spray[1250]) that is capable of phase transformation to the separate sodium (Na^+) and chloride ions. To exemplify the point with a well-studied corrosion instance, the high mobility of the chloride ion with its single negative electrostatic charge drives its subsequent migration through CP layers until it reaches the corroding metal. The anodic metal's imbalanced charge caused by parting electrons requires balancing by negatively charged species such as chlorides[1251]. The water solubility of ions (Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}), proposed to be attributable to dissolved species in sea-spray[1252] or in gypsum[1253], potentially discounts these ions from being *ideal* superior limitos markers. The preferable insolubility of solid pollutants in water makes their use as superior limitos markers more suitable, even more so due to the established high RH atmospheric environment of the Palace Armoury[1254]. As previously outlined[1255], the same principle of using exogenous, water-insoluble material (specifically quartz, SiO_2[1256]) from the terrestrial burial environment has already been used to assist delimiting the original surface limits of archaeological iron artefacts.

[1249] 3.3.1.1.3 Corrosion accelerant

[1250] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1251] Selwyn et al. 1999, p. 218, 2.2.2.3.4 Ferrous corrosion products & 2.2.3.3.1 Pitting corrosion mechanism

[1252] Florian 1987, p. 4

[1253] Van Grieken, 2006, pp. 44, 66

[1254] 2.2.2.3.2 Atmospheric water, Time of wetness/dampness & humidity cycles

[1255] 2.3.1.2.1 Localisation of the limitos

[1256] Only soluble in specific and highly acidic solutions (i.e. hydrofluoric acid) CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 82)

In pH neutral conditions calcium carbonate (i.e. calcite in limestone/limewash) might provide the characteristics for a suitable superior limitos marker since it is highly insoluble in water (0.00066×10^{20}g/100g H_2O)[1257]. However, unfortunately for these diagnostic purposes, calcium carbonate is soluble in dilute acids[1258] and acidification of atmospheric water is common. Acidification of water occurs via the absorption of atmospheric carbon-dioxide during the carbon cycle (Equation 5-1)[1259] and via interactions with pollutant aerosol species[1260]. It is proposed that acidification of atmospheric water would facilitate calcite's dissolution; making transcorrosion product layer mobility via aqueous solutions possible and thereby *restricting* its effectiveness as a superior limitos marker.

$$CO_{2\,(g)} + H_2O_{(l)} = H_2CO_{3\,(aq)}$$
$$H_2CO_{3\,(aq)} = H^+_{(aq)} + HCO_3^-{}_{(aq)}$$
$$HCO_3^-{}_{(aq)} = H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Equation 5-1 Production of carbonic acid by absorption of atmospheric carbon dioxide into water[1261].

The high detection rate of silicon (77.8%) and aluminium (61.1%) suggests their prevalence might also be useful as superior limitos markers. Their attributed source, like the others, remains open to question. With EDS their structural composition with allied elements can only be hypothesised and the assertion of their subsequent usefulness as superior limitos markers (as further hypothesised from the typical properties) tenuously hinges on such a series of suppositions. If the silicon is present as quartz (either from local soil or limestone-derived materials or Sirocco winds) then their potential usefulness could be high due to silicon dioxide's high water insolubility, while still relying on a high prevalence. Potential confusion with silicon and aluminium in the metal's inclusions[1262] and from sample polishing abrasives[1263] is not discounted, although particular morphologies and concentration gradients might help discrimination.

The main problem with accepting either barium (16.7%) or lead (11.1%) as superior limitos markers that absolutely define the limitos is that their abundance and

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[1257] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 48

[1258] Ibid.

[1259] Brimblecombe, 1996, p. 86

[1260] e.g. production of acids in atmospheres polluted with nitrogen and sulphur dioxide (2.2.2.3.3 Atmospheric pollutants, Gaseous aerosols)

[1261] Brimblecombe, 1996, p. 86

[1262] 2.1.2.1.1 Direct process: bloomery furnace

[1263] 3.2.3.2.3 Armour cross-section sample preparation distribution was so low that an identifiable uniform surface coverage might not always be present to form a relatively continuous line. Nonetheless such elements might be considered as useful additions to the range of superior limitos markers. The radio-opacity of these heavy metals would also facilitate their preliminary observation via SEM using the backscatter electron detector[1264]. The extreme insolubility of barium sulphate in water (0.0003120g/100g H_2O)[1265], inertness in acids[1266] and alkalis[1267] make its properties as a potential superior limitos marker preferable to calcite. The contamination of CP layers with barium, as barium sulphate, would also depend largely on the time of its introduction to the PA environment, whereas calcite has probably been present as a pollutant since the PA's inception. Lead in the form of *lead white* pigment, basic lead carbonate, ($2PbCO_3.Pb(OH_2)$) is insoluble in water, but soluble in acids[1268] and so suffers from similar solubility issues as calcium carbonate.

Evidently, the usefulness of iron (11.1%) cannot be considered as a discriminating element of the superior limitos layers in ferrous corrosion products, while the scarcity of phosphorus (5.6%) and chromium (5.6%) on the aerosol samplers indicates their value might only be in isolated areas, rather than a continuous line in the stratigraphy.

5.1.2.2.1 Summary of Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties

To conclude this preliminary evaluation of potential superior limitos markers, although calcium carbonate's atmospheric water solubility is not ideal, its contained calcium is highly prevalent and is therefore thought to be the most useful superior limitos marker available from the series of elements detected in the Palace Armoury aerosol pollutants.

Calcium's prevalence and transcorrosion product layer mobility was noted in the corrosion product layers of the armour samples investigated by cross-section and calcium made a decisive contribution to further specifying the diagnostic location of the limitos in ZOI $3a_4$ of PA RC 166[1269].

[1264] Feller, 1986, p. 60

[1265] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 45

[1266] Barium sulphate is slightly (0.01-0.02%) soluble in strong acids (Feller, 1986, p. 51)

[1267] Feller, 1986, p. 51

[1268] CRC Handbook of Chemistry and Physics: 85th Edition, 2004, p. 4 – 64

[1269] Figure 4-23

5.1.3 AUTHENTIC MUNITION ARMOUR CORROSION/CORROSION PRODUCT MORPHOLOGIES: LABORATORY INVESTIGATIONS OF SURFACES & STRUCTURES

The main discussion based on the results from laboratory investigations performed on the surfaces and cross-sections of the authentic armour is made here.

5.1.3.1 Armour surface observations: macrophotography & photomicroscopy

The greater correlation of secondary to tertiary developed filiform with local to general corrosion is perceived to occur, since over time, the locally defective coating that induced the filiform corrosion became so defective by the propagating filiform that a more general surface corrosion started under the coating[1270]. The process of progressively disrupting the coating's effectiveness is similarly applicable to the local to general corrosion as it developed from the primary to secondary to tertiary development classifications[1271].

On the microscopic scale, the irregular orientation of filiform on more *randomly* flawed surfaces presumably really followed the adjacent surface imperfections[1272], which provided a surface and/or coating defect that was conducive to producing a differential aeration cell necessary for the filiform corrosion mechanism[1273].

5.1.3.2 Armour corrosion cross-section observations & analyses

5.1.3.2.1 Armour cross-section sampling site surface macrophotography & photomicroscopy

PAULDRON (PART) PA RC 166

The previous non-intervention on the corrosion products present on the outer surface of PA RC 166 is assumed to have occurred since the fragment could no longer serve its purpose; either in functional dynamic armed-service or as a piece of static armour worthy of aesthetic display. It is probably for this reason that the fragment is stored in the reserve collection, as denoted by its registration number prefix RC. This sample provided a larger thickness of corrosion products for investigation. Such a relatively overlooked armour-piece is important since the

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[1270] Table 4-2
[1271] Table 4-2
[1272] Table 4-3
[1273] 2.2.3.2 Filiform corrosion/corrosion product morphology

limitos, compared with the other samples, is likely to date further back due to the lack of human interventions. Such a corroded, and corrosion product covered, armour could also possibly represent inaccessible areas on other munition armour that preserved their CPs in place over a long duration. Due to the multicomponent nature of armour, inaccessible areas are commonplace: for example, between static lames (e.g. cross-section from PA 316) or under rivets[1274].

PAULDRON PA 316

Similar to PA RC 166, the site on Pauldron PA 316, from which the sample was extracted, is also perceived to represent outer surfaces that might have had few historical interventions. In this case, a possible cause for a lack of interventions is its provenance from the inaccessible surface between armour lames. However, it is noted that surfaces between lames might have generally experienced abrasion of the surface by the superimposed lame, especially during its dynamic lifetime. In the particular case of PA 316, the site of sample extraction appears to *now* have sufficient tolerance to have avoided wear of corrosion products and metal caused by any such friction with the lame above.

BACKPLATE PA 329

The pitted outer surfaces adjacent to the sample extraction site for armour Backplate PA 329 were deemed to represent a previously corroded, yet metallic surface that had possibly been more recently intervened upon and had not yet allowed corrosion redevelopment (largely due to its vertical surface orientation). The pitting could be attributable to former corrosion processes and/or etching of the metal by corrosive solutions used to strip the surface of its CPs[1275].

5.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy

PAULDRON (PART) PA RC 166

Factors contributing to the thickness of this sample include the non-perpendicular embedding angle and its sampling from the former centre of the armour plate[1276]. The apparent absence of a coating makes sense since the fragment of armour has probably previously not been as valued as unbroken armour, which

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[1274] 2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour

[1275] 2.1.3.4 Recent history: museum typological collection & tourist site, Restoration

[1276] 4.1.3.2.1 Armour cross-section sampling site surface macrophotography & photomicroscopy, Pauldron (part) PA RC 166 featured coatings[1277]. The internal surface-parallel corrosion probably propagated in the direction of slag inclusions and forging planes.

The reported ordered colouring of the corrosion product layers (lower dark-brown-black & upper red-brown) is typical of iron CP stratigraphies, since as noted earlier on atmospherically corroded iron and steel, the black corrosion product magnetite (mixed with iron oxyhydroxides)[1278] is associated with the atmospherically isolated internal layers next to the metal, while external layers feature more iron oxyhydroxides (brown, orange, yellow CPs; i.e. ochres)[1279].

The lines (associated with probable internal forging planes) of unpolished dark brown-black CPs along the supposed inclusions[1280] might have been more atmospherically isolated and thus did not predominantly reach the higher oxidation state of the iron oxyhydroxide ochres[1281]. Meanwhile, the brighter orange appearance of the outermost edges of the CPs that bordered the embedding resin[1282] are perceived to be due to their relative thinness, which permitted light from behind to transmit through via the transparent embedding resin[1283].

On first inspection of the various colours observed in the corrosion product stratigraphies in Figure 4-8 & Figure 4-9 one might have been tempted to interpret these visually differing layers simply as different CP species, or indeed different mixtures and proportions of CP species. However, differing colours could have also been due to surface properties attributable to compactness/porosity. The unpolished CPs reflected (and absorbed) incident visible light at angles according to their inherent crystal structures and probably exhibited different colours to the flattened and polished surfaces of the same material. It was apparent via the standard optical microscope that the brown-black surfaces were often those that had been polished flat (since they were more compact and/or closer to the metal?), while those that were orange-brown featured in recessed and therefore unpolished areas (since they were more porous, further from the metal and/or tended to detach easily). It is difficult to ascertain whether the perceived colours of the ochre corrosion products are only attributable to inherent porosities that were simply exposed after sectioning

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[1277] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron PA 316 & Backplate PA 329

[1278] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1279] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1280] Figure 4-9

[1281] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1282] Figure 4-9

[1283] As per footnote 1041, this sample was previously embedded on a non-perpendicular angle.

or if these interfaces were caused by poor edge retention during polishing/grinding. This possible optical effect brought about by differing responses to surface preparation exemplifies the difficulty of correctly interpreting colours in ferrous corrosion product layers[1284]. This difficulty can also be encountered with ferrous CP surfaces under non-embedded plan observation, such as that confronted by a conservator with an artefact. Markers complementary to perceived colours are therefore required for proposing any existence or location of the limitos.

PAULDRON PA 316

It is probable that the thin metal core is a result of sampling from an edge formed during manufacture, and possibly differentially worn during use[1285].

