4.43 Preservation of Metallic Cultural Heritage

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4.43.1 Introduction to Conservation of Metals

4.43.1.1 Cultural Heritage Context

Cultural heritage is an industry that significantly contributes to the economy of nations via tourism, employment, and taxation. Whole communities rely on it for their economic welfare. Cultural objects and structures document developments and events within a society, offering a bridge to the past and providing important markers for individuals, religions, and cultures. To continue their contribution to the welfare, stability, development, and understanding of societies, cultural objects must be actively preserved. Age, origin, and use mean that historical, archaeological, industrial, and art objects are often decayed, corroded, and prone to further deterioration. The diversity of contexts from which cultural heritage metals originate presents a significant preservation challenge. This chapter briefly defines conservation and provides an insight into the goals and ethical constructs that underpin its decision-making rationale. This is followed by an overview of how corrosion processes relate to treatment design and assessment. Conservation strategies for metals are revealed using selected examples of treatments to illustrate conservation research and practice.

Metals conservation involves the preservation of cultural objects and conservators are its practitioners. Their goal is to preserve objects while retaining evidence of their cultural context and integrity. Ideally there should be minimum change to an object while achieving this and restoration to the former state is rarely carried out. Refinishing, replacement of parts and repairing of metal objects with new corrosion-resistant materials are not normally options within the conservation process. While preservation appears to be a straightforward material science problem, involving elucidation of the structure and corrosion of metals to develop conservation procedures that prevent or control corrosion, it is constrained by ethics, aesthetics, and cultural contexts that may complicate, constrain, and ultimately direct preservation strategies.

The goal of conservation is normally the preservation of an object using minimum intervention, although in some instances arguments for partial or total restoration are valid and professional guidelines aid rationalization here.

Research into the corrosion and conservation of historic and archaeological metals is developing significantly due to the increasing contribution of dedicated specialists and funding of large collaborative research programs that have a specific focus and the challenges of large complex objects. An influx of corrosion scientists has improved the methodology of research and the understanding of conservation methods by widespread introduction of electrochemistry into corrosion and treatment studies. As conservation is a blend of art and science, it utilizes data and publications generated by many disciplines to devise its preservation strategies. Literature sources within conservation focus mainly on conference proceedings and research project publications dedicated to specific themes that provide discussion forums for developing, interpreting, and reporting metallic corrosion and the conservation process. Metals conferences are organized and published by national conservation groups, museums, universities, and the International

4.43.1.2 Conservation: Definitions and Rationale

4.43.1.2.1 Conservation rationale

Conservation of metals can be broadly split into interventive methods, which involve adding or removing something from an object in order to preserve it, and preventive techniques that aim to prevent corrosion by controlling the environment. Both approaches require an understanding of the physical and chemical structure of metals, their interaction with environmental variables and the properties of their corrosion products. This information is used to design safe storage environments and to develop, implement, and assess interventive treatments. Conservation does not have its own universally defined preservation standards and generally works towards goals generated to satisfy prevailing situations.

4.43.1.2.2 Preservation goals

The ultimate conservation goal of indefinite preservation has driven conservation rationale for many years. Stabilization is a much used word in conservation literature and a reassessment of its meaning and context are long overdue. Since few metals are inherently stable in ambient conditions, corrosion prevention for metals and alloys requires some degree of environmental control. Depending on the degree of control required, significant capital outlay and ongoing energy consumption may be called for. This will carry a carbon footprint and may be beyond the financial means of many museums. Qualitative and quantitative control of environmental parameters, backed by relevant research to identify the environmental needs of the metals in question, underpins the concept of preventive conservation. Unstable metals are merely prevented from corroding using environmental control and they remain inherently unstable. Since they have not been stabilized by an interventive treatment, any changes to the environment could once again favor their decay. This minimalist approach to preservation is now much favored in conservation practice. Previously, environmental control was normally employed as the end point of an interventive process focused on enhancing the chemical and physical stability of an object by attempts to remove corrosion accelerators and apply coatings and inhibitors. Interventive treatments should only be used where there is evidence that they enhance the stability and lifespan of an object without contravening ethical guidelines.

Preservation strategies should be designed to support the role and function of the object in a society. This may involve public accessibility, which will require provision of oxygen, light, and heat. All of these are agencies of decay that can contribute to corrosion. Access to metal objects may mean it is necessary to accept the concept of limited lifespan, although this will depend on the metal in question and its condition. Alternatively, never viewing an unstable metal object while knowing it is preserved in deoxygenated storage may be an acceptable preservation strategy if the mere knowledge of its existence is sufficient for it to fulfill its cultural role. This may be the case for iconic objects that form cultural cornerstones within societies and history timelines.

4.43.1.2.3 Standards in conservation

Few defined preservation and test standards exist within conservation at the time of writing (2008). The concept of indefinite preservation still pervades conservation thinking for metals. A move towards a rationale that pragmatically measures conservation outcomes as a function of resources, treatment success, cost, and object context is required to facilitate the defining goals that can be used to create standards. To produce attainable standards requires research that provides quantitative evidence of the success of treatment. Within metals conservation there is currently limited quantitative data that could be translated into hard currencies of object longevity, stability, and survival.

Standards grow from attainable and reproducible quantified outcomes. Gaps in our understanding of corrosion processes, treatment mechanisms, and treatment success hinder the production of conservation standards. There is a need for more research that definitively identifies corrosion mechanisms, quantifies treatments and measures their success relative to defined goals. International agreement on what constitutes realistic treatment success is required, as is a
recognized body that defines or approves standards with the support of the conservation profession. Thus, if a standard does not prevent decay there must be an indication as to the extent to which it protects from corrosion or prolongs lifespan. This requires a definition of lifespan reliant upon identifying the function of a cultural object and defining when it ceases to fulfill this function. These are difficult questions but until they are answered conservation cannot develop models that quantitatively define goals and offer a framework of standards to achieve them. There is a case for the conservation profession to devise its own standards for use in research and quality assurance, as ISO and ASTM standards are often inappropriate for use in conservation research and practice.

4.43.1.2.4 Ethics
Ethics both guide and constrain conservation practice. National guidelines define generic rules for good practice that include minimum intervention with objects, reversibility of conservation materials and of treatments applied to cultural objects, as well as retention of the cultural integrity of an object and the information it contains. Situation ethics prevail when determining the level of intervention required to preserve objects. Within archaeological conservation, significant intervention is normally essential for understanding the technology and function of a metal object or for revealing its shape from a corroded metal conglomerate. Ethical dilemmas abound when devising treatment procedures. While a blistering paint surface on a working engine comprising cast iron and steel might be removed and the surface repainted to approved international standards, accessioning such an object into a museum changes this and the paint now constitutes part of the object history. An ethical preservation process for such an object might involve the local stabilization treatment of pits in the paint layer, followed by application of an unobtrusive protective coating and storage in a controlled relative humidity. This is more expensive to execute and offers a less predictive corrosion control strategy than stripping the metal to an SA standard and repainting.

4.43.2 Corrosion
4.43.2.1 The Influence of Corrosion on Conservation Strategies
The nature and extent of corrosion strongly influences conservation strategies. Understanding how metals corrode within specified environments such as museum interiors, enclosed storage boxes and the atmosphere is central to developing treatments and identifying realistic conservation goals. It may be necessary to understand more than one corrosion model to devise conservation procedures. For instance, understanding how archaeological metals corrode during burial is essential for developing a model of their corrosion in the atmosphere following excavation. Equally, elucidating the corrosion mechanisms on a historical pewter salt cellar facilitates an understanding of how this object corrodes in a museum environment. It may no longer contain salt, but the legacy of its original function influences its future survival. Corrosion models also contribute to understanding object aesthetics and developing conservation ethics. Research into corrosion mechanisms informs conservators about the stability of objects, their rate of decay and their conservation needs.

4.43.2.2 Corrosion of Archaeological Metals
Although reviews of archaeological and historical metal corrosion exist, aspects of corrosion relevant to the treatments discussed here are briefly outlined. Archaeological metals normally corrode extensively during burial to form corrosion products related to their burial environment and alloy composition. Environment, alloy composition and the mechanisms of ionic and electron transfer during corrosion dictate the nature of the corrosion layer formed and whether corrosion products are passive or unstable. Smooth dense patinas or voluminous disfiguring corrosion layers may form. Some corrosion layers can retain good approximation of the shape of the object and surface details like wear marks or engraving (see Figure 1). These layers have been loosely referred to as representing the original surface of the object but are now more often called marker layers. They are often hard and compact and may be overlaid with softer more voluminous corrosion.

Conservation is not just about preservation. Archaeological metals are subjected to investigative conservation that involves analysis designed to answer questions on technology, provenance, and trade. Mechanical cleaning employing hand tools like scalpels and micro air abrasion techniques, which utilize powders such as aluminum oxide, are often employed to remove overlying corrosion to reveal the marker layer. Guidance in this process is helped by X-radiography. By detecting differences in density juxtaposition of differing corrosion products are shown, along with dissimilar metals, technological detail and evidence
of residual metal\textsuperscript{7} (see Figure 2). This information-sensitive marker layer may be physically weak and infused with soluble corrosion accelerators, but it must remain undamaged by any treatment, whether it has been revealed or is left covered with corrosion products. Chemical treatments that strip off all corrosion products to remove the soluble corrosion accelerators they contain cannot be used to treat archaeological metals, as the remaining metal rarely represents the original shape of the object\textsuperscript{7} (see Figure 3).

Post-exavation corrosion processes usually differ from those occurring in the burial environment, as the atmosphere contains more oxygen and is normally less damp than soil\textsuperscript{2,10}. To develop a preservation plan it is essential to understand how the corrosion model changes, especially how corrosion products form in the burial environment, respond to the new environment and influence the metal they are associated with.

The instability of archaeological iron offers a clear example of how an understanding of corrosion mechanisms is essential to treatment design. It is used here to illustrate conservation thought processes for metals containing soluble corrosion accelerators. During burial, chloride is attracted to anodes as a counter ion to balance charge from Fe\textsuperscript{2+}\textsuperscript{2,10}. In damp burial conditions it exists as a Fe\textsuperscript{2+}/Cl\textsuperscript{−} solution at the metal surface. Chloride content may be typically 0.1–1.5 wt % of object, but can be significantly greater for marine metals\textsuperscript{7,10–12}. Soluble chloride acts as an electrolyte making the iron inherently unstable. Overlying the corroding metal core is a dense corrosion product layer (DPL) identified as comprising a goethite (\(\alpha\)-FeOOH) or sometimes a siderite (FeCO\textsubscript{3}) matrix in which are embedded magnetite (Fe\textsubscript{3}O\textsubscript{4}) or maghemite (\(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}) strips\textsuperscript{2} (see Figure 3). This is effectively the marker layer for the surface of the object and is also present in totally mineralized objects, which present no ongoing corrosion problem, but remain a conservation problem due to their fragility and the need to reveal their original shape.

Moisture and oxygen in the post-exavation environment facilitates the formation of \(\beta\)-FeOOH...
(akaganeite) in the acidic chloride rich solution sited at anodes on the metal surface. Chloride is incorporated into tunnels within the hollandite-type \( \beta \)-FeOOH crystal structure and adsorbed onto its surface. Growth of these voluminous tower-like \( \beta \)-FeOOH crystals pushes off the overlying DPL and is catastrophic for the object as an information resource, as it destroys evidence of the original surface and shape leaving only an unevenly corroded metal core (see Figure 4). While conservation strategies aim to reveal the shape of the object they must also prevent the corrosion of metallic iron, as the consequent formation of \( \beta \)-FeOOH would remove the information retaining DPL. Totally mineralized iron is stable, as there is no more metal to oxidize and this has allowed soluble anodically held chloride to diffuse out of the object.

Corrosion of nonferrous archaeological metals presents different conservation problems. Most are alloyed with other metals as; bronze (copper/tin sometimes with added lead); brass (copper/zinc); pewter (lead/tin); and precious metals (silver/gold, silver/copper, gold/copper). This facilitates preferential corrosion. Thus, gold may lose the copper it is alloyed with and be covered in copper corrosion.

Figure 3 A cross section of a medieval nail shows it retains a substantial metal core and differing corrosion layers (a). Images (b) and (c) show how the dense corrosion product layer (DPL) retains the shape of the nail, which is overlaid with a corrosion matrix containing soil. Stripping the nail of all corrosion would lose the shape of the object and its surface detail. Totally mineralized iron retains the shape of the object as a corrosion layer, visible in this Roman nail (d).

