Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge

L. Selwyn

Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario K1A 0M5 Canada

Abstract

This paper contains a brief overview of iron corrosion, including a summary of what happens to iron during burial and after excavation. Also included is a discussion of the iron oxyhydroxide, akaganéite. Following this, there is a critical review of the key factors that play a role in the effectiveness of various iron treatments used to treat archaeological iron. Key areas are identified where there is a need for further research. The information is based on research carried out at the Canadian Conservation Institute and by others worldwide.

Keywords: Iron corrosion, archaeological iron, conservation treatments, akaganéite, chlorides, sodium hydroxide, alkaline sulphite, electrolysis.

1. Introduction

An ongoing problem with archaeological iron is continued corrosion after excavation caused by the accumulation of salts during burial. The treatment of archaeological iron is often based on immersing the object in an aqueous solution and waiting for the chloride ions to diffuse out. This paper addresses the current understanding of archaeological iron corrosion and treatment. Reviewed first are the corrosion processes that iron undergoes during burial and after excavation, including a discussion of the critical role of chloride ions and the formation of chloride-containing akaganéite. Two diffusion models currently used to interpret the time-dependence of the chloride ion concentration in treatment solutions are briefly described. Next, two key factors, which influence chloride ion diffusion, are discussed. These are whether the iron continues to corrode during immersion, and the porosity of the corrosion layer. Included in this discussion are how pH, Fe(II) ions, electrolysis, temperature, and the removal of dissolved oxygen contribute to continued iron corrosion, the corrosion layer porosity, and ultimately to the success or failure of an aqueous iron treatment.

2. Corrosion

2.1 During Burial

When iron is exposed to moisture during burial, it corrodes by an electrochemical process. The anodic reaction of iron dissolution takes place at the surface of the metal; the anodic half-reaction is Fe(s) → Fe^{2+}(aq) + 2e\(^-\); designations are solid(s), aqueous(aq), and gas(g). In aqueous solutions with pH greater than 4, this half-reaction is counterbalanced by the reduction of dissolved oxygen; the cathodic half-reaction is O\(_2\)(g) + 2H\(_2\)O + 4e\(^-\) → 4OH\(^-(aq)\). At the iron surface, iron(II) ions dissolve and accumulate. Each Fe\(^{2+}\) ion is hydrated with six coordinated water molecules [Fe(H\(_2\)O)\(_6\)]\(^{2+}\) (or, for simplicity, written as Fe\(^{2+}\)). The +2 oxidation state is favoured at low levels of dissolved oxygen. The water associated with hydrated Fe\(^{2+}\) ions can react (e.g. undergo hydrolysis) and cause local acidification (e.g. Fe\(^{2+}\)(aq) + H\(_2\)O → Fe(OH\(^-(aq)\) + H\(^+(aq)\)). The rate of hydrolysis increases with increasing temperature. Different iron(II) species can form, depending on the pH. Hydrolysis of Fe\(^{2+}\) ions starts above pH 6 and involves the release of one or more protons from the coordinated water. In solutions containing only iron in the +2 oxidation state, the predominant species are: hydrated Fe\(^{2+}\) below pH 9; Fe(OH\(^-(aq)\) at pH 9-10; and...
Fe(OH)$_3^-$ (also written HFeO$_2$·H$_2$O) and Fe(OH)$_2^+$ (also written FeO$_2$·2$	imes$2H$_2$O) above pH 10 (Blesa et al. 1994). In the presence of dissolved oxygen, the Fe$_{2}^{+}$ ions can be oxidized to Fe$_{3}^{+}$ ions. These hydrated Fe$_{3}^{+}$ ions, [Fe(H$_2$O)$_6$]$_{3}^{3+}$, can also undergo hydrolysis, starting at about pH 1. In solutions containing only iron in the +3 oxidation state, the predominant species are: hydrated Fe$_{3}^{3+}$ below pH 2; Fe(OH)$_{2}^{2+}$ at pH 2-3.5; Fe(OH)$_{3}^{+}$ at pH 3.5-8.5; and Fe(OH)$_{4}^{-}$ above pH 8.5 (Blesa et al. 1994).