The respective presence and absence of the coating on this sample's outer and inner surfaces[1286] raises a point for further discussion. The absence of the coating helps to define the possible effect of this missing element (variable) in the stratigraphy's constituents. In this case, it would appear (assuming all other factors being equal) that the absence of the coating layer on the inner surface did not affect the essential corrosion product stratigraphy when compared to the stratigraphy observed on the coated outer surface: the apparent CP stratigraphies were the same. On each side of the armour from the metal core upwards, the corrosion product stratigraphies were both firstly composed of a DPL that was then followed by a TM, which was again composed of two parts: the inner compact red-brown layer and the orange-brown porous fragmented outer layer. Due to the unknown history of the armour, it is yet again difficult to draw reliable and definitive conclusions on the phenomena responsible for this CP layer orientation.

BACKPLATE PA 329

Like the sample from Pauldron PA 316, the thinness of the metal is possibly also due to its sampling site from a manufactured and worn edge[1287].

It appears that, at some time prior to being coated, the microscopically corrugated outer surface[1288] was created. This alteration could have possibly involved

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[1284] 2.3.1.2.1 Localisation of the limitos

[1285] 4.1.3.2.1 Armour cross-section sampling site surface macrophotography & photomicroscopy, Pauldron PA 316

[1286] Figure 4-12

[1287] 4.1.3.2.1 Armour cross-section sampling site surface macrophotography & photomicroscopy, Backplate PA 329

[1288] Figure 4-16 & Figure 4-17

either removing (by physical or chemical means) any present CPs from any corrosion pits and/or simply by abrading the metal surface.

In sample PA 329, the location of the coating within the corrosion product stratigraphy of the inner surface differed from the previous sample, PA 316. The inner surface of PA 329 appears to have had little or no preparation prior to coating application since it can be seen that the coating layers were directly on top of all the CPs. This supposition is made since a mixture of non-CP particles featured under the coating: including a large white particle[1289] presumed to be exogenous. This implies that the TM was present before the application of the coating. Consequently, this differing location of the coating in the armour CP stratigraphy is alleged to be more as a result of human intervention with the coating application on differently prepared surfaces, rather than due to differing corrosion mechanisms. Yet again, such a supposition is unverifiable due to the unknown precise history of the armour.

5.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS)

Some of the discussion from the results obtained from Pauldron (part) PA RC 166 and their interpretation is also of relevance to the subsequent samples (Pauldron PA 316 & Backplate PA 329) and is therefore not repeated in detail. Of particular note is the extended discussion on the validity of inferior limitos markers in these authentic samples exposed to the real environment of the Palace Armoury.

PAULDRON (PART) PA RC 166

The heterogeneous morphology and composition determined from zone of interest $3a_1$[1290] is typical of wrought ferrous metal and corrosion products; especially of armour where slag can still be present, but in lesser proportions than expected with structural wrought iron[1291].

The greater proportion of exogenous materials indicated by particle morphologies in the outer stratigraphy is logical since this area represents the surfaces most recently accumulating particulate deposits from the atmosphere. These areas, and materials deposited therein, have also had less time for subsequent potential transformations and envelopment within precipitating CPs; making the

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[1289] Figure 4-17

[1290] Presented in Figure 4-20 and corresponding with ZOI 3_1 & ZOI 3_2 represented in Figure 4-9 & Figure 4-10

[1291] 2.1.2 Munition armour fabrication: materials & techniques deposits more recognisable towards the atmosphere interface. The lower limit to where these exogenous deposits vertically extend in the CP layers remains unrecognisable. Due to possible transformations of these deposits, it is hypothesised that only water insoluble solid atmospheric pollutants from the display and storage environment have persisted in their deposited state[1292].

The major phase material present in the dense product layer was indeed the ferrous corrosion products. Metallography performed by Vella et al. previously determined that the metal core of this sample was a ferritic iron[1293]. This implies that metallographic microstructures requiring the carbon to form steel were non-existent. The grain structure of ferritic iron therefore consists of only one phase, ferrite[1294], and is only noticeable in etched metal by ferrite's grain boundaries. When observing the now corroded metal, this former phase singularity appears to have made it impossible to distinguish between multiple similar grain microstructure phases. The absence or non-observation of former metal microstructure phases makes it impossible to identify them as potential candidates for inferior limitos markers.

The extended discussion regarding the validity of the proposed inferior limitos markers is now made in the context of the matters emanating from the results obtained from Pauldron (part) PA RC 166. Inside the dense product layer the inferior limitos markers determined from PA RC 166 cross-section SEM observation and EDS analyses included the:

- nodules of uncorroded metal; and
- slag[1295].

As previously introduced[1296], the uncorroded metal nodule surrounded by the DPL corrosion products provides an indication that this CP area is below the original surface limit i.e. it is an inferior limitos marker. Relative to its original position in the uncorroded artefact, the precise location of the metal nodule might have moved, but this is expected to have occurred in tandem with the surrounding area as it has expanded during the metal's transformation into CPs. It is not expected that the metal

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[1292] 5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties

[1293] Vella et al. 2004, p. 223 & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[1294] 2.1.2.1.1 Direct process: bloomery furnace

[1295] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

[1296] 4.1.3.2.2 Armour cross-section optical & metallographic photomicroscopy, Pauldron (part) PA RC 166 has been ejected upwards and out of these dense CP layers since a transport mechanism driving such an action cannot currently be supposed. Uncorroded metal nodules cannot be expected to act as a corresponding limitos marker since their frequency is too low and distribution too scarce to be considered always present at the limitos interface (and where atmospheric corrosion is usually most pronounced[1297]). So generally, it can be said that, at best, the usefulness of uncorroded metal as inferior limitos markers depends largely on their prevalence. Notably, such prevalence depends logically on their durability (i.e. permanence). They can be considered as potentially unstable components of the stratigraphy since these metal nodules are obviously also capable of transforming into corrosion products, thereby becoming less prevalent over time. It is therefore proposed that metal nodules are likely to be more useful inferior limitos markers on less corroded materials or where corrosion mechanisms permit residual metal near the surface. In any case, the ability to consistently rely on uncorroded metal as an inferior limitos marker is heavily dependent on and overridden by its inherent instability and consequential non-permanence.

The permanence of slag inclusions, however, provides a useful contribution to the collection of potential inferior limitos markers. From the morphology (shape, features) and composition (vanadium, titanium, chromium, aluminium, for PA RC 166) of the small and larger globules in the uncorroded metal core and in the dense product layer[1298], it is clear that these features are slag remaining from manufacture or the ore. Such slag inclusions composed specifically of these elements in the form of vanadium and chromium oxides (V_2O_5, Cr_2O_3) have been reported in the literature to appear in the wüstite phase of slags together with manganese and aluminium. The presence of this type of slag is possibly explained by the smelting of the metal from the "…magnetite ore, which is known to contain accessory chromite and vanadium-titanium minerals"[1299, 1300, 1301]. As outlined previously[1302], the proposed predominant

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[1297] 2.2.3.2 Filiform corrosion/corrosion product morphology & 2.2.3.3Uneven local to uneven general corrosion/corrosion product morphology

[1298] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

[1299] Buchwald & Wivel 1998, pp. 91-92

[1300] As an aside: the *concentrations* of titanium, vanadium and chromium in vanadium and chromium oxides slags have been claimed to be indicative of the ore smelting process applied to derive the metal: greater concentrations (of 1-2 orders of magnitude) occur in slag inclusions found in metal obtained via the indirect process as opposed to via the direct process (Dillmann et al., 2002, p. 332)

[1301] 2.1.2.1 Metal extraction & processing pollutant source, limewash, also contains the aluminium, titanium and other elements found in the slag and therefore potentially poses confusion regarding its attributed source. It is the morphology of these vanadium-rich slags with their concurrent distribution isolated inside the uncorroded metal[1303] that proved their origins and valid discrimination as inferior limitos markers. The distribution of the inclusions here in the DPL of PA RC 166 is irregular, so they cannot be used alone as a definitive corresponding limitos marker.

The major phase present in the transformed medium, by both observed morphology and analysed composition, was the ferrous corrosion products (indicated by iron and oxygen[1304]), but notably with greater porosity than the DPL. The TM's irregularly striated/laminated morphology made a strong contrast with the compact DPL below and the recurring distribution of this striated feature helped identify it as one overall part distinguishable from the DPL. The TM's striated morphology resolved with the SEM[1305] is unexplained, but is thought to maybe correspond with the layered formation over time of CPs by precipitation during alternating wet and dry cycles[1306]; more specifically, during the theoretically established cyclical precipitation of ion pairs out of supersaturated liquid layer solutions during CP formation[1307].

A revised proposition of the TM/DPL interface was based on the porosity of the CP layers as marked by calcium concentration gradients[1308]. It is proposed that the mobility of calcium species (dissolved Ca^{2+}?) and the relative porosity of the CP layers permitted its migration, but only until the impermeable metal. The increased calcium (from limewash?[1309]) concentration in the revised area is thought to be attributable to the greater porosity of the transformed medium, when compared with the dense product layer. Separate electrochemical studies on the porosities of the dense product layers of archaeologically buried iron[1310] and unalloyed hypoeutectoid steel[1311] demonstrated a capability of species transport (particularly dissolved

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[1302] 4.1.2.1 Armour Hall aerosol pollutants' SEM-EDS: results

[1303] Figure 4-20 & Table 4-4: Spectrum 2

[1304] Figure 4-20 & Table 4-4, Figure 4-21 & Table 4-5, Figure 4-22 & Table 4-6

[1305] Figure 4-20, Figure 4-21 & Figure 4-22

[1306] 2.2.2.3.2 Atmospheric water, Time of wetness/dampness & humidity cycles

[1307] 2.2.2.2.4 Corrosion product precipitation & 2.2.2.2.5 Corrosion product coalescence

[1308] Figure 4-23

[1309] Table 5-1

[1310] Vega et al, 2007, pp. 94, 98

[1311] Pons et al, 2007, pp. 78, 90

oxygen) in these DPLs that is facilitated by its porosity. Studies on porosity of atmospherically corroded ferrous artefacts demonstrated a greater porosity in atmospherically corroded materials (circa 50%) when compared with archaeological materials (circa 25%)[1312] suggesting greater capability of species transport in atmospherically corroded ferrous materials. It would appear here that the form of calcium present in the sample is the antitheses of barium sulphate, in terms of its prevalence and solubility. It is possible that the solubility of calcite could reduce its long-term morphological observation in the form of particles and permit the permeation of the dissolved calcium though the porous striated/laminated corrosion product layers of the transformed medium (transcorrosion product layer mobility[1313]). An alternative explanation, or indeed more likely, a dual explanation for the presence of calcium in the TM corrosion products is the precipitation of CPs onto surfaces already containing deposited calcium species. Eventually over time the voluminous corrosion products emanating from the DPL and metal to form the TM have incorporated the calcium-based material into the TM's structure.

On the one hand, the apparent lack of human intervention on Pauldron (part) PA RC 166 meant that its CP formation could be more readily interpreted since less doubt was introduced by unknown interventions. Momentarily removing this large indeterminable variable, which is of high significance for this collection of largely historically intervened surfaces provided more solid foundations for the cases where the nature of interventions on CP layers is more uncertain (e.g. Backplate PA 329). On the other hand, such a sample could not represent those recently or historically intervened armour.

PAULDRON PA 316

A major distinction between samples from Pauldron PA 316 and Pauldron (part) PA RC 166 was the presence of the coating (circa 20µm thick) that separated the dense product layer from the transformed medium. The transformed medium of PA 316 was also different from Pauldron (part) PA RC 166: the TM on this sample did not feature the striated layers of corrosion products running parallel with the DPL interface as noted previously[1314]. Instead, the morphology of the TM on this sample

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[1312] Vega et al, 2007, p. 98

[1313] 5.1.2.2 Armour Hall aerosol pollutants' SEM-EDS: evaluation of potential superior limitos marker properties

[1314] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

was characterised by lumps or spheres of corrosion products with a comparable atomic contrast to the minority lighter phase in the DPL counterpart below[1315]. The absence of the parallel striations of the TM on PA 316 was perhaps a consequence of the coating positioned between the DPL and the TM. Perhaps the coating prevented this surface-laminated appearance because corrosion product deposition could only occur where the coating was defective; thereby permitting local CP extrusion.