Figure 4 Corrosion at the metal/DPL interface results in loss of overlying corrosion products and the information they contain.
products. Chemically removing these copper corrosion products leaves a soft porous copper depleted layer of gold on the surface of the alloy. Mechanical removal of corrosion leaves copper corrosion products embedded in the metal surface alongside the gold, but produces a stronger surface.

Corrosion processes, products, and rates can vary according to the proportions of metal within alloys and the burial conditions. This can prove advantageous, although bronzes often decuprify the corrosion of alloyed tin, producing an insoluble and poorly mobile tin oxide to act as a marker layer for the original surface of the metal. Lead forms very stable lead carbonates in neutral to alkaline burial conditions and insoluble chloride compounds that are stable following excavation. Silver is also stable after excavation due to the highly insoluble silver chloride and silver sulfide formed on its surface. Lead and tin have similar corrosion potentials and both corrode in pewter to produce a lamellar wart-infested surface with powdery corrosion products that are unlikely to form marker layers. Copper that forms sparingly soluble cuprous chloride (CuCl) next to the metal surface can be unstable following excavation if there is sufficient water to hydrolyze it to voluminous $\text{Cu}_2\text{OH}_2\text{Cl}$ known as ‘bronze disease’.

Conservation procedures will be dictated by the stability of the corroded metals, corrosion mechanisms, and the presence or absence of marker layers.

### 4.43.2.3 Corrosion of Historical and Modern Metals

Historical metals are found in outdoor and indoor environments and may be decorative objects d’art, functional artifacts, or large industrial items. Metals kept indoors since their fabrication may have very little corrosion and retain their original surface finish. Conservation aims to retain such surfaces. This can be achieved by monitoring environments, simple good housekeeping and environmental control in relation to corrosion threshold values for the metals in question.

The context of the object is important and the nature of a corrosion patina (see Section 4.43.5.2) may be seen as an important aesthetic value of the object or part of its life history. This will dictate whether it is removed or retained during conservation and heavily influences the choice and success of treatments. Analysis aids decision making in conservation. Sometimes it may be necessary to replace metals if they are performing a structural function. Analysis detected dezincification of brass (70:30) in nails used to join the planks in the hull of the yacht Asgard (see Figure 5). Built in 1905 by Colin Archer the renowned Norwegian shipwright for Robert Erskine Chalder the yacht is now an important part of Irish history. The analysis provided information that aided conservation decisions for nails that otherwise appeared to have only surface corrosion.

Modern metals increasingly occur in museum collections and are the fabrication materials of many cultural icons and monuments. These include zinc, aluminum, magnesium, and their alloys. Conservation of protective and technologically informative surface finishes on metals like aluminum may be equally as important as preserving the metal itself. Air quality, relative humidity, and temperature are important for metal stability within museums. The Oddy test was devised to determine if materials used to construct boxes and showcases give off gas pollutants that will cause metals within them to corrode over long-time periods. It can also be applied to show if metals and...
alloys corrode in polluted environments, thus aluminum and Duralmin (Al/Cu) corrode in the presence of formic acid and magnesium and AZ31 (Mg/Al/Mn/Zn alloy) corrode in the presence of a wide range of materials that include oak, plywood, formic acid and wool, which may all be found in museum environments. Lead and copper are also susceptible to corrosion from carbonyl pollutants. Equally studies must examine what occurs when objects are handled, as chloride corrosion products on zinc coins and Indian Bidri ware (zinc alloy) in museum collections were attributed to handling. The influence of handling on corrosion is evident for tarnishing of silver by sulfur compounds, where fingerprints can act as a focus for corrosion (Figure 6). Conservation has moved some way towards developing standards for showcase design and the use of corrosion-safe construction materials, but much more remains to be done.

Outdoor corrosion patterns on metals are predominantly influenced by alloy composition, environment, climate, and the object morphology. Out of doors iron produces a corrosion layer mostly comprised of loose $\alpha$-FeOOH rather than form the shape retaining DPL that occurs on archaeological objects (see Figure 3). Sulfurous gases can produce a FeSO$_4$ corrosion cycle that is humidity sensitive. While conservation of iron that has corroded in the atmosphere may involve removal of corrosion layers, rather than their retention, outdoor copper alloys may develop patinas considered to be aesthetically desirable and conservation planning takes account of this (see Section 4.43.5.2). Humid air containing SO$_2$ will attack copper alloys dissolving passive layers and supporting electrochemical corrosion of the alloy, which is problematic for statuary and architectural fittings. Establishing the precise role of patinas and corrosion product layers in the corrosion process is currently underway for many metals, which will facilitate better long-term planning and improve treatment design.

4.43.3 Environmental Control of Corrosion: Preventive Conservation

4.43.3.1 Desiccation

A common preservation strategy for cultural metals is to prevent their electrolytic corrosion by controlling one of the agencies essential for this process to occur. Normally, removal of moisture is used to prevent electrolyte formation, although in some instances the oxygen necessary to support cathodic processes and form corrosion products is removed. Removal of electrolyte ions from corroded metals involves interventive treatment. It is easier, cheaper, and more user friendly to control corrosion by desiccation than to remove oxygen. The degree of desiccation necessary to prevent corrosion differs according to the corrosion mechanism of the particular metal or alloy and dictates the cost of corrosion control as capital outlay on plant, fuel, and personnel. Despite the importance of understanding corrosion mechanisms for optimizing preventive conservation strategy, only chloride infested iron has been extensively researched to identify relative humidity (RH) no-corrosion thresholds for reactions within its corrosion mechanism.

4.43.3.1.1 Relative humidity – Threshold corrosion values

Ambient humidity can supply moisture to solvate ions within corroded metals and create electrolytes. Conservation of metals examines corrosion as a function of RH rather than absolute humidity. It is well known that hygroscopic or deliquescent salts such as sodium chloride can lower the RH threshold for corrosion to occur. The RH at which the formation of electrolytes begins is the threshold corrosion value. On corroded iron the surface adsorbed chloride on hygroscopic $\beta$-FeOOH becomes mobile within atmospheric moisture and corrodes iron in contact with it at 15% RH (see Figure 7). Additionally, ferrous chloride may form in the low pH and high Fe$^{2+}$/Cl$^-$ environment created as damp chloride infested iron, dries (see Figure 8). Any FeCl$_2$·2H$_2$O that forms contains enough water to corrode iron in contact with it, but once FeCl$_2$·2H$_2$O forms at 20%, RH corrosion ceases (see Figure 7). Storage standards

Figure 6 The influence of a fingerprint on the pattern of sulfur tarnishing on this silver surface is clearly visible. A protective coating on the surface would have prevented this.
for chloride infested iron at 20°C have been defined as: at 12% RH no corrosion; 15–20% RH β-FeOOH causes slow corrosion of iron; above 21% RH both β-FeOOH and FeCl₂·4H₂O contribute to corrosion \(^{20}\) (see Figure 7). Corrosion increases significantly above 25% \(^{19–21}\) and several times faster above 30% RH than at 25%.\(^{20,21}\)

In contrast controlled storage of corroded iron from historical contexts has received scant attention in conservation research, as it will tolerate higher humidity values before incurring corrosion if it is chloride free. No conservation studies have examined how iron contaminated with sulfates from SO₂ pollution would respond to RH.

Corrosion of archaeological copper alloys can occur when cuprous chloride (CuCl) close to the metal surface hydrolyses to form basic cupric chloride (Cu₂(OH)₂Cl) polymorphs, usually clinoatacamite or atacamite with an accompanying molar volume increase.\(^6\) This pressure or undermines the overlying hard and dense corrosion layers that predominantly comprise malachite (CuCO₃·Cu(OH)₂), breaking their contact with the CuCl/Cu₂O mixture next to the metal and ultimately causing their exfoliation. Scott\(^6\) observed no reaction over the relative humidity range 42–46% but rapid corrosion at 70%, leading him to recommend storage below 45% relative humidity in contrast to the anecdotal 39% commonly cited in conservation. The CuCl/Cu corrosion model merits closer scrutiny to define both the critical no-corrosion humidity and corrosion rates above this value.

Unless it has already corroded by aggressive ions such as chloride and sulfate, aluminum offers minimal conservation challenges provided it is stored at around 55% relative humidity.\(^{16}\) Reaction of chloride infested aluminum alloys to relative humidity has not been examined in relation to safe storage thresholds. Similarly, the role of soluble tin chlorides in the corrosion of tin and tin alloys merits detailed study, since tin chloride solutions are prone to hydrolysis.

4.43.3.1.2 Practical humidity control

Humidity control either employs active dehumidification using mechanical plant or passive desiccation using desiccants like silica gel to control environment in fixed storage or display areas.\(^9,14,21–23\) A significant advantage of controlling corrosion of cultural metals by desiccation is that they remain easily accessible, especially if an entire store room is desiccated as opposed to individual storage boxes. Although maintaining low humidity using mechanical desiccation plant demands finance and energy, it is capable of controlling large spaces that will require only one or two telemetric sensors to monitor relative humidity. These can immediately and remotely detect any failure to maintain target relative humidity on a macroscale, which allows for rapid remedial response. Thus mechanical corrosion control is a low risk corrosion control strategy for cultural metals, provided resources exist to underpin its continuing operation and management.

In contrast the small scale control of climate by silica gel for storage within enclosed polyethylene boxes and for display in sealed showcases appears to offer a cheap conservation strategy for small metal objects. Gradual hydration of the desiccated silica gel will occur as a function of air exchange rate, external relative humidity and initial moisture content of the metals being desiccated.\(^{21–24}\) This eventually raises internal humidity within the controlled space to values that support corrosion, which will speed up as internal relative humidity continues to rise until it equilibrates with the external environment. The metals now rest in a continually aggressive environment. Determining when to replace the silica gel relies upon knowing the threshold corrosion value of the metals in question and detecting when the interior of the box exceeds this value.

Research to evaluate the complex equation of storage, hardware performance, air exchange, monitoring, maintenance time, and human error is needed.
to offer a realistic and practical assessment of this corrosion control strategy. Enclosure design largely controls air exchange rate which is the governing factor in passive desiccation systems.\textsuperscript{24} Assessment of enclosure performance can produce predictive life spans for specified passive desiccation storage systems.\textsuperscript{21,24,26} Showcases designed for desiccation maintained relative humidity below 20\% for 1 year without a change of their silica gel desiccant, when external relative humidity fluctuated between 60\% and 95\%.\textsuperscript{22,24} As telemetric monitoring of showcase performance is easy to initiate and financially viable, this system offers potentially reliable low energy consumption corrosion control for unstable metals on display. The major cost will be an initial outlay to meet the showcase specification. Further work could establish performance of the showcase with age and use. This requires real-time testing that may take several years. Attempting to define long-term effectiveness by extrapolating a one year study or short-term laboratory results cannot provide a definitive guide to performance.

\textbf{Figure 8} Brunel’s iconic SS Great Britain was the first ocean going screw driven iron hulled passenger liner and is now preserved by a mechanical desiccation system that maintains relative humidity to 20\% and allows visitors to walk around the hull. Reproduced from Watkinson, D.; Tanner, M.; Turner, R.; Lewis, M. \textit{The Conservator} 2005, 29, 73–86.\textsuperscript{25}
The performance of polyethylene storage boxes as desiccated depositories for archaeological iron has been studied as functions of manufacturer, age, use, silica gel performance, and ambient relative humidity. The study confirmed earlier studies on threshold corrosion values and determined most air leakage was via lid seals, making storage protocols important in relation to the stacking of boxes compromising their seals. Storage in polythene boxes suffers from a reliance on the limited accuracy of moisture sensitive indicators to detect the internal relative humidity of boxes for gel regeneration cycles. Individual telemetric monitoring of the interior of the box is financially prohibitive for the several hundred polyethylene boxes normally housed in a storeroom. Good management is also necessary if the gel is to be changed as required. It is essentially a low cost, but high risk corrosion control strategy when the frailties of human nature are taken into account.

Relating corrosion rate to increasing relative humidity provides opportunity for pragmatic management decisions. The degree of corrosion control implemented can be matched to resources available to produce a package that will reduce, but not prevent corrosion. This reasoning was used to control corrosion of Brunel’s famous 1843 wrought iron steamship SS Great Britain, whose chloride-ridden lower hull is preserved in a mechanically desiccated dry dock maintained at 20% relative humidity with a goal of retaining its structural integrity for at least 100 years (see Figure 8). This allowed public access to the hull and avoided employing costly and environmentally unfriendly alkaline washing methods (see Section 4.43.4.2) in attempts to remove chloride corrosion accelerators from the 324 ft long hull. The conservation challenge required a scientific investigation to identify the influence of RH on corrosion, followed by an engineering project to design an envelope to maintain the operating RH.

