"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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VOLUME I of II

A dissertation submitted in partial fulfilment of
the requirements for the degree of:

Master of Conservation
in Applied Conservation Studies
(M. Cons.)

University of Malta – Heritage Malta,
Institute of Conservation & Management of
Cultural Heritage

May 2008

99 300 words (excl. footnotes, references, & appendices)
132 700 words (incl. footnotes, references, & appendices)

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"Case studies in the determination of the original surface limits of the ferrous armour of the Order of St John, Palace Armoury, Malta"

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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.

ACKNOWLEDGEMENTS

Particular acknowledgements to:

Christian Degrigny for fulfilling his large component of this Masters programme, his proposal of the dissertation topic and his inspiration and drive for science in heritage conservation.

Daniel Vella for our numerous chemistry and corrosion discussions, his and the University of Malta's Department of Metallurgy & Materials Engineering's preparation of the steel coupons and his related doctoral and Promet project research.

Michael Stroud & Emmanuel Magro Conti for their concerned custodianship, trust and making the time to enable this curator-conservator collaboration.

Lawrence Spiteri for his consistent laboratory support and SEM-EDS operation.

Martina Caruana for her support, availability and making possible the Masters programme at ICMCH, Heritage Malta.

The European Commission 6th Framework Programme, the former Malta Centre for Restoration & Heritage Malta, for funding the complementary Promet project research, without which this part-time study would not have been financially viable.

The European Commission Promet project co-ordinator, Vasilike Argyropoulos & Workpackage 3 leader, Christian Degrigny.

Further acknowledgements to:

Duncan Abela for his contribution to the statistical analysis of the questionnaire on ferrous munition armour corrosion products and to numerous information technology matters.

Badidou Abdallah Hadj Amar, Dana Ben-Israel, Oliver Mamo, Michelle Marsh, François Mirambet, Edwin Sciberras, Maryse Pierrard & Annick Texier for providing access to their reference libraries.

Ivan Barbara, Joseph Darmanin, Karmenu Debono & Joseph Vassallo for providing their skilled technical support.

Régis Bertholon for his inspiration, correspondence and continued work on the modified original surfaces of archaeological metal artefacts.

Louis Borg, Tony Borg & Raymond Jones for providing logistical and material support.

JoAnn Cassar, Francis Chetcuti & Elizabeth Galea for their discussions on Maltese limestone-based/derived materials.

Roslyn DeBattista, Matthew Grima & Valentina Lupo for their operation of the SEM-EDS and for assisting with the laboratory accelerated corrosion regime of the armour analogues.

Anne-Claire de Poulpiquet for providing French-English translations.

Philippe Dillmann, Judith Monnier & Delphine Neff for their interest and assistance in the dissemination of their and their colleagues' research on corrosivity of atmospheric ferrous corrosion products and its interpretation to the heritage conservation domain.

Stavroula Golfomitsou for her interest, perspectives and advice.

Stefan Michael for providing German-English translations.

Judith Monnier for performing the Raman micro-spectroscopy and spectra interpretation of the Raman micro-spectroscopy & micro-x-ray diffractometry.

Jesmond Pace & Pierre Vella for the CNC milling of the acrylic sample-tray mould.

Jean-Pierre Reverseau & his armour restorers for their discussions and tour of Le Musée de L'Armée, Les Invalides.

Robert Smith for his communications, generosity and interest in armour conservation.

Daniel Vella, Elizabeth Galea, David Scott, Gertie Jensen, Mark Dowsett & David Thickett for communications on optimising corrosion product/metal sample cross-section embedding procedures.

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].

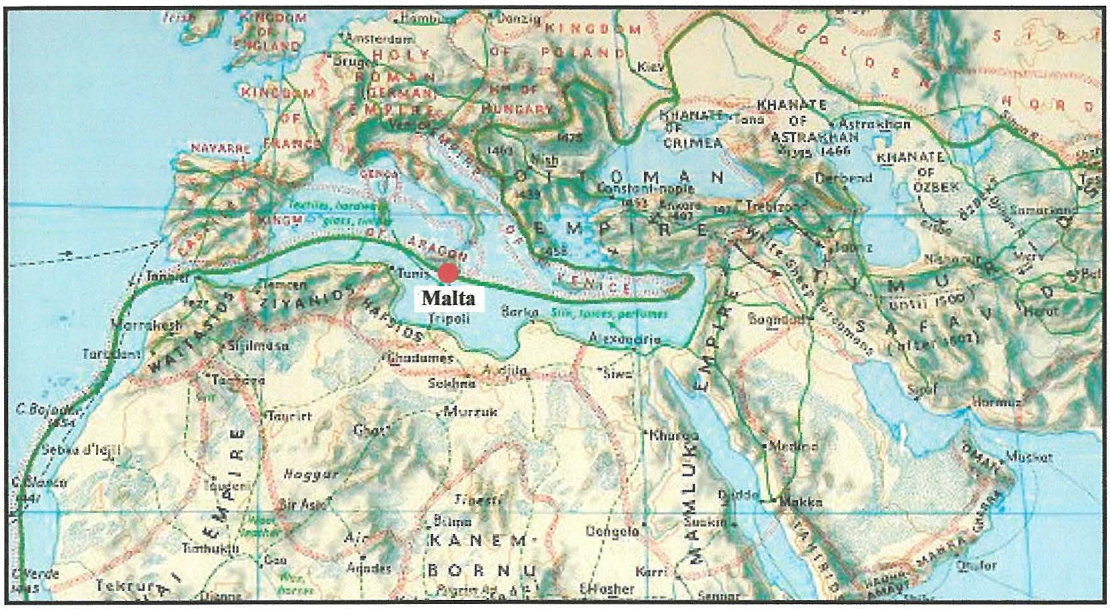

Figure 2-1 The Islamic world circa AD 1500 (below broad green line) and Malta on the Christendom frontier[8]

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.

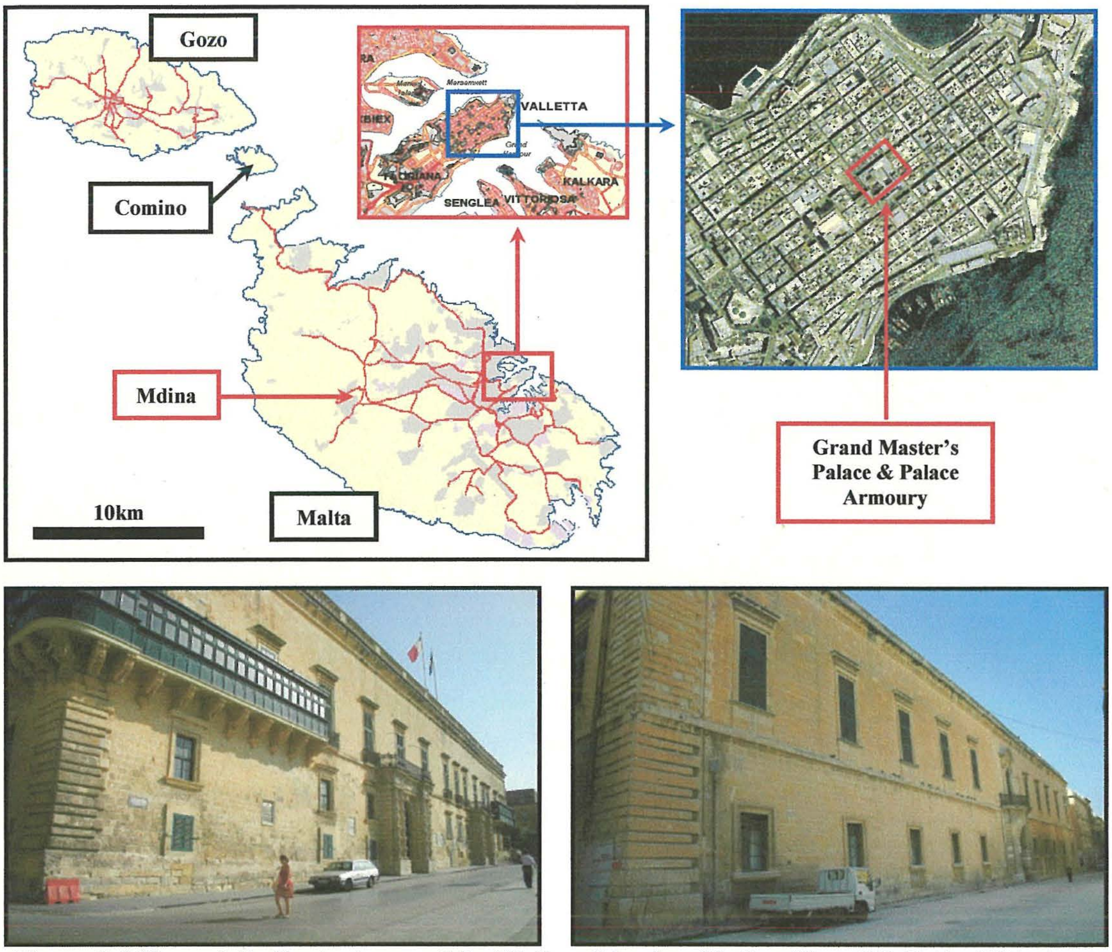

Figure 2-2 Upper left: Context map of the Maltese Islands with the cities of Valletta, Vittoriosa & Mdina[12] Upper right: Context aerial view of the Palace Armoury in Valletta[13] Lower left: Exterior of Grand Masters' Palace, Republic Street[14] Lower right: Exterior of Grand Masters' Palace Armoury,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

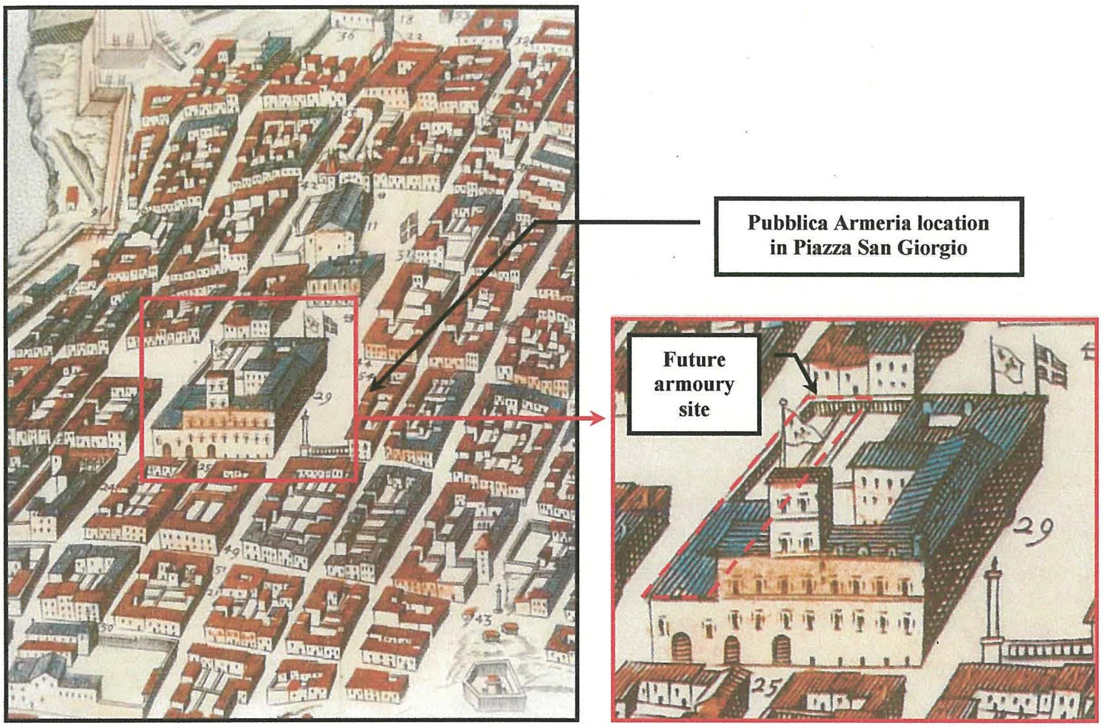
[13] Ibid.

[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].


Pubblica Armeria location in Piazza San Giorgio

Future armoury site

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].

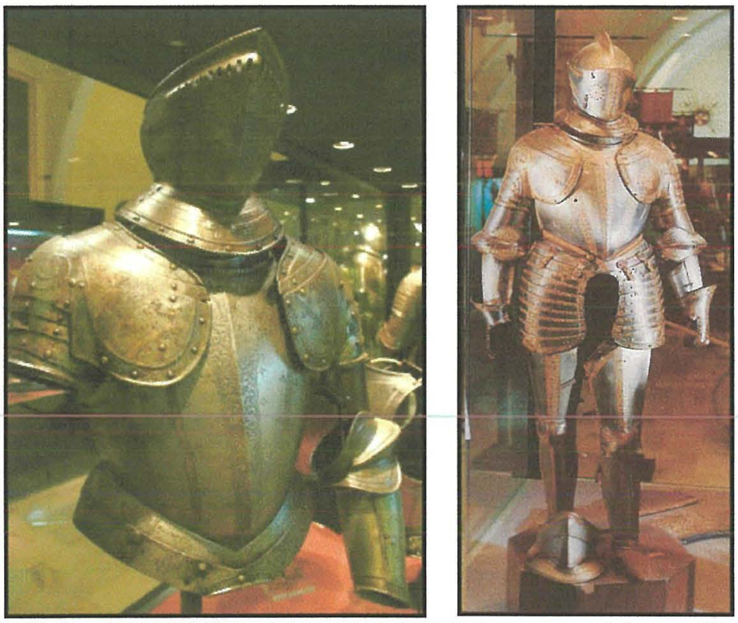

Figure 2-5 Left: Northern Italian-style etched Knight's Armour (circa 1570-1580)[35] Right: Northern Italian Pisan style gilt parade armour of Grand Master Verdelin (circa 1580)[36]

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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.

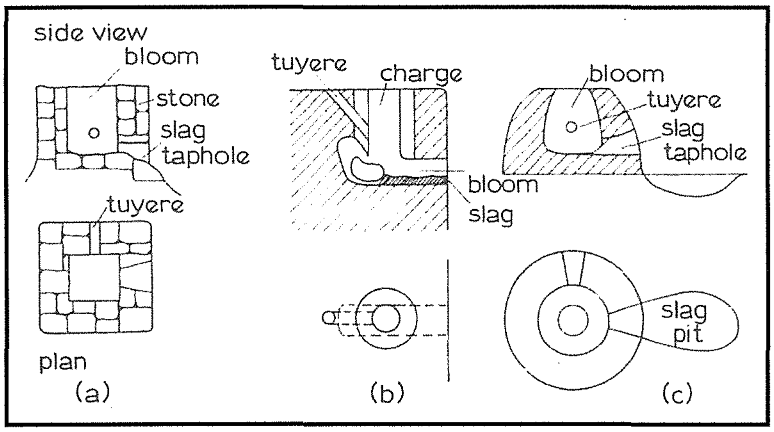

Figure 2-6 Section and plan perspectives of three bloomery furnaces dating from the Middle Ages[70]

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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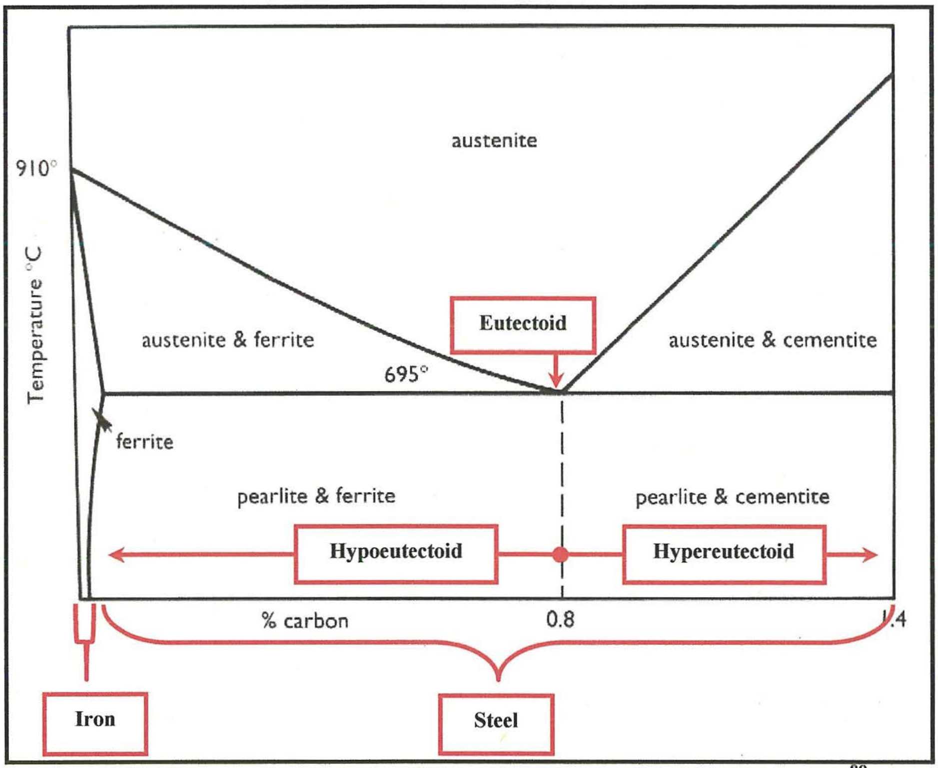
[68] Williams, 2003, p. 4
[69] Tylecote, 1976, p. 88
[70] Tylecote, 1992, p. 76
[71] Ibid., p. 96 & Williams, 2003, pp. 4, 879
[72] Buchwald & Wivel, 1998, pp. 80-81
[73] Williams, 2003, p. 4
[74] *ferrite* = a solid solution in body centred cubic iron, and carbon being the typical solute (Chandler, 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].