BACKPLATE PA 329

This sample represents surfaces of armour that have been previously corroded, then partially or completely stripped of corrosion products, but not (yet) recorroded. Figure 4-32 & Figure 4-33 are good examples of where the previously stated[1316] context-adapted definition of the limitos for these historically intervened armour is most marked. In these examples, the limitos, or rather the sub-surface remnants of the limitos, can at best be proposed to be located in the compact corrosion products inside the largely/partially stripped corrosion product pits. These remnant DPLs are not expected to exhibit surface information from the last metallic state, since any such surfaces would have likely been removed during the former corrosion product removal intervention. For armour surfaces that have previously been stripped of most corrosion products (thereby only leaving remnants of the dense product layer inside pits) nothing can be done for preserving the limitos since this has already been lost. The remnant limitos substrate should however be conserved by a conservator who is assessing the condition of such an armour.

5.1.3.2.4 Armour cross-section Raman micro-spectroscopy

PAULDRON (PART) PA RC 166

Compared with the darker[1317] corrosion product phase, goethite, it would be expected that the whiter appearance of the phase identified as ferrihydrite could potentially be attributable to its molecular formula and its higher percentage atomic weight of iron. However, "…there is no consensus on the crystal structure of this mineral[1318]" and "No single formula is widely accepted for ferrihydrite and this is attributed to variable water content and a lack of a known crystal structure"[1319]. On

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[1315] Figure 4-25

[1316] 2.3.1.2.2 Definition of the limitos for the Palace Armoury's historical munition armour

[1317] Observed by either OM or SEM BSE.

[1318] Michel et al., 2007, p. 1

[1319] Ibid.

the one hand, according to the formula for ferrihydrite ($Fe_5HO_8.4H_2O$) given by Cornell & Schwertmann (2003)[1320], the percentage atomic weight of iron present in the compound should be 58%. Meanwhile, Antony et al. quote a past edition of Cornell & Schwertmann (1991) with ferrihydrite having a formula of $Fe_2O_3·4–5H_2O$[1321], making an atomic weight of 45-48% iron. Both of these cited formulae for ferrihydrite imply an atomic weight percent of iron that is below goethite's iron content: 63% atomic weight[1322]. Indeed, if a difference in atomic contrast between unmixed phases of goethite and ferrihydrite would be discernable via SEM BSE imaging on these polished samples, then it would be expected to be the opposite of the contrast observed. That is to say goethite should be lighter than ferrihydrite. On the other hand, in possible agreement with this study's observations, the more recent work of Michel et al. (2007) reports the ideal molecular formula of ferrihydrite as being $Fe_{10}O_{14}(OH)_2$[1323], making a higher percentage atomic weight of iron content (68%) than for goethite and the previous citations for ferrihydrite.

The recurring outer layer position for akaganéite in the corrosion product stratigraphy is probably due to a source of chlorides (from the atmosphere) necessary for its formation. The location of akaganéite close to the atmosphere is in agreement with Monnier's finding on the Amiens iron[1324].

PAULDRON PA 316

The apparent association of unmixed ferrihydrite in the lighter minority DPL phase[1325] proposed to contain carbides could merely be coincidental or perhaps be an influential result of carbides on the corrosion processes[1326].

BACKPLATE PA 329

The limited results obtained from the Raman micro-spectroscopy on PA 329 did not further discussion.

[1320] Cornell & Schwertmann, 2003, p. 2

[1321] Antony et al., 2007, pp. 7757, 7759

[1322] Ibid, p. 7757

[1323] Michel et al., 2007, p. 2

[1324] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1325] Figure 4-26 & Figure 4-40

[1326] 2.2.2.3.5 Ferrous metal type

GENERAL RAMAN MICRO-SPECTROSCOPY DISCUSSION

Results obtained for the predominant species of ferrihydrite and goethite are reflected by the published results from indoor architectural iron fastenings atmospherically corroded in France and Belgium[1327].

The CP phases of this current study on munition armour have either been detected separately or as mixtures. This could mean that the beam (circa 3µm[1328]) has overlapped different adjacent phases or more likely, given the frequency of occurrence, different phases were intimately mixed on a sub 3-micron scale. A difference in the physical arrangement of the CP layers (porous versus compact), rather than any differences in their chemical composition (similarly ferrihydrite and goethite), appears to form a more promising means of assisting determination of the limitos in these atmospheric ferrous corrosion products: the complex, unparallel and intimate mixtures of atmospheric ferrous corrosion products cannot simply be discriminated as discrete layers of differing CP phases. These proven intimate mixtures of CP phases further emphasise the difficulties one would have if using colours alone as an indication of the limitos[1329]. Alone, physical qualities (e.g. porosity/compacity) of the CP layers appear to provide a more significant contribution than chemical composition or phase colours.

The precise cause for the fluorescence phenomenon encountered from these cross-sections is worthy of further investigation and without this work confident interpretation of its specific cause/s cannot be made. The cause could be the presence of an organic coating/embedding resin or from the inherent asperity of the transformed medium[1330]. It has been suggested that the fluorescence corresponds to possible interventions on the armour such as the addition of a coating[1331]. However, considering the numerous cited examples where fluorescence coincided with asperities and also with areas where it is supposed coatings could not penetrate, it is hypothesised that such fluorescence is in most cases exclusively attributable to surface asperities. Indeed, it appears that fluorescence interference, the instrumental limitation of Raman micro-spectroscopy, has serendipitously indicated[1332] a further means of discriminating between the dense product layer and the transformed

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[1327] Neff et al 2006, pp. 1228-1237

[1328] 3.5.3 Raman micro-spectroscopy

[1329] 2.3.1.2.1 Localisation of the limitos

[1330] 3.5.3 Raman micro-spectroscopy

[1331] Monnier, 2005a, p. 14

[1332] Figure 4-38 & Figure 4-39

medium: it is possible that the roughness and porosity of the transformed medium could provide a means for differentiating between it and the dense product layer below. And if the limitos is definable by the interface between the DPL and the TM, then the predominating differential surface roughness/porosity of these layers could indeed be detected with a Raman spectrometer, or another instrument better suited to the task. Such an application would only function for diagnostic purposes where cross-sections are available and would therefore not be deemed appropriate as an everyday conservation tool where conservators approach the artefact by a plan perspective.

The identification of the corrosion products formed on these three munition armour samples elicits some discussion concerning the stability of the CP layers and their specific influence on possible corrosion of the remaining metal. The predominant presence and association of goethite and ferrihydrite might suggest that the ferrihydrite is converting to the thermodynamically stable state of goethite[1333]. Also of particular note is the presence of akaganéite and lepidocrocite; two iron oxyhydroxides having particular corrosive properties in addition to the generally adverse physical properties afforded by the other common ferrous corrosion products[1334]. The presence of some akaganéite on the samples that could have developed after contamination with chlorides from the marine atmosphere is of major concern to the armour's longevity and should provoke action regarding the Palace Armoury's environmental conditions and investigation of possible means of interventive stabilisation treatments to remove or counteract chlorides. The presence, albeit comparatively small, of lepidocrocite next to the metal[1335] and within the corrosion product layers[1336], suggests possible corrosion activity via Stratmann's atmospheric corrosion model involving lepidocrocite reduction[1337].

The non-detection of magnetite by Raman micro-spectroscopy on these samples is surprising considering the typically reported composition of atmospheric ferrous corrosion product layers, where magnetite is often located between the metal interface and iron oxyhydroxides nearer the atmosphere[1338], and is in contrast with previous μXRD results from the same armour. These μXRD studies detected

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[1333] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1334] 2.2.2.3.4 Ferrous corrosion products

[1335] ZOIs $3b_1$ & $3d_1$ on PA RC 166 (Figure 4-37 & Figure 4-39)

[1336] ZOIs $3a_1$ & $3c_1$ on PA RC 166 (Figure 4-38 & Figure 4-36)

[1337] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1338] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products magnetite on 42% of the *total (n = 52) samples extracted from various locations* on the same three armour studied here[1339]. Moreover, the µXRD results from the *one sample*[1340] *extracted from the same side and zone adjacent to the cross-section sampling site* did indeed reveal magnetite. Notably, the µXRD analyst provided a relative-quantitative indication[1341] of a smaller amount of magnetite compared with the other detected phases of goethite, akaganéite and lepidocrocite[1342]. In spite of the unsatisfactorily small statistic, this non-detection of magnetite in areas where its presence would actually be suspected could be attributable to the known limitation of Raman spectroscopy; where spectra peaks from larger concentrations of goethite are known to mask identification of smaller magnetite spectra peaks[1343]. To fully characterise the corrosion products' phases, the complementary technique of XRD[1344] would have been desirable to perform on cross-sections[1345] of the CP stratigraphies. However for the principle aim of this research, determination of the limitos, this was not necessary since it appears the limitos cannot simply be determined from structural composition.

5.1.3.2.5 Conclusions from armour corrosion cross-section observations & analyses discussion

The heterogeneous composition of the armour is typical of past forged ferrous metals[1346]. Strong similarities between the three samples were evident especially in terms of the overall layout of the ferrous CP stratigraphy and the presence of slag inclusions. The possible locations of the limitos hypothesised from these cross-section perspectives depended on each particular armour and the interventions that it had historically experienced. Of the superior limitos markers identified from the armour cross-sections, the protective coating is undoubtedly the most useful one for a conservator who is assessing the position of the limitos. The typically complete surface coverage of a coating is useful not only for distinguishing the corrosion products that are above it, but with the appropriate solvent, also helps their removal as their underlying supporting substrate is dissolved and removed. The problem

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[1339] Table 2-1
[1340] i.e. sample 58 from PA RC 166
[1341] µXRD sample 58 (PA RC 166): goethite, akaganéite, lepidocrocite, magnetite (un peu) = a little
[1342] Monnier, 2006
[1343] 3.5.3 Raman micro-spectroscopy
[1344] 3.5.3 Raman micro-spectroscopy
[1345] Reflection on the existing embedded samples or transmission on thin sections
[1346] 2.1.2 Munition armour fabrication: materials & techniques

remains, however, that it is difficult to know which CPs below the coating belong to the limitos and which ones are still superior to the limitos.

The observed boundary (marked by compactness/porosity differences) between the transformed medium and the dense product layer on local to general corrosion product morphologies probably represents the corresponding limitos marker that is required to localise the limitos. Since the basic composition of these two layers has been proven to be comparable (i.e. essentially complex mixtures of goethite and ferrihydrite[1347]), their morphology difference (i.e. varying porosity) rather than compositional difference, appears to provide a form of layer delineation. Structural differences of the layers, if sufficiently thick, might facilitate sensitive means of their physical separation i.e. by cleavage. Capitalising on these observed micrometric morphological differences between layers, especially when observed by plan perspective, might not prove so easy. However, before this is attempted it must be ascertained that the interface between the DPL and the TM truly corresponds to the limitos: from the armour cross-section investigations the boundary *appears* to form a corresponding limitos marker.

Of the three types of inferior limitos markers (i.e. slag inclusions, uncorroded metal nodules, carbide microstructures) identified on the armour cross-section samples, none could be considered as potentially useful to a conservator who is cleaning corrosion products from armour. While the slag inclusions and carbide microstructures were nonetheless useful for the diagnostic purposes of this investigation, slag inclusions and metallographic microstructures in armour are far too small to be observable to a conservator, even when assisted by a binocular microscope during localised stratigraphic probing. Detecting such small features requires the higher magnifications of non-standard binocular microscopes and they also rely on sequential polishing of surfaces to optimise their detection. Meanwhile, uncorroded metal nodules, due to their reflectivity in CPs, could possibly be observable; depending on their size and the magnification used. However, the practical value of metal nodules as inferior limitos markers is doubted since their size is small (the largest was circa 0.1mm or 100µm wide[1348] and the smallest ones were 0.01mm or 10µm wide[1349]), their distribution is low (i.e. they were generally located

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[1347] 4.1.3.2.4 Armour cross-section Raman micro-spectroscopy

[1348] Figure 4-10

[1349] Figure 4-35

in isolated areas) and they experience low-permanence[1350]. If it is eventually proven that the DPL is actually an inferior part of the limitos then the overall presence of this continuous and relatively compact material would be the most appreciable quality of the limitos a conservator could use as an inferior limitos marker.

Although inferior and superior limitos markers were identified on the armour cross-section samples, the main problem they presented was the absence of an indisputable corresponding limitos marker. Often the identified inferior markers were already obviously below the profile of the last metal surface; as the higher positioned uncorroded metal surrounding the corrosion pit indicated. Only the sample from Pauldron (part) PA RC 166 featured corrosion products that were significantly above the corrosion pit level.