4.43.3.2 Deoxygenation

Ageless™ is a commercial oxygen absorber that has been used in conservation to deoxygenate enclosed spaces. It is expensive to use and the exothermic reaction that expends oxygen produces water, which should offer no corrosion risk provided the storage environment remains oxygen free. Despite technical challenges, high cost, and reduced accessibility, archaeological iron has been stored in heat sealed low linear density polyethylene tube, with barrier properties 2000 times better than polypropylene, deoxygenated with oxygen scavenging RP-A™ (mordenite/CaO/PE/activated carbon). This study showed that iron objects, which had been pretreated in aqueous NaOH to wash out chloride (see Section 4.43.4.2), remained visibly unchanged over a 5-month period but untreated iron had a 12% failure rate attributed to poor seals and bag punctures. Although the researchers predict a storage lifespan of 4–6 years, the high initial cost of materials and labor and a one-shot storage system make it unlikely that it will displace desiccation in popularity. A long-term quantitative testing program comparing its effectiveness, ease of use and global cost with desiccation techniques would define the relative merits of these two treatments. Using a flow of nitrogen gas through an enclosed container offers a no-corrosion environment for damp high status archaeological objects prior to their conservation.

4.43.4 Interventive Treatments

4.43.4.1 Removing Ions that Act as Corrosion Accelerators

Interventive treatments aimed at reducing or preventing corrosion of unstable metals mostly focus on removing chloride and other soluble ions that are capable of acting as electrolytes in high humidity environments. Entirely removing soluble ions should prevent corrosion, while their partial removal enhances the stability of the object by reducing electrolyte availability. Additionally, some washing treatments may aim to remove or modify sparingly soluble or insoluble corrosion products that promote corrosion. From an ethical standpoint, merely enhancing stability without controlling environment to prevent corrosion may not be considered an appropriate corrosion control strategy. Even a small amount of corrosion occurring at anode sites on the metal can interfere with adhesion of important overlying corrosion layers, whose loss destroys the object as an information resource despite the survival of the metal core (see Figures 2–4). Delaying this for a short time by reducing corrosion rate could be viewed as a very limited goal, when measured against the ideal of indefinite preservation. Equally, treatments that partially remove corrosion accelerators could be seen as unnecessary, since post treatment storage must be similar to that provided for untreated metals. Why bother trying to remove electrolytes if the objects still need to be subjected to the same stringent storage conditions? One possible advantage is that failure to maintain the controlled environment will lead to a slower corrosion.
rate, as compared to untreated iron objects. Quantitative understanding of treatment efficiency and effectiveness is essential for facilitating informed decisions about their use.

To optimize treatments designed to remove corrosion accelerators that are normally predominantly comprised of chlorides, it is necessary to: identify the corrosion mechanism; devise appropriate chloride removal procedures; quantify the removal of chloride as an absolute value of chloride contained in the metal; use this value to calculate extraction efficiency; determine the extent to which the metal is stabilised. While the concept of removing soluble ions to prevent electrochemical corrosion is logical, no studies provide quantitative assessment to show how stable metals like iron become following attempts to remove their soluble chloride. Equally, there is limited information as to what percentage of chloride present within objects is extracted by a particular treatment and how consistently this occurs.\(^1\text{1,12,29}\)

4.43.4.2 Washing Methods in Practice

Washing methods are applied to metals to solvate soluble corrosion products and soluble ions adsorbed onto corrosion products. Iron is the most unstable archaeological and historical metal, due to its ability to attract chloride and retain it in a highly soluble form.\(^10\) Washing methods will solvate chloride ions and this allows them to diffuse out of the object.\(^7,11\) This process is hampered by the DPL limiting solution access to the iron surface, where wash solutions must enter pits and micro cracks to exchange with chlorides at anode sites. Chloride removal is diffusion controlled, slow, and is unlikely to be 100% efficient, although efficiency can be improved using chemical additives.\(^11,12,29\) Evidence from a qualitative study of the long-term stability of treated archaeological iron revealed simple washing with hot deionized water to be a poor stabilization system, with 68% of treated objects recorrodin.\(^30\) Recent study quantitatively confirms washing in deionized water is an unpredictable treatment that never extracts large amounts of chloride\(^11\) (see Figure 9).

Their ease of use and low aggression to iron has meant that inhibited wash solutions have been chosen to treat large objects. HMS Holland was the first submarine used by the British Navy. It was fortunate that she lost her tow en route to the breakers yard and sank, as when she was discovered and salvaged many years later she had become an important historical object. Her 19 m length offered challenges to removing the chloride that infused her structure. Health and safety and cost augmented against the use of strongly alkaline wash treatments (see below) and electrolytic desalination (see Section 4.43.4.3). A purpose built treatment tank containing 820 000 dm\(^3\) of Na\(_2\)CO\(_3\) was used to provide an inhibited wash relying on diffusion to extract chloride that was continually monitored.\(^31\) Treatment was followed by storage in a building constructed for this purpose maintained at 35% RH to slow down any corrosion from residual chloride. While new study indicates storage at 25% RH would slow iron corrosion significantly more than 35% RH,\(^11,20,21\) any environmental control program must be related to the finance available to sustain it and 35% RH will restrict corrosion better than higher values. This is a typical finance/corrosion control cost benefit assessment that is a factor in the conservation equation. It is often used to influence selection of treatment options and should be considered when developing standards of treatment. Equally object size may dictate which treatments are feasible, as in the case of the Holland.

Alkaline wash systems act as inhibitors and optimize chloride removal.\(^6,11,12,29\) Inhibition provided by alkalis such as NaOH reduces corrosion during treatment. This releases chlorides from their charge balancing role at anodes and allows them to diffuse out into the wash solution, while at the same time the alkali supplies OH\(^-\) ions to replace them and associate with Fe\(^{2+}\). Solvation of solid ferrous chloride and surface adsorbed chloride on β-FeOOH occurs,
reducing β-FeOOH hygroscopicity and preventing post-treatment corrosion of iron in contact with it. In strong alkali β-FeOOH can transform and this will advantageously release chloride into the wash solution. Since the ionic size of chloride occluded in tunnels within β-FeOOH crystals exceeds the diameter of tunnel entrances it remains trapped and presents no post-treatment corrosion threat, unless conversion of β-FeOOH to α-FeOOH releases this chloride. Post-treatment hydrolysis of residual β-FeOOH to α-FeOOH can occur but is little studied. A 23-year-old dry sample of β-FeOOH was assayed as being 1% α-FeOOH and 99% β-FeOOH. A major study currently underway aims to identify physicochemical transformations of corrosion layers as a function of treatment regimes, using microanalysis techniques to characterize the corrosion products. This will significantly contribute to an understanding of treatment and post-treatment corrosion.

Further improvements in chloride extraction can be produced by deoxygenated NaOH solutions (see Figure 9). Passivation of iron in oxygenated NaOH solutions is likely to be incomplete, as NaOH needs to reach all anodes sited at the metal surface to be effective. Consequently, chloride continues to be held as a counter ion and is difficult to wash out. Deoxygenating NaOH solutions with an SO$_4^-$ oxygen scavenger or nitrogen gas stops corrosion and improves chloride extraction. Anecdotal reporting indicates undesirable softening of corrosion products in NaOH solution, but no studies offer quantitative evidence of this or address the influence of any chemical treatment residues on iron corrosion products. This merits further attention. Objects should be washed post-treatment in deoxygenated water to flush out chemicals.

A promising variation on alkaline washing currently under investigation is the use of a subcritical high pressure alkali treatment for treating the American Civil War submarine Hunley, which was recovered from a marine environment where she had lain since she sank immediately after becoming the first submarine to sink a warship. Treatment transforms corrosion promoting β-FeOOH to the α-FeOOH, Fe$_3$O$_4$, and Fe$_2$O$_3$, chloride-free phases that are nonaggressive to iron.

Other inhibitors have been tried, notably aqueous washing of archaeological iron with ethylene diamine. Inhibition and a high solution pH (11.5 at 5% (v/v) aq.) aim to prevent corrosion during treatment and aid chloride removal. It is an inferior chloride extractor as compared to 2% NaOH aq., but has been cited as offering good long-term stability to iron in a qualitative study of treated objects. There is limited information available regarding the amount of chloride removed by treatments as a function of total chloride within the iron, since determining residual chloride requires post-treatment digestion of objects. The small amount of quantified data available indicates that some wash methods are significantly better than others and consistently extract within fixed percentages of chloride. The limit of detection for measuring chloride extracted into wash baths cannot guarantee iron is chloride free. Although it is important to determine whether small residues of chloride are capable of causing significant corrosion of iron, testing the susceptibility of washed iron to corrosion has received little attention. For guaranteed no-corrosion all washed iron should be stored in a controlled environment to a standard equaling that used for unwashed iron, but this makes storage costs the same as for untreated iron.

Studies that qualitatively examine the stability of washed and unwashed iron within museum collections have offered comparative assessment of treatment effectiveness. While these types of survey offer a genuine insight into treatment outcomes, they are limited by their retrospective nature, wide range of uncontrolled variables and a lack of quantified data. Computer monitoring of RH now offers an opportunity for precise recording of storage environment and new studies of long-term performance of treated objects are overdue. It would also be worth interpreting past studies using new data available on corrosion mechanisms. Until quantitative long-term post-treatment stability testing is carried out and outcomes are linked to chloride residues within objects, washing treatments remain empirical applications best described as having an unpredictable and unknown capacity to remove chloride and enhance object stability. Such studies will prove hard to fund because of their time commitment.

Aluminum alloys are becoming increasingly common in museum exhibits and include aircraft and boats rescued from extreme environments. Once the highly protective nonconducting Al$_2$O$_3$ layer on aluminum fails the metal will corrode. This may cause pitting or intergranular corrosion according to alloying and metallography. Chlorides exacerbate corrosion by attacking the Al$_2$O$_3$ film and concentrating in pits where they cause low pH, hydrolysis of Al$^{3+}$ and voluminous disfiguring corrosion product at the mouth of the pit. The shape of the object is obscured and ultimately lost with eventual perforation of the metal. Washing to remove soluble chloride can be carried out on objects retaining significant amounts of metal, but those without large quantities of metal...
will be beyond recovery as corrosion products are non-adherent and friable.

Chemically aided washing was innovatively used to treat a Duralumin (3–5% copper) seaplane float belonging to a Junkers W33 infused with chloride, exhibiting extreme pitting and redeposited copper on its surface that could act as a cathode for continuing corrosion of the aluminum. 17 Washing conditions were carefully manipulated using \((\text{NH}_4)_2\text{SO}_4/\text{NH}_3\) buffer solution to complex \(\text{Cu}^{2+}\) ions to \(\text{Cu}(\text{OH})_3^{2+}\) and \(E_0\) of the system was lowered to allow corrosion that removed redeposited copper, provided oxygen was present. 17 Thermodynamic data revealed \(\text{Al}_2\text{O}_3\) was stable in the treatment solution. Its presence on the metal surface protected aluminum at the treatment pH of 9.6 and chloride diffused out of the object following hydrolysis reactions within pits. As with most washing methods employed in conservation, assessment of the success of the treatment was qualitative and reported that the object appeared to be stable 4 months after treatment.

Washing has been employed for copper alloys to deal with the problem of \(\text{CuCl}\) hydrolyzing to form \(\text{Cu}_2(\text{OH})_3\text{Cl}\) polymorphs that damage and disfigure copper alloy objects. 6,10 Fortunately \(\text{Cu}_2(\text{OH})_3\text{Cl}\) is not hygroscopic and does not cause corrosion of metallic copper in contact with it, although its growth can undermine and lever off overlying patina. Not all copper alloys containing chloride are unstable. MacLeod 38 argues that there is a minimum chloride ion concentration required to support corrosion. The low solubility of \(\text{CuCl}\) and its positioning within or under \(\text{Cu}_2\text{O}\) means chloride solvation by simple aqueous washing can last years. Washing for up to 2 years in sodium sesquicarbonate (\(\text{NaHCO}_3/\text{Na}_2\text{CO}_3\)) at 5% (w/v) pH 10 has been employed to slowly solvate \(\text{CuCl}\) and supply \(\text{OH}^-\) to form cuprous oxide (\(\text{Cu}_2\text{O}\)). 68 Basic copper carbonate (\(\text{CuCO}_3\text{Cu}(\text{OH})_2\)) and chalconatronite \(\text{Na}_2\text{Cu}_2\text{CO}_2\cdot2\text{H}_2\text{O}\) may also form and darkening of patina may make the treatment undesirable when aesthetics are an important consideration. It is now more likely to be used as an inhibited wash solution following other treatments like electrolysis (see Section 4.43.4.4).