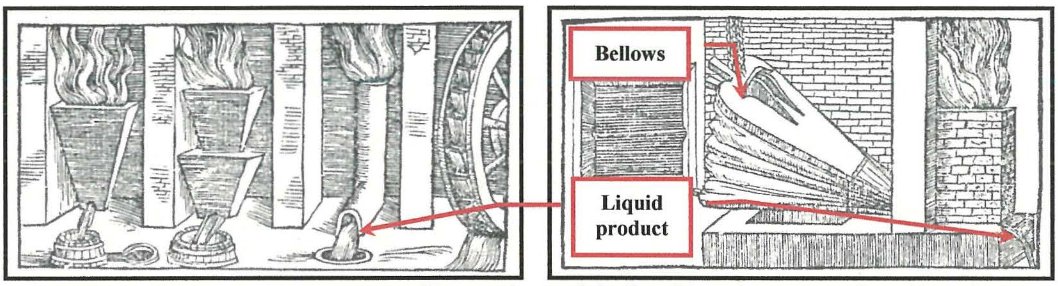

Figure 2-7 Left: Sixteenth century illustrations of Italian blast furnaces of various shapes powered by a watermill[94] Right: A bellow and blast furnace[95] Note all furnaces are producing liquid material

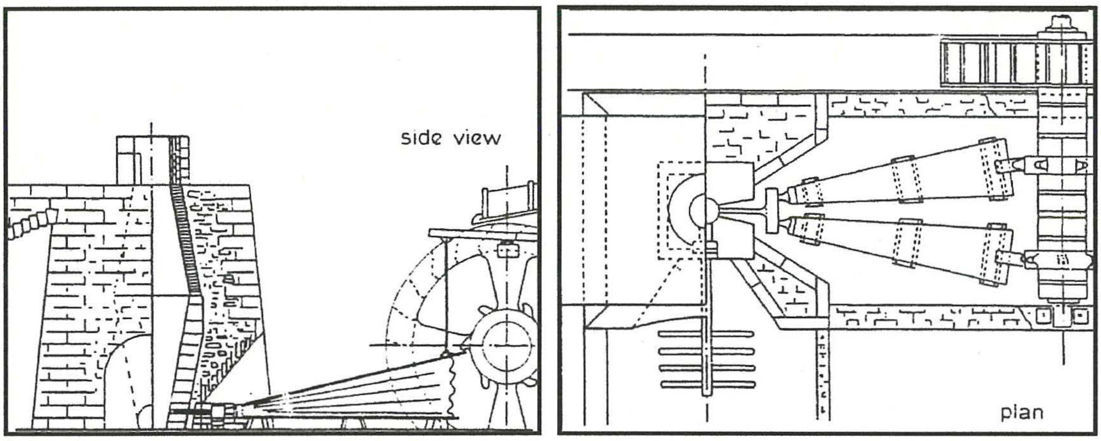

Figure 2-8 Left: & Right: Contemporary technical elevation and plan of a hydraulic blast furnace (circa 16th century)[96]

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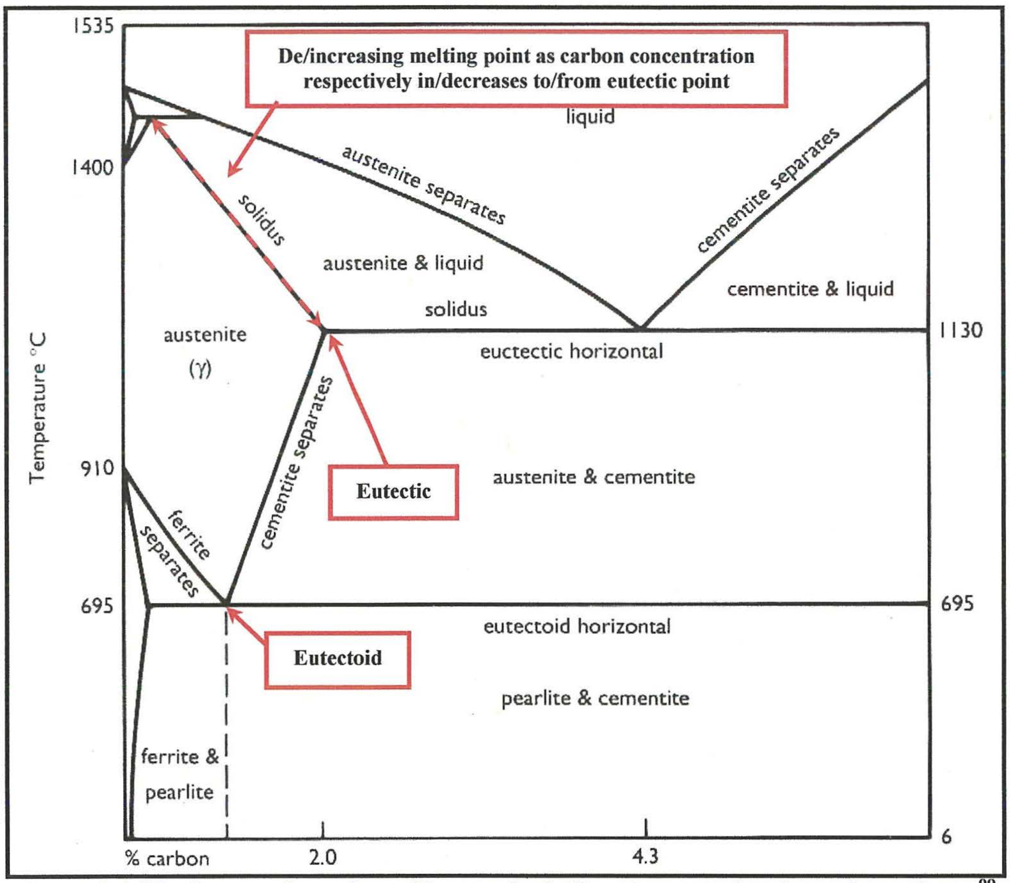
[92] Tylecote, 1992, p. 97
[93] Biringuccio, 1990, pp. xiv, 22
[94] Ibid., p. 150
[95] Ibid., p. 64
[96] Tylecote, 1992, p. 97
[97] Williams, 2003, p. 880 & Buchwald & Wivel, 1998, p. 74
[98] Buchwald & Wivel, 1998, p. 74 & Dillmann et al., 2002, p. 327



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.

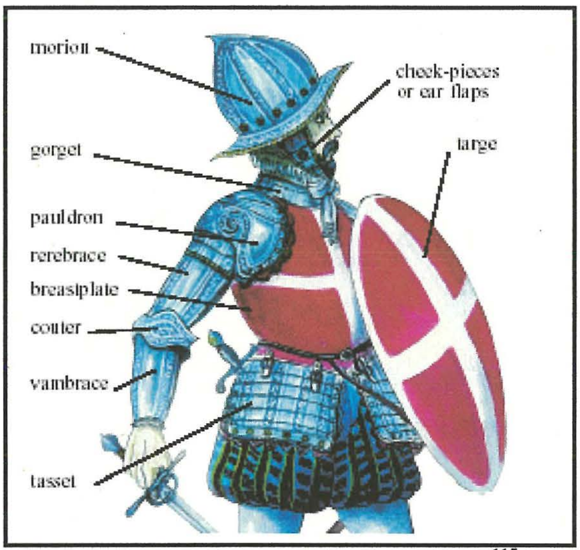

Figure 2-9 Left: Annotated appellation of worn etch-decorated[115] half-armour (breast and backplates are covered by a surcoat marked by the Order of St. John ensign)[116]

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

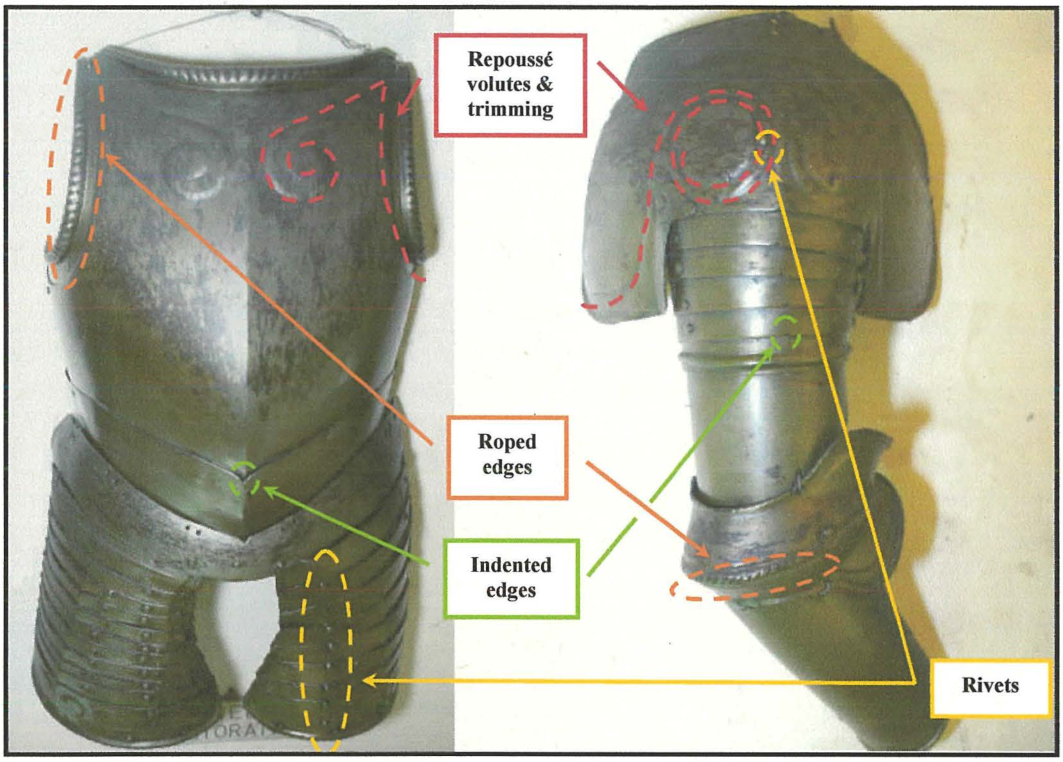

Figure 2-11 Typical mid 16th-mid 17th century northern Italian-style munition armour at the Palace Armoury[121]. Left: Breastplate and tasset. Right: Pauldron, upper cannon (rerebrace), couter and lower cannon (vambrace)

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. "<u>Rough from the hammer</u>: 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. "<u>Rough filed</u>: This is not common, but surfaces exist which have been planished and then rough filed smooth: file marks are still evident."
3. "<u>Polished</u>: 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 <u>Hausbuch der Mendelschen Zwölfbrüderstiftung</u> (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].

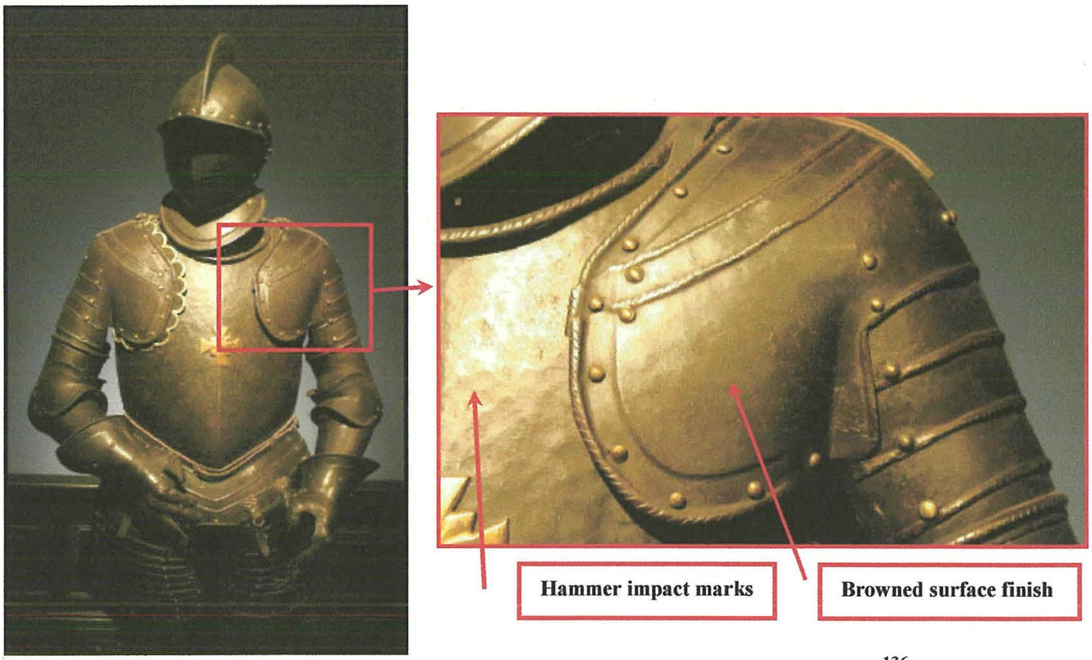

Figure 2-13 "Northern Italian foot soldier/infantry armour (c. 1560-1570)" [136] at Vienna's Kunsthistorisches Museum[137]

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).

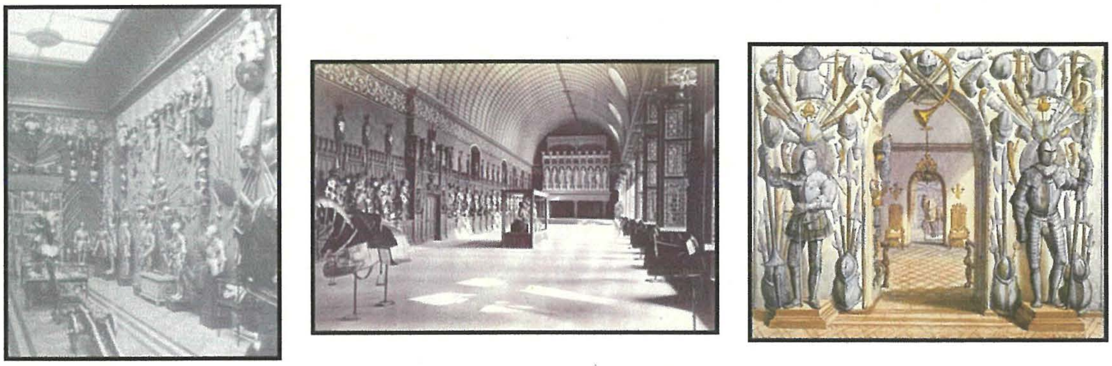

Figure 2-14 Examples of trophies of arms across Europe. Left: Hertford House (circa 1873-1897), Sir Richard Wallace, United Kingdom[163]. Centre: Pierrefonds (published 1867), Viollet-le-Duc, France[164]. Right: *Cabinet des armes et armures* (n.d.) of Prince Soltykoff in St Petersburg, Russia[165].

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.

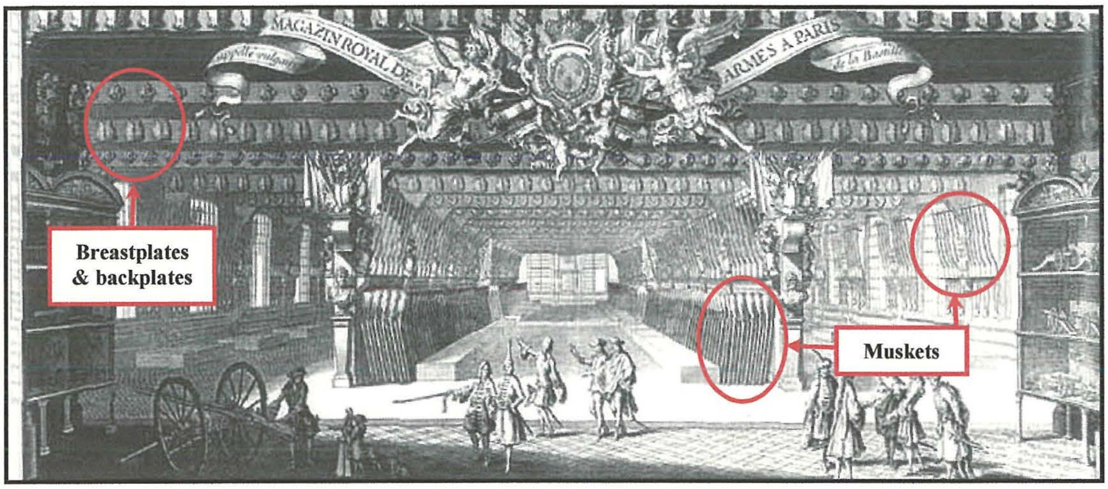

Figure 2-15 ***Le Magazin Royal des Armes à Paris*****, circa 1686**[172]**.**

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.

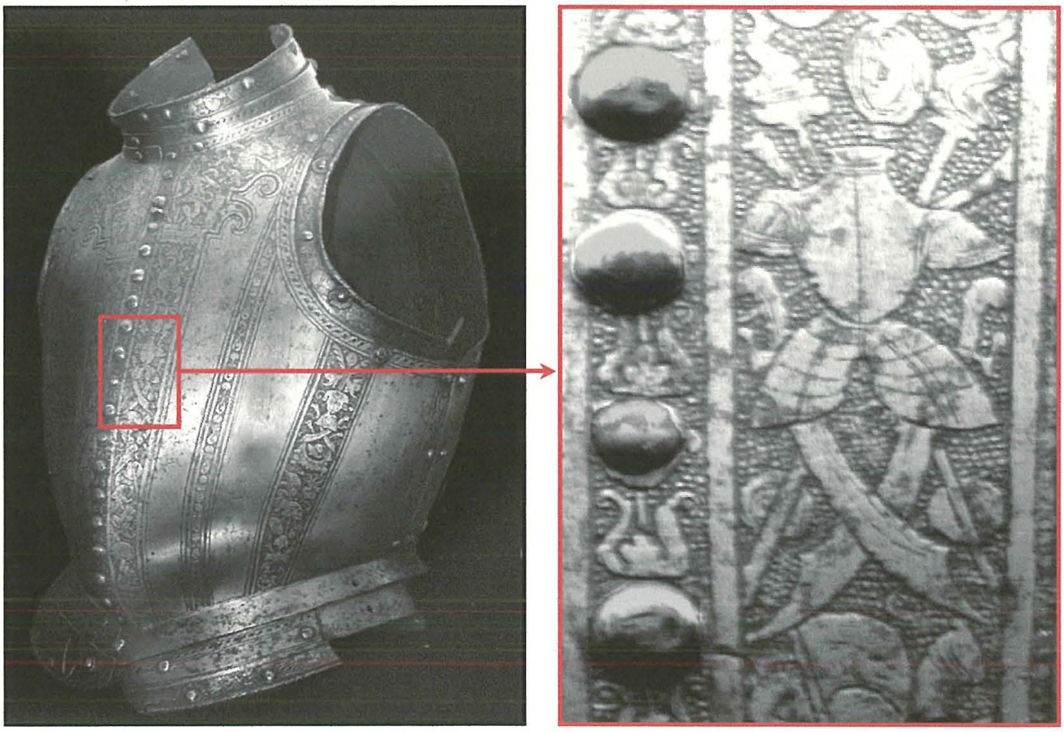

Figure 2-16 Acid-etched decorations on more elaborate armour (circa 1590) indicate trophy of arms display formations[188].

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

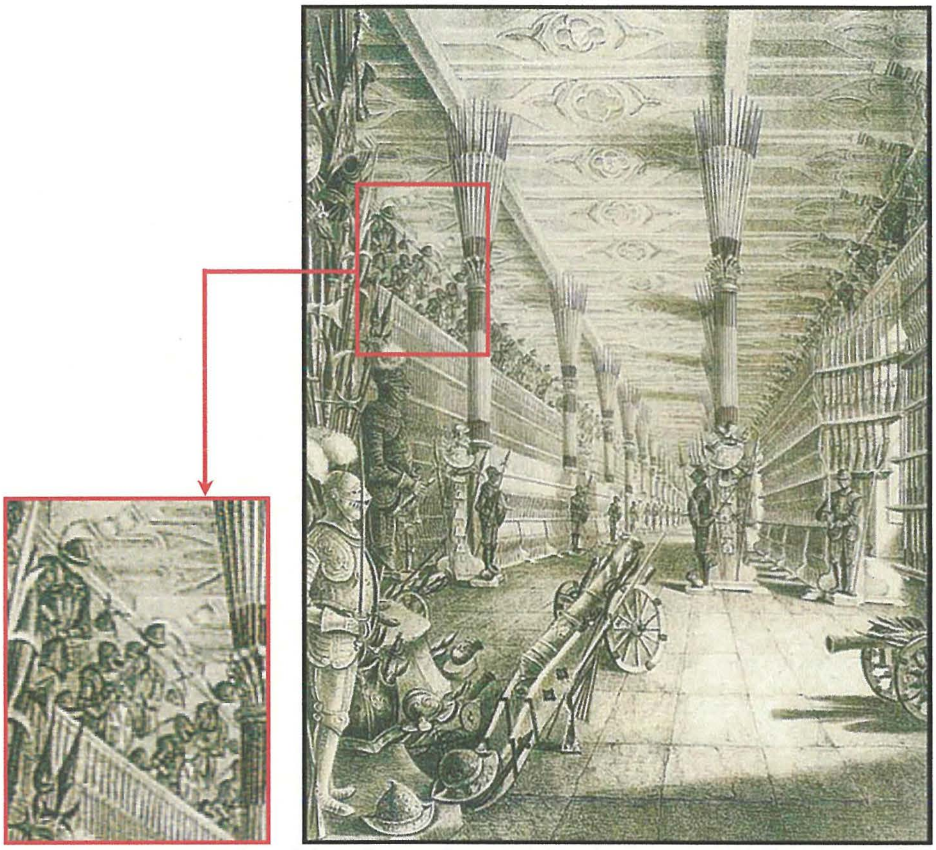

Figure 2-17 Left: Detail of trophies of arms from Right: *Armoury in the Governor's Palace in Valetta*, lithograph by Charles Frederick de Brocktorff, circa 1840[207].