Since potentially present former metal microstructures were unobservable in the CPs. it was not possible to ascertain any similarities differences in the location of the limitos pertaining to the three types of metal microstructures[1351] in the armour samples[1352].

Overriding all these factors in diagnostically determining the presence of the limitos in these authentic armour is the inherent uncertainty that the armour presents. That is to say, it is difficult to have confidence in hypotheses that are drawn from the condition of materials that have been subjected to unknown histories and environments. It was for this reason it was decided to fabricate the armour analogue materials and observe the degradation and change of the metal's original surface to the original surface limit supported by corrosion products. Controlling the history and environment of the armour analogues was anticipated to facilitate confident interpretation of the corrosion mechanisms that alter the metal's surface when transforming into CPs. It was anticipated that a corresponding limitos marker might be identifiable on these purposefully designed diagnostic experimental materials.

[1350] 5.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

[1351] Iron, ferrite; steel, ferrite with carbides; steel, Widmanstätten ferrite-pearlite (Table 3-1) & Appendix E – Microstructures of the three Palace Armoury munition armour samples selected for cross-section investigations

[1352] Although it is not expected varying locations for the limitos would be present on these similar ferrous metals.

5.1.4 AUTHENTIC MUNITION ARMOUR CORROSION PRODUCT REMOVAL: THE PALACE ARMOURY TECHNIQUE

There are several noteworthy points on the Palace Armoury's munition armour cleaning technique:

- The deep, yet narrow diameter pits probably caused the incomplete removal of corrosion products from step 5 of the Palace Armoury CP cleaning technique.
- The grey metal colour observed on the acetone-moistened toilet tissue, which was used to remove the rottenstone, abraded "grit & dirt" and oil (3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique: image 5b), probably evidenced erosion of the metal surface. It is expected that the grey metal colour came mainly from the armour surface since it is less abrasive than the steel wool.
- Cleaning is performed without magnification (i.e. by the naked eye)

5.1.4.1 Conclusions from the Palace Armoury's corrosion product removal technique

Several important issues can be concluded from observing the current corrosion product removal technique, which is currently performed on the munition armour by staff at the Palace Armoury:

- Distinction between limitos and non-limitos corrosion products cannot be made without magnification
- The combination of localised corrosion products with non-localised CP removal techniques results in polishing adjacent metal
- The extent of corrosion product removal is more limited by the practical inability to remove CPs from deep pits without damaging the adjacent metal; rather than being governed by a philosophical intent such as conservation of any preserved original surface limits or levelling with adjacent metal profile

5.2 MUNITION ARMOUR ANALOGUES: LABORATORY CORROSION CASE STUDIES & DESTRUCTIVE INVESTIGATIONS

5.2.1 ARMOUR ANALOGUES, LIMITOS DETERMINATION: CORROSION/CORROSION PRODUCT MORPHOLOGIES & LIMITOS INVESTIGATIONS

This first objective for the armour analogues, "Characterisation of corrosion product stratigraphy and metal leading to limitos determination", was the most important component of the current research question since it aimed to diagnostically determine the limit of the original surface in CPs in a laboratory, hence controlling otherwise largely indeterminable variables of history and environment. This vastly improved certainty is the most outstanding contribution that these contemporary coupons could provide to complement the information provided by the authentic armour.

5.2.1.1 Plan perspective investigations

Because of the thin nature of the corrosion product layers it is supposed that the more practically determinable markers were observed features on layers (i.e. micro-grooves), instead of layer interfaces (i.e. tactile characteristics). These thin layers did not always have significantly appreciable differences via the manual senses employed during physical cleaning[1353]. Furthermore, inconsistencies in the physical tenacity, or indeed fragility of otherwise similar appearing CP structures (CP6c from Coupon Series 1) sometimes made these properties unsuitable for helping delineate between corrosion product layers by manual means. Micro-grooves provided a more certain marker than sensitive properties, which like all markers ought to be used in conjunction with as many complementary markers as possible.

It was thought that the non-observation of micro-grooves on the surface of CP6c that featured CP4s might be attributable to the destruction of any micro-grooves during the formation of the bright orange caps (CP4s). This is even more convincing when considering that the otherwise identical black domed and smooth blisters (CP6c) without any bright orange caps (CP4s) always featured micro-grooves[1354].

Although it is deemed highly probable that CP5c is a corresponding limitos corrosion product, there is, at present, no conclusive evidence to support this supposition. Evidently, assertions made via indirect evidence are not as reliable as those made via direct evidence, but in the practical scenario of a conservation laboratory decisions must be made and retaining such supposed limitos CPs is a safer, more conservative intervention choice.

Superior limitos markers obviously included the exogenous applied superior limitos materials, including the deposited barium sulphate[1355] (or respectively zinc oxide/barium sulphate and gold for Coupon Series 4 & 6) and the Paraloid B-72™ coating[1356]. Unlike most buried archaeological artefacts, the coating and its use as a superior limitos marker is especially relevant to armour and other similar historical artefacts that are coated/painted (contemporarily). It seems logical that the corrosion products that have perforated and/or deposited on top of the coating cannot

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[1353] 2.3.1.2.1 Localisation of the limitos

[1354] Table 4-10 & Figure 4-48: Images 5 & 6

[1355] Figure 4-48, image 2: D3s

[1356] Figure 4-48, image 3: D2s

correspond to the limitos as outlined earlier[1357]. If further time (i.e. years) was permitted during acceleration corrosion, then it might be expected that further CP precipitation on top of the coating would occur and the coating's value as a superior limitos marker would increase significantly.

The thick filiform with shallow corrosion that left micro-grooves relatively uncorroded[1358] was in contrast with the quoted theory stating that thicker filaments are indicative of "…more vigorous corrosion"[1359]. The micro-grooves under the thicker filiform filaments are theorised to have remained since corrosion was simply too superficial to fully corrode these surface details; demonstrating the obvious notion that corrosion does not corrode all details if the details are high enough and corrosion is sufficiently superficial.

Of significance to conservation practice, particular limitos structures, such as CP5c[1360] and fragmented versions of CP6c and CP7c[1361] were considered very fragile. Therefore these structures would be difficult to preserve during routine surface interventions, like surface dusting and coating removal and replacement.

Several corrosion product morphologies from Coupon Series 1, classified as CP5c, CP6c and CP7c, were very similar in morphology. It is suggested they were formed from the same or similar corrosion processes and that they represented different stages or extents of the corrosion process. They could be considered variations or evolutions of the same classification. Even CP8c (filiform morphology) was very similar to corrosion product morphologies CP6c and CP7c since they all featured a red-dark brown outer crust with corresponding limitos micro-grooves. Filiform corrosion has indeed been referred to in the literature as a type of pitting corrosion that spreads laterally, rather than vertically into the metal[1362]. To exemplify this point, a sample exhibiting filiform corrosion was polished to remove superior CP layers; a series of consecutive pits became evident (Figure 5-2). The depth of each pit varied, but, as according to the filiform corrosion mechanism, the metal corrosion was superficial and proceeded laterally to new corrosion sites across the surface, rather than more or less vertically into the substrate, as for pitting corrosion.

[1357] Figure 4-48, image 1: CP1s

[1358] Figure 4-52: Bottom right

[1359] 2.2.3.2 Filiform corrosion/corrosion product morphology

[1360] Figure 4-47 & Figure 4-48: globular tubercle corrosion products

[1361] Figure 4-50: black domed and rough irregular corrosion products

[1362] 2.2.3.2.1 Filiform corrosion mechanism

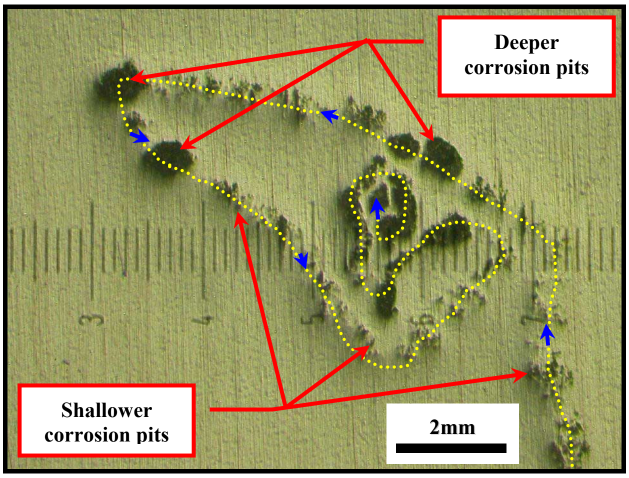

Figure 5-2 Armour analogue lateral-section, Coupon Series 1: Subsurface laterally polished metal with filiform corrosion filament (that has self-terminated as indicated by direction of blue arrows).

It is suggested that the brief, discontinued activity of the corrosion pits of the transient filiform corrosion filament was responsible for maintaining the limitos in the resulting CPs. If, like pitting corrosion, filiform corrosion could also continue further into the metal, then subsequent production of corrosion products would force the CP limitos layer to fragment under the pressure of new underlying and expanding CPs. Indeed, this phenomenon also potentially explains why examples of the micro-grooves on local to general corrosion product morphologies varied widely in preservation condition. Accordingly it can be summarised that:

> Preservation of former ferrous metal surface details in corrosion products, which evidence the limitos, decreases with an increase in the extent of corrosion occurring underneath.

The displacement of limitos CPs on wrought iron buried in an archaeological environment has already been noted[1363]. Based on these present experimental observations, it is thought that corrosion of rolled low-carbon steel, even in an atmospheric environment, is quite similar, but is of course generally less detrimental to the metal due to a less aggressive environment and usually shorter exposure time. Such parallels should not be unexpected, providing fundamental conditions of corrosion between the atmospheric and burial conditions are the same; whether an oxidising (aerobic) or reducing (anoxic) environment is present. Anoxic, as well as aerobic conditions, can occur in burial environments and depend largely on the burial medium.

[1363] Figure 2-47

5.2.1.1.1 Summary of plan perspective investigations' discussion

The visual clarity, and therefore reliability, of the micro-grooves contributing as a corresponding limitos marker depended largely on the corrosion morphology (and the underpinning corrosion mechanism). For the case of local to general morphologies (pitting corrosion mechanism?), a deeper and longer corrosion duration probably decreased the limitos' preservation. Whereas filiform corrosion's superficial and lateral propagation ensured the limitos was preserved. The corrosion mechanisms and resulting morphologies were affected by surface conditions such as the presence and type of applied superior limitos marker.

The determined limitos location for the munition armour analogues i.e. the interface between the dense product layer and the transformed medium is comparable to the location published for archaeological wrought iron[1364] and possibly that supposed from the authentic munition armour cross-sections[1365].

5.2.1.2 Cross-section perspective investigations

As mentioned previously[1366] and as probably exemplified in Figure 4-56, since the coating had an adhesive effect and it was applied directly onto the applied superior limitos markers, it can be expected that these markers might have also followed the coating when the underlying and expanding corrosion products displaced it. In the given cross-section (Figure 4-56 & Table 4-12) it is unclear whether the interface of the coating faithfully corresponded with the limitos, especially since the isolated particle of barium sulphate (Spectra 3) could not mark the whole width of the stratigraphy. Also, the barium sulphate marker was positioned too off-centre to assist determination of the limitos position in other areas; particularly in respect to the interface between the morphologically differing corrosion product phases of CP4s and CP6c.

By inference with the results from Coupon Series 1, in 4.2.1.1 Plan perspective investigations, it is supposed that the corrosion products presented in Figure 4-56 probably correlate with those already observed in Figure 4-48 (images 5 & 6) and documented in Table 4-10: the orange acicular CPs in Figure 4-56 are likely to represent CP4s, while the domed structure represents CP6c and the

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[1364] 2.3.1.2.1 Localisation of the limitos
[1365] 4.1.3.2.5 Summary of armour corrosion cross-section observations & analyses results
[1366] 4.2.1.2 Cross-section perspective investigations

corrosion products underneath represent CP9i. During other results interpretation, CP structures between different Coupon Series (e.g. filiform or globular tubercle morphologies) were also considered alike. The valid transferability of assessments made on corrosion product structures between differently prepared experimental substrates (such as Coupon Series 1 & 6), or even between identically prepared substrates could be questionable, especially since a multitude of CP morphologies exist; each with their varying extents of development.