### 4.43.4.3 Removal of Corrosion Products

Stripping techniques may be employed when ethical arguments allow removal of corrosion, such as preparing lightly corroded industrial and historical steels to receive protective coatings. They may also be used to free archaeological objects from corrosion conglomerates provided substantial amounts of metal remain, as heavily mineralized objects will lose their identity when corrosion is removed. 8,39 While there are several studies looking into the action of stripping agents there is no single definitive comparative assessment that identifies a preferred method for specified alloys. Conservators must evaluate studies or themselves test stripping agents relative to the object they are planning to treat. That stripping is ethically acceptable at all, illustrates how situation ethics dictate conservation procedures.

Traditional acid stripping solutions are aggressive to metal and corrosion products alike and are now largely ignored, except where it is ethical to remove all corrosion products. Copper alloy coins have been separated using complexing agents exhibiting low aggression to metallic copper to remove copper corrosion products. Citric acid is reported as being best in this respect, when compared to alkaline glycerol, alkaline Rochelle salt, sodium hexametaphosphate, and sulfuric acid. 40 Elsewhere alkaline Rochelle salt is reported as being less aggressive than reagents like methanoic acid, alkaline glycerol and alkaline dithionite. 39 Electrochemical assessment of these reagents would help indicate which reagents offer the best removal of corrosion for the least aggression to the parent alloy. Dealloying is a problem. Predictably, metallic lead is lost from copper alloys by alkaline stripping systems and organic acids. Stripping corrosion from copper alloys 38 and iron 41 has been achieved using thiourea (\(\text{SC(NH}_2)_2\)) inhibited citric acid washes. Thiourea controls the aggressive action of citric acid by complexing unstable \(\text{Cu(I)}\) species, to prevent them forming metallic copper, and by forming stable complexes with \(\text{Cu(II)}\). 8,38 Phosphoric acid (\(\text{H}_3\text{PO}_4\)) has been used for stripping ferrous metals to leave a ferric phosphate protective film, as has hydrochloric acid with hexamine corrosion inhibitor. 41 All stripping methods require post-treatment washes to remove residual chemicals that would continue to corrode metals. This is often followed by application of a protective coating.

Following citric acid/thiourea treatment of copper alloys, washing in sodium sesquicarbonate is used to neutralize acid and remove \(\text{CuCl}\) left in crevices and cracks, but this is likely to be incomplete. 39 Washing marine copper alloys revealed the benign nature of this treatment method, as tin, zinc, and lead compounds were not removed from either the corrosion products or copper alloy, whereas washing in deionized water removes metallic lead as the purity of the water prevents formation of protective \(\text{PbCO}_3\). 38 Washing of iron in inhibited chromate or nitrite
solutions following citric acid/thiourea stripping is not environment-friendly, so ecologically superior alkali metal salts of organic carboxylic acids (secacic acid – NaOOC(CH$_2$)$_2$COONa) have been used to provide washes of similar efficiency. They can also provide long-term inhibitive properties (see Section 4.43.6.3) and offer promise for widespread use in conservation following more in-depth testing.

Chelating and sequestering agents, such as the sodium salts of ethylenediaminetetraacetic acid (EDTA), have been used extensively in conservation in attempts to dissolve corrosion products without attacking metal. However, they can be slow to act and may be too selective in their action on corrosion products. Careful selection of commercial products is essential to obtain suitable pH values for optimizing complexation. A study examining reaction of disodium edetate (2NaEDTA) on copper corrosion products and copper metal revealed that chelation rate varied according to corrosion product. This would result in differential removal of corrosion products leaving exposed copper open to the treatment solution. Fortunately, metallic copper was barely attacked by 2NaEDTA over a 30-h period. Dissolved sodium salts of EDTA have also been frequently used to remove corrosion from iron and lead and its alloys. Using compresses allows stripping agents to be used in a controlled manner. Degrigny treated a Citroen caterpillar tracked vehicle used on the trans-Saharan crossing of 1922/23 by this method. It still retained much of its original paint layer. Corroded areas that had sustained paint loss were treated with compresses of tetrasodium edetate (4NaEDTA) to remove iron corrosion products. This was followed by application of inhibitor (see Section 4.43.6.2) and a protective wax coating (see Section 4.43.5.4.2) to provide a typical stripping-inhibition-coating treatment regime. All treatment methods were assessed using electrochemical measurements prior to their use. Treatment success was gauged in the usual qualitative manner of visually checking for corrosion as a function of time and no corrosion was visible after 6 months of indoor display. Developing standards for assessing time weighted visual success of treatments set against conservation criteria would produce a useful tool for conservation practice.

Removal of corrosion from copper alloys may also be achieved by alkaline dithionite (Na$_2$S$_2$O$_4$) solutions, which provide electrons to reduce corrosion products to finely divided metallic copper. Weak heavily corroded objects may be consolidated by this conversion, but there is also a chance they will disintegrate. The skill and knowledge of the conservator are essential as treatment is fast, lasting only a few minutes followed by a wash of several days to remove residual chemicals.

### 4.43.4.4 Electrolytic Techniques

Electrolysis is employed in conservation either to entirely remove corrosion products from a metal or to aid diffusion of soluble corrosion accelerating ions into an electrolyte, while retaining corrosion layers on the metal. These differing outcomes are achieved by careful control of current density (CD) and in some instances current delivery. The metal is immersed in a suitable electrolyte and made cathodic relative to an inert anode, which protects it from corrosion during electrolysis. Different metals are electrolyzed in differing ways according to the nature of their corrosion products and the treatment goal. It is an extremely useful technique provided its use matches ethical goals and research identifies optimum treatment methodology. Its context within conservation has only been quantitatively established over the past 15 years since the application of potentiometric electrochemical analysis within conservation research.

Procedures vary from metal to metal. Iron is immersed in an electrolyte in which it will remain passive, such as NaOH. Using an imposed current to cathodically protect the iron frees chloride from its counter ion role, allowing it to solvate and diffuse out of the object. Chloride is drawn to the inert anode and delocalized from the object by diffusion. Maintaining a low CD retains the information rich DPL by avoiding polarization that would produce hydrogen gas which physically dislodged corrosion layers. Reduction of FeOOH corrosion products to Fe$_2$O$_4$ can occur and the accompanying increase in density increases porosity which is said to contribute to facilitating diffusion of chloride out of the object.

Most quantitative assessment of chloride removal by electrolysis has been carried out on cast iron, whose even corrosion matrix is different to the lamellar structure of corroded wrought iron. Tests on small cast iron chloride infested samples reveal significant migration of chloride to the anode during electrolysis. Quantitative measurement has shown that electrolysis (CD 10 mA dm$^{-2}$) in NaOH solution is no better at extracting chloride than aqueous washing in NaOH solution. While washing is easier to carry out than electrolysis, full inhibition of iron corrosion in a 1% NaOH wash solution cannot be
Electrolytic treatments are often favored for large iron objects, as they will remain cathodically protected during the long treatment times required to remove deep-seated chloride. Treatment may take from 1 to 4 years for large cast iron cannon and wrought iron anchors from marine contexts as well as very small cast iron samples required over 200 days to desalinate. As with most metal treatments, there is no report of any quantitative long-term assessment of post-treatment stability of electrolyzed iron as a function of relative humidity. Intentionally using a high CD to remove all corrosion layers may be ethical for certain Industrial and historical objects, provided their corrosion layers contain no information and they retain substantial metal cores. Such treatment would usually be a precursor for the application of protective coatings (see Section 4.43.5).

An advantage of electrolytic treatments is their degree of control, as the imposed potential can be matched to specific reduction processes. They are also useful for large objects, as electrolytic treatments can be run for long periods of time with little input from the conservator thereby saving labor. Circumstance must dictate whether electrolysis is possible. HMS Minerva was a big gun monitor launched in 1915 and sold as a visitor attraction in 1984. Removal of the high levels of chloride inside her hull was achieved by flooding it with Na₂CO₃ electrolyte and making it cathodic (35 mA m⁻²) relative to stainless steel mesh anodes placed directly above it. Electrolysis can be used to remove all corrosion from lightly corroded lead to reveal fine details on the metal surface. This is normally carried out in sulfuric acid electrolyte. A brief reversal of the electrode poles upon completing treatment makes the lead anodic and forms an invisible PbSO₄ coating that has protective properties in the atmosphere. The final 'fresh metal' appearance of lead treated in this way would influence any decision to use this method. Electrolysis of copper alloys to remove potentially reactive CuCl and all other corrosion products is now considered to be aggressive and difficult to control, with a high risk of redepositing reduced copper. Simple electrolysis of copper alloys in water is advocated as deserving of more research, as it can retain the copper corrosion product patina and offer cathodic protection of the metal during treatment.

The inherent insolubility of the silver corrosion products Ag₂S and AgCl prevents the formation of electrolytes on corroded silver exposed to high relative humidity. Consequently their removal is largely an aesthetic act or an information revealing strategy, according to whether the layer is a thin Ag₂S tarnish or a thicker layer of AgCl/Ag₂S that might be found on archaeological silver objects. Once silver is returned to a shiny metal finish the challenge is to apply coatings or control environments to prevent sulfur-based pollutants tarnishing it (see Section 4.43.5). Electrolysis removes silver corrosion products within a wide range of operating parameters using electrolytes such as formic acid (5–30%, w/w) or NaOH (5–15%, w/w) with CD of 0.3–20 mA cm⁻² at 3–12 V.

Very low current densities have been used to slowly reduce corrosion on mineralized brittle silver objects to metallic silver, which is retained in situ to produce a consolidative effect. This method uses a third reference electrode to control the potential of the cathode and a polarization plot is used to identify reduction potentials of the corrosion products, which are then reduced by setting the object potential to match the reduction potential of the corrosion product. It is a finely controlled system that avoids any unwanted reactions such as hydrogen reduction and is useful for tarnish (Ag₂S) removal.

Once corrosion begins on aluminum and its alloys they corrode rapidly in the atmosphere. Electrolysis can be used to remove chloride corrosion accelerators and unstable corrosion products. Degrynge developed a treatment that cathodically polarized aluminum to constant potential in a buffered deaerated slightly acid citrate solution, with treatment parameters optimized to avoid pitting corrosion from the chlorides extracted into the treatment solution and cathodic corrosion of the metal. Composite aluminum objects associated with other metals like iron are problematic, as significant galvanic couples can be established during treatment. For this type of composite metal object electrolysis is modified. Active polarization of the composite object in an inhibited solution protecting the aluminum alloy from corrosion produces a potential that facilitates formation of a protective magnetite coating on the iron fittings. This is followed by polarization of the object in citric acid solution (pH 7) to remove aluminum corrosion products and chloride. Finally, polarization in deionized water washes out chemicals introduced during treatment. The object is dried and coated with a suitable protective coating (see Section 4.43.5.4.2).
Treatments are often fine tuned to the needs of an object. Adaptation of electrolyzing aluminum omitted the magnetite forming step to treat a WWII Japanese Oscar Ki43II fighter retrieved from a saline swamp. The design utilized a swimming pool, 55,000 l of water and 800 kg of chemicals with expanded stainless steel mesh anodes conformed to the shape of the aircraft and sited 30 cm above its surface (see Figure 10). The inevitable post-treatment flash rusting of ferrous components was dealt with by a tannic acid inhibitor. Original paint and penciled notes on the cockpit fascia were masked prior to treatment. Success was assessed by ongoing observation, as opposed to quantifiable measurements of change or residual chloride in objects.