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].

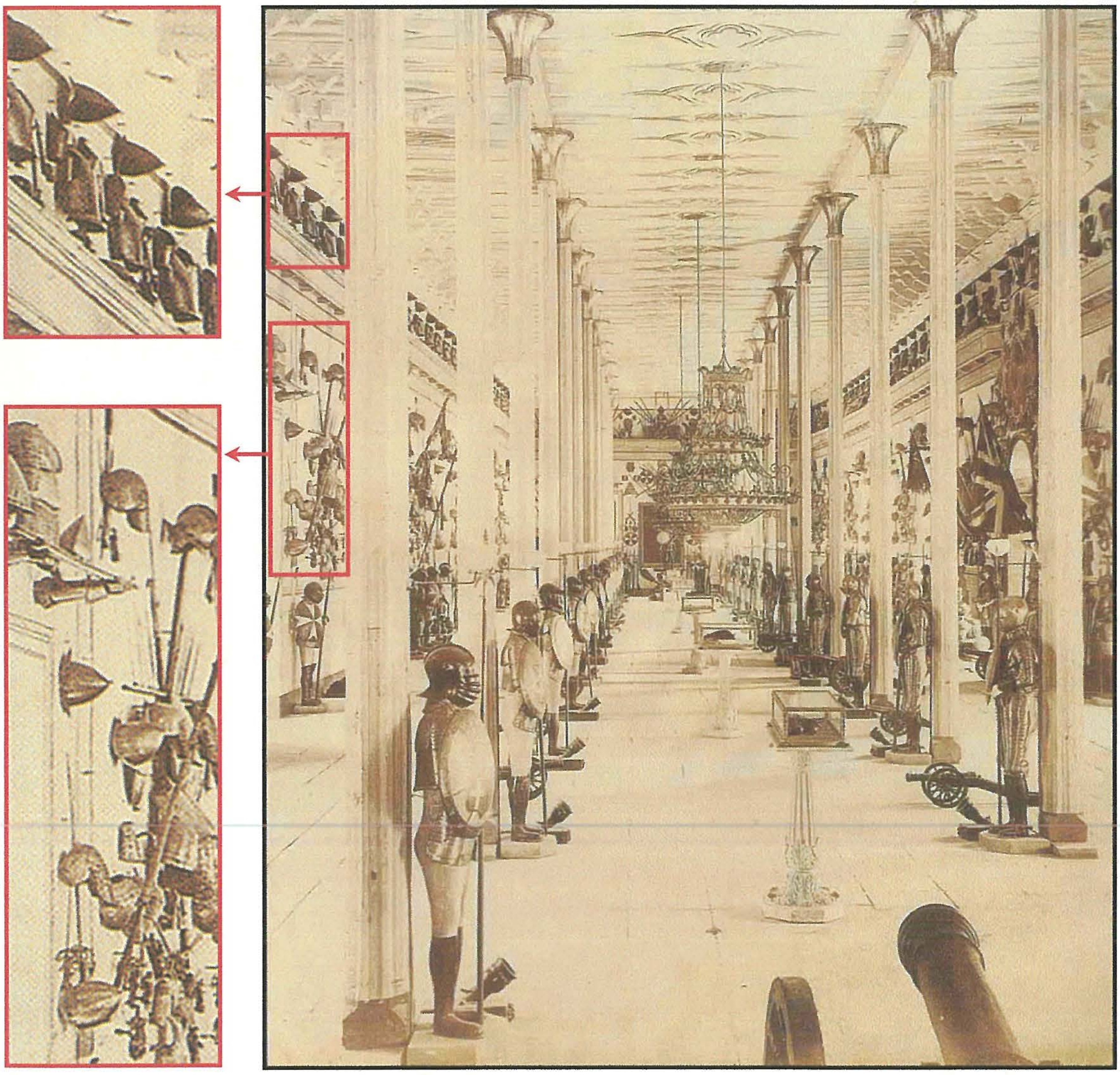

Figure 2-18 Upper and lower left: Details of trophies of arms from Main: The Palace Armoury circa 1900[213]

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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.

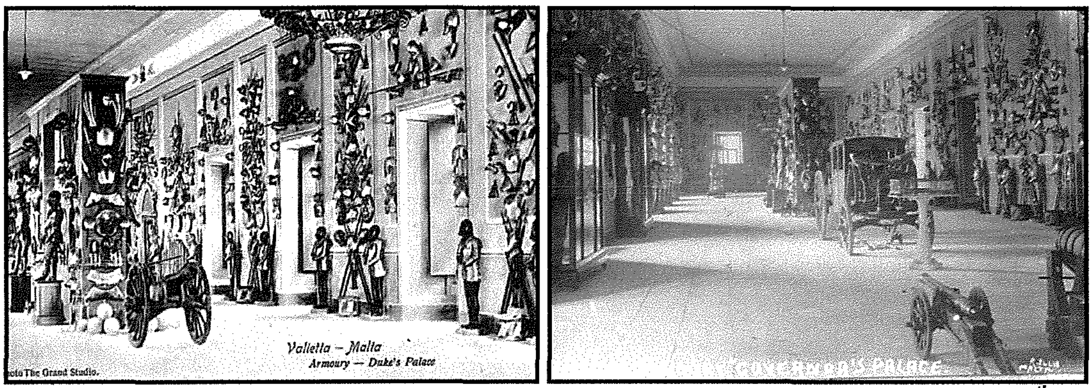

Figure 2-19 Postcards depicting the Palace Armoury during the British period of the 20th century[220]. Note the multitudes of trophies of arms (and armour) on walls and furnishings

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

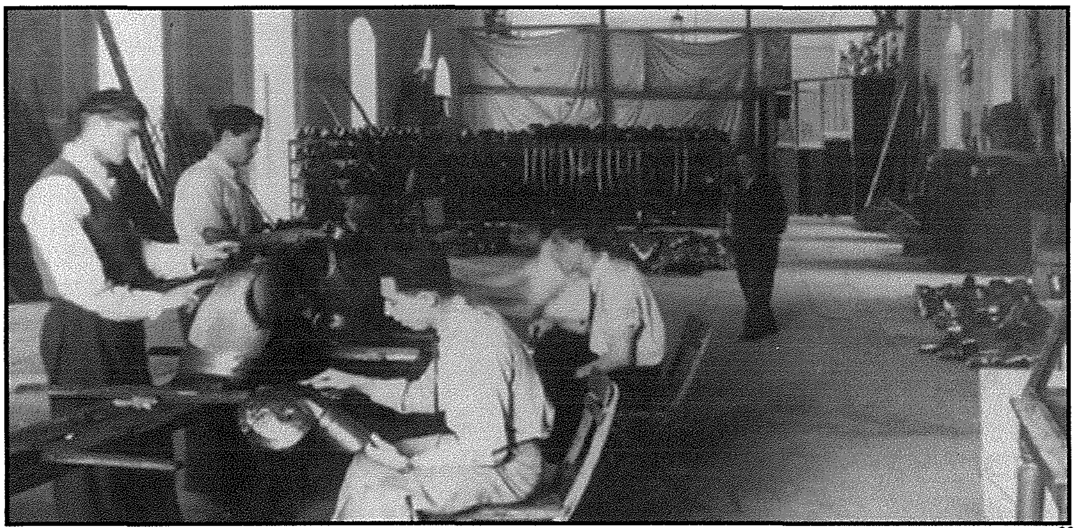

Figure 2-20 Armourers polishing armour at the Palace Armoury after the Second World War[223]

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

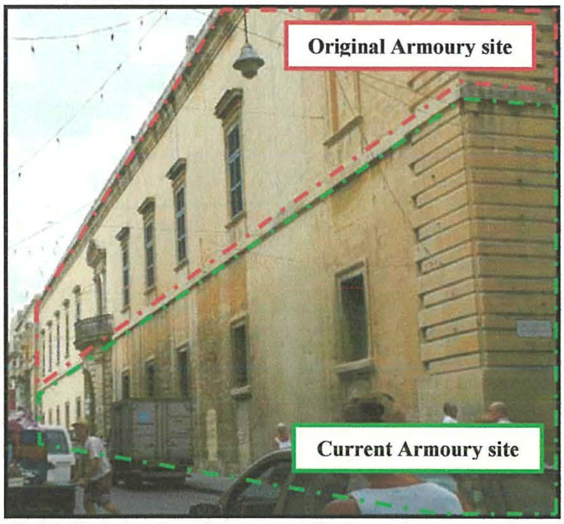

Figure 2-22 Original and current Palace Armoury locations[248]

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

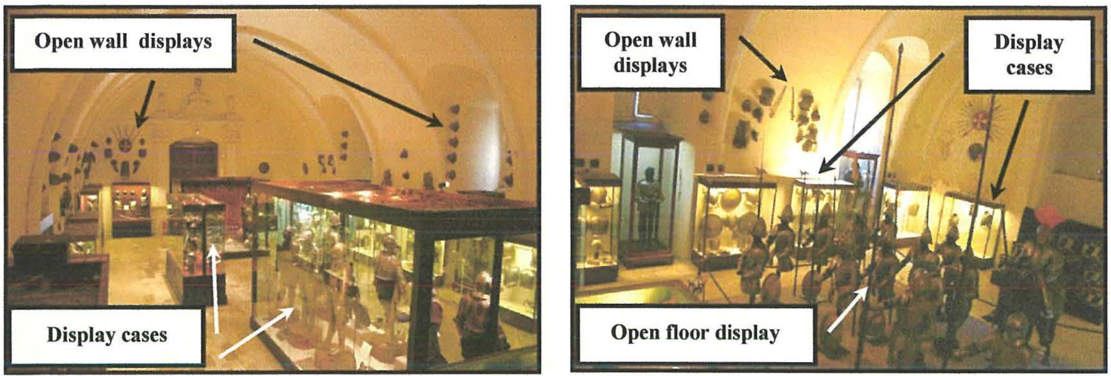

Figure 2-23 Palace Armoury Armour Hall exhibition space in 2006 marked with display types[253]

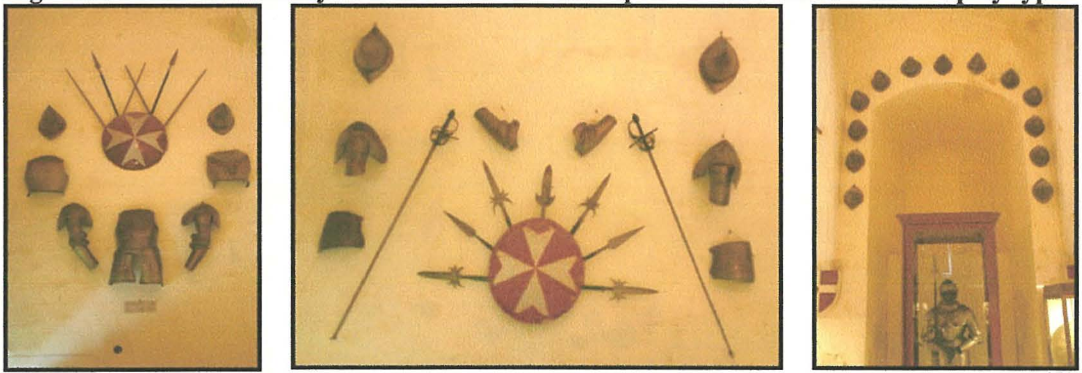

Figure 2-24 A selection of the wall-displayed trophies of arms in the Armour Hall in 2006[254]

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).

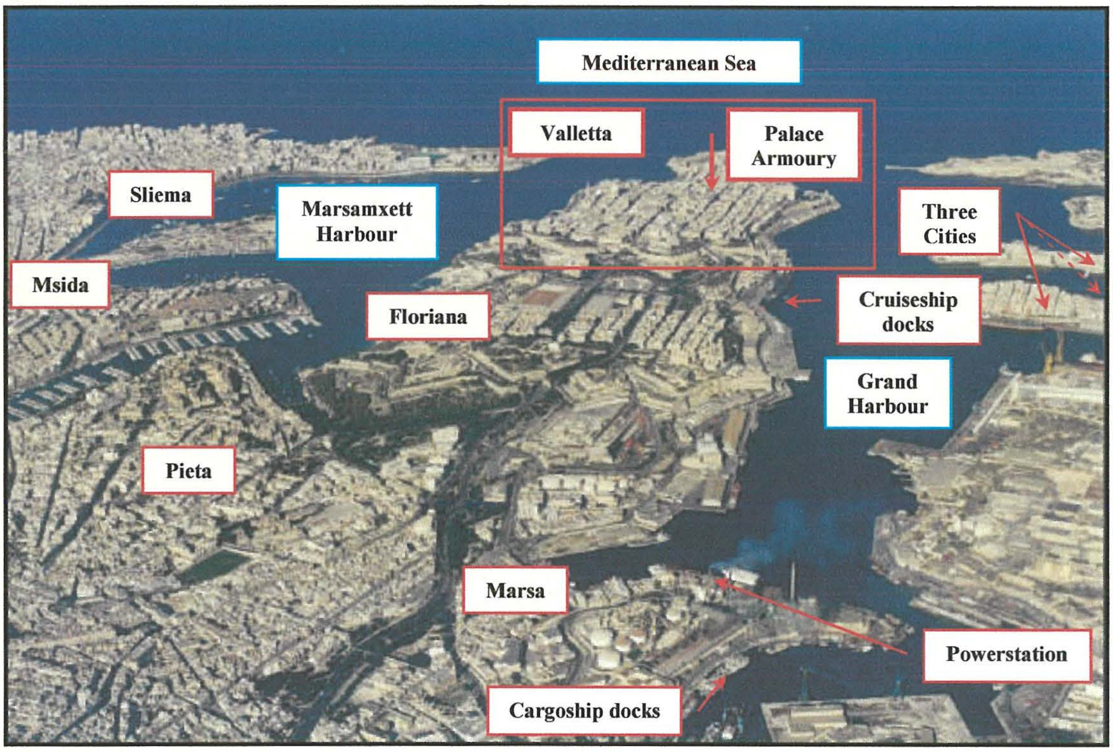

Figure 2-25 The coastal, urban and industrial regional environment of the Palace Armoury, Valletta[263]

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).

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

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 Surface hydroxylation & water adsorption

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].

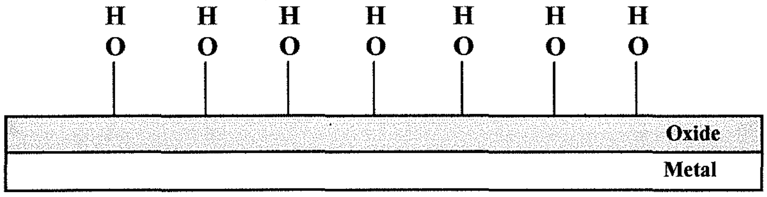

Figure 2-26 “A schematic depiction of surface hydroxyl (OH^-) groups on a metal oxide surface” after Leygraf & Graedel[275]

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.

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

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.

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

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]:

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

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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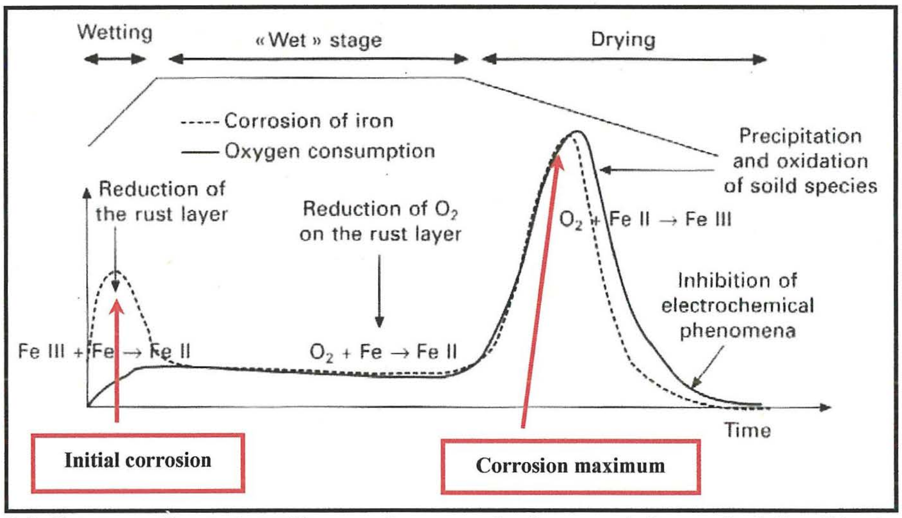
[319] Uhlig & Revie, 1985, p. 173 & Rowlinson, 1977, p. 23
[320] Pohlman, 1998, p. 81
[321] Cassar, 1995, p. 45
[322] Getty Conservation Institute, 1994, p. 86
[323] Magro Conti, 2007, pers. comm.
[324] Pohlman, 1998, p. 80
[325] Vella et al., 2006b, p. 12
[326] Pohlman, 1998, p. 82 & Uhlig & Revie, 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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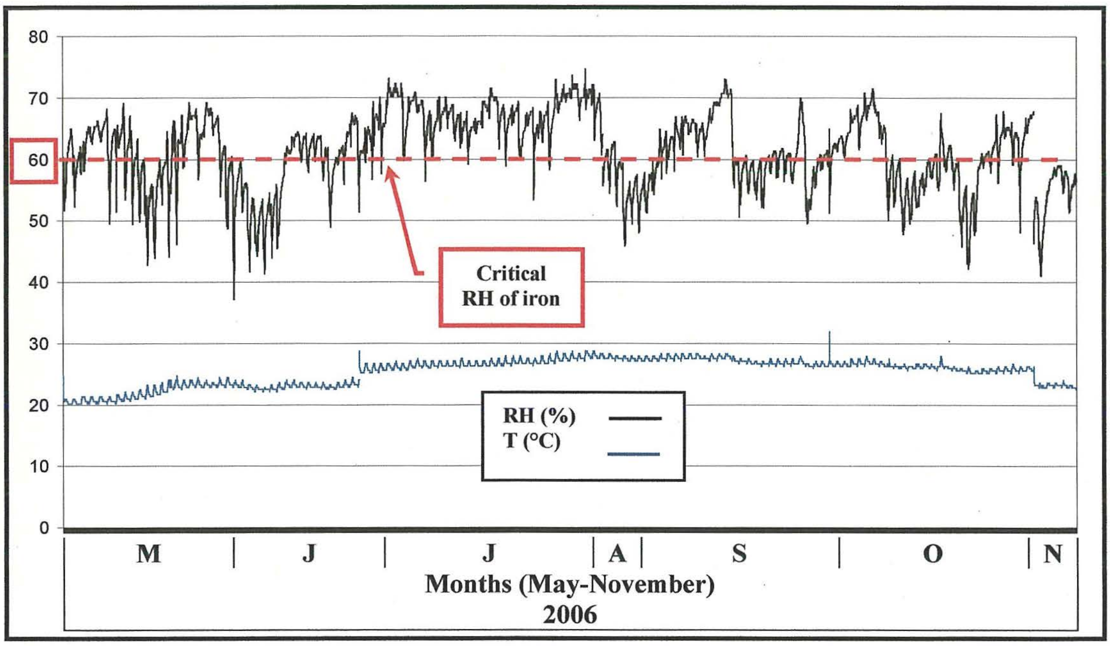
[330] Ibid., p. 126
[331] Ibid., p. 110
[332] Though air-exchange rates can be calculated.
[333] Stroud, 2006-2007, pers. comm.
[334] Stratmann & Streckel, 1990, p. 695
[335] Maréchal et al., 2007, p. 23
[336] Ibid., p. 22
[337] Leygraf & Graedel, 2000, p. 14