It is tentatively surmised, based on the SEM-EDS investigations and the bright orange aspect (Figure 4-56 & Table 4-12), that some iron hydroxyoxide/s could be present in the acicular CPs. Structural characterisation analyses like XRD and Raman-spectroscopy are required for confirmation. It is reminded that the precipitation of some iron oxyhydroxides physically damage structures during formation[1367] and this could help explain any such possible disappearance of the normally present micro-grooves as noted in 4.2.1.1 Plan perspective investigations and discussed in 5.2.1.1 Plan perspective investigations (i.e. CP6c capped with CP4s).

Based on the cross-section results from the authentic steel armour (PA 316 & PA 329)[1368], it was similarly expected and subsequently evidenced[1369] that the steel armour analogue's metal microstructures (i.e. ferrite-pearlite and Widmanstätten ferrite platelets with pearlite[1370]) would not be resolvable in any of the expanded corrosion products. The fragmentation of CPs in Figure 4-60 (Middle & Bottom) and Figure 4-61 could be attributable to the embedding preparation process, but it is instead suspected that it is evidence of the fragmentary nature of the expanded voluminous CPs. Such fragmented corrosion products could help explain why very few traces of micro-grooves were found in the CPs on Coupon Series 4 and why microstructures were not observed in cross-section on any Coupon Series.

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It would appear that one or more explanations are responsible for the absence of discernible trends in the presence of manganese in the metal and corrosion products in the preliminary survey:

[1367] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products

[1368] 4.1.3.2.5 Summary of armour corrosion cross-section observations & analyses results

[1369] 4.2.1.2 Cross-section perspective investigations

[1370] 3.3.1.1 Metal selection & substrate preparation & Appendix F – Microstructures of munition armour analogues.

1. The manganese concentration is too low for the EDS detection limits; and/or
2. The manganese concentration is too heterogeneously distributed for point analyses and small area analyses.

For a thorough evaluation of the use of manganese as an inferior limitos marker the distribution of manganese in the uncorroded metal and corrosion products would need to be further studied and with instrumentation with lower detection limits.

The zones surveyed with EDS[1371] represented corrosion products areas that could be considered under the proposed limitos, i.e. within the dense product layer. Notably, analyses on a site featuring the very outermost CP phases of the transformed medium are still required and might suggest that the manganese is indeed exclusively an inferior limitos marker. Such investigations would again require more sensitive instrumentation since it is probable that the relative percentage of manganese in the steel after corrosion has decreased furthermore due to the significant addition of oxygen and contamination of the TM with superior limitos markers. This would push the relative concentration of manganese below the optimum detection range on the EDS; introducing greater uncertainty in results.

This preliminary experiment by EDS point and area analyses determined that the detection of manganese distribution under the limitos was extremely variable and the technique requires further development especially in surveying greater quantities of zones of interest corrosion products above and below the proposed limitos and on greater quantities of cross-sections from all of the Coupon Series. Since the relative quantity of manganese in the metal is already at the detection limits of the EDS confidence in the results found for manganese above the metal should be regarded with scepticism.

5.2.1.3 Applied superior limitos markers review

The validity of using the applied materials ($BaSO_4$, $ZnO/BaSO_4$ & Au and also the Paraloid B-72™ coating) as superior limitos markers is subject to some discussion since it was not always clear that they corresponded to a limitos interface immediately below: indeed there were cases of corrosion morphologies where it was probable the limitos corresponded to a corrosion product layer further down in the CP strata[1372]. With the present applied superior limitos protocol it was clear that the

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[1371] Figure 4-64, Figure 4-65, Figure 4-66 & Figure 4-67

[1372] Figure 4-57, Figure 4-58 & Figure 4-59 validity of each marker needs to be judged on each specific marker and corrosion case. The Paraloid B-72™ coating that was applied on top of all the investigated applied superior limitos markers also had its influence since it effectively adhered to these applied superior limitos markers. If the uppermost corrosion product morphologies only consisted of a dense product layer, then this effect did not pose a problem in the determination of the limitos. The filiform and globular tubercle corrosion product morphologies (Coupon Series 6: Figure 4-54 & Figure 4-55) are good examples of unambiguous determination of the limitos between the applied superior limitos marker and the micro-grooves since an intermediate layer of CPs had not formed between these features.

Overall, gold, although not yet fully developed as an applied superior limitos marker, was the best performing of the three types trialled and has the most promising potential for further development. Gold's superior performance is attributed to the thin and even vertical and lateral distribution, and possibly also its chemical non-reactivity. In plan perspective, gold's thinness conformed to the micro-grooves and therefore did not mask them from optical observation or SEM observation/EDS analyses[1373]. The finer and complete surface distribution of gold on the globular tubercle corrosion product morphologies on Coupon Series 6[1374] can also be seen to be of greater diagnostic use than the white powdered superior markers. The upward displacement of the formerly flat surface is perceptible thanks to the gold marker present on the globular tubercle CPs.

As expected from the preliminary glass slide tests[1375], in cross-section perspective at high (1500x) SEM BSE magnification the sputtered gold with its sub-micron thickness was immediately contrasting and visible even on corroded and deformed surfaces (Figure 4-59). However, with the quantities of gold applied in this experimentation, the gold superior limitos marker layer was not clearly resolvable in cross-section at the highest magnifications provided by the optical microscope (200x) (i.e. without objective lens solutions). Occasionally, an isolated point of gold reflection was discernable via optical microscopy, but this was considered insufficient for diagnostic purposes. During stratigraphic probing in plan perspective, the minute gold particles were quite difficult to remove from the corrugated surfaces

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[1373] As expected due to its usual application in sample preparation for SEM-EDS

[1374] Figure 4-55

[1375] 3.3.1.1.4 Applied superior limitos markers and were not always removable without damaging some CP structures; this was not considered a problem for these diagnostic purposes.

It is probable however that the gold acted as a galvanic catalyst due to its far superior placement to iron in the electromotive force series[1376]. Providing it remained a catalyst and was thus not involved in the corrosion product precipitation and morphology formation, then gold's presence is not deemed to be of significance. As with any porous, surface applied material, it was possibly an initiator of differential aeration corrosion[1377]. Since differential aeration was to be encouraged during the laboratory accelerated corrosion regime, and since the resulting corrosion product morphologies were representative of the armour they were attempting to emulate, any such effect does not appear to have been detrimental.

As for the white pigment markers ($BaSO_4$ and $ZnO/BaSO_4$), their white appearance proved a useful contrast to the iron oxides observable while under optical microscopy with visible light. The staining of the white pigment with ferrous ochres was obvious; thereby evidencing outward migration of CPs. However, their uneven (i.e. thick to absent) vertical and lateral distribution was unsatisfactory and was responsible for obscuring the surface from observation prior to stratigraphic probing. It was earlier[1378] hypothesised that the superior limitos marker pigments, $ZnO/BaSO_4$, on Coupon Series 4 had an effect on the corrosion process and also reacted together with the corrosion products; consequently forming a conglomeration that was difficult to remove. The only difference in surface preparation and corrosion exposure between Coupon Series 4 ($ZnO/BaSO_4$) & 6 (Au) was the applied superior limitos marker materials; thereby demonstrating the significant influence of surface materials on corrosion processes and limitos preservation.

As already detailed[1379], the addition of zinc oxide to the marker did not prove as useful as anticipated under the optical microscope with ultra-violet light excitation, since contamination of the zinc oxide with the ferrous corrosion products inhibited fluorescence in the areas where it was required most for diagnostic purposes. Regarding the barium sulphate applied superior limitos marker under SEM in BSE mode, the x-ray opaque barium proved visually easily identifiable due to its extreme white appearance compared to the grey CPs. Energy dispersive spectrometry

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[1376] 3.3.1.1.4 Applied superior limitos markers

[1377] 2.2.2.3.3 Atmospheric pollutants, Solid aerosols

[1378] 4.2.1.1.1 Summary of armour analogue corrosion plan perspective investigations results

[1379] 4.2.1.2 Cross-section perspective investigations

confirmed this distribution as the contained sulphur correlated with the barium signal.

The thin film (5%m/v) of Paraloid B-72™ could also be considered a superior limitos marker[1380], although this was not its principal intention. Despite its intended benefits of simulating organic coating covered authentic artefacts, and the causal effects on corrosion mechanisms by the Paraloid B-72™, the coating appears to have prevented some corrosion products from depositing above it[1381]. Coatings can therefore only be definitively used as a superior limitos marker and not definitively used as a corresponding limitos marker in corrosion product stratigraphies. The Paraloid B-72™ coating had more acute implications for the three intended applied superior limitos markers ($BaSO_4$, $ZnO/BaSO_4$ & Au): the coating consolidated or bound them into a relatively consistent polymeric film. Even though the film was intentionally very thin[1382] and was very often perforated by CPs, this film layer has limited to an undetermined extent the effectiveness of the superior limitos markers in their role to delineate the limitos between the superior and inferior limitos corrosion products.

5.2.1.4 Armour analogue discussion & corrosion/corrosion product morphologies' validity

The following discussion cautiously links the results interpretation into the practical scenario of applied conservation, such as that faced by a conservator responsible for the partial removal of corrosion products from corroded and polymer coated ferrous munition armour such as those present at the Palace Armoury. The characteristics typical of corrosion products on the three Coupon Series of armour analogues that are considered advisable to retain (since they are proposed to correspond or be inferior to the limitos CP structures) can generally be described as either:

1. Supporting micro-grooves;
2. Being hard, brittle, dark red-brown to black *and* being under the Paraloid B-72™ coating *and* being under the applied superior limitos markers. If necessary for confirmation, limited destructive probing would indicate these morphologies are on top of localised corrosion pits (i.e. of pitting or filiform morphologies); or
3. Typically being granulated porous black-brown and/or bright orange and positioned underneath the corrosion product structures described in the above two classification points.

[1380] 5.1.3.2.5 Conclusions from armour corrosion cross-section observations & analyses discussion

[1381] Figure 4-57, Figure 4-58 & Figure 4-59

[1382] 3.3.1.1.5 Protective coating

Some corrosion products did not exhibit micro-grooves (the most definitive corresponding limitos marker found in this study) since they were either destroyed in the formation process or because they were covered with CPs.

In conservation practice, a comparison might prove difficult to achieve if the adjacent metal does not (or the former metal did not) feature minute surface topography differences like micro-grooves. However, it is possible smooth surfaces could still be of use since any preserved smoothness would be in contrast with the rough and irregular surfaces of the most disrupted ferrous corrosion products morphologies. In the cases where a topographical reference point is absent the location of the limitos needs to be presumed by inference from similar structures (and their associated properties) that do exhibit evidence by way of the corresponding limitos.

The characteristics typical of corrosion products on the three Coupon Series of armour analogues that are considered permissible to remove (since they are proposed to be superior to the limitos CP structures) can be described as either:

1. Being above or in the Paraloid B-72™ coating and/or the applied pigment markers;
2. Not supporting micro-grooves *and* being above the B-72™ and/or the applied superior limitos markers;
3. Being powdery orange and being present on the metallic surfaces and/or on top of the defined limitos corrosion product structures; or
4. Being brittle and fragmented and being present on top of the defined limitos corrosion product structures.

The four points above encompass the corrosion product structures referred to as the transformed medium. As usual, greater certainty with the limitos determination is attainable by determining CPs that feature combinations of one or more of the above characteristics.