Imposed currents are used industrially to protect large homogenous steel structures, but heterogeneity and corrosion in historical metal objects produce discontinuities that limit applications of this method for corrosion control. The American Civil War submarine CSS Hunley was recovered in 2000 and stored in a holding tank containing chilled (10°C) filtered water (see Figure 11). Storage involves the hull being protected by an impressed current monitored by five electrodes, with two large anode segments running the length of the tank. Comparing corrosion rates of an unprotected mild steel test probe with a similar probe with an imposed current indicated that the post-excavation corrosion rate had been reduced by a factor of 8 and now matched pre-disturbance corrosion rates recorded on the seabed. Protection of the hull by sacrificial anodes was rejected as a preservation option, as it would have required 50 cumbersome 20 kg anodes to be attached to the hull. Impressed current was used to reduce corrosion of the USS Monitor’s steel structure from 254 μm year^{-1} to as little as 25 μm year^{-1}. Measuring the in situ corrosion rates of ship and aircraft wrecks to identify the role of galvanic couplings, concretions, coatings, and environment on their longevity has been extensively studied by MacLeod to develop predictive corrosion control strategies in marine contexts.

4.4.3.4.5 Hydrogen Reduction

Removal of chloride from iron using hydrogen reduction at temperatures of over 800 °C was once seen as a way forward for large chloride contaminated marine objects but is now rarely used. The treatment uses a hydrogen/nitrogen gas mix to reduce chloride bearing compounds at around 350 °C, iron oxides above 570 °C and fully volatilizes iron chlorides and any NaCl present on marine iron at 800 °C. High capital outlay, stringent safety measures designed to prevent oxyhydrogen explosions and ethical concerns that changes to metallographic structure compromise technological data and object history limit its use. It may be argued that it is still a viable treatment for cast iron cannon from marine contexts, where technology is well reported and where objects may be considered to be effectively untreatable in any other way due to the amount of deep-seated chloride within them. The technique is reported to provide good post-treatment stability, but suggestion that the method can offer stabilization by reducing corrosion product to metallic iron is challenged by the instability of the reactive pyrophoric iron it produces. Another heat assisted expensive reduction process used in conservation is gas plasma. It has been used...
to aid chloride removal from iron by reducing FeOOH to denser Fe₃O₄ to produce a more porous corrosion product layer that aids removal of chloride in subsequent aqueous alkaline treatments.¹⁴

4.43.5 Coatings

4.43.5.1 Coating Rationale and Research

Conservation coatings are normally applied as barriers to combat ingress of gaseous, aqueous, or particulate agencies of decay. They may be treatments in their own right or form part of a treatment regime, such as when they are applied as moisture barriers following attempts to remove chloride from iron using washing treatments. Coatings applied to silver must have good gas barrier properties to reduce ingress of H₂S and thereby prevent tarnish.¹¹ Resistance to vapors such as volatile carbonyl pollutants is important for lead, copper alloys, zinc, and aluminum.¹³,¹⁶,⁴³

The role of a coating, environment in which it must be effective and the nature of the metal surface dictate coating choice. An absence of standardized procedures for testing coating effectiveness on cultural metals hinders the use of published material for comparatively identifying the most suitable coating for use in a specific context. While some popular coatings still mostly have qualitative data to support their use, there exists a considerable amount of useful information within conservation literature and there is a move toward providing quantitative data and standardized testing.¹ Both qualitative and quantitative assessment of coating performance within conservation now employs electrochemistry and modern methods of instrumentation in conjunction with increased collaboration with corrosion scientists.²–⁴,⁵⁵

The concept of manufacturing conservation specific coatings is largely a redundant approach, since conservation viability is cultural rather than commercial as there is no significant financial gain for potential manufacturers in such a small market. Increasing collaboration with industrial partners would benefit conservation and reveal its links to industrial applications. Both industry and conservation seek low toxicity, easy application, predictive performance, and low cost for their coatings. Additionally conservation has stringent ethical guidelines that require coatings to have enhanced life span, long-term reversibility and minimal visible impact to the object upon application or ageing. Object context may modify these goals to some extent. Coatings that offer good protection from corrosion, but are aesthetically displeasing, may be acceptable for objects in long-term storage provided they are easy to remove for display purposes. Since the conservation ideal is for indefinite preservation coatings should be long lasting and low maintenance during their lifespan. Demand for long-term durability and guaranteed reversibility
remain at odds with coating design. While cross-linking polyurethanes have renowned barrier properties their irreversibility, without significant mechanical action coupled with aggressive solvents, rules them out for most conservation applications. Since minimal intervention with an object is contravened by applying a coating and by its future removal, its application is only ethical provided there is evidence that it significantly improves corrosion protection.

Conservation coatings must often perform well on porous, uneven oxidized metal surfaces that may be fragile and chemically unstable. No coating is perfect and this type of surface will result in a large number of coating imperfections. This complicates the testing of coatings for conservation applications, as producing test samples with suitably corroded surfaces to match corrosion patinas developed over years or centuries in the ground or air may be impossible. The alternative of using original materials suffers from reproducibility problems and may be subject to ethical constraints. In some instances actual objects are used to test products. The baton from the bronze equestrian statue of the famous fifteenth century mercenary Bartolomeo Colleoni (see Figure 12), which is sited opposite the Ospedale San Marco in Venice, was used to compare the performance of organo-silane coatings (see Section 4.43.5.4.4), synthetic waxes (see Section 4.43.5.4.2) and acrylic (see Section 4.43.5.4.1) coatings in tandem with tests on naturally aged metal samples. This approach links the intrinsic properties of coatings to real-life applications and contexts. Samples are not reproducible but performance can be linked to tests on prepared and reproducible samples. Two-phase test systems, where materials are laboratory tested on reproducible samples by accelerated and natural ageing, then tested on objects in real life environments were employed in the PROMET project. This system should be applied to generate evidence-based advice for practical conservators regarding contextual use of materials.

Coatings on metals are used extensively within conservation, but the absence of industry standards makes it difficult to identify the best coating for defined contexts. Much published work produces useful standalone data. This usually compares groups of coatings using highly specific goals and personalized test regimes to deal with the multiple numbers of variables within the test procedures. The demands and complexity of coating use in metals conservation means that many studies naturally attempt to review many aspects of a chosen group of coatings. A stepped study that examines and compares the performance of coatings in relation to a single variable then moves onto the next would gradually build into a detailed review of materials. Unfortunately, this approach demands significant time and resource commitment and would necessarily be a team project requiring long-term major coordination. Conservation research is not lavishly funded. Collaborative research projects are currently underway or recently completed. Their work could offer platforms for movement towards industry recognized standards for testing. Significant coordination and standardization were evident in the recent EU 6th Framework PROMET project. It sought to identify suitable coatings for use on metals within museums surrounding the Mediterranean basin and aimed to identify a methodology for developing and testing inhibitors and coatings for use on iron and copper alloys in museum environments. Additionally it was looking towards environment friendly inhibitor systems.

Many researchers modify international standards or use them unchanged for testing materials and designing experiments. Overall, there remains a
need for developing test procedures that support conservation goals and facilitate comparative performance testing of coating materials for use in conservation. A conservation-specific accelerated corrosion test standard could be used to model the demands of conservation practice. Coating performance in its operational environment is of crucial importance, as it determines its maintenance requirements and life-span. Although laboratory studies, instrumental analysis and electrochemistry can establish intrinsic performance characteristics of coatings according to a set of fixed variables, they cannot offer quantitative assessment of real-time in situ performance within museum stores, display cases and outdoor environments. Laboratory testing is useful for establishing which coatings are unsuitable for use and for comparative performance testing in specified conditions. Coatings identified as good performers within the laboratory may fail in the field because certain parameters could not be effectively replicated in the laboratory. However, appropriately designed accelerated ageing normally offers an indication of the relative performance of materials.

Within testing processes examining coating performance a recurring theme is that application methods often dictate whether a coating performs well or badly. The procedure here may be critical. Inappropriate coating methods may negate differences between coatings. A coating with intrinsically better barrier properties may fail at the same rate as one that offers poorer barrier properties because of application methods. Standardizing application methods to ensure variable control is an appropriate experimental procedure, but it may not reflect how the coating will perform in practice where the condition of the object, surface morphology and positioning can dictate whether application is by spray, brush, or cloth. How coatings perform as a function of their application method is as important as their intrinsic properties and should form a major part of testing. A coating with only mediocre barrier properties may perform well if its physical properties suit a particular application procedure. Spraying is often a favored coating method, but coatings of the cellulose nitrate lacquer Frigline™ on silver were found to fail unevenly due to thickness variations and discontinuities that resulted from spraying. Brushing is known to offer preferential failure in troughs created by the brush stroke and solid wax coatings may have to be applied as polishes. The nature of the surface of the object may also favor different methods of application and mobile self-healing films may be essential in certain environments. The coating itself may dictate which application methods are possible to use. This overall complex equation must be effectively worked into research studies if results are to be of maximum practical use.

4.43.5.2 Metal Surfaces and Patinas

A major hurdle to the successful application of coatings within conservation is surface preparation. Only in specific circumstances is it ethical to remove patinas and corrosion from surfaces. Within museums equipped with dedicated micro- or macroenvironmental control and monitoring, bare metal surfaces on historical metals may be left uncoated. However, without environmental controls silver tarnishes rapidly in the presence of very low concentrations of sulfur pollutants like H₂S and forms Ag₂S and lead and copper alloys are attacked by low concentrations of organic acids. Preventive conservation is the preferred option to control pollutant availability and attack, but coatings offer an alternative strategy where sources of pollution cannot be eliminated. Potential for disaster exists in mixed displays or with composite objects, such as when an unstable cellulose acetate object emits acetic acid into an enclosed showcase it shares with a lead object.

Patinas on many metals offer an information resource and provide aesthetic attraction. They may be deliberately applied or naturally formed corrosion layers. Deliberately patinated or polished copper alloy statuary is often modified by corrosion from pollution, rain, and particulates that form corrosion products that may undermine, obscure, or destroy the original patina and outermost metal surfaces (see Figure 12). The extent of corrosion will relate to metal composition, climate, location, preexisting patina and the solubility, morphology, uniformity, and adherence of new corrosion products. Run marks, differential corrosion from pitting, differing colors and textures produced by climate, pollution, composition, and object morphology can entirely ruin object aesthetics and offer a porous uneven surface that will not accept a continuous coating. Wear marks on patinas can be important to retain as part of the history or present life of an object (see Figure 13). Whether total or partial removal of patina is appropriate, in return for improved object stability and surface preparation for coating, presents ethical and aesthetic dilemmas for the conservator.

Apart from ethical considerations, establishing the role of a patina in the corrosion process can help decide whether to remove it as part of a corrosion control strategy. Equally an understanding of patina stability
and protectiveness contributes to developing corrosion control strategy by offering a measuring point for monitoring, assessing, and predicting patina deterioration with time.

Nondestructive in situ analysis has been used to identify variance of electrochemical stability within patinas to locate areas that offered high stable electrode potential relative to the base metal, as they provide good corrosion protection. Results revealed that unsightly black crusts offered more protection than visually acceptable blue/green corrosion product layers. This creates an aesthetic dilemma for conservation strategies based on patina retention. Understanding the contribution of corrosion layers to the corrosion process makes it easier to determine if interventive treatments are a better corrosion control option than noninterventive monitoring strategies.

Disfiguring, unstable and aesthetically displeasing patinas formed by corrosion may be removed, either to reveal metal or a selected corrosion product layer in preparation for repatination and/or adding a protective coating. Repatination may even form part of a corrosion control strategy, as some patinas may offer a degree of protection by acting as partial barriers to moisture, electrical conduction, and gases. Instrumental analysis and historical research to determine the original appearance of a metal object is a prerequisite to selecting a repatination process. Working objects and industrial equipment that never developed a patina or were frequently repainted may in some instances be stripped to the metal surface, provided their history is not compromised by loss of data such as paint layer sequences. Analysis of paint layers would determine if this was likely to occur. Stripping processes like electrolysis, chemical dissolution and complexation, which remove corrosion prior to applying coatings should provide for lower maintenance of coatings, all other factors being equal. Yet there remain ethical dilemmas concerning the stripping of historical metals. During its working life a cog may have uncorroded teeth that developed a surface finish from work, with a corrosion patina on its ‘noncontact’ body that can also be associated with its working life; should conservation retain both these layers?

4.43.5.3 Preparing Surfaces on Cultural Objects to Receive Coatings

Surface preparation of objects may take the form of mechanically removing disfiguring corrosion to reveal the ‘original’ surface of the object or the marker layer for this. In archaeology it is normal to use mechanical systems to remove corrosion to reveal the object shape and surface detail. For historical metals preparation may involve mechanical cleaning systems, chemicals, or electrolysis. Precious metals may be polished to a high shine as the goal of coating is to ensure that future repolishing occurs as infrequently as possible. In all cases it is best to remove soluble corrosion accelerators before applying coatings.