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

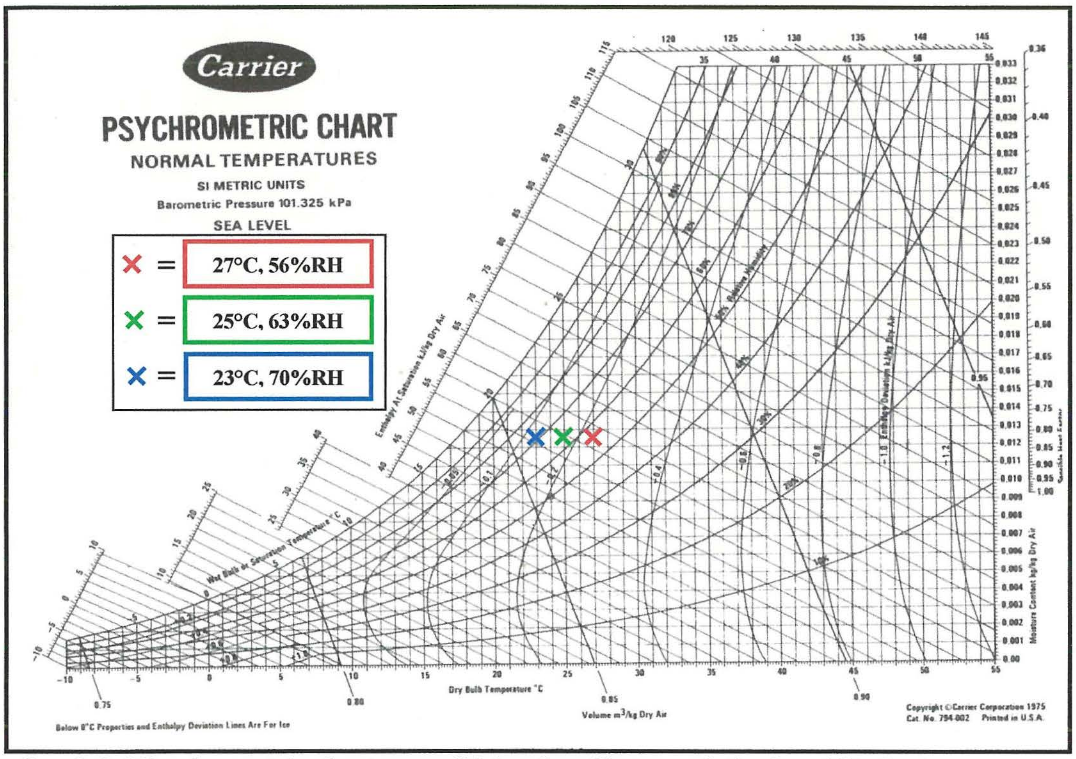
[340] Ibid., p. 12

[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

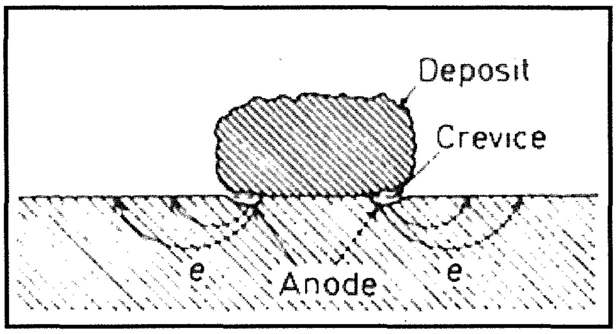

Figure 2-27 Schema of differential aeration corrosion caused by a surface deposit particle[356]

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].

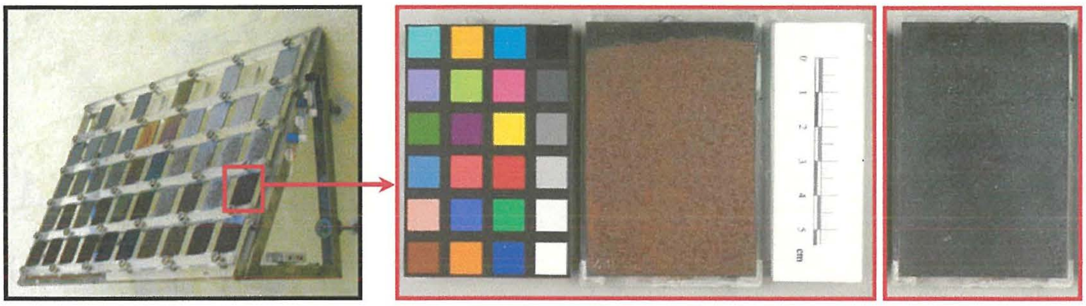

Figure 2-28 Left: Rack containing low-carbon steel coupons exposed at an inclination of 30° to the vertical in the Palace Armoury, Armour Hall[371]. Centre: Very corroded particle-collecting upper side of unprotected coupon after 17 months exposure[372]. Right: Slightly corroded inverted side of corresponding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

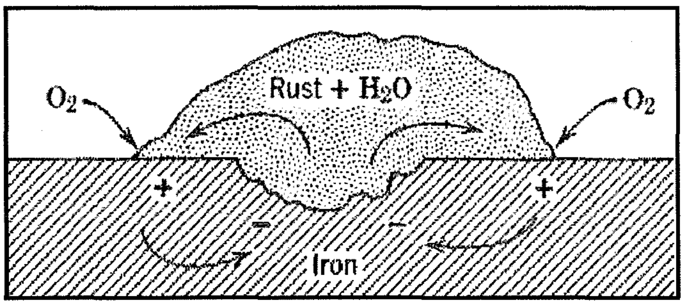

Figure 2-29 "Differential aeration cell formed by rust on iron"[402]

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.

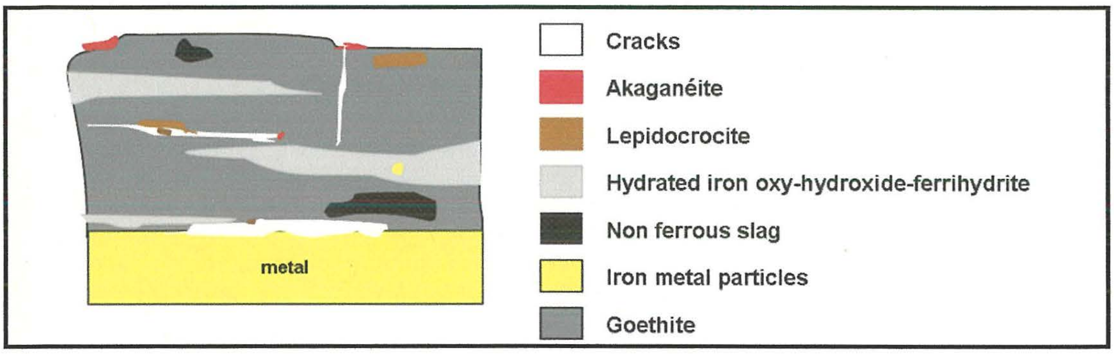

Figure 2-30 "Schematic view of the corrosion layer developed on the Amiens iron chains"[430].

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

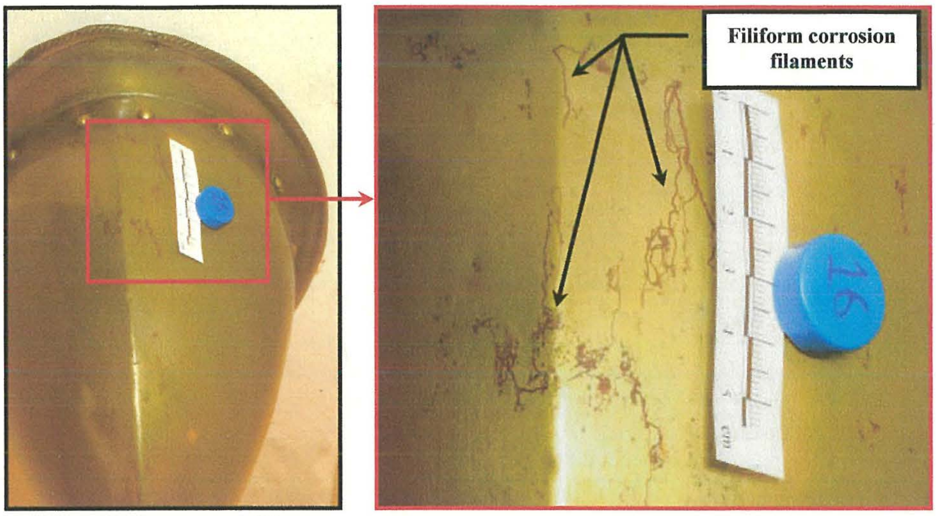

Figure 2-31 Left: *Varnished*[510] helmet *in-situ* on a wall display at the Palace Armoury. Right: Detail of the same helmet featuring filiform corrosion[511]

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

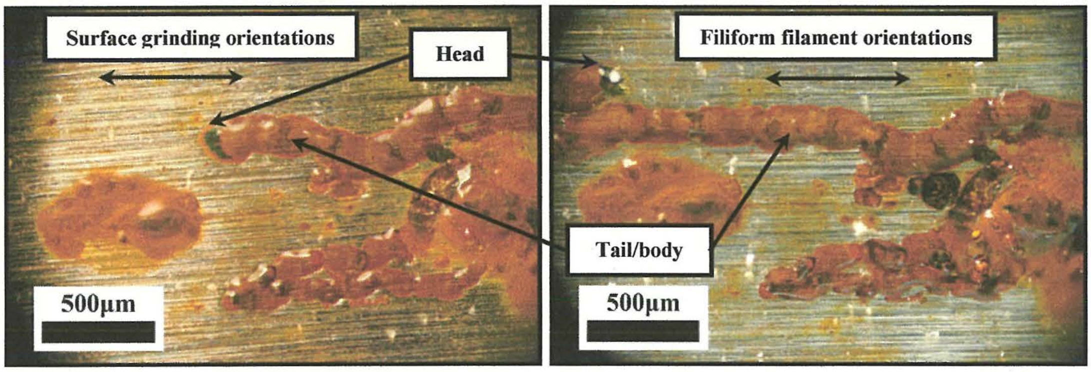

Figure 2-32 Filiform corrosion progressing on contemporary low-carbon steel coated with Paraloid B-72™ [512] (15%m/v in acetone) during laboratory-based accelerated corrosion protective system efficiency tests. Left: Filament after 14 daily cycles & Right: Same filament after 22 daily cycles[513]

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

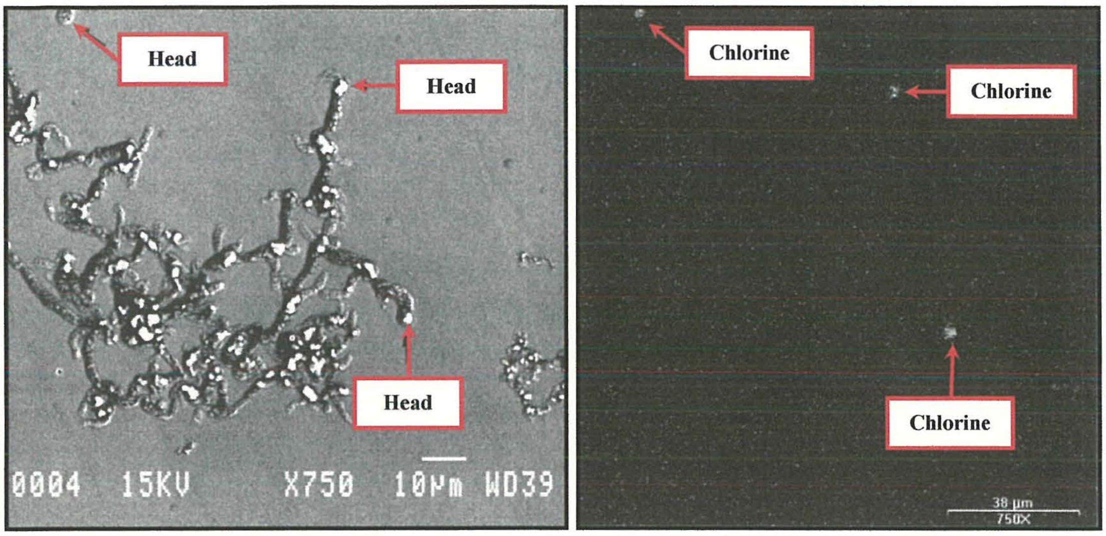

Figure 2-33 Left: Scanning electron microscope image of filiform corrosion on iron. Right: Filiform heads enriched with chlorine as determined by corresponding mapping with energy dispersive spectrometry[516]

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

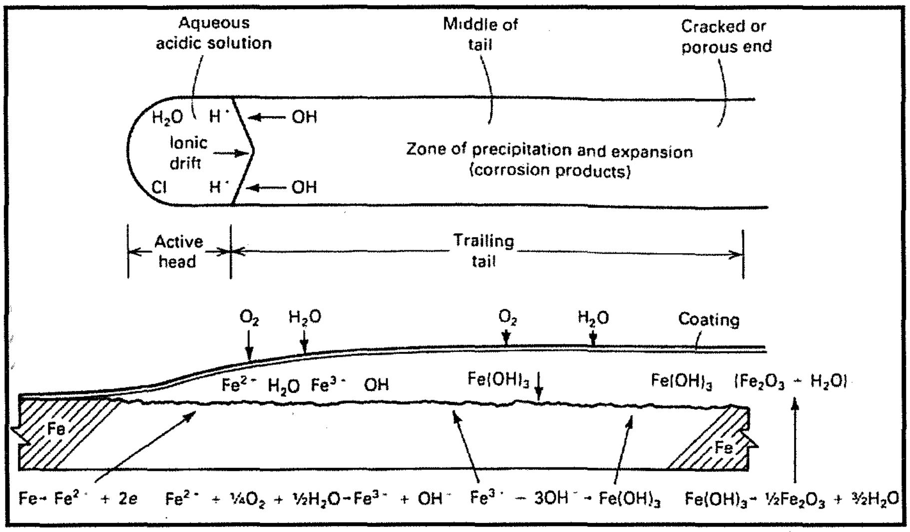

Figure 2-34 Plan and profile of filiform corrosion mechanism on coated steel[521]

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).

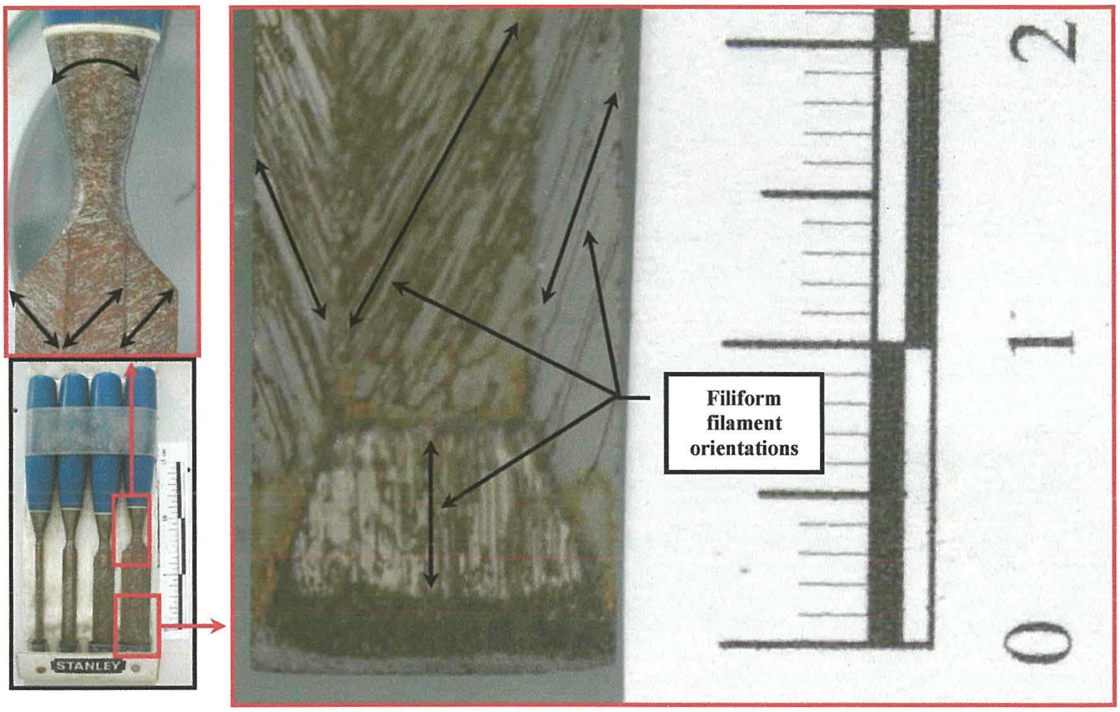

Figure 2-35 Lower left: Contemporary set of four varnished steel carpentry chisels[530] featuring filiform corrosion products oriented parallel with the grinding directions on each facet. Top left and right: Details of a single chisel's facets and filament orientation

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[526] Ibid.
[527] Ibid.
[528] Ibid.
[529] Ibid., p. 104
[530] Courtesy of J. Camilleri-Polidano

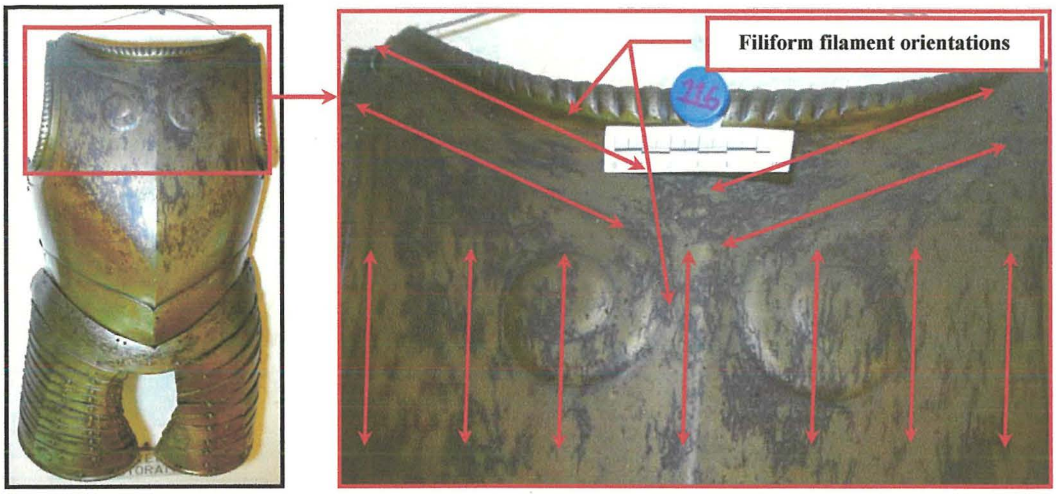

Figure 2-36 Corrosion product filaments that are oriented parallel in respective areas on Palace Armoury munition armour[531]

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

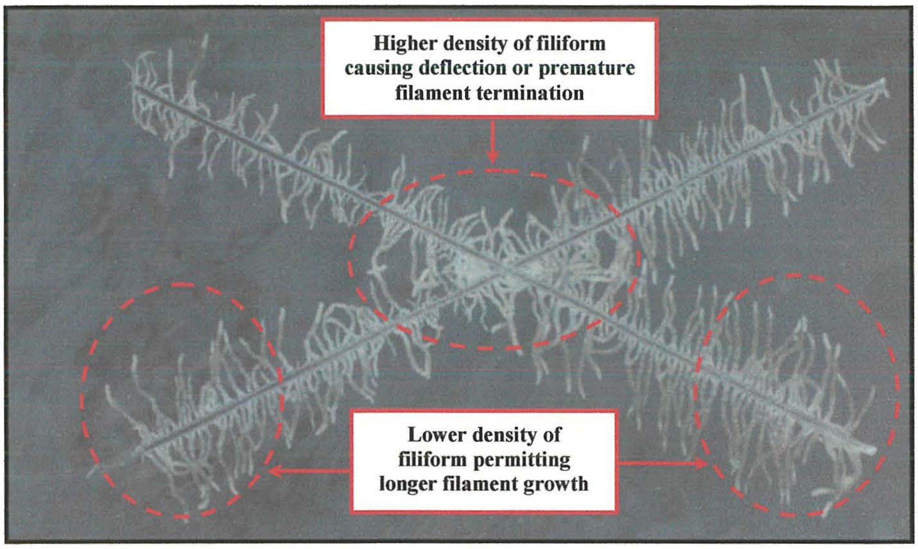

Figure 2-37 A coated unspecified metal with filiform corrosion propagating from deliberate coating incisions[537]

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].