The accelerated corrosion regime of the low-carbon steel armour analogues was relatively short if compared with the long-term basis of years to decades for the natural corrosion occurring to the authentic armour at the Palace Armoury. This difference in extent of corrosion raises some important points of discussion regarding the limits of valid comparability of the armour analogues and the authentic armour. It has already been stated that the armour analogues only initially aimed to represent the primary to secondary local to general corrosion product development classifications[1383]. Ultimately, the resulting laboratory corrosion procedures acquired

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[1383] 3.3.1.2 Armour analogue selection & 4.1.3.1 Armour surface observations: macrophotography & photomicroscopy, Table 4-2 & Table 4-3 corrosion/CPs equivalent to the primary classification. Therefore, the results presented do not claim to represent the more advanced heavily corroded classifications of secondary or tertiary development. Qualified commentary on the preservation of the limitos on corrosion to a secondary or tertiary development (local to general or filiform) cannot be made. Some limited speculation can be made however. Bertholon concurs in principle about the potential similarities of same metal types in varying states of corrosion. He states, specifically for the case of contemporary and ancient bronzes, “Nevertheless, recent studies have revealed that some of the features observed on heavily corroded metal artefacts correspond to some of the surface properties of freshly corroded metal”[1384, 1385]. So speculating, it might be expected that identifiable traces of the limitos (e.g. former surface features like micro-grooves) in filiform filaments formed to the primary development classification might survive into the secondary and tertiary filiform classifications if these stages of observed CP creation result purely from surface deposition by precipitation from adjacent corrosion sites. But identifiable traces of the limitos in filiform CPs would not be expected to survive if corrosion of the underlying metal recommences. Underlying corrosion in the longer-term might occur, resulting in further expanding corrosion products, which would eventually disrupt limitos surfaces. Similarly, pitting corrosion occurring over longer durations would be expected to destroy micro-groove traces of the limitos as further subsurface CP evolution proceeds. To continue the speculation on the survival of the limitos in low-carbon steel with secondary to tertiary developed local to general or filiform corrosion, it could be expected that the limitos might indeed be recoverable, if only without the evidence of the micro-grooves or other former surface features. The limitos would instead need to be ascertained by association and still be expected to correspond with the interface between the dense product layer and the transformed medium. Such limitos determination by inference was already performed on those structures exhibiting the more distorted corrosion product state. The micro-grooves might not be present, instead a vertically displaced TM/DPL interface would represent the limitos as a more generalised corrosion takes over.

[1384] Bertholon, 2001a, pp. 241-242

[1385] Suggesting identical physical formation/transformations of corrosion products between ferrous and cupreous metals is not the objective of this citation. The citation is simply used to support the notion that features in corrosion products formed on less corroded metal can persist/also exist on heavily corroded metals.

Other areas of consideration regarding the valid comparability between the authentic armour and the armour analogues are based on the inherent differences between these ferrous materials. The armour analogues, of low-carbon steel, can be expected to more closely represent the corrosion phenomena of the armour composed of steel rather than iron; although the literature did not furnish any citations claiming differences in the possible corrosion product *morphologies* between these two ferrous metals[1386]. If there should eventually prove to be any significant differences, the armour analogues research results will be more applicable to the slight majority of the Palace Armoury munition armour. This claim is only based on the current and admittedly small statistics (n = 8) available from the only metallography performed on the Palace Armoury munition armour: 62.5% are steel and the remainder (37.5%) are iron (i.e. 5 steel & 3 iron)[1387]. If, dubiously including the metallography of the decoratively etched and therefore non-munition armour, then the statistic (n = 10) and proportion of steel is slightly increased: 70% steel & 30% iron[1388].

The second potential difference, worthy of greater acknowledgement, is the possible influence of the relative homogeneity of contemporary rolled steel used for the armour analogues. This homogeneity might increase rolled steel's likelihood of exhibiting a limitos in corrosion products when compared to wrought ferrous metals. Heterogeneity of the bulk metal composition and inclusions due to the mid-late Early Modern Period smelting processes, forging action and impurities of wrought ferrous metal might make it more susceptible to more localised, discontinuous and internally located corrosion actions. These corrosion actions could be seen as being potentially more susceptible to developing an irregularly corroded surface, or more particularly, a delaminating surface parallel to slag stringers that could destroy traces of the limitos as previously outlined[1389]. Nevertheless, without comparative research of these dissimilar materials in the same testing environments such assertions remain speculative[1390].

A third potential difference between the authentic armour and the armour analogues is their evolved corrosion products or more specifically, physical properties like adhesion/cohesion of CPs. Such physical properties are important to

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[1386] 2.2.2.3.4 Ferrous corrosion products
[1387] Vella et al. 2004, p. 230
[1388] 3.2.3.2.1 Armour cross-section sample selection
[1389] 3.3.1.1 Metal selection & substrate preparation
[1390] 3.3.1.1 Metal selection & substrate preparation

interventive conservation procedures like coating renewal, and of course, corrosion product removal/retention. These properties would depend not only on composition, but formation processes (e.g. rate, pollution). Regarding comparability of composition between the CPs on the authentic armour and armour analogues, the armour analogue component of this research did not have an available means of corrosion product structural characterisation on a micrometric scale (e.g. μRaman spectroscopy and/or μx-ray diffractometry). However, micrometric structural characterisation of CPs produced from an identical test metal used in parallel studies[1391] had been made[1392], and proved to feature the predominant corrosion products that were also detected on the Palace Armoury munition armour (goethite, ferrihydrite, lepidocrocite, magnetite[1393]). Although the corrosion environments of these other studies on the same low-carbon analogue metal were not identical to that used in this research[1394], they were similar[1395]. The identified corrosion products of the prior studies provide, at least, an indirect indication of the similar corrosion product composition between the authentic armour and the armour analogues in this research. Direct investigations of the armour analogues' CPs would be preferable to definitively ascertain their composition, and also their distribution within the TM and the DPL.

5.2.2 ARMOUR ANALOGUES, PALACE ARMOURY TECHNIQUE: CURRENT ARMOUR CORROSION PRODUCT REMOVAL PRACTICE

Coupon Series 1 was not included in the post-cleaning examination because it had previously been corroded and cleaned of its CPs during its preparation before accelerated corrosion. Such previously intervened surfaces resulted in partly emptied corrosion pits that were deemed to limit the confident discrimination between this preparatory procedure and the later cleaning performed by the PA.

Comparison of the amount of CPs retained or removed between Coupon Series cannot be made since this would necessitate incorrectly assuming the extent of corrosion and CPs was initially the same. It is necessary to highlight that all artefacts/analogues present their unique composition and condition. Like armour, the subsequent properties of the armour analogues dictated the tools and technique

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[1391] The European Commission Promet project (refer to Preface)
[1392] 2.2.2.3.4 Ferrous corrosion products, Types of atmospheric ferrous corrosion products
[1393] Table 2-1 & 4.1.3.2.4 Armour cross-section Raman micro-spectroscopy
[1394] 3.3.1.1.6 Laboratory accelerated corrosion
[1395] Footnotes 421 & 422

followed. The Palace Armoury staff member, who practically cleaned the coupons using the same tools and materials as for the armour, did not raise any points where he considered the analogues to be different to the armour. Some differences, however, included the relative cleanliness (i.e. particulate pollution) of the surface and the single and readily soluble protective coating[1396]. This meant the dust removal step was unnecessary and only one solvent step for coating removal was necessary. These differences are not expected to make techniques applied to the armour analogues incomparable to those normally applied to the armour. The relative size difference of the smaller armour analogues did not pose problems since the template facilitated its manipulation and the PA techniques do not involve long strokes.

Although effecting partial excavation of the CPs in pits forms part of the aim and strategies employed by the Palace Armoury, generally, the corrosion products were mostly retained level with their pit edge, intentionally or otherwise. Since CP removal on munition armour is performed by the naked eye, it is not expected that such minor topographical differences would have been noticeable to the conservation practitioner. Because the Palace Armoury's corrosion product removal technique essentially created a profile more or less even with the adjacent metal surface, it is not expected to be able to retain the previously determined limitos. The limitos and its inherently high topography ascertained from Armour analogue objective 1, Limitos determination[1397] make it subject to removal by the PA's cleaning techniques. For example, the consecutive corrosion pits partly filled with corrosion products in Figure 4-71 suggest the former presence of a filiform filament. Normally this corrosion product morphology on Coupon Series 6 would furnish micro-grooves as evidence of the limitos. After corrosion product removal by the PA, the superficial part of these filament structures were completely removed, only leaving the consecutive pits and CPs below[1398]. This supposition is in agreement with the documentation of the corrosion product cleaning process of the authentic armour where the quite deep "worming things" were not completely removable after the scalpel cleaning stage[1399]. The highly displaced surfaces of the limitos corrosion products need to be considered when cleaning armour surfaces. Palace Armoury and

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[1396] 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique

[1397] 4.2.1 Armour analogues, limitos determination: corrosion/corrosion product morphologies & limitos investigations

[1398] Similar to Figure 5-2

[1399] 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique

international laboratory armour cleaning practices have been shown[1400] to make corroded surfaces as flat (or even as recessed) as possible. Removal of all displaced surfaces therefore does not respect the limitos determined by these studies.

The effect of the corrosion product removal procedure on the metal surfaces was not objectively measured since the focus of these investigations was on the corrosion products, but it is expected by the localised nature of the corrosion pits and corrosion products that polishing/abrasion of the metal surface is unavoidable with the employed objectives and techniques. The very minute metal surface scratches in circular shapes noticed on the armour analogues could correspond with the circular action taken when using the steel wool and/or Pre-Lim™[1401]. All of the physical techniques employed (by the Palace Armoury or indeed any other practitioner) could be seen as being potentially erosive to the metal surface and subsurfaces. In particular, the use of Pre-Lim™ polishing paste, with or without steel-wool, for homogenising the metal surface sheen and *perceived* dirt removal is certainly a procedure contributing to the removal of metal surfaces. The rate of metal removal depends of course on the mode of application, but also on the frequency of application.

The use of Pre-Lim™ paste appears to have also had a supplementary role. Intentionally or unintentionally, the residual presence of the light coloured Pre-Lim™ inside partly emptied corrosion pits had a masking effect of the underlying dark corrosion products and could therefore be seen to play a role in aesthetics by lessening the contrast between the metal and remaining CPs[1402].

5.2.3 ARMOUR ANALOGUES, LIMITOS APPLICATION: CORROSION PRODUCT REMOVAL TO THE LIMITOS

On a macroscopic scale the surfaces still with limitos corrosion products[1403] did not look as though they were cleaned of many, or possibly any of their CPs, since the majority of retained CPs were considered to represent the limitos. This is in contrast to the results obtained by the practices established in the literature review and the questionnaire: where the remnant red-brown corrosion products representing

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[1400] 2.4.2.1 Laboratory questionnaire summary & conclusions, 3.2.4 Authentic munition armour corrosion product removal: the Palace Armoury technique & 3.3.2.3.2 Armour analogues, Palace Armoury technique: current armour corrosion product removal practice

[1401] 3.3.2.3.2 Armour analogues, Palace Armoury technique: current armour corrosion product removal practice, steps 4a & 5a.

[1402] Figure 4-70

[1403] Figure 4-71 & Figure 4-72 & Figure 4-73 the limitos are normally considered superfluous to those retained on munition armour[1404].

Fragility of the limitos corrosion products is an important consideration when determining if, or how, to remove CPs. Discussion on the level of fragility and approaches to sympathetic cleaning is only pertinent if cleaning is performed under magnifications that permit selective application of techniques to accommodate such differences in fragility. To selectively remove the non-limitos corrosion products it is estimated that it would take *at least* ten times longer to perform the work in this manner. Timed surveys are required to properly estimate this.

It must be stated that the relatively thin layers of corrosion products and superior limitos markers made it difficult, but not impossible, to manually differentiate between layers even in spite of binocular magnification. The amount of time to undertake this task was the determining factor.

The minute areas of corrosion products observed at 200x optical microscope magnification[1405] were useful for demonstrating that even though some CPs might have initially appeared to the naked eye to have deposited on top of uncorroded metal from adjacent corrosion sites, they can in fact be born from the metal surface immediately underneath, which has thinly corroded. Since they formed a part of the modified surface, such superficial corrosion products should be retained if the limitos is to be respected. When viewed on a macro scale it is the assembly of numerous microscopic sites that form the surface observed by the naked eye.

On the armour analogues (especially Coupon Series 4) there were numerous corrosion product forms where direct evidence of the limitos (by way of the micro-grooves) was simply not apparent and the limitos was only presumed via deduction and similarity with morphologies and properties of other limitos CPs. The retention of corrosion products not showing micro-grooves, but featuring similar characteristics raises an important point about the limitos. Should the limitos be preserved only when it is apparent and proven by way of evidence such as micro-grooves (or other) in corrosion products? Deduction via similar CP morphologies and properties is an important method of reasoning, if only less certain, since armour surfaces can be relatively smooth and do not always provide convenient

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[1404] 2.4.1 Literature review on ferrous armour corrosion products & 2.4.2 Laboratory questionnaire on ferrous armour corrosion products

[1405] Figure 4-75

corresponding limitos markers by way of micro-grooves. Further research with much greater quantities of experimental material is required to establish the validity of this assertion.