Outdoor statuary is cleaned according to the goals of the conservation process, taking account of ethics and aesthetics. Preparing surfaces by stripping patinas is normally unacceptable due to ethical constraints and aesthetic outcomes (see Figure 14). All processes must involve minimum loss of material. Choosing a cleaning method normally relates to how it physically modifies surfaces and alters appearance, rather than its impact on metal stability by removing corrosion accelerators or making a surface more coating friendly, unless it is being prepared for paint. Cleaning methods...
will influence the effectiveness of coatings, as leaving corrosion products and patinas in situ influences their adhesion and distribution. Most studies qualitatively compare the effects of cleaning methods on specific metal surfaces. Dry particulate abrasion, pressurized water and chemicals have variously been compared for cleaning patinated copper.\(^\text{61}\)

One study serves to illustrate some of the decision making associated with cleaning surfaces. It compared cleaning of a patinated copper alloy token by abrasion techniques employing glass beads, walnut shell, corn cobs, and sodium bicarbonate delivered at pressures between \(1.38 \times 10^5\) and \(5.52 \times 10^5\) Pa with simple abrasion using \(\text{Al}_2\text{O}_3\), pressurized water and chemical cleaning by complexation (solution comprising \(\text{KNaTartarate}, 2\text{NaEDTA}, \text{NaOH},\) and fumed silica applied in a cellulose ether gel pack).\(^\text{61}\) Postcleaning samples were exposed to synthetic rain and their corrosion was monitored.

Results of these tests reveal the general dilemma produced when trying to balance effectiveness with aesthetics and ethics. Although chemical cleaning offered the most stable substrate, as observed after 1 year, it produced the most visually altered surface by removing all overlying green corrosion products to leave only orange/brown \(\text{Cu}_2\text{O}\) in situ. Predictably the softest corrosion products disappeared from the mechanically abraded objects, which were less stable than the chemically treated sections. Pressurized water produced the least visual change, but removed the most soluble corrosion products leaving the metal actively corroding after a year. None of the methods entirely stabilized the metal and various corrosion products were left in situ, neither did they remove all corrosion accelerators. Other workers have expressed concern at indiscriminate surface preparations that fail to recognize the importance of original coatings on metals like aluminum.\(^\text{16}\) Glass beads have been cited as being too damaging on finishes on aluminum alloys, but airbrasion can be retained by use of plastic beads at \(1.0 \times 10^5\) Pa.\(^\text{16}\)

Preparing historical metals and objects d’art that traditionally carry a shine for the application of coatings involves either chemical or physical removal of tarnish. Removing \(\text{H}_2\text{S}\) tarnish from silver can be achieved by chemicals or abrasion.\(^\text{13}\) Chemicals are aggressive and may lead to differential corrosion and surface enrichment of alloys such that loss of copper alloyed with silver leaves a soft and porous silver enriched surface. They may also leave residues that are too aggressive and these have been tested to determine their impact on the object and develop a protocol for treatment. Polishes remove metal and produce surface scratching. Studies of polishing methods concentrate on the loss of metal incurred and scratching of the surface, with \(\text{CaCO}_3\) being a favored inert polish for silver.\(^\text{62}\) Chemicals are normally only preferred for heavy tarnish due to the risks of preferential leaching of alloying components and the need for acidified complexing agents to remove \(\text{Ag}_2\text{S}\).\(^\text{12}\) Potentiometric methods mentioned earlier can also be used to remove silver tarnish (see Section 4.43.4.4). Focus should be on identifying the least interventive method that offers the best surface for receiving a coating.

### 4.43.5.4 Coatings in Conservation Practice

There are a small range of generic coatings in general use within conservation and there is no definitive comparative study which clearly identifies the most successful coating for any given context. Preferences and trends exist for various chemical groupings and products.\(^\text{3}\) Coatings are reviewed below by chemical affiliation, rather than their application to specific metals. Trade names are used in general discussion, having initially defined the chemistry of the product.

#### 4.43.5.4.1 Acrylic coatings

The Paraloid™ range of acrylics, known as Acryloid™ in USA, is commonly used within conservation practice. Other acrylcs are used according to availability, which means geography can dictate choice of materials. Survey reveals that only a few coatings are routinely used, with Paraloid B72™ (70 methyl methacrylate/30 ethyl acrylate copolymer) being one of the most popular general purpose surface coatings.

![Figure 14](image.png)
for cultural metals. Its long-term reversibility and application as a coating, consolidant, and adhesive make it a workhorse within conservation and a comparative performance standard in many test procedures. Performance of Paraloid B72™ and an ethylene based commercial coating Poligen ES 91009™ were compared, both alone and with added inhibitor as coatings on fresh and precorroded coupons of steel exposed to cycling γ (90% at 35 °C to 55% at 25 °C) to simulate extreme museum environmental fluctuations. Performance was assessed qualitatively by visual interpretation and quantitatively using EIS and polarization techniques. Poligen ES 91009™ was more effective than Paraloid™, and added inhibitors failed to significantly improve the performance of either coating. Long-term exposure of similar test coupons in museum environments confirmed that although Paraloid B72™ gave ‘quite satisfactory results’, it failed at edges producing filiform corrosion. This was recognized as being problematic where much cultural material like edged weapons and armor had multiple thin edge sections. The importance of environment was revealed in these tests as matched sample sets performed differently over similar exposure times within museums in differing Mediterranean countries. Application method was again revealed as being an important variable. In one test, a 250 µm layer of polyurethane (Rylard™ boat varnish) performed much better than either Paraloid B72™ (40 µm) or an innovative physical vapor deposition system (<1 µm). Standardizing test methodology by employing aged coupons and using laboratory and onsite real-time testing in monitored environments offers a solid test platform for cultural metals and for the evaluation of assessment standards. Yet outcomes discounted certain products due to outright failure, it proved difficult to quantify the performance of some of the more successful coatings. Overall, the study revealed weaknesses in the performance of traditional conservation materials and identified the newly tested Poligen ES 91009™ as offering promise for the future.

The inability to separate lead organ pipes from oak supporting frames emitting organic acids in European Baroque organs led to a research program that tested the ability of coatings and inhibitors to prevent the corrosion of lead by organic acids. Using an aqueous washing strategy to remove soluble lead methanoates and ethanoates acting as electrolytes failed to reduce the corrosion rate upon reexposure of the lead to the methanoic (170 ppb Pb(CHOO)2) and ethanoic acid (195 ppb Pb(CH3COO)2). Coatings alone produced limited protection, with Paraloid B72™ offering no protection, microcrystalline wax providing uneven protection and various inhibitors had little effect. This is of concern as Paraloid B72™ has long been used as a coating on lead. Treatment must be effective for the long term, due to the cost and logistics of coating the organ pipes. Nanotechnology is now being tested in a preventive treatment using Ca(OH)2 nanoparticles to control acid emission from the wood.

Incralac™ lacquer comprises Paraloid B44™ (ethyl methacrylate/butyl acrylate copolymer) with added epoxidised soya bean oil as a leveling agent and benzoiazole as a UV absorber and is industry designed for protecting copper alloys. It has been extensively used both on archaeological and outdoor copper alloys since the 1960s. Its application aesthetically changes bronzes by darkening their surface. However, outdoor exposure is likely to result in optical changes to most coatings as they weather and collect dirt. Good electrochemical impedance measurements recorded for fresh Incralac™ coatings on polished and unpolished bronze, implied good coverage and low porosity, but after natural ageing on a rooftop in Canberra for 4 years impedance was the same as for uncoated metal. Although two coats improved performance the time-related failure remained the same. Poor long-term performance was also found in 10-year-old Incralac™ coating on a gilt bronze statue in New York. It was entirely cracked and its insolubility was likely due to cross linking exacerbated by the loss of the BTA UV stabilizer which was absent in the aged lacquer, which required strong solvents and physical intervention to reverse it. Inhibitors such as benzoiazole (see Section 4.4.3.6.1) have been used to prime bronze surfaces prior to applying Incralac™. The manufacturer reports a 5-year lifespan with removal instructions recognizing its reduced solubility with age, but a 2-year lifespan on outdoor copper alloy monuments is more common. The outdoor performance of Incralac™ is limited when measured against conservation goals of low maintenance, good protection, and reversibility but it continues to be used in the absence of any quantitative proof of significantly better performing alternatives. Survey suggests Incralac™ is now less commonly used on historical and archaeological metals inside museums, apparently in favor of Paraloid B72™.

Solvent-based acrylic resins and their aqueous dispersions have been tested as H2S barriers in a program comparing them to vinyl acetates, cellulose nitrate and microcrystalline wax. Acrylic dispersion systems performed better than the acrylic resin solutions and were equal performers with vinyl acetate and cellulose nitrate, but the defining factor in protectiveness of all
the coatings tested was their evenness and thickness. Uneven coatings produced differential tarnishing. Microcrystalline wax (Renaissance Wax™) produced the worst result because its solid state made it difficult to apply. The conflict between good experimental procedure and practical use of coatings is reflected by drying coatings for 8 months prior to testing them with H₂S₈, as this is unlikely to reflect the procedure within museum contexts.

Fragile metal objects are held together by impregnating them with polymers using immersion systems. Acrylic polymers like Paraloid B72™, microcrystalline waxes and occasionally, epoxy resins are used for fragile iron.⁷,⁶⁻¹⁶ Unsurprisingly, long-term survey reveals that iron objects washed to remove chloride and then consolidated with epoxy resins survive better than washed iron that remained unconsolidated.⁶⁻¹⁶ Epoxy resin coating offers a degree of protection against moisture ingress and its strength as an adhesive retains the physical integrity of the iron even if it corrodes.⁶⁻¹⁶ While the insolubility of epoxy resins appears to contravene the central conservation concept of reversibility, its use is measured against increased longevity of the iron as a cultural resource. The influence of ethics on treatment choice takes account of both the prevailing situation and the ultimate goal of prolonging the functional life of an object.

In reality even the use of a reversible consolidant is effectively an irreversible process. Since its use implicitly acknowledges it is essential for retaining the physical integrity of an object, overcoming consolidant/metal interactions to remove it would likely result in object fragmentation. While there have been no conservation studies on the influence of epoxy resins on the corrosion of metals, less viscous short chain aliphatic epoxy resins suited to consolidation processes produce more OH groups upon cross-linking than aromatic epoxy oligomers, which means they attract more water from the atmosphere and this may facilitate greater corrosion. Trapping moisture within iron objects by using consolidants and coatings runs the risk of creating microclimates that may accelerate and localize corrosion.

4.43.5.4.2 Waxes
Microcrystalline waxes are commonly used as coatings in conservation, especially on smooth even steel surfaces such as armor⁷ and patinated outdoor monuments.⁶⁻¹⁶ Recent Ecorr studies revealed one such wax offered little or no protection when compared to the acrylic Paraloid B72™ and polyethylene wax Poligen ES™ on smooth steel in contact with electrolytes.³ Interpreting this failure illustrates the importance of taking account of environment and metal substrate, as when microcrystalline waxes were tested on lead exposed to atmospheres containing organic acid vapor they performed significantly better than Paraloid B72™.⁶⁻¹⁶

Renaissance™ and Cosmoloid 80H™ waxes are the most commonly cited microcrystalline waxes in conservation literature. Typically in conservation, particular commercial products tend to be preferred for use over long time periods.⁷ In what is often a nonevidence-based manner the perception grows that they are ‘proven’ products. Replacing popular coatings that are no longer being manufactured presents a problem. An extensive study was set up to find the best commercially available alternative for a microcrystalline wax being phased out of production. A range of microcrystalline waxes and a low melting point (80–100 °C) polyethylene wax were compared using electrochemical impedance spectroscopy and immersion in 0.1 M NaCl, supported by real-time atmospheric exposure.⁵⁵,⁶⁵ BeSq 2095™ microcrystalline wax performed similarly to TWA 2095™ which was being phased out. Real-time testing was an essential part of this study and identified complete failure of the waxes over a 4-year exposure period. As reported for many other test procedures it was the application method that once again provided a significant influence on performance. BeSq 2095™ microcrystalline wax performed better when applied in a molten state, which produced crystalline lamellae, whereas polyethylene wax offered best protection when buffed onto bronze surfaces.