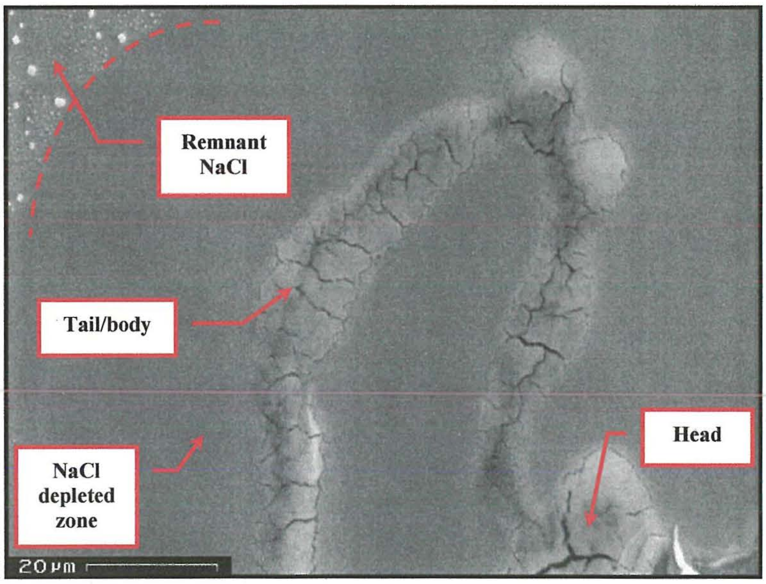

Figure 2-38 Scanning electron microscope image of a small filiform corrosion filament on iron coated with halite, rather than a coating[540]

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

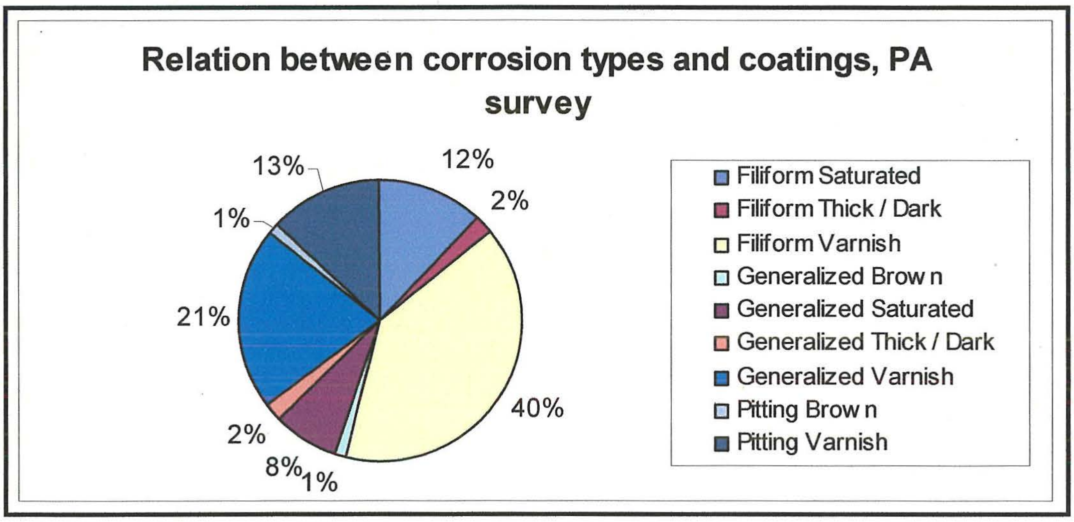
[538] Weissenrieder & Leygraf, 2004, pp. 165-171

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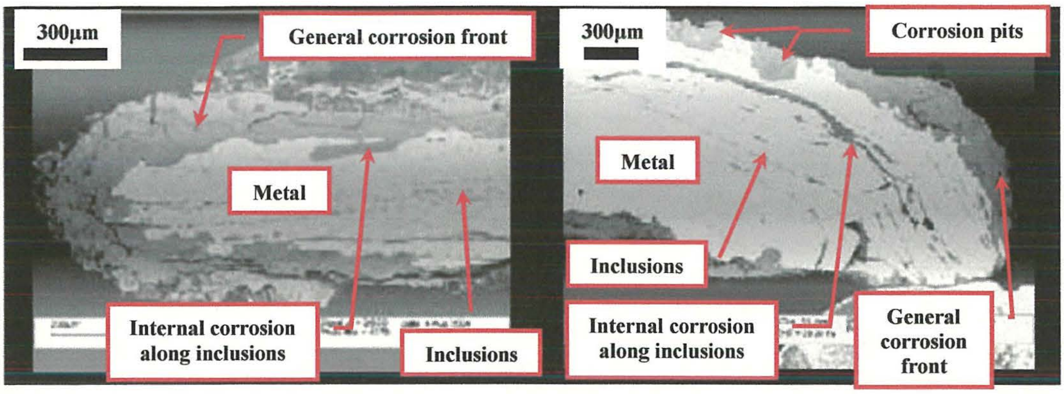
[541] Uhlig & Revie, 1985, p. 257

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

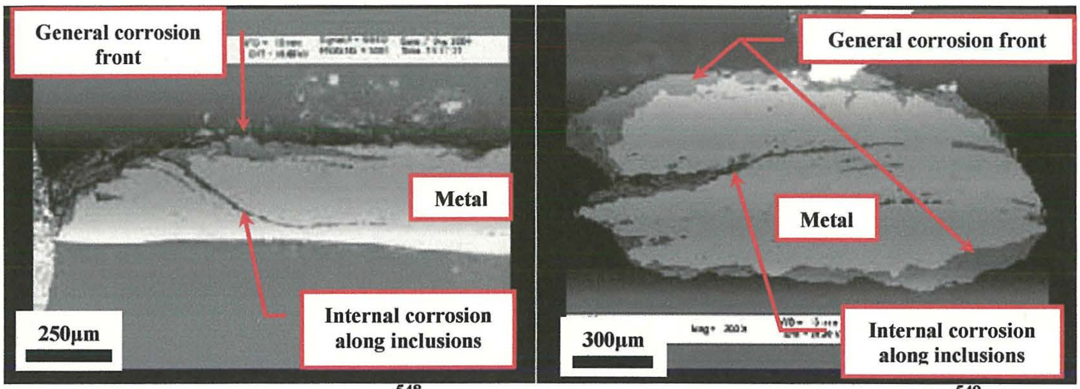
[543] Argyropoulos, in press, Chapter 5, p. 17

[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

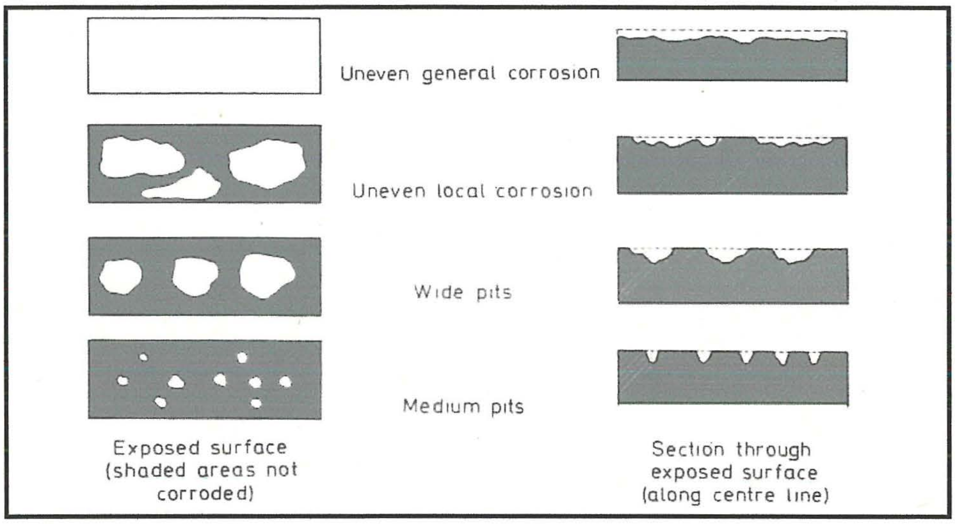

Figure 2-40 Schematic classification of types of metal corrosion: excluding corrosion products[550]

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].

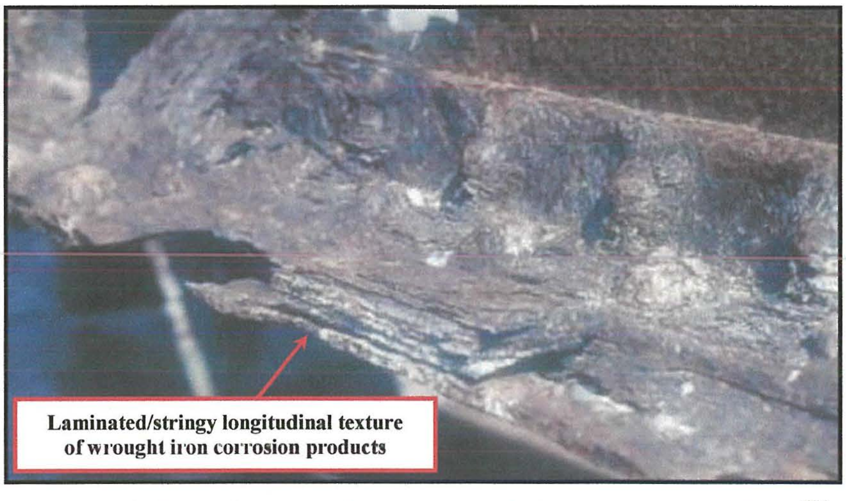

Figure 2-41 Excessive corrosion to a wrought iron construction beam[554]

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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.

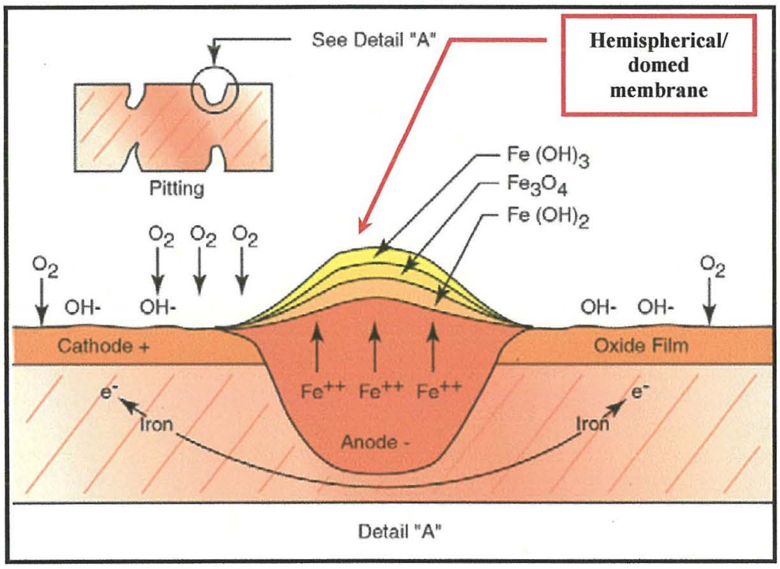

Figure 2-42 Schematic depiction of pitting corrosion by differential aeration on a ferrous metal with a previous oxide layer[567]

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.

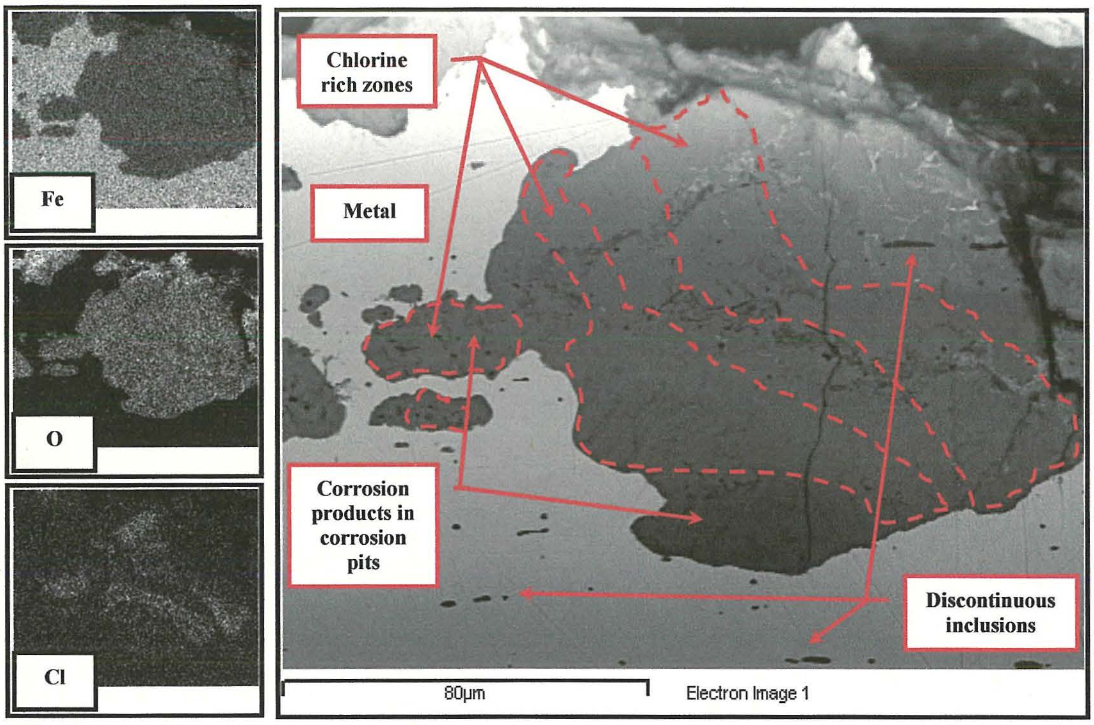

Figure 2-43 Left: Energy dispersive spectrometry mapping of a cross-section of more heavily corroded Palace Armoury armour (PA RC 20) with increased chlorine concentration inside a corrosion pit below the adjacent metal. Main: Corresponding SEM BSE image[579].

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.

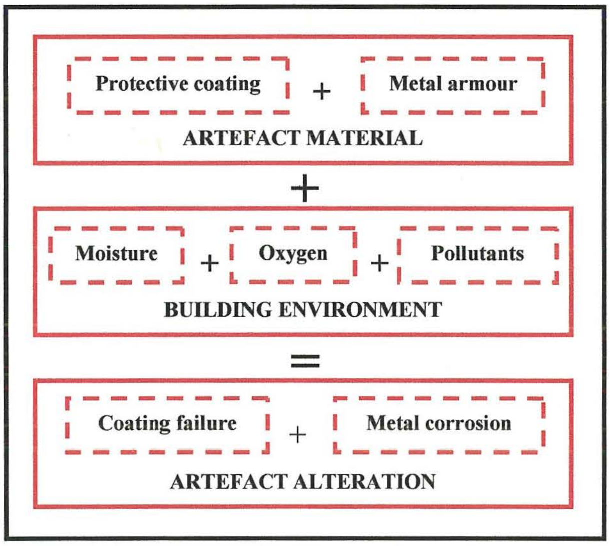

Figure 2-44 A conceptual representation of the principal components of the material-environment system contributing to the metal artefact alteration by corrosion

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).

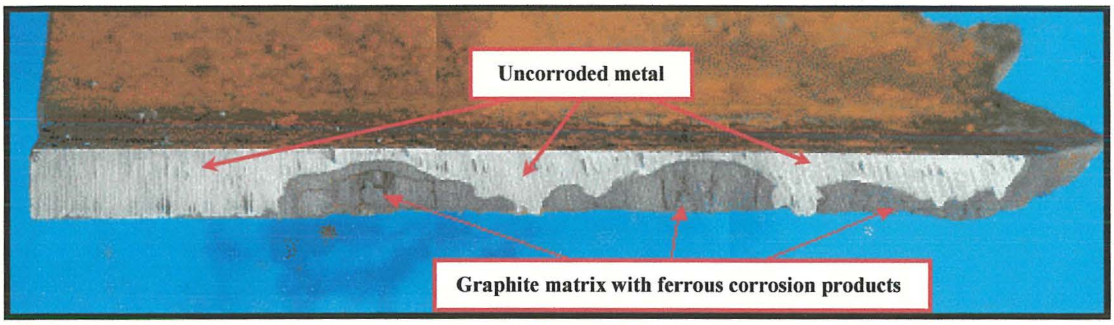

Figure 2-45 "Longitudinal cross-section through the wall of a cast iron pipe, exhibiting severe graphitic corrosion, i.e. dissolution of the iron from the cast iron pipe leaving behind layers of intact graphite"[651]

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].