Coating removal by solvent immersion, as performed on Coupon Series 6, would be considered inappropriate for large and sometimes incompatibly multi-composite artefacts like armour. However, the higher prevalence of the orange weeping droplets on these particular armour analogues is not quantitatively comparable to the Palace Armoury munition armour collection and it was the CP morphologies underneath that were more representative of authentic armour.

5.2.3.1 Curatorial perspectives on corrosion product removal to the limitos

In a contemporary museum context, the results of this research need to be considered on several levels. The examples of the major cleaned coupons and mini reference coupons from the Palace Armoury technique and Limitos application experiments[1406], formed the basis of the collaborative discussion with the Senior Curator[1407] and Curator[1408] of the Palace Armoury

The discrepancy in curatorial opinion over what can be considered the *original* appearance highlights the subjectivity of object interpretation. The absence of specific armour treatment documentation makes it even less achievable to ascertain which surface finishes relate to respective periods. It could even be argued that the retention of corrosion products might reflect the (unintentional) appearance of unmaintained surfaces that would probably appear more closely related to periods of their more neglected static lifetime[1409].

The influence of aesthetics, and public perception and acceptance of aesthetics, appear to be motivating factors in CP removal in the past and present: the documented armour cleaning campaigns of 1860 and post-Second World War[1410] that occurred before major reopenings to the public were neither simply coincidental nor serendipitous. Aesthetics are an important issue in conservation; especially if they inhibit object interpretation. Aesthetics are however a largely subjective concept and the current acceptability of altered surfaces depends on the artefact genre.

[1406] Figure 4-77

[1407] Mr Emmanuel Magro Conti

[1408] Mr Michael Stroud

[1409] 2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques, 2.1.3.3 1964, Independence: remnants of a colonial history & 2.1.3.4 Recent history: museum typological collection & tourist site

[1410] 2.1.3.2.1 Restoration

Corrosion products comprising the surfaces of archaeological metals are increasingly more easily accepted by the public since they are deemed as being truly antiquated and therefore should *look* correspondingly old. However, historical artefacts like armour face a more critical and demanding public since the adjacent uncorroded surfaces (i.e. still metallic) are a reminder of how the entire surface probably once generally appeared. It is only with prior professional acceptance of corrosion products on surfaces that the public can start to be convinced of the possible necessity to maintain these alteration products. Gradually the appeal from the public for more homogenise surfaces will lessen. Communicating any such needs is the responsibility of curators in their role as interpreter of material history. It is the role of the conservator or conservation scientist to raise the curator's awareness of the stability and the potential information that certain materials possess.

Do limitos structures that were retained by inference rather than evidence of surface modification (i.e. micro-grooves or other topographical markers) have a value or significance? What can these irreparably modified surfaces bring to a curator or metallurgist who are, after all, interested in conveying the human-artefact story or determining paleometallurgy? Perhaps they cannot presently or will never furnish useful information and the usual accessibility of uncorroded metal surfaces on these partly corroded surfaces makes the metal itself a preferable source of more reliable information. Preservation of unintelligible surfaces remnant from corroded materials, similarly with glass or plastics, is a matter of major significance for the implications of this research. Possibly, compounding this matter for other curators might be the issue surrounding the unattributable dating of historically intervened surfaces. These concerns are beyond the immediate scope of this research and are matters warranting a larger continued debate in conservation ethics and philosophy. Nonetheless, such decisions are of considerable significance to the practical application of these research results and it is hoped that presentation of this research's results will further the debate, and moreover aid the decision making process so practical conclusions can be made to this contentious philosophical arena with important implications for practical heritage management.

Ferrous artefacts from the buried archaeological environment have limitos corrosion products (or indeed CP's that the limitos is superimposed on) that can be very thick since they feature on semi/completely corroded/mineralised substrates. Relative to archaeological artefacts, the limitos corrosion products on ferrous artefacts from an atmospheric environment are relatively thin. The thickest DPL recorded in the authentic armour investigations was circa 250µm or 0.25mm[1411], while the thickest *definable*[1412] DPL measured and presented on the armour analogues was 90µm or 0.09mm)[1413]. Due to the expansive nature of the DPL only about half of this thickness can be considered as a corroded volume lost from the metal substrate and is in agreement with the previously theoretically quoted iron metal to corrosion product volume ratio of at least 1:2.1[1414]. The removal of the upper half of the DPL to effectively level the corrosion products to any adjacent metal level will not entail a drastic dimensional change of an armour as for the more corroded archaeological artefact. But such a degree of CP removal will remove the superiorly positioned limitos. Nor will complete removal of CPs from pits have a drastic dimensional change of an armour. However, it is reminded that these armour are comprised of circa 1mm thin plates, which will not tolerate much corrosion pitting and CP excavation, without the eventually inevitable consequences of perforations of the sheet metal. Examples of armour backplates with thinning metal and penetrated holes are already numerous[1415].

The ability of corrosion products to directly and indirectly contribute to further corrosion has been outlined[1416]. Medical analogies for corrosion products and their treatment, such as the removal of gangrenous elements, are typical[1417], but simplistic since they only address the symptoms and secondary cause of the *disease*, not the primary causes. If it is agreed that certain CPs should be retained, since they either feature evidence of the limitos or are at least indicative of the limitos, then consideration of this major point of stability is required. Stability depends not only on the materials involved, but the environment[1418].

The potential retention of these normally removed corrosion products on armour implicates much broader questions:

[1411] Figure 4-10

[1412] Thicker corrosion product layers were observed (e.g. 150µm in Coupon Series 4, Figure 4-60), but defining the location of the upper limits of the DPL associated limitos was not so easily definable.

[1413] Figure 4-58

[1414] 2.2.2.3.4 Ferrous corrosion products

[1415] Stroud, 2006-2007, pers. comm.

[1416] 2.2.2.3.4 Ferrous corrosion products

[1417] Bertholon, 2001c, p. 10

[1418] Figure 2-44

- Are preventive conservation procedures, such as controlled indoor environments, and/or interventive techniques, such as coatings and corrosion inhibitors, sufficient to limit the adverse effects of ferrous corrosion products?; and significantly,
- Are these resolutions always practically achievable?

Separate thorough investigations about corrosion products and their influence on preventive conservation and interventive conservation techniques could be one path to initiate to determine any such effects. However such further detailed investigations are deemed superfluous since it is already known that the addition of particulate matter and its progressive surface accumulation makes a marginally corrosive environment significantly corrosive[1419]. Although being potentially beneficial, it appears that attempting to control the relative humidity in this large ground floor site, which lacks a damp course, might simply not be achievable. Moreover, such an environmental control intervention might not be considered the priority nor the most feasible immediate action; especially since the effect of ambient relative humidity on inverted surfaces (i.e. where dust does not prevail) appears to have a comparatively insignificant corrosive effect as evidenced by uncorroded inverted armour surfaces[1420]. At present, the Palace Armoury environment is not only too humid, but importantly polluted with solid aerosols including chlorides. It is these particles, not corrosion products, which appear to make the major critical difference in corroding the non-inverted surfaces of the wall-displayed munition armour.

5.3 PRELIMINARY NON-INVASIVE OBSERVATION OF THE DETERMINED LIMITOS ON AUTHENTIC MUNITION ARMOUR

Comparison of the authentic armour surfaces with the armour analogue results proved that direct evidence of the limit of the original surface, by way of surface micro-grooves, also exists in the corrosion products of the mid-late Early Modern Period wrought munition armour at the Palace Armoury[1421]. Even though the CPs on the munition armour were not probed, so as to maintain the non-invasive nature of these research foundations, it can still be stated that these CPs must have

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[1419] Figure 2-28
[1420] Figure 4-1
[1421] Figure 4-78

been sufficiently physically resilient to tolerate the coating removal procedure that involved surface swabbing with solvent on cotton swabs[1422].

The more frequent occurrence of filiform CPs with limitos micro-grooves on the armour reflected another similarity with the armour analogues. Given the direction of each corrosion mechanism (i.e. filiform propagates laterally, while pitting propagates vertically), it is presumed that the more numerous examples of micro-grooves observed on the filiform filaments, rather than on pitting CPs, is both a result of the filiform mechanism's inherent capability to form the limitos and also its capability to subsequently retain the limitos.

5.4 SUMMARY & CONCLUSIONS TO DISCUSSION

Due to the imprecisely known history of the armour and its corrosion product removal interventions, the armour presented doubts regarding reliable interpretation of the corrosion formation processes and the subsequent ability to reliably determine the limitos. On the one hand, the manufacturing of the armour analogues from available contemporary materials and their corrosion to morphologies previously established to be representative of the munition armour provided a means to study much more reliable experimental materials. On the other hand, such contemporary, homogenous and rolled materials could not yield useful metallurgical markers[1423], nor help replicate the typical laminated appearance of wrought iron's upper corrosion products to differentiate between the superior and inferior limitos CPs[1424]. Another limitation of using contemporary test materials was the limited timescale permitted to generate atmospheric ferrous corrosion products that were representative of a collection that features up to decades of naturally evolving corrosion products. Nonetheless, the CP morphologies and the extent of their development were sufficient to represent the initial stages of corrosion of the PA munition armour.

So it was established that the micro-grooves in corrosion products in the surface of the dense product layer were proposed to represent the limitos from the last metallic state. The great uncertainty about the point in time (and the implied curatorial significance of the respective historical period) that this surface was last metallic should be of high consideration when the curators decide which surface

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[1422] Lemasson et al. 2004, pp. 40-41

[1423] 4.2.1.2 Cross-section perspective investigations

[1424] 4.1.3.2.3 Armour cross-section scanning electron microscopy-energy dispersive spectrometry (SEM-EDS), Pauldron (part) PA RC 166

interface to reveal or even *create* (as via the more intensive CP cleaning procedures). Do these surfaces reveal information about the types of surface maintenance and care of these artefacts? Yes, they do, but can this information be dated and therefore be of greater curatorial interest? As yet, in the absence of greater documentation, it seems not. Further open discussion about the objective of the corrosion product removal procedure and the curatorial intent regarding armour interpretation or storage is required so as to decide the level of cleaning undertaken by conservators.

The removal of greater quantities of corrosion products (thereby disregarding the limitos) might be preferred so as to limit the aesthetic detraction and to re-establish the *look* of maintained surfaces, which would probably appear more similar (on a macro scale) to those surfaces exhibited during their dynamic lifetime (initial 100-200 years[1425]). The retention of the majority of corrosion products (thereby respecting the limitos) might continue the appearance of unmaintained surfaces that would probably appear more closely related to neglected periods of their static lifetime (latter 200 years[1426]). As always, each armour (and discrete areas within) should be considered on its individual basis, but also in the context of the greater collection and any matching components.

The results of this research suggest that if the limitos corrosion products present on the authentic 16th-17th century northern Italian-style wrought ferrous munition armour are to be respected, then a more conservative level of corrosion product cleaning will be required at the Palace Armoury. But before taking into consideration any new and more conservative techniques of corrosion product removal it is recommended that preventive conservation approaches are adopted and maintained. After assessments of the improved PA environment are made, the stability of a sample of munition armour with and without their limitos corrosion products can be made and future policies developed accordingly. Fundamentally improved environmental conditions will not only reduce the detrimental effect ferrous corrosion products have on the metal, but in parallel will limit the reoccurrence of corrosion of metal that is unassociated with corrosion products.

From an experimental methodological perspective, the testing of the innovative applied superior limitos markers proved to be worthwhile in making a

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[1425] 2.1.3.1 Mid 16th century-1798, Order of St John: functional, symbolic & obsolete arsenal

[1426] 2.1.3.2 1798-1964, French & British occupation: decorative romantic trophies to academic antiques, 2.1.3.3 1964, Independence: remnants of a colonial history & 2.1.3.4 Recent history: museum typological collection & tourist site contribution to the diagnostic determination of the limitos. The effectiveness of the applied gold superior limitos marker as a diagnostic tool was demonstrated when examining these armour analogues in cross-section and plan perspective. The gold marker did not obscure the micro-groove markers and confirmed, as suspected, that some corrosion product elements (namely porous granulated CPs and weeping CP droplets), could be validly removed when they featured above this permeable superior limitos marker. At best the gold superior limitos marker indicated an interface location that corresponded with the limitos immediately below, but this assessment was not assured since the reliability heavily depended on the absence of the transformed medium. The potential unreliability of all the applied superior limitos markers was not least due to the probably small, yet significant, adhesive effect of the coating, which was used to assist propagation of corrosion products.