Protection of bronze ethnographic and artistic objects with waxes provides a transparent coating with a degree of color saturation that meets aesthetic goals. Sticky aesthetically displeasing mobile wax coatings that alter color saturation of surfaces are not used in conservation, unless the object is to be stored. A number of commercial products comprising wax and volatile corrosion inhibitor additive were ranked as better performing coatings for outdoor bronze sculpture, as compared to the conventional microcrystalline wax Besq 195™ using electrochemical impedance spectroscopy.⁶⁷ Dinitrol 4010™ performed best. It is used by the aerospace industry to protect engines in storage.⁶⁸ and it is a preferred choice for electrolyzed aluminum alloys,⁵⁶,⁶⁷,⁶⁸ although a note of caution was expressed on the use of inhibited commercial waxes for aluminum alloys without first examining their relationship with the corrosion processes taking place.¹⁶ A Focke-Wulf 190 aero engine treated by electrolysis was coated with a 40 μm layer of Dinitrol
4010™ post treatment, which has good protective properties and is favored by the aircraft industry because it has no adverse affect on rubber and plastics. Wax coatings are considered to be high maintenance options for outdoor bronzes, as compared to acrylics. However, they are used as sacrificial topcoats on outdoor bronze statuary where they protect the underlying acrylic layer from degradation. A threephase system of Benzotriazole inhibitor primer, Incralac™ main coat and microcrystalline wax topcoat has been employed by a number of workers and offers a more robust protective system.6

4.43.5.4.3 Cellulose nitrate
Before the introduction of the Paraloid™ range of acrylics, cellulose nitrate was commonly used in conservation as an adhesive and a coating. It has proven long-term reversibility and its properties and decay have been extensively reported. Long-term performance studies discounted its effectiveness as a coating on archaeological iron.3,14 Although it has been in long-term use as an antitarnish coating on silver the cellulose nitrate lacquer Agateen™ only equaled the performance of acrylic and vinyl acetate emulsions in laboratory tests.66 As with many other coating studies on silver, tarnishing from sulfur was strongly influenced by coating methods and the quality of their application.57,66 Anecdotal reporting suggests recoating silver to protect against tarnishing is necessary every 10 years. This is an expensive and time consuming exercise for a large silver collection, so coating lifetime has been explored using accelerated ageing tests.69 These revealed that light and relative humidity had a pronounced effect on the lifetime of the commonly used cellulose nitrate lacquer Frigilene™. Extrapolating the results of the accelerated tarnishing tests indicated that Frigilene™ should still protect from tarnishing after 10 years in mid-range relative humidity values. Calculations did not account for thermal effects inherent in accelerated ageing tests, so lacquer lifetime was expected to be greater than 10 years’ exposure at room temperature.

Appropriately these laboratory tests are being evaluated by English Heritage using real-time monitoring of the Waterloo silver centerpiece in Apsley House, London. In several years’ time the final outcome will offer insight into the effectiveness and value of the test procedures, as much as the performance of Frigilene™ lacquer as a gas barrier. Focused pragmatic studies such as this offer tangible evidence for choosing materials fit for task and for devising long-term conservation planning and budgeting. The reported testing supplied sufficient information for the production of a predictive conservation strategy. Benign impact on metal, proven reversibility, and long operational lifespan are the main essentials for conservation planning, which, in this instance, revealed that cellulose nitrate was a good choice for antitarnish coatings on silver. Although investigations into the surface chemistry relationships between cellulose nitrate and silver would offer insight into mechanisms of protection and failure, it is not necessary in order to devise a preservation strategy.

4.43.5.4.4 Silanes
While organosilicon compounds are extensively used in industry,70 they have received limited attention in conservation practice. It appears that there is much scope for employing them on cultural metals as hydrophobic barriers, as they are largely invisible on surfaces, are good water repellents and are capable of bonding to corrosion products.33 Barrier properties of silanes can be improved with the inclusion of inorganic additives like silica plates, which can reduce water permeability and aid reversibility. Eventually silanes will be broken down by water reaching the metal—silane interface, where it reverses the Si–O–Me bond that was formed by hydrolysis to protect the metal. Applying thicker films cannot be used to counter this as they tend to be too brittle and application difficulties are experienced.70

Organic–inorganic polymer systems produced by hydrolysis and condensation reactions of alkoxysilanes and organo-functional alkoxysilanes have been tested on bronze, fresh, and precorroded steel in the form of the Ormocer™ (ORGanically MODified CERamic) family of lacquers produced by the Fraunhofer Institute in Munich.71 Good adhesion to metal surfaces and their hydrated corrosion products should occur due to the presence of Si–OH and Si–O–R groups in the polymer and an organic polymeric network results from the cross linkable functional groups of alkoxysilanes (R–Si(OR)3). Ormocer™ lacquers can be modified to produce differing elasticity, by reacting their main cross linkable component glycidoxypropyl trimethoxy silane with alkoxysilanes.71

These lacquers significantly outperformed waxes in laboratory-based accelerated (SO2) corrosion tests and outdoor exposure using various international standards.72 Application method and concentration proved important to performance. Monolayers (4–8 μm) and bilayers (10–12 μm), applied by spray, darkened metals and the monolayer performed better
than the bilayer on patinated metal. This data indicates that it may be a promising coating for corroded metals, but technical and ethical boundaries must be crossed when using it. Ormocer™ requires methylene chloride paint stripper to reverse it. Testing this lacquer in SO₂ contaminated environments reflects its initial conception for use within industrial contexts, where polluted environments offer significant threat. Despite the siting of many cultural metal objects in urban contexts surprising few studies within conservation examine coating performance in SO₂ contaminated conditions.

As in other areas of conservation comparative studies dominate conservation research into silanes. An EU research project (ARCHITECH) seeking to identify better coatings for outdoor art works is examining silane coatings, copper oxalate patinas and increasing the thickness of Cu₂O layers to improve the natural protectiveness of patina on copper alloys. Comparing selected silanes to the commonly used Incralac™ acrylic coating revealed them to perform only equally well, which is not encouraging given the overall weak outdoor performance of Incralac™ (see Section 4.43.5.4.1). The fact that Incralac™ altered the chroma of the metal surface more than the silanes does not seem to offer strong support for using silanes. The fact that Ormocer™ showed better adhesion than Incralac™ in high humidity may be of use, but such conditions are likely to more readily induce its hydrolysis. The PROMET project included Silane A (5% γ-mercaptopropyltrimethoxysilane; 2%bis-(trimethoxysilylpropyl)amine; 1% hydrated tetraethoxysilane; 92% ethanol) in its comparative testing regime. This offered best protection for bronze in long-term real-time testing, as compared to Paraloid B72™ and selected corrosion inhibitors. However, all systems failed over the test period. There are many difficulties to overcome if silanes are to be successfully used on cultural metals.

4.43.6 Inhibitors in Conservation

Inhibitors are used selectively and, in many cases, empirically in conservation practice, either alone or in combination with coatings. While their use is governed by the usual ethical constraints of appearance and reversibility, fashion also has an input. For instance the blackening of iron by tannate inhibitors may be deemed to be ethically acceptable on archaeological iron, as it could be argued that visual changes do not stray too far from the appearance of the gray/black DPL layer retained on objects. This encapsulates the flexible nature of ethics and aesthetics within conservation, as the slight darkening of patinas on copper alloys caused by the use of benzotriazole is cited as being of concern by some authors. Whether inhibitor use in conservation can be reconciled with the goal of stabilizing metals is debatable, as inhibitors slow rather than prevent corrosion.

No inhibitors have been specifically developed for use in conservation practice. They are borrowed from industrial contexts, where they have been assessed for use in specific operational environments on particular alloys. As with protective coatings inhibitors are required to be effective in the presence of corrosion products. This presents difficulties, as soluble corrosion accelerators like chloride ions normally interfere with their action. Low inhibitor toxicity is also a requirement, as objects remain in the public domain where they must be accessible and easy to handle. This tends to rule out many vapor phase inhibitors, as these are often based on volatile and toxic amine base compounds. Attempts have been made to find less toxic alternatives and cheap natural inhibitors. Recently extract of seed oil from the cactus Opuntia ficus indica was used to formulate an inhibitor that contained long chain fatty acids, triethanolamine, and potassium hydroxide but it failed to offer protection when compared to a range of coatings. This is likely due to poor film formation, as a continuous film reportedly constitutes its inhibitive properties. In the same tests, adding corrosion inhibitors to films failed to improve their protective properties significantly.

4.43.6.1 Benzotriazole (BTA)

1,2,3-Benzotriazole is the most successful commercial inhibitor used in conservation practice. It is applied to prevent corrosion of chloride contaminated copper alloys. There is some discussion whether it is the inhibitive properties of BTA or the barrier properties of Cu–BTA films that infer protection to patinated chloride containing copper alloys. The Cu(I)–BTA inhibitor complex films formed on copper, copper alloys, and Cu₂O surfaces have excellent adhesion from primary and secondary bonding and likely play the dominant role in the protection of patinated copper alloys by limiting water, ion, and oxygen ingress to reactive metal and mineral surfaces. The film tolerates chloride ions and low-pH environments and reacts with CuCl to produce a BTA–chloride compound that is stable at high humidity (see...
Figure 15. Benzotriazole was specifically applied in conservation practice to combat ‘bronze disease’; the growth of voluminous Cu$_2$O$_2$Cl polymorphs at the Cu$_2$O–CuCl interface beneath shape-retaining overlying corrosion layers. Their loss is visible on this Roman pin.

Figure 15). Compared to a range of other nitrogen or sulfur-containing organic compounds it is more effective (99%) at inhibiting hydrolysis of CuCl to Cu$_2$(OH)$_3$Cl and although both 2-mercapto-benzimidazole (98% effective) and 2-mercapto-benzothiazole (97% effective) approach its inhibitive properties, they form aesthetically unacceptable white and yellow complexes with CuCl. The black-green coating BTA produces when it reacts with CuCl is probably why BTA is noted for darkening patinas on copper alloys. This is a small trade-off for its proven effectiveness at preventing corrosion.

There is no definitive agreed and tested protocol for its use. It is normally used as a 3% solution in alcohol or 1% in water, with no quantitative evidence to support suggested treatment times that range from paintbrush application through a few hours in vacuum to several days soaking. Archaeological and deeply pitted copper alloys often prove difficult to stabilize using BTA solutions, as hydrolysis within pits creates a low pH that interferes with the formation of an effective Cu–BTA coating. This is overcome by pretreatment of pits with Na$_2$CO$_3$ but at an aesthetic cost of producing brown-colored spots.

Factors influencing copper–BTA reactions and the nature of the resulting film include the condition and oxidation state of the reacting surface, potential, temperature, pH, and chloride and oxygen concentrations. Thus Cu(I) complexes formed in acid corrosive environments tend to be thicker, less polymerized, and more permeable to oxygen than equivalent films formed in neutral and deaerated conditions. This diversity in film formation indicates that there would be considerable benefit in tests designed to examine the nature of the films formed to determine optimum application conditions. For instance, it appears that deoxygenated solutions may offer an advantage over current oxygenated treatment environments and short treatment times could explain why BTA sometimes fails to inhibit corrosion. Tests on artificial patinas have shown that it takes several days for reaction with brochantite (Cu$_4$SO$_4$(OH)$_6$), which is a common corrosion product on outdoor statuary in urban areas, to go to completion. Although the acid by product of this reaction lowers pH as concentrations of BTA increase, a dilemma exists as treatment must ensure there is excess BTA present to repair any damage to the protective BTA polymeric film formed.

Use of BTA on outdoor statuary requires a regular maintenance program, as BTA is likely to be lost from effects of rain-wash due to its solubility and volatilization because of its low vapor pressure. The use of BTA as a primer coated with protective lacquer(s) should prolong its effectiveness. Additionally, BTA also forms Pb–BTA and PbO–BTA compounds as crystalline polymeric films which have been shown to protect lead within leaded bronzes from corrosion by organic acids and Zn(II)–inhibitor complexes have been detected on copper alloy. In contrast electrochemical measurements showed silicon bronzes had lower organic inhibitor efficiency as silica is poorly reactive towards BTA. It is clearly important to know what copper alloy is being treated to assess likely inhibitor effectiveness.

Whether copper alloys routinely require treatment with BTA is questionable. What percentage of objects would have remained stable, even if they had not been treated with BTA, is unknown. Many patinated copper alloys treated by BTA appear stable in museum environments, although this observation remains unsupported by quantitative data. A study of surface chemistry reactions with the typical corrosion profiles found on copper alloy objects and quantitative long-term studies of copper alloy object stability following treatment with BTA would determine its inhibitive powers relative to the conservation goals of longevity and predictive success.