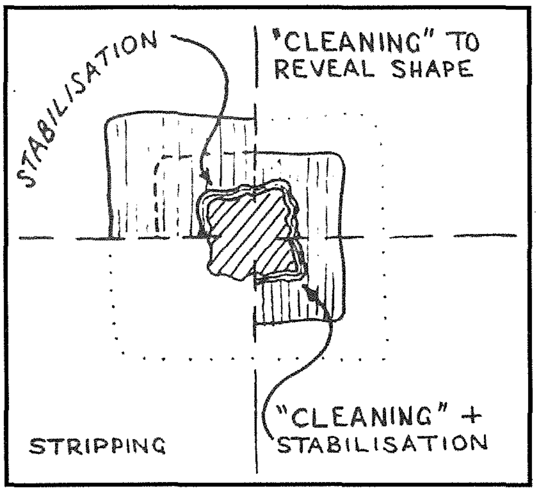

Figure 2-46 "Diagram showing four options the conservator may choose in cleaning a bronze object"[655]

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

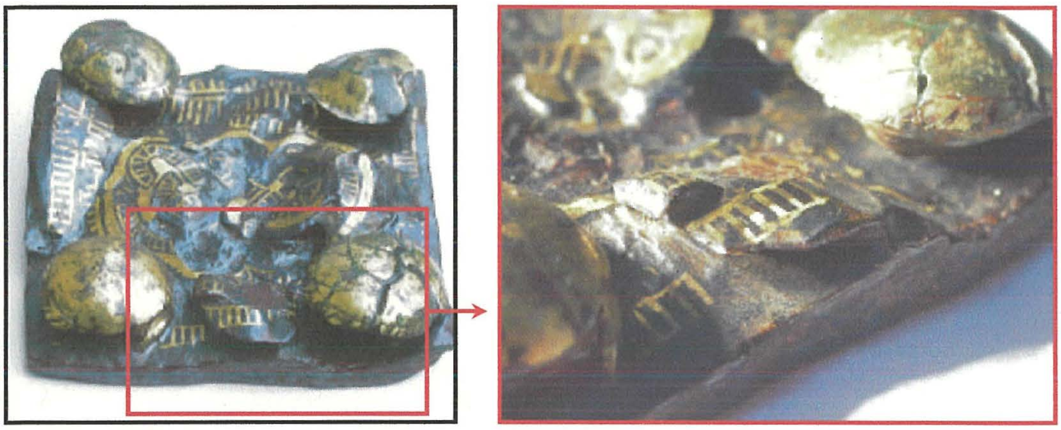

Figure 2-47 Left: Overall view of a Merovingien (5-8th century AD) wrought iron plate inlaid with brass[696]. Right: Detail demonstrating the vertical displacement of the corroded iron and contained brass.

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.

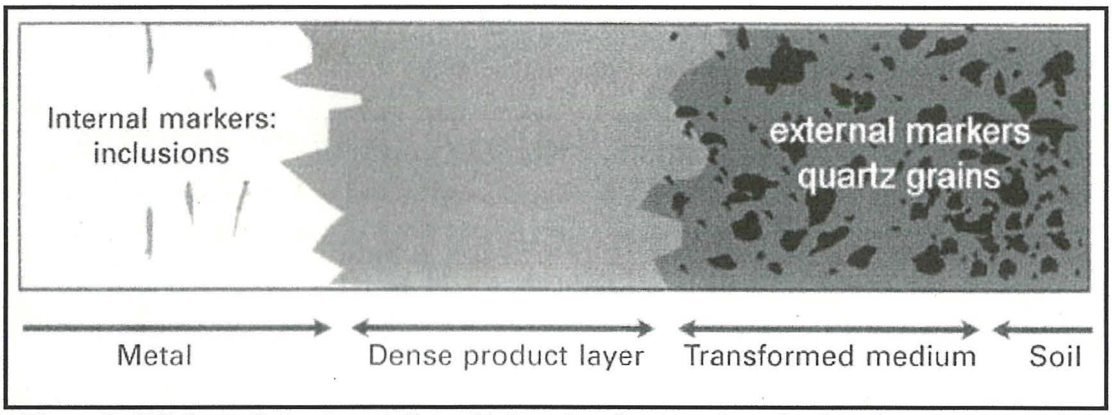

Figure 2-48 Schematic representation of internal and external marker locations on a wrought ferrous metal in a burial environment[708]

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.

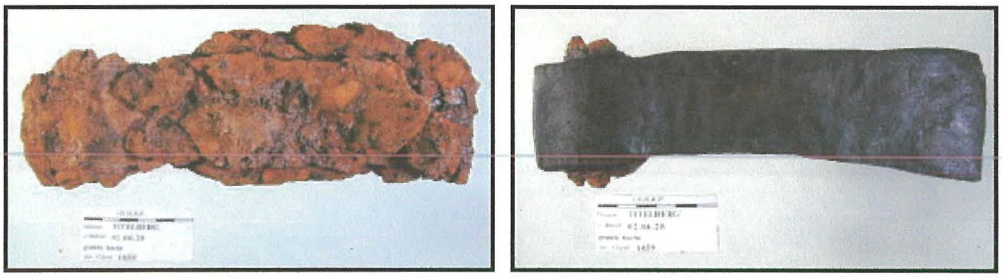

Figure 2-49 Left: Wrought iron axehead dating from the Middle Ages after terrestrial excavation with corrosion products fixed into sediment. Right: Same axehead after removal of sediment fixed with corrosion products[709]

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[707] Neff et al. 2004, p. 743

[708] Reguer et al, 2007, p. 174

[709] Crawford, 2003

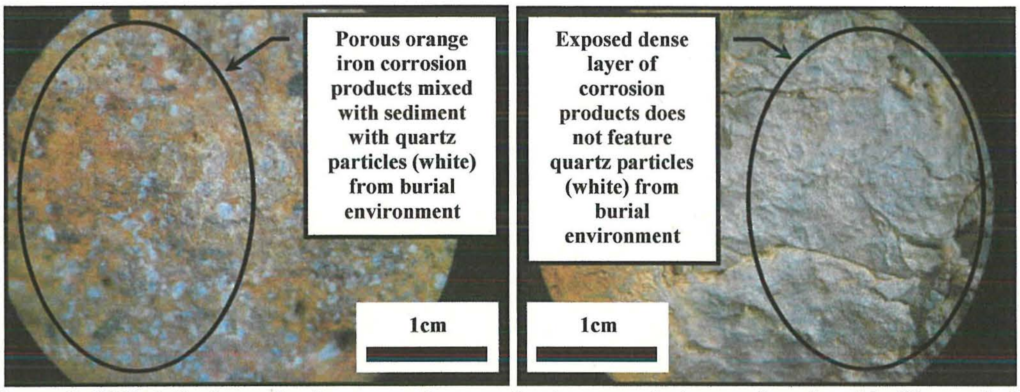

Figure 2-50 Details from during corrosion product removal stages of axehead in Figure 2-49. Left: Quartz sediment superior limitos markers in external corrosion product layers. Right: Determined limitos of axehead without quartz sediment superior limitos markers[710]

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

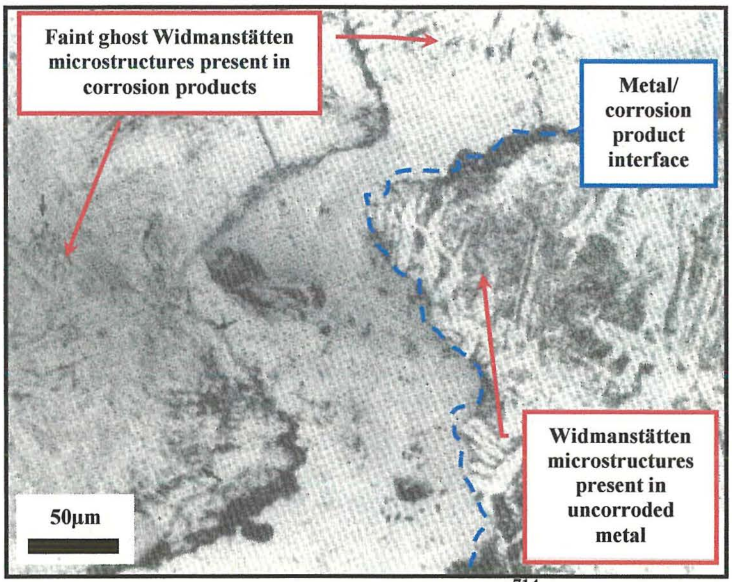

Figure 2-51 Widmanstätten microstructures present in metal[714] and corrosion products (200x)[715]

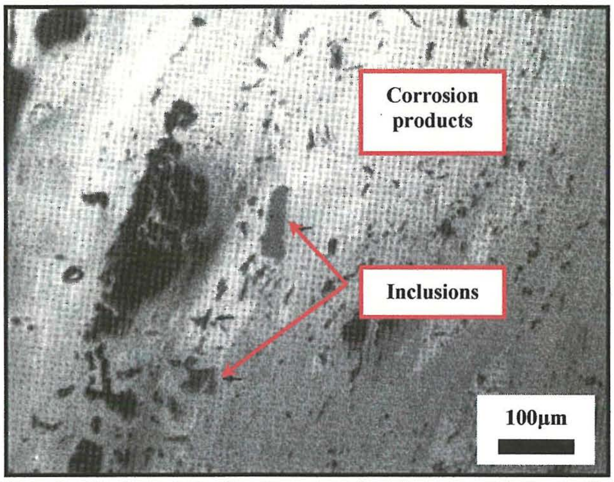

Figure 2-52 "Slag inclusions wholly surrounded by corrosion products (100x)"[716]

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

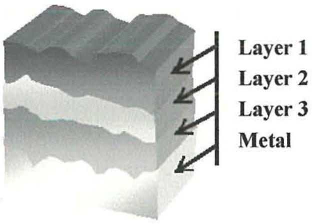
[715] Scott, 1989, p. 13

[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.

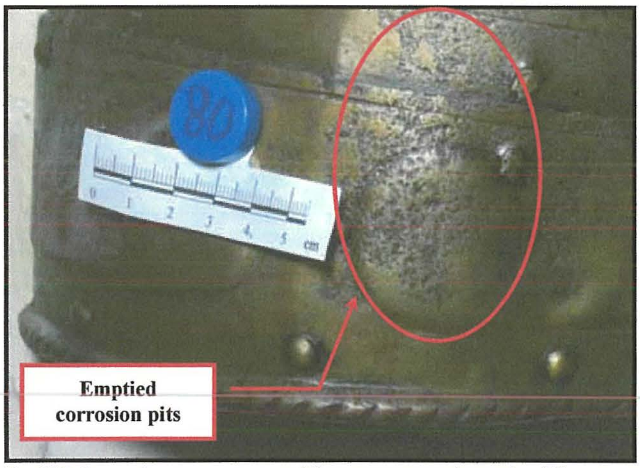

Figure 2-55 Detail of Palace Armoury munition armour tasset with corroded surface area largely devoid of corrosion products[754]

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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

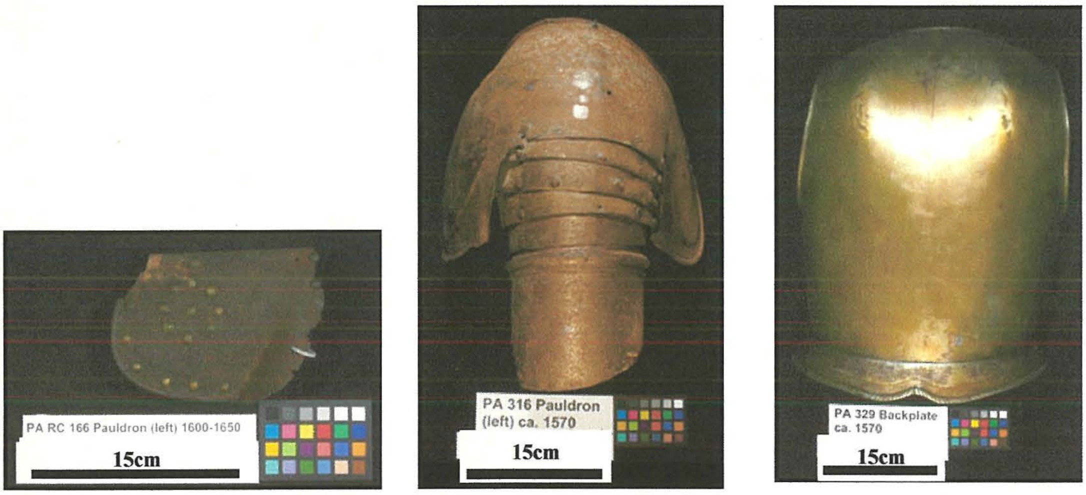
[820] 3.2.3.1.1 Munition armour selection

[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]).

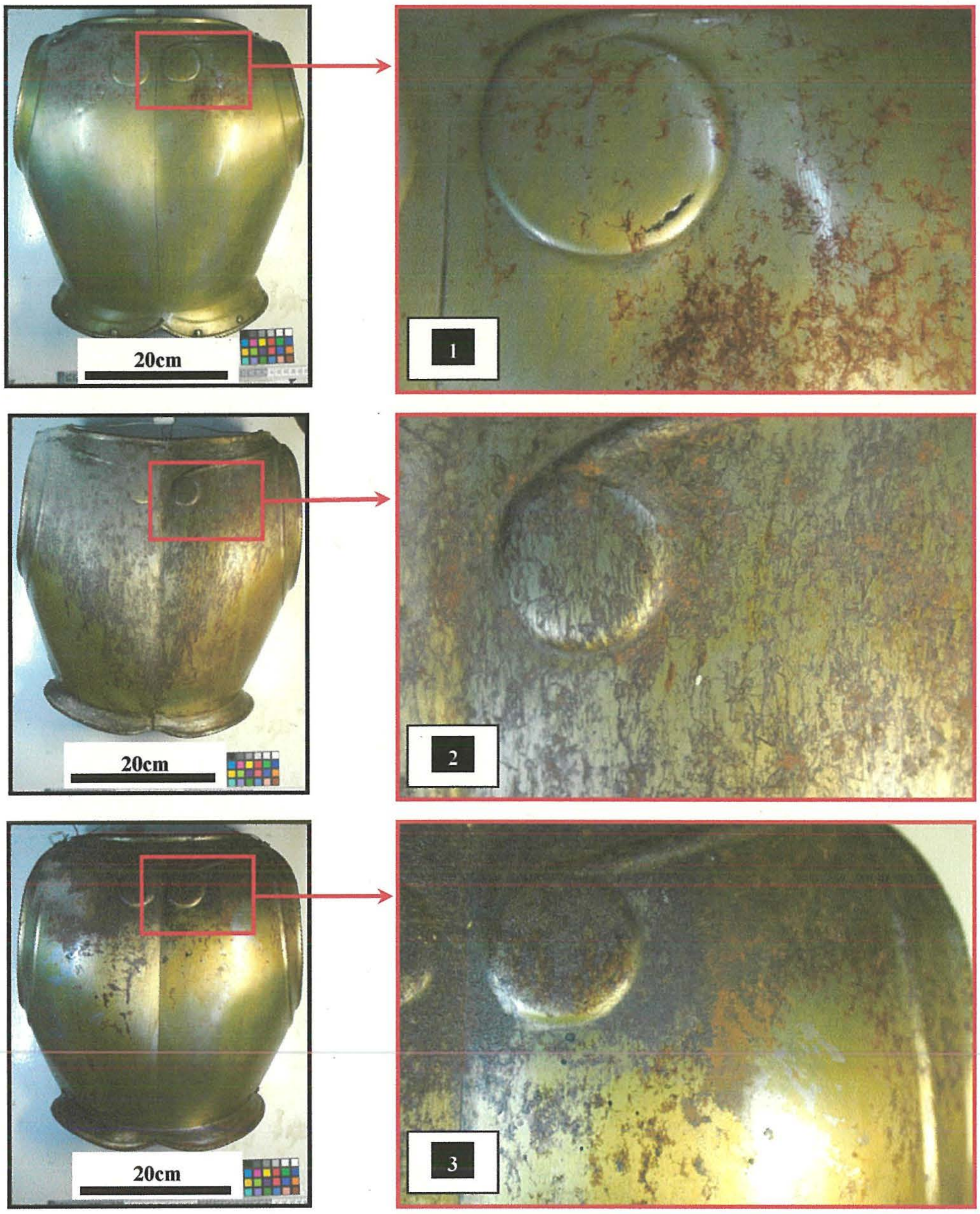

Figure 3-2 Three backplate armour selected to be representative of the corrosion extent on the wall displays

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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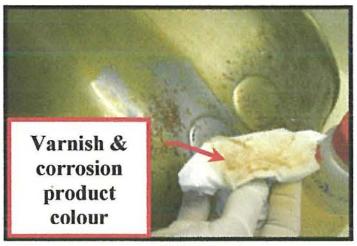
[847] This is in contrast with approaches to decorated armour (Stroud, 2006-2007, pers. comm.).
[848] Stroud, 2006-2007, pers. comm.
[849] Ibid.

3c.

3d.



3d.

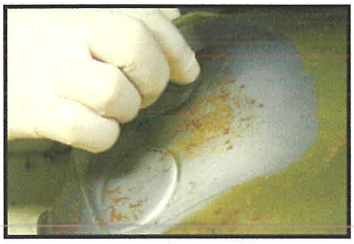
4. <u>Upper (i.e. positioned above adjacent metal profile) corrosion product removal</u>
   a. Adherence of "hard rust attached to the surface" checked by probing with the custom-made acrylic plastic wedge. This physical process also "removed varnish remnants trapped in the rust". "Rust is hard, but 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.

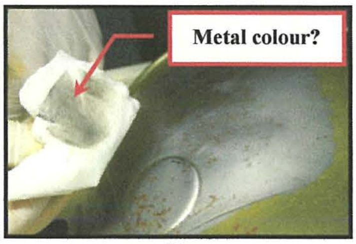

4f.


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"

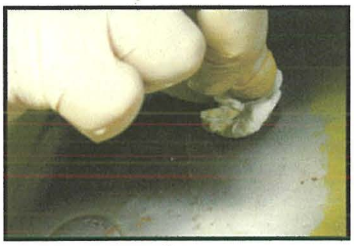

5a.


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).

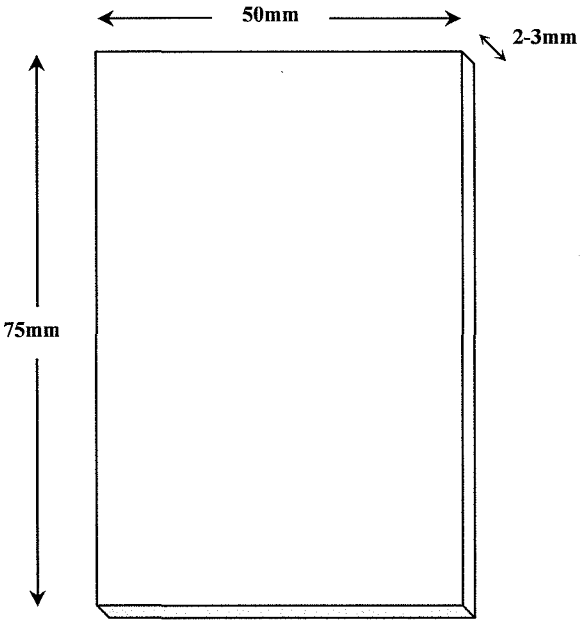

Figure 3-4 Dimensions of low-carbon steel armour analogues

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.

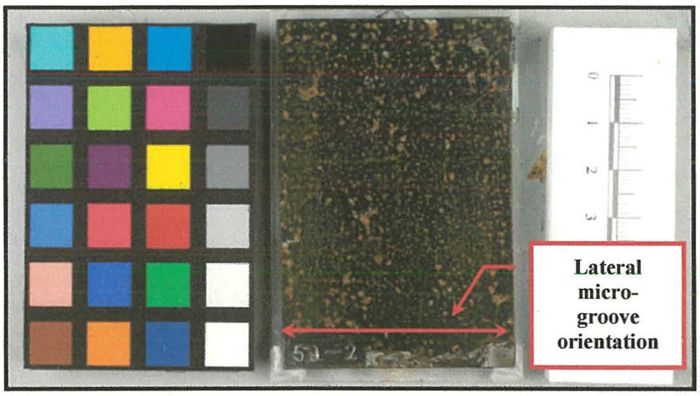


Figure 3-5 Armour analogue representative of Coupon Series 1 after pre-existing coating and partial corrosion product removal

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).