Since evidence for the limit of the original surfaces has already been established in the conservation field for corroded archaeologically buried wrought iron, it is not too surprising that similar evidence is observed on similar materials, which are in a comparatively less aggressive environment, i.e. in the atmosphere. A proposed possible negative effect, however, on the corrosion associated with atmospheric artefacts might be a more localised action that disrupts the continuity between remaining uncorroded and corroded surfaces; particularly with active local to general corrosion at a tertiary corrosion extent[1427]. Local sets of differential aeration cells might develop on historical ferrous plate artefacts due to local CPs, dust deposition, or coating defects and cause localised corrosion adjacent to stable metal. The effects of failed coatings and particles on historical artefacts could therefore cause greater disruption of the limitos bordering stable metal in a more localised manner than with archaeologically interred artefacts. Comparatively, an uncoated artefact in a moist (often condensing RH) and aerobic burial environment would feature a more complete liquid electrolyte layer. This more or less complete distribution of corrosion sites on an archaeological artefact enables a greater, yet more even, displacement of the limitos. This is not to say that localised corrosion product eruptions destroying the limitos in archaeological wrought iron do not occur; they do, as observed from personal experiences.

[1427] Table 4-2 & Table 4-3

6 CONCLUSIONS

The results of this applied research proved that particular corrosion product morphologies on contemporary rolled low-carbon steel and later validated on an authentic 16th-17th century northern Italian-style wrought ferrous munition armour can mimic, in a modified and mineralised manner, the metal surface as it was before corrosion. Here the limitos was typified by a localised upward displacement of the surface; similar to a blister on living skin tissue.

It has been demonstrated that in collaboration with conservators, curators can have their attention drawn to examples of atmospherically corroded ferrous surfaces that have the potential to exhibit evidence of their earlier metallic surfaces. The recognition that atmospherically corroded mid-late Early Modern Period wrought ferrous metals and contemporary rolled steel can indeed preserve surface information originating from the metal provides cause for reasoned deliberation for conservators and curators alike when they are faced with making decisions about corrosion products on wrought ferrous armour, or artefacts based on similar ferrous materials (including contemporary rolled low-carbon steel) and exposed in similar atmospheric environments.

A conservator, who is identifying the limitos on an armour artefact, or similar ferrous surface, can be assisted by the texture or *fingerprint* of the metal surface before corrosion. The typical co-existence of uncorroded metal surfaces on atmospherically corroded munition armour provides this reference. Fine grinding grooves conveniently and definitively traced this corresponding limitos marker on steel armour analogues and on the Palace Armoury's authentic armour. Local variations in topography became more perceptible after solvent-removal of protective coatings and evidently, during magnification.

The determination of filiform corrosion on low-carbon steel as an atmospheric corrosion product morphology that consistently retained surface characteristics can assist conservators in readily identifying the probable location of the limitos resulting from this type of corrosion. Practically, the greater majority of these corrosion product structures were physically resilient and therefore did not pose much risk of being physically damaged. Whereas, the determination of local to general corrosion on low carbon-steel as an atmospheric corrosion product morphology (probably driven by the pitting corrosion mechanism) that inconsistently retained some original surface characteristics can serve as a warning to conservators that limitos determination is going to be much more difficult. Also, this is most likely to only be achievable in association with some of this morphology's relatively few domed (as opposed to rough) CP structures. The traces of any limits of the original surfaces in pitting corrosion products will probably become more distorted as underlying corrosion continues, and corrosion products expand. For the relatively thin corrosion product layers relevant to this research, the sometimes brittle and fragile nature of the dense corrosion product layer on local to general CP morphologies will likely make tactile responses felt by manual probing riskier than determination by observation of features characteristic of the limitos.

For those armour that have already had all of their upper corrosion products removed, as evidenced by CPs only remaining in the corrosion pits, any limitos emanating from the armour's preceding corrosion phase has been irretrievably lost. There is little the conservator can do; only the substrate of the former limitos can be preserved.

This research proposes, for continued debate, consideration of a potential future approach to corrosion products that respects the modified surfaces of wrought ferrous metal artefacts from and continuously exposed to indoor atmospheric environments. Due to the size of the munition armour and their numerous quantity, the implications of this research's findings mean that if the limitos is to be respected then the time taken to selectively clean the armour under binocular microscope could be amplified by at least one or more orders of magnitude. This is where an important curatorial decision needs to be made that assesses the value or significance of the surfaces of the numerous munition armour, which have been intervened over the centuries. The value or significance of the surface features preserved in corrosion products on these usually partly corroded surfaces needs to be made by the curator on a case-by-case basis, while also viewing the abundant munition armour as an assembly. It is the curator's responsibility to establish if these cyclically intervened surfaces warrant the extra resources required to preserve these CP structures and adjacent metal. Curators might consider that since the adjacent inverted surfaces generally remain uncorroded then the corroded surfaces could be sacrificed on the grounds of pragmatism. If such decisions are made, they would now be made knowing that evidence of former surface materials would be effaced. It would also demonstrate that limitos corrosion products, and metal surfaces alike, continue to be lost with every corrosion and corrosion product removal cycle. This should act as an alert to museum administrators: this sequence will persist and holes will continue to develop in the 1mm-thin sheet metal. If there is a significant element of doubt in the curators' minds regarding the value of the munition armour's surfaces then it is advised to act on the side of caution and intervene with the low interventionist approach exemplified by the determined limitos. Such findings might also prompt curators to revaluate the priorities of the collection and remind administrators of the need to allocate the appropriate resources (personnel and infrastructure) to mitigate immediate concerns and to permit long-term strategic conservation planning.

The appearance of metallic armour surfaces contrasted with rusty red-brown corrosion products is not one that is currently deemed acceptable in the genre of historical arms and armour and might not ever be accepted by all museum professionals despite the corrosion product's indisputable association and similarity with the metal. The curator-conservator relationship must involve a dialogue about the rational objectives of an artefact treatment and collectively inform museum staff and the wider public of its consequences. Together they can aim to reason out subjectivity towards aesthetics and conservation-restoration approaches; a goal that might not ever be fully achievable, nor desirable to all, as after all, these are humanity's cultural artefacts, which are representative of the subjective and variable human condition. The question remains open as to whether the 16th-17th century northern Italian-style wrought ferrous munition armour will continue to embody the subjective and variable human condition of the past and the present.

7 RECOMMENDATIONS

A holistic perspective on the conservation and management of the munition armour at the Palace Armoury is recommended. This entails considering the material-environment system of the museum, not just the armour material, when making decisions about this large assembly of culturally significant armour that is highly susceptible to the local environment. The adverse effect of ferrous corrosion products can be mitigated by many of the same rational measures that need to be employed to prevent the further corrosion of the munition armour's metal. It is the conservator's responsibility, in conjunction with environmental engineers, to advise and advocate for feasible and pragmatic solutions that improve environmental conditions and maintenance procedures. It is advised as a base for preventive conservation or more simply, good housekeeping, that the environment of the Palace Armoury is reviewed and human resources are provided at the PA to maintain relatively dust-free surfaces for the non-display case armour. Reversing the direction of ventilation (i.e. extraction to induction) and installing renewable filters on the window fans (already installed in each exhibition hall) could also be considered for reducing outdoor solid and gaseous aerosol induction. Requiring greater funds, automatic entrance doors would reduce aerosol induction, while an outlet for the window-inducted air would be required to exhaust air when the automatic doors are closed. As regards the source of indoor limewash particulates, the use of limewash could be restricted to the lower walls: where it is needed most against rising damp[1428]. Upper walls and ceilings, where rising damp is less of an issue, could be painted with non-lime based paint systems such as acrylic emulsions; thereby sealing the majority of particles originating from the walls and ceiling.

Lastly, in terms of the artefact, any continued use of applied barrier coatings should be considered to only serve as an interim barrier between the pollutants and

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[1428] It is understood that previous research investigations for a limewash substitute have not *yet* been successful (Stroud, 2006-2007, pers. comm.).

the armour surface until the next scheduled dust removal. If left uncleaned the coating ultimately fails and corrosion pursues. The armour metal loss and corrosion product removal cycle thus continues at an unnecessarily accelerated pace.

It is recommended that the approach to ferrous corrosion products on the munition armour is assessed *after* the environmental management of the Palace Armoury and its preventive conservation practice have been satisfactorily improved and the relative stability of the armour in this new environment is established. In short, the environment at the Palace Armoury needs to be adjusted to better suit the conservation of the munition armour, rather than perpetually addressing the rust that is symptomatic of, and implicated into, the real environmental problem.

Such cursory suggestions on the environmental management of the Palace Armoury and prolonging the effectiveness of the munition armour's coatings are of course not the focus of this research, but they highlight the requirement that for successful resolutions, conservation problems should not be viewed in isolation. Gaining a holistic perspective of the Palace Armoury's material-environment is highly recommended when the Palace Armoury Curators, and possibly Heritage Malta's management, further consider the results of this research's determination of the original surface limits of the munition armour.

8 FUTURE RESEARCH

Invasive investigations (i.e. coating removal and subsequent CP probing) on the authentic munition armour are the next necessary progressive steps to be considered so as to increase the statistic of armour studied without surface coatings, and to further conclude the level of comparability of the important characteristics of adhesion/cohesion between the CPs on the armour analogues and authentic armour.

Raman micro-spectroscopy and x-ray diffractometry of the dense product layer and the transformed medium on the armour analogues could provide direct confirmation, or otherwise, if the CP composition created on the armour analogues is representative of the authentic armour CP layers. Further analyses of these CP layers could determine if the relative differences in their fabrication (i.e. wrought by hammer versus wrought by rollers as for the contemporary metal) and composition (relative amount of inclusions, minor and trace alloy metals) significantly affects the distribution of differing CP phases.

Future diagnostic investigations on artefact analogues atmospherically corroded over years to more extensive levels and under time-lapse digital photomicroscopy would help trace the typical location of the limitos in more developed corrosion cases not studied here with the armour analogues. The application of this research's sputtered gold superior limitos marker on unprotected surfaces (i.e. no barrier coating) could be considered for achieving this task. Tests without the adhesive effect of protective coatings would determine whether or not the gold applied superior limitos marker is still too impervious to permit the transmigration of all corrosion products attributed to the transformed medium layer. Since the determination of the limitos for underfilm filiform corrosion product morphologies has been established during this research, the subsequent use of a coating film is less imperative. The expected results of such future investigations on more heavily corroded substrates might determine that coherent surface features would be less likely to be preserved in the corrosion products; only the displaced position of the former metallic surface might be determinable in complex and irregular ferrous stratigraphies.

Further research on the extent of limitos preservation in varying ferrous metal-medium interfacial environments would also be of interest in resolving the extent of corrosion differences and the survival of the limitos between similar wrought ferrous metals in burial environments.

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LIST OF ABBREVIATIONS

AIC	American Institute for Conservation
ASM	American Society for Metals
ASTM	American Society for Testing & Materials
AEAIS	atomic emission arc induced spectroscopy
BSE	backscatter electron/s
C	coating
CEA	Commissariat Energie Atomique
CNC	computer numerical control
CNRS	Centre National de la Recherche Scientifique
CP/s	corrosion product/s
CS	cross-section perspective
D	deposit
DPL	dense product layer
EA	electron acceptor
ECCO	European Confederation of Conservator-Restorers' Organisations
EDS	energy dispersive spectrometry/spectrometer
FTIR	Fourier transform infra-red
HM	Heritage Malta
ICMCH	Institute of Conservation & Management of Cultural Heritage
limitos	limit of the original surface
LADIR	Laboratoire de Dynamique, Interaction et Réactivité
M	metal
MP	melting point
n.d.	no date
OM	optical microscopy
P	plan perspective
PA	Palace Armoury
R	refractive index
RH	relative humidity
SE	secondary electron/s
SEM	scanning electron microscopy/microscope
SHE	standard hydrogen electrode
SR	synchrotron radiation
TM	transformed medium
UKIC	United Kingdom Institute for Conservation
UNESCO	United Nations Educational, Scientific & Cultural Organization
UV	ultra-violet
VOC/s	volatile organic compound/s
XAS	x-ray absorption spectroscopy/spectroscope
XRD	x-ray diffractometry/diffractometer
XRF	x-ray fluorescence spectrometry/spectrometer
z	valence/number of electrons
Z	atomic number
ZOI/s	zone/s of interest

APPENDICES