Despite its proven inhibitive success, workers still seek alternatives to BTA mainly due to toxicity worries and its high cost. While no better inhibitor for cultural corroded copper alloys has been recorded, synergistic inhibitive effects have been identified when using BTA with other inhibitors that included 5-amino-2-mercapto-1,3,4-thiadiazole. Caution is
required when mixing inhibitors as the formation of differing BTA complexes can lower performance of BTA. Recently BTA with a hydrophobic alkyl side chain (C6-BTA) has been tested on the basis that the side chain will better repel aqueous electrolyte. A more novel use for BTA is as an inhibitive washing procedure for marine iron, where it forms Cu(I) complexes and Cu(II) species and prevents corrosion while the water wash extracts chloride from CuCl. A big advantage of using a BTA preservation strategy on copper alloys is that it can be applied without any surface preparation, which is ideal where patina is part of the intrinsic value of the object. Ensuring access to the Cu2O layer that is normally situated next to the metal or integrated with CuCl sited there will provide the best opportunity for treatment success, due to the ability of BTA to react with this oxide. Unfortunately, removing the overlying green brochantite/antlertite/malachite patinas to reveal orange/red Cu2O would be visually unacceptable in many instances.

### 4.43.6.2 Tannins

As conservation seeks to balance its goals with global concerns regarding toxicity and carbon footprints, testing low toxicity inhibitors derived from natural sources like plant extracts is of interest. Tannin plant extracts have been used intermittently in conservation since the 1960s and are reported to act as rust converters, leaving a black inhibitive film on the metal. Treatment involves either immersion in tannin solutions or, more likely, painting onto objects. Currently there is no quantitative in-depth study of their action within conservation contexts or any data that offers quantified guidance for optimum treatment concentrations or application procedures.

It is well known that condensed tannins applied either in water or solvent to rust-covered iron offer inhibitive properties by forming ferric–tannate complexes that act as insoluble barriers and phosphoric acid is said to improve inhibitive properties. Tannate-coated iron performed well in long-term storage according to a qualitative survey of archaeological iron. While this provides useful information, post-treatment stability studies for determining treatment success should be controlled and semiquantitative with clear links to environmental variables, rather than retrospective examinations of treated objects.

Iron stripped by 4NaEDTA was coated with a mixture of phosphoric and tannic acids to inhibit further corrosion, following electrochemical testing to determine optimum concentrations and combinations of inhibitor. A recent study identifying optimum concentrations of tannin and phosphoric acid for inhibiting corrosion of rusted iron in a 3.5% NaCl solution indicates the importance of research and testing to optimize tannin applications to meet the prevailing circumstances. In this study, $E_{corr}$ values showed that phosphoric acid reduced the inhibitive properties of mangrove tannins at low pH (0.5 and 2.0), yet when used alone at higher pH (5.5) it offered improved inhibition as compared to tannin/phosphate mixtures. Corroding archaeological iron has varying pH across its surface due to hydrolysis of anodically produced Fe(OH)$_{3}$ and its thick corrosion layers. Any testing of tannins for use in conservation practice should be tailored to the corrosion model extant.

As with other protective surface coatings testing the stability of treated objects at typical storage humidities is necessary and, until this is achieved, application of tannins in conservation will retain a degree of empiricism. To date, no inhibitor has been shown to have effective long-term inhibitive action on chloride-contaminated archaeological iron retaining its corrosion layers and exposed to mid to high relative humidities. Commercial tannate-based inhibitors have been tested and shown to be effective for inhibiting internal corrosion of boilers in the working nineteenth-century paddle steamer PS Enterprise between its weekly use on lake Burley Griffin, Australia (see Figure 16). In these closed systems the boiler retains its water and inhibition results from a combination of reducing the availability of oxygen, formation of iron tannate film and precipitation of dissolved salts as sludge.

### 4.43.6.3 Carboxylates

Sodium carboxylates (CH$_3$(CH$_2$)$_n$–COONa – usually $n = C_{10}$ or $C_{12}$) derived from vegetable oils have been used on copper alloys and iron to form inhibitive copper and iron carboxylates. Like tannates, they are environmentally friendly. They have been linked to conservation in tests on corroded iron and copper coupons and blank standards. Potentiodynamic curves revealed they offered slightly better inhibition than mimosa tannin solutions and considerably better protection than phosphates tested on bare clean steel coupons. A further advantage is that the nanomeric hydrophobic iron carboxylate soap layer formed by reaction with iron cations is not aesthetically disfiguring, as is a black iron tannate layer. Carboxylates readily reverse in ethanol, which may mean they are best suited to indoor applications. Long-term
real-time testing using pre-corroded metal coupons indicated that sodium decanoate offers temporary protection on partially oxidized historic steels and may be considered as an alternative to Paraloid B72™. It also offered good protection for copper alloys.

Carboxylates were originally tested in conservation as inhibitors for preventing corrosion of lead by volatile organic acids. Polarization plots produced by modeling corrosion of inhibited lead by these acids indicated that sodium decanoate and undecanoate protected best against corrosion, whereas phosphate inhibitors actually increased corrosion rates. Real-time X-ray diffraction studied the resistance of lead carboxylate (\(\text{CH}_3\text{(CH}_2\text{)_8\text{COO})_2\text{Pb}}\)) films to acetic acid vapor and revealed considerable protective properties, but ultimate failure. Carboxylates appear to delay corrosion by organic acids, but ultimately they cannot prevent it. As in other areas of conservation, contextual needs dictate preservation strategies, while these tests showed carboxylates as being unsuitable for preserving church organs, they may be considered suitable where lead is more accessible and easy to monitor to determine if retreatment is necessary.

4.43.7 Painted Metals

4.43.7.1 Removing Paint

Conservation ethics normally dictate that original or later paintwork that offers either a record of the history of the object or milestones in its life should be preserved. The preservation of fragmentary original paint surfaces is challenging, as pitting and corrosion undermining paint are a threat to paint integrity and are difficult to stabilize. In such instances environmental control may be the only option guaranteed to prevent ongoing corrosion beneath the paint layer. There are instances where ethical arguments support refinishing the surfaces of cultural objects either to their original specification or to an improved standard in order to offer the best opportunity for longevity. This should not compromise the future interpretation of the object.

Refinishing may be acceptable when there is no original paint layer remaining and replicating an original finish offers significantly increased object longevity. A combination of refinishing and preservation of original surfaces may be adopted in some instances. If the condition of the metal allows, refinishing offers opportunity for highly specified surface preparation. It may also be possible to apply modern paint systems if visual appearance rather than replication of the original recipe is deemed to be the most important interpretive factor. Stripping to the bare metal for repainting should involve minimal loss of the original metal.

4.43.7.2 Refinishing Painted Surfaces

Preparation of historic metal surfaces to receive paint must always minimize loss of metal. Commercial conservation programs often adhere to international
standards for preparing surfaces, such as SSPC, NACE, and Swedish Standards. This offers the client a defined measuring point within the contract of work. Repainting the upper hull of the SS Great Britain was justified on the basis of continual repaints during the working life of the ship and the presence of a failing modern paint layer. The hull above the waterline was to be exposed to the British climate and merited the best possible protection from the elements. It was stripped to near white metal (SA2.5) using high pressure water lances (2500 bar) and for weaker areas crushed Australian Garnet (8 bar) in preparation for painting (see Figure 17). Although this removed several microns of original wrought iron, it was reasoned to be ethical as this thickness of metal would inevitably be lost through future corrosion if preparation was not so stringent. The paint system chosen was typical for creating a durable, long-lived outdoor protective coating on a well prepared surface. A three-phase treatment comprising a 2-pack zinc-rich epoxy primer followed by 2-pack high-build main coat paint system with a urethane UV-resistant topcoat, produced a total paint thickness of 225–250 μm (see Figure 17). The preferred method of application involved an airless spray at 207 × 10^5 Pa with brushing when the spray could not be used. Life expectancy of this layer with appropriate maintenance is predicted at 15 years.

Often it is not possible to prepare corroded metal surfaces to a high standard. In this instance original lead-based paints are preferred, both to replicate original paint layers and because of their perceived longevity. Since health and safety considerations make their manufacture costly and their use has environmental implications, aluminum-based primers are normally used instead. Ferro zinc (HMG Paints) is a rust conversion paint that was used to paint the monitor HMS Minerva after electrolysis. The range of historic alloys and the inability to effectively prepare many surfaces beyond SA 1 or 2 means that each surface offers a unique coating problem. Consequently conservation designs often test paint adherence using a pull-off test (ASTM D 4541-02 or ISO 4624) before applying it to an entire surface. Reports on the longevity of painted surfaces relative to the prepainting condition of the surface and the paint system applied are not reported and this offers another area for research that could act as a platform for designing industry standards. Silanes are used for preparing metals for paint within industry, but this has not been reported in conservation practice.

Where sections of metal have entirely corroded away, decisions regarding a course of action have to account for ethical, technical, and corrosion considerations. Structural problems require structural solutions but care must be taken not to create galvanic cells by repairing with alloys of differing potential from the original metal. Equally, where structural

![Figure 17](https://example.com/figure17.png)
integrity is not a concern it is possible to use glass reinforced plastics and epoxy systems.\(^\text{25}\)

4.43.8 Overview

The overall equation for preserving cultural metals is a complex mixture of material science, context, and ethics. During the past 40 years, conservation has developed links with corrosion science that have led to greater understanding of corrosion processes, which, in turn, supports investigation into treatment mechanisms and methods. This has been extensively boosted over the past 15 years by increased application of modern instrumental analysis in conservation

Figure 18  Challenges in metal conservation extend beyond museum interiors to whole sites such as housing at Valparaiso (UNESCO World Heritage site) and abandoned factory settlements like Stromness (South Georgia) whaling station. Images courtesy of Eura Conservation Ltd.
research. Much greater opportunity exists for collaboration between conservators and corrosion scientists to develop a synergistic relationship for solving the problems of preserving 'metallic heritage.'

Within conservation there are normally multiple preservation options, either due to insufficient evidence to identify one treatment as being significantly better than another or because of differing, but equally valid ethical arguments allow for a range of conservation routes and outcomes. Thus, within this review, large iron chloride-infested naval vessels were treated in four different ways in attempts to stabilize them. HMS Holland was washed in an inhibitive solution to extract chloride\(^1\), CSS Hunley will be treated by a newly researched washing method employing alkali and pressure\(^1,2,28,29\), HMS Minerva was electrolyzed to remove chloride\(^1\), SS Great Britain used environmental control to prevent corrosion.\(^1,11,25,32\) All methods are either supported by new research or utilize universally applied treatment techniques. They also have a strong treatment rationale with practical arguments to support the course of action taken. While there will always be diverging views and arguments on appropriate ethical strategies, there remains the opportunity to ensure treatments are researched and optimized. Conservation is a staged process with systematic treatments. There is initially a rationalizing process to decide a course of action, which is then split into treatment stages. As an example, chloride removal from iron might be followed by an inhibitive treatment, over which a coating is applied and the result is subjected to long-term monitoring that assesses outcomes and provides data for future action. Large-scale complex contextual combinations will challenge this approach. At Valparaiso ad hoc steel houses form a world heritage site (see Figure 18). They are lived in and offer the challenge of corroding sheet steel, galvanized structures and various paint regimes. Besides finding safe, proven treatment procedures, complex decisions exist on retention of paint, set against a backdrop of what the occupants want and expect, relative to their standard of living. Should the structures eventually become a museum or continue to be lived in? Deserted, but equally daunting, are the remains of a whaling station at Stromness, South Georgia. Remoteness, climate influences, and cost offer significant challenges here. An overarching consideration is climate change and how it will influence corrosion.

Conservation should define standards of preservation, starting with costly indefinite survival of metals down to the guarantee of only a few months preservation. Developing such a scale goes beyond the science of preservation to its ethics. It may be argued that national icons providing cornerstones in societies merit the cost of indefinite preservation, but commonplace archaeological iron that is to be analyzed, recorded, and published is preserved only for the duration of the analysis and publication process. Counter arguments would focus on the importance of future research into material such as archaeological iron. Suggesting a scale of importance will necessitate extensive ethical debate about how to define importance. In the modern world of diminishing resources, carbon footprints and concern over environmental impact, there are difficult decisions to make and responsibilities to accept for the action taken. Focused coordinated research in collaboration with corrosion scientists can contribute towards informing these decisions for metals preservation.

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