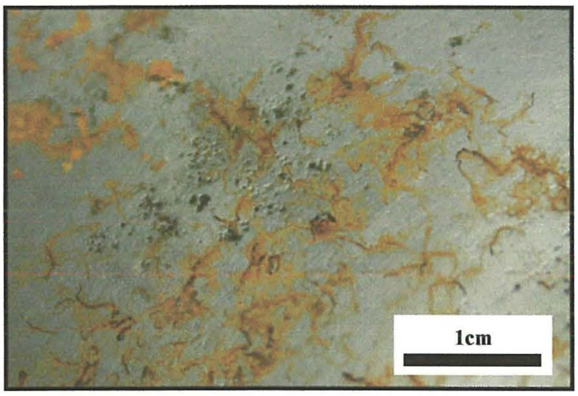
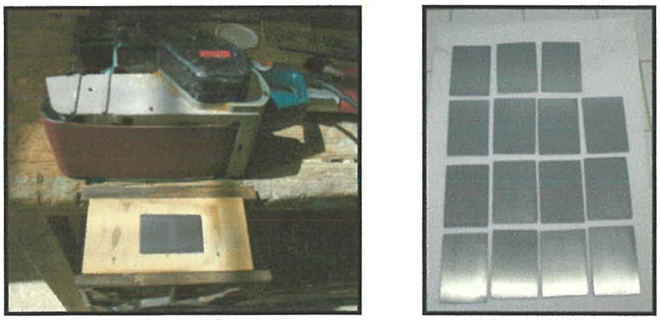


Figure 3-6 Filiform corrosion filaments (orange-brown) proposed to have initiated from former corrosion pits (black areas) on munition armour

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.

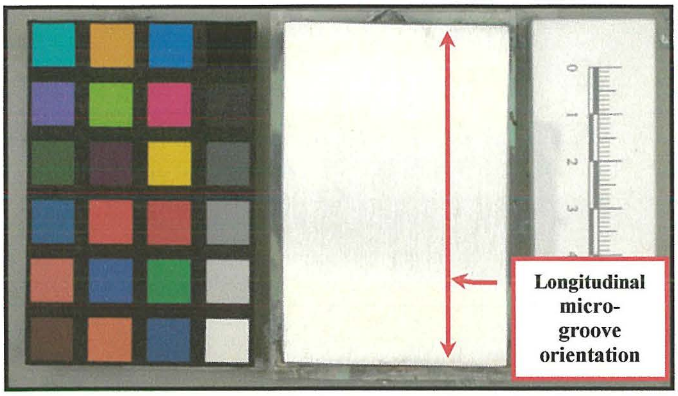


Figure 3-8 Armour analogue representative of Coupon Series 2-7 after pre-existing coating and corrosion product removal

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.

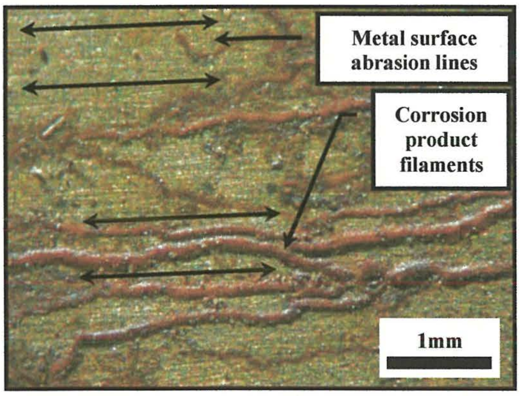


Figure 3-9 Filiform corrosion propagating along parallel metal surface abrasion lines on PA munition armour

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).

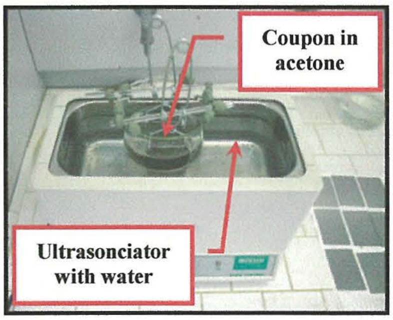

Figure 3-10 Removal of surface matter from armour analogues by ultrasonication

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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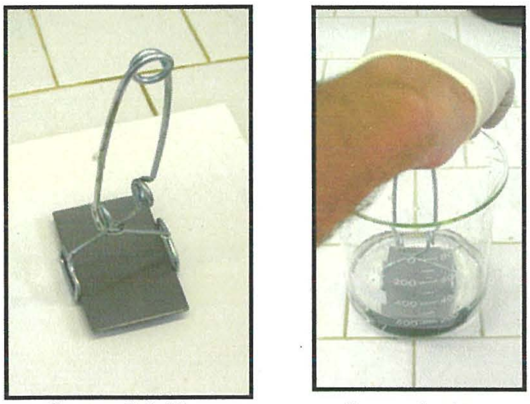
[889] 2.3.1.2.1 Localisation of the limitos

[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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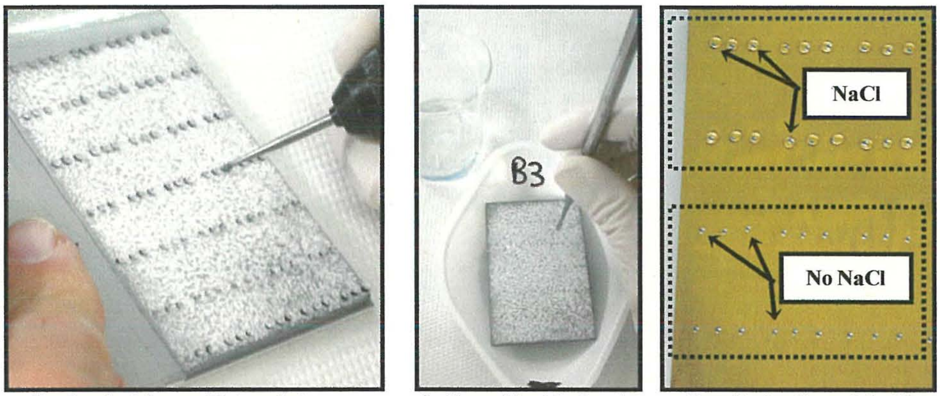
[891] In spite of sodium chloride's much lower solubility in ethanol (0.055 g/100g at 25°C) compared with in water (26.483g/100g at 25°C) (Pinho & Macedo, 2005, p. 30). Repeated applications would therefore be required.

[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).

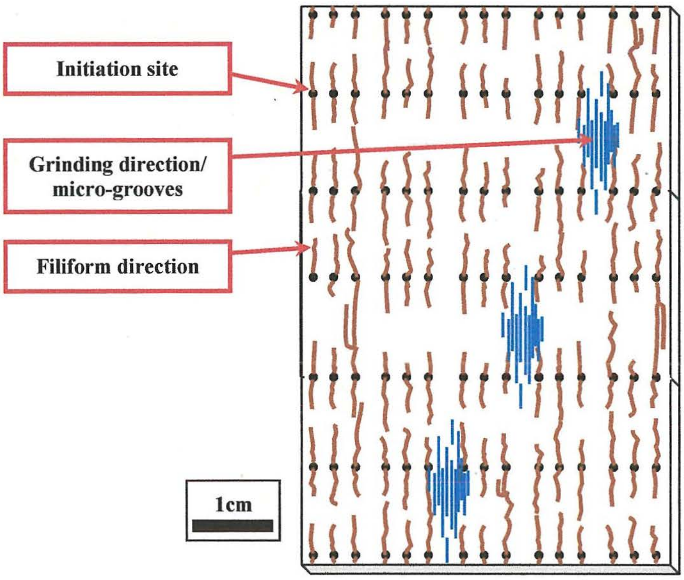


Figure 3-13 Schematic representation of coupons designed for filiform corrosion

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 ($0.00031 \times 10^{20} g.100g^{-1} H_2O$)[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 25°C, 1M)[914] and iron ($Fe^{2+} + 2e^- \rightarrow Fe$, -0.440V/SHE at 25°C, 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).

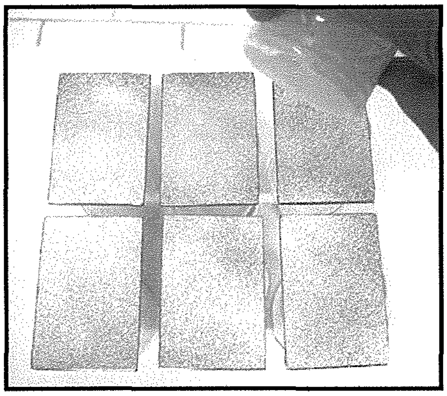

Figure 3-14 Application of zinc oxide/barium sulphate applied superior limitos marker to armour analogue Coupon Series 5

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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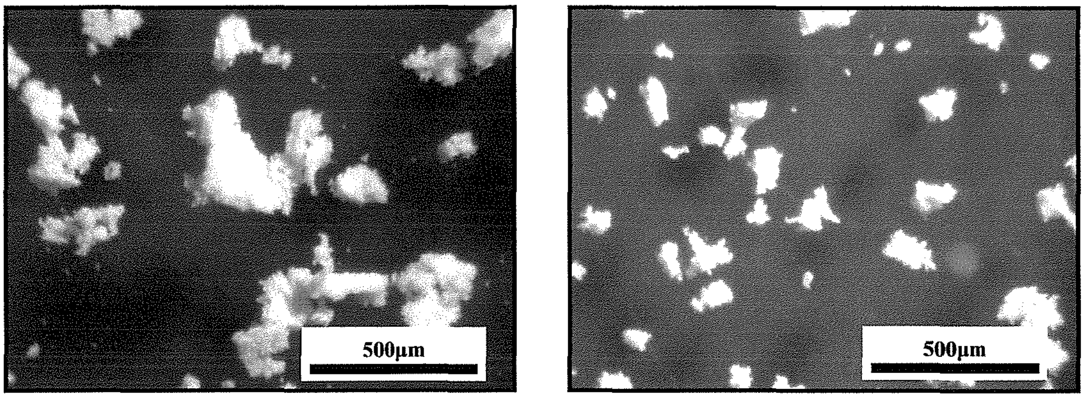
[938] Feller, 1986, p. 54

[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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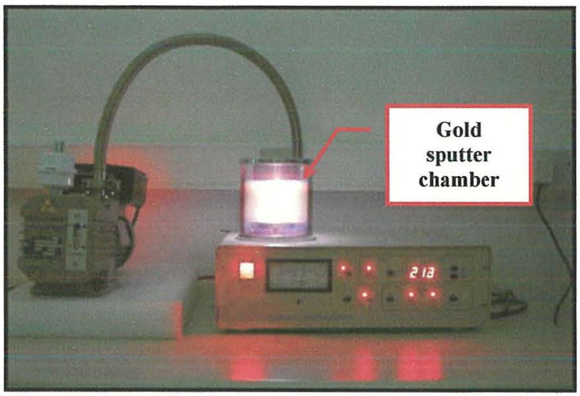
[940] Biella, 14/03/07, pers. comm.

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 ($mg.cm^{-2}$)		
$BaSO_4$ (n = 12)	ZnO / BaSO4 (n = 12)	Au (n = 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 (T°C)**	**Relative Humidity (RH%)**	**Temperature (T°C)**
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 35°

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.

$$R = [\sqrt{(100 + A)^2 + A^2 - (H + A)^2} - A] \times 1/715.3 + 1.3333$$

$A = 25.60 - (0.1950 \times T) + (0.0008 \times T^2)$
$R =$ 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).

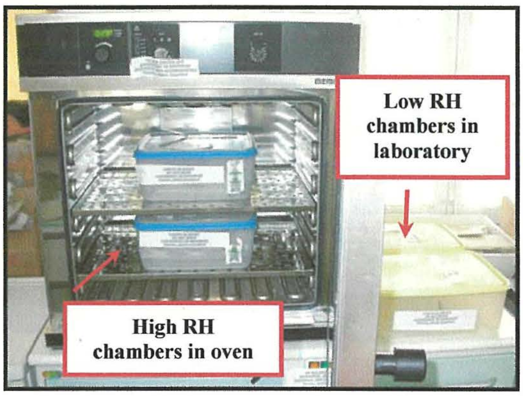

Figure 3-17 Polypropylene chambers and oven used for relative humidity and temperature cycling (2-week regime)

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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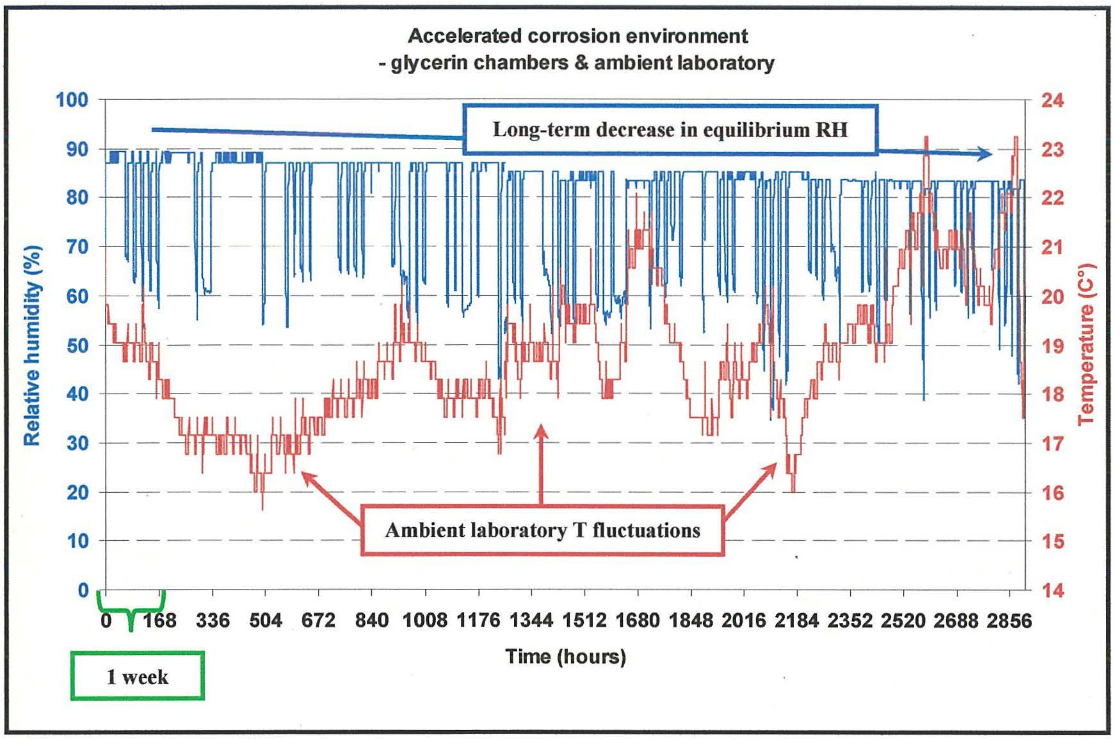
[959] Concentration of glycerin/water solution when with 1.3785 RI (at 20°C) (Ibid.). Data at 35°C could not be sourced.

[960] ASTM, 2003, p. 2

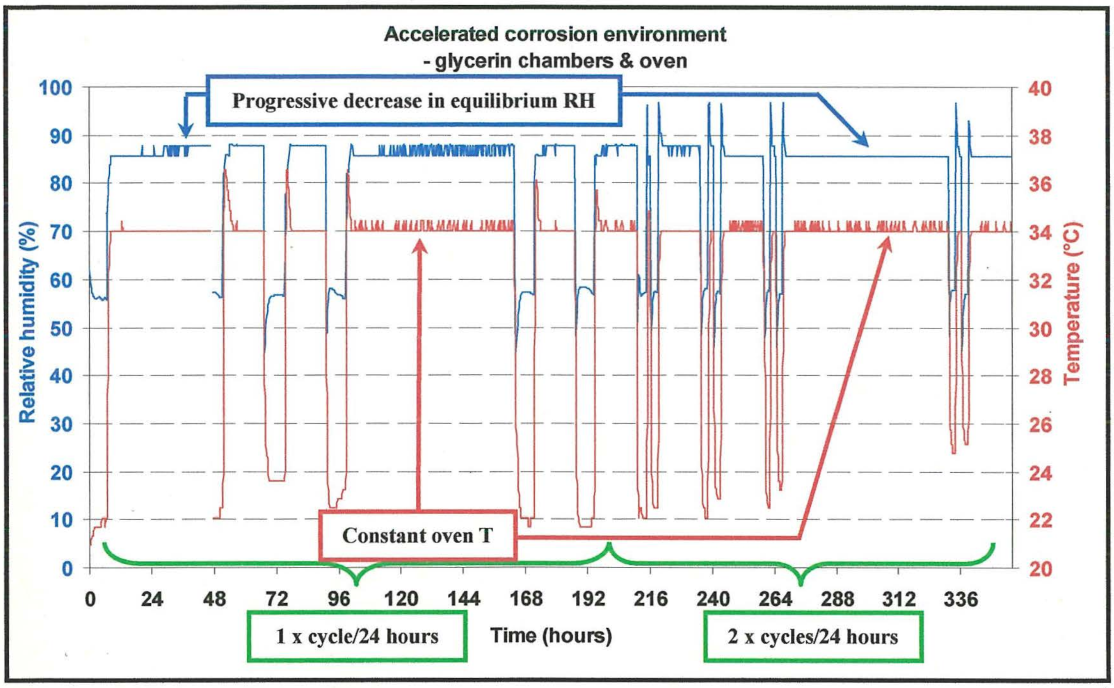
[961] Onset, 2003

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].