The solids that precipitate from solutions containing any of the above-mentioned iron(II) and iron(III) ions depend on the pH (e.g. some cathodic half-reactions produce OH$^{-}$ ions), the level of dissolved O$_2$, and the presence and concentration of environmental anions. Solid iron(II) hydroxide, Fe(OH)$_2$, starts to precipitate above pH 6 and has low solubility over the pH range 9-14, with its minimum solubility at pH 11. Under reducing conditions in the presence of carbonate or phosphate ions, siderite (iron(II) carbonate, FeCO$_3$) or vivianite (iron(II) phosphate, Fe$_6$(PO$_4$)$_2$·8H$_2$O) can also form.

Once Fe(OH)$_2$ has precipitated, it is easily oxidized by dissolved oxygen and forms intermediate Fe(II)-Fe(III) compounds (e.g. magnetite Fe$_3$O$_4$, green rusts). Magnetite, an electronically conducting mixed Fe(II)-Fe(III) iron oxide, is a common corrosion product identified on archaeological iron. Green rusts can form in the presence of chloride ions, carbonate ions, or sulphate ions; these compounds have well defined layered structures of positively charged iron hydroxide sheets and negatively charged anions (Refait et al. 1997). Because green rusts are oxidized to iron oxyhydroxides when exposed to air, they are rarely identified as corrosion products.

Iron(II) hydroxide can also be oxidized to iron(III) compounds such as iron hydroxide Fe(OH)$_3$ or iron oxyhydroxides, Fe$_2$(OH)$_3$. Freshly formed Fe$_2$(OH)$_3$ is amorphous but, over time, transforms into crystalline material, typically one of the iron oxyhydroxides. Lepidocrocite γ-FeO(OH) usually forms first, but it can transform into goethite, α-FeO(OH), which is thermodynamically more stable (Stratmann 1990). Iron(III) oxyhydroxides are orders of magnitude less soluble than iron(II) hydroxide. Goethite, for example, has a solubility product $10^{-41}$ whereas Fe(OH)$_2$ has a solubility product of $10^{-15}$ (Cornell and Schwertmann 1996). The iron oxyhydroxide, akaganéite β-FeO(OH), can form in the presence of chloride ions (Cl$^{-}$), but it does not appear to have been reported as a corrosion product that has formed on archaeological iron during burial. Iron(III) oxychloride, FeOCl, was once thought to be a major chloride-containing corrosion product on archaeological iron (North and Pearson 1975), but its identification was probably a mistake (Gilberg and Seeley 1981).

Archaeological iron is usually covered by a layered structure of corrosion products. The outer layer is a mixture of iron corrosion products (e.g. iron(III) oxyhydroxides, typically goethite) and extraneous material such as small rocks, sand, clay and soil minerals. Below this is another layer of iron corrosion products in a lower oxidation state, usually magnetite, lying on top of any remaining metal. When iron corrodes in a marine environment, it usually becomes covered with concretions, primarily calcium carbonate CaCO$_3$. The Fe$_{2}^{2+}$ ions tend to react and precipitate in the concretion rather than on the surface of the object. Because of the acidity that develops beneath the concretion of marine iron, there may not be many corrosion products retained on the surface of wrought iron or cast iron. Wrought iron will have its characteristic fibrous structure while cast iron will usually have its original shape maintained by the remaining porous matrix of soft graphite filled with some iron corrosion products.

As long as iron is corroding, it is forming Fe$_{2}^{2+}$ ions at the interface between the remaining metal and the corrosion products. These Fe$_{2}^{2+}$ ions dissolve, accumulate, and depending on the local pH, undergo hydrolysis. Electrical neutrality must be maintained. This is achieved by anions diffusing in from the surrounding environment to balance the charge of the Fe$_{2}^{2+}$ and H$^{+}$ cations. Chloride ions, in particular, tend to concentrate at the interface. The Cl$^{-}$ ions remain in solution or are adsorbed onto the corrosion products. The degree to which Cl$^{-}$ ions are adsorbed depends on the pH. The maximum adsorption of Cl$^{-}$ ions occurs at low pH (acidic conditions) because of a net positive charge produced on the surface of iron oxyhydroxides by excess H$^{+}$ ions. The net result of on-going iron corrosion during burial is that the cracks, pores, and open spaces within the corrosion layer or beneath concretion become filled with an acidic iron(II) chloride solution, with the Cl$^{-}$ ions depending on the pH (e.g. some cathodic half-reactions produce OH$^{-}$ ions), the level of dissolved O$_2$, and the presence and concentration of environmental anions. Chloride ions, in particular