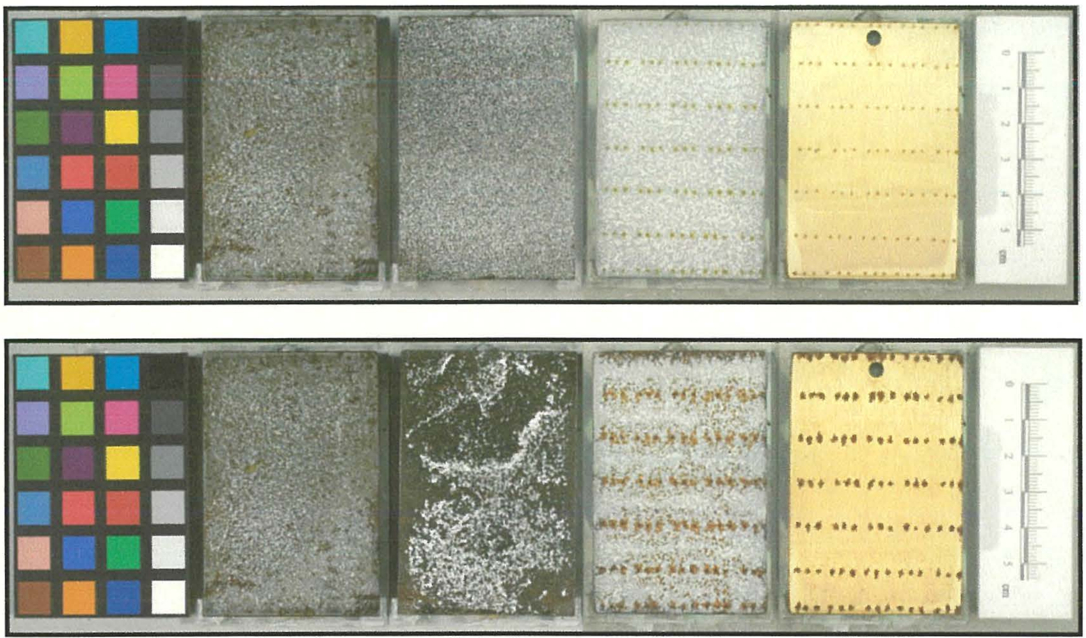


Figure 3-18 Representative armour analogues from the four Coupon Series *not* selected for continued investigation Top row: Before accelerated corrosion regime Bottom row: After accelerated corrosion regime

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

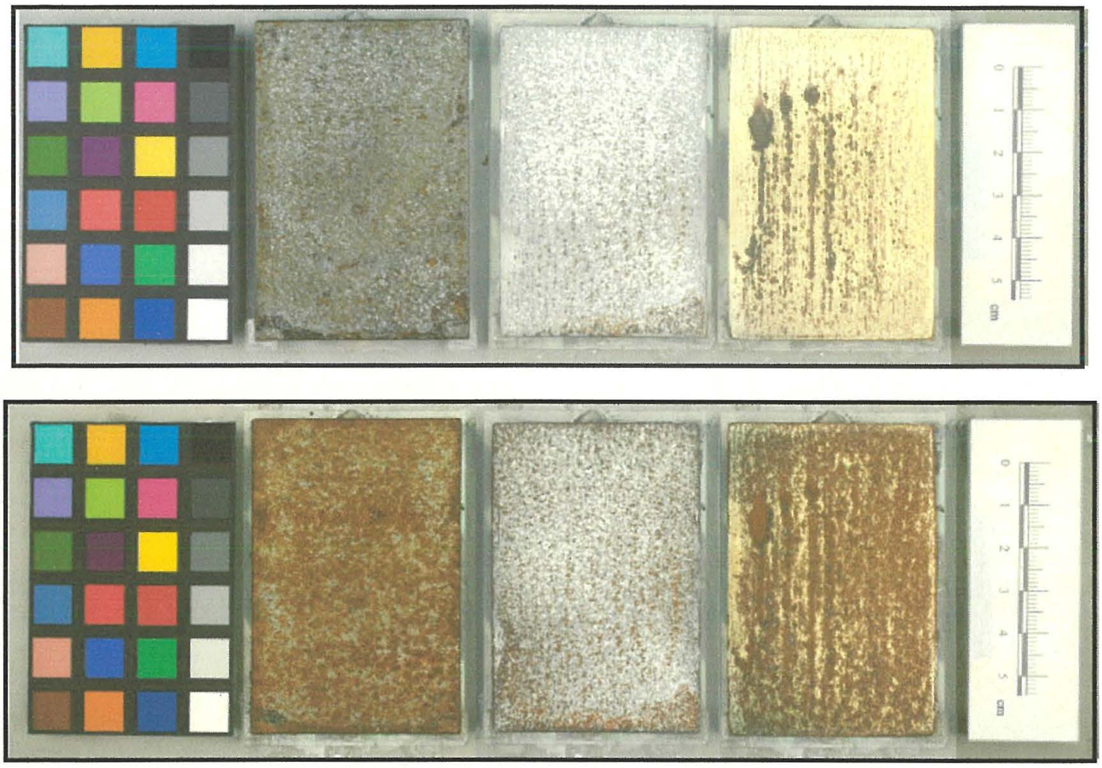

Figure 3-19 Representative armour analogues from the three Coupon Series selected for continued investigation. Top: Before accelerated corrosion regime Bottom: After accelerated corrosion regime

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

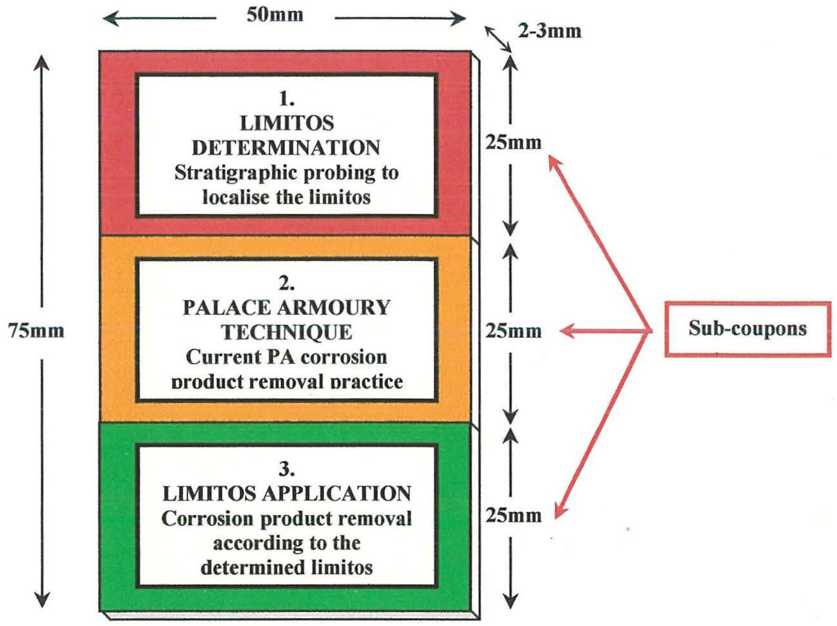
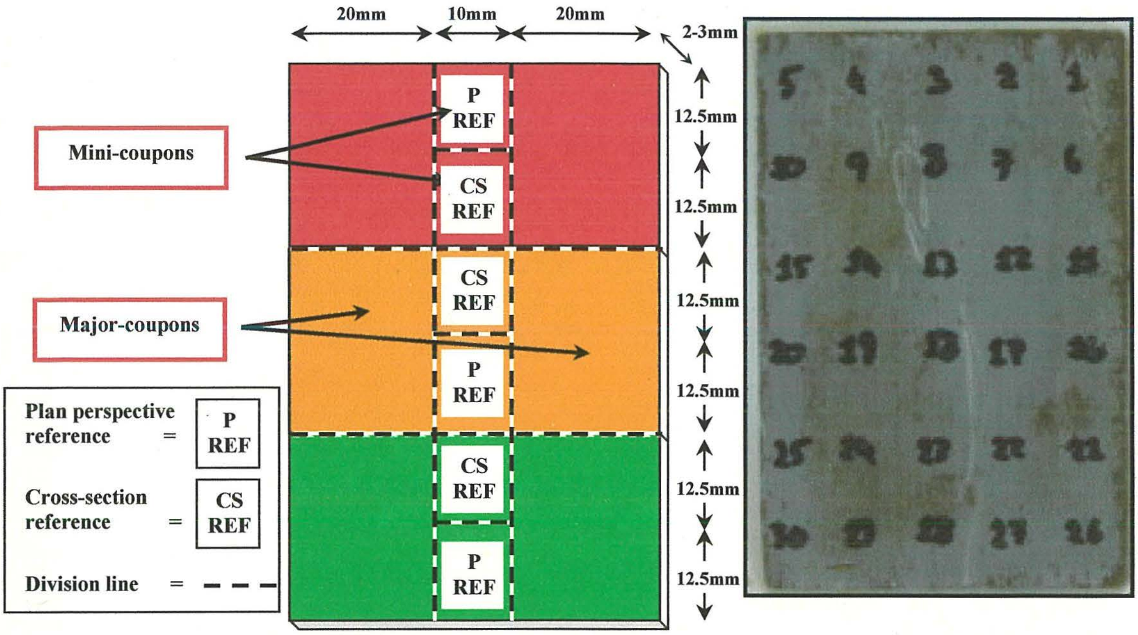


Figure 3-20 Schematic summary of armour analogue coupon with sequential objectives

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

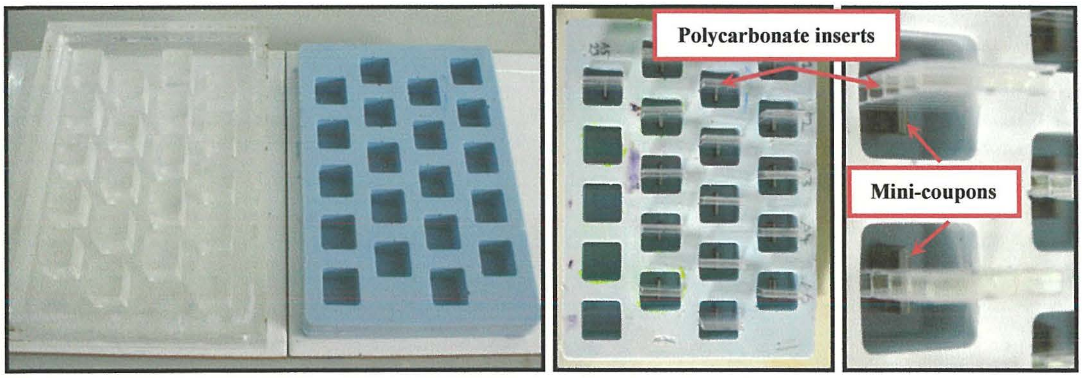

Figure 3-23 Left: Computer Numerical Control (CNC) machined acrylic positive mould and cast silicone negative mould custom-designed for dimensions of armour analogue sections Centre & right: Overview and detail of mini-coupons (i.e. cross-section samples) in embedding tray before resin application

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.

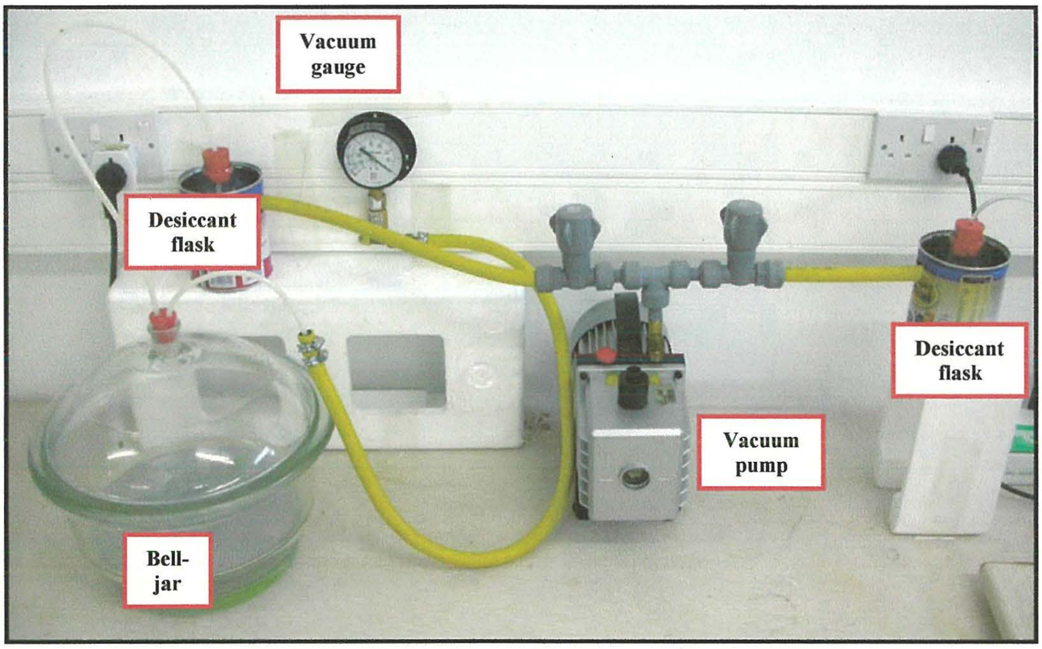

Figure 3-24 Laboratory constructed vacuum resin embedding system

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.

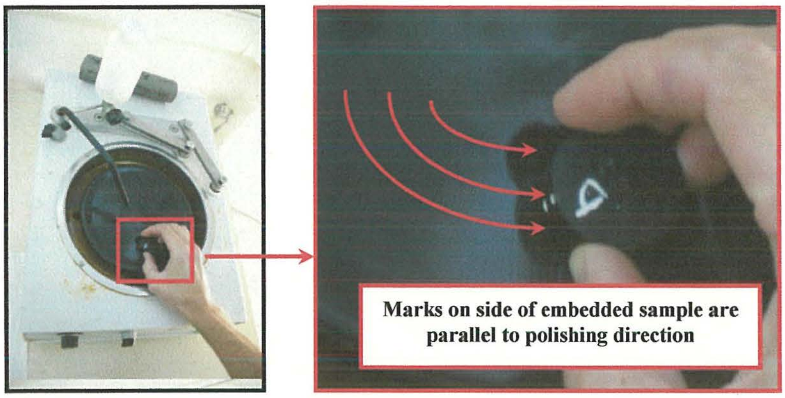
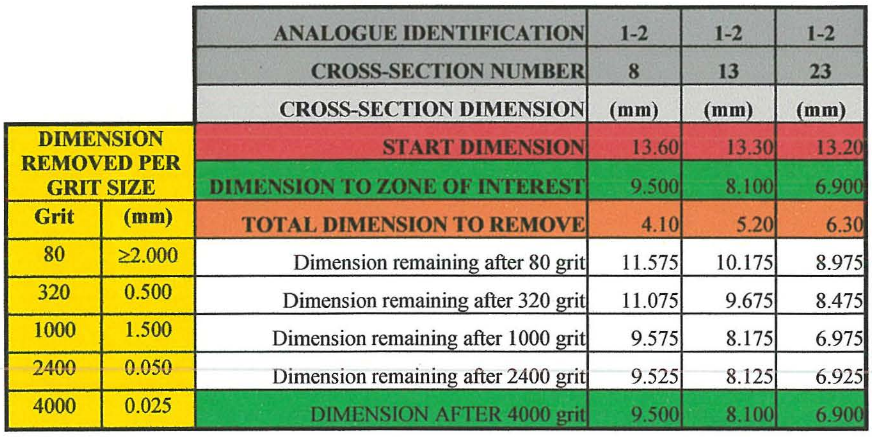


Figure 3-25 Sample polishing table and example detail of sample orientation and abrasive wheel direction

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].

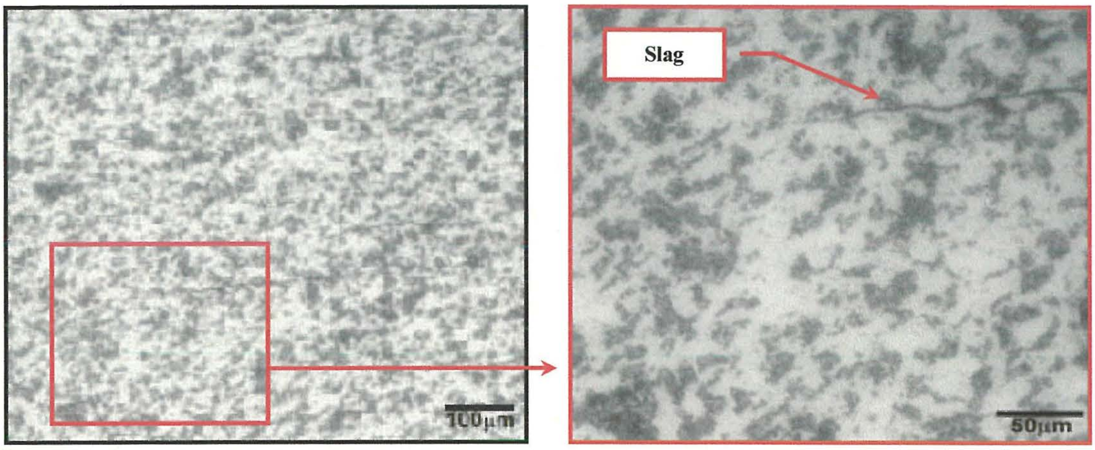

Figure 3-26 Slag in metallographic cross-section of armour analogue[982]

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 Armour analogue objective 2, Palace Armoury technique 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. Coating (i.e. Paraloid B-72™) removal
    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. Upper (i.e. positioned above adjacent metal profile) corrosion product removal
    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. Lower (i.e. positioned in pits below adjacent metal profile) corrosion product diminution
    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. Surface polishing
    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).

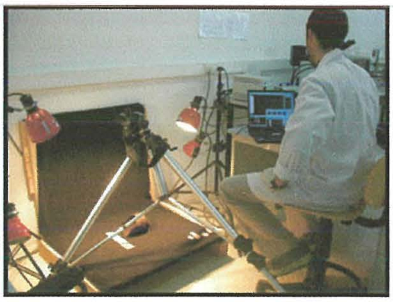

Figure 3-29 Macrophotography of overall armour

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

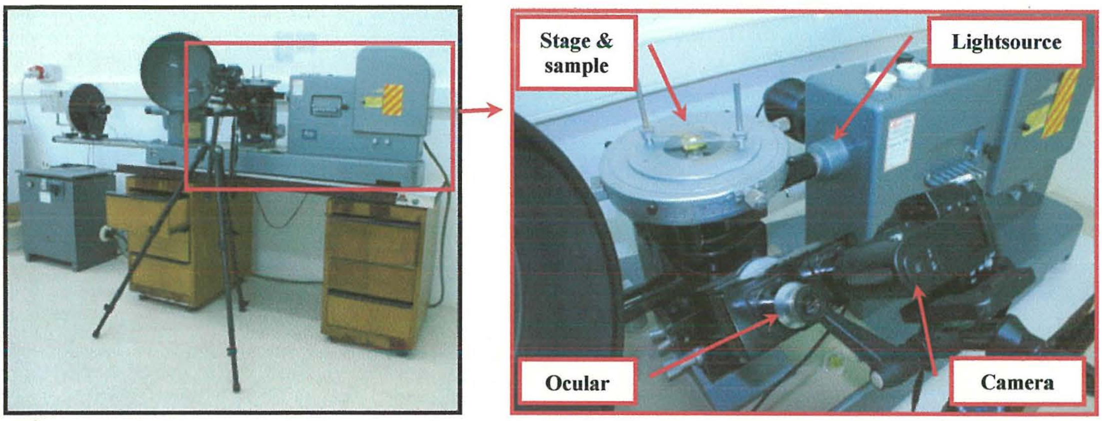

Figure 3-30 Photomicroscopy configuration: Leitz MM5 inverted metallographic microscope and tripod mounted Nikon Coolpix 4500 digital camera

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

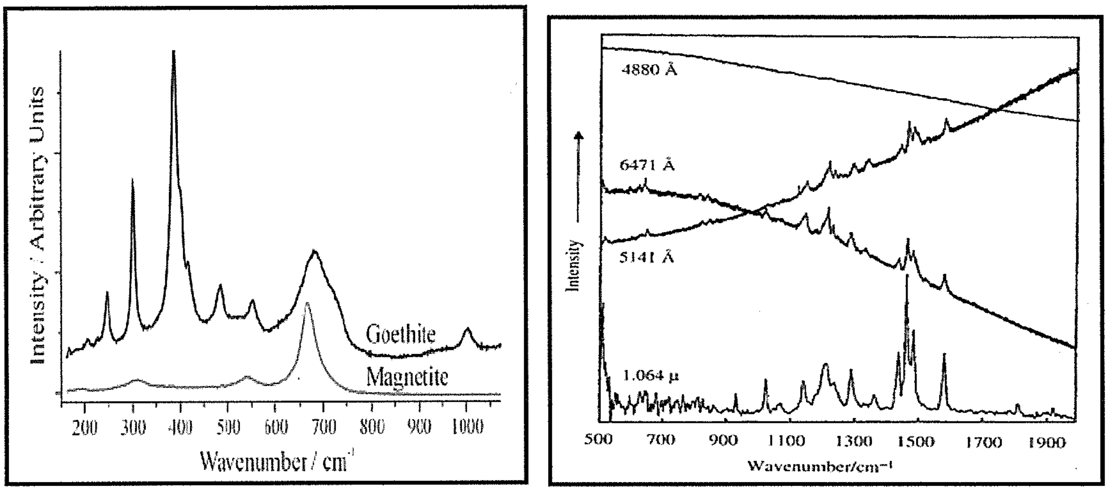
[1021] Monnier, 06/10/2007, pers. comm.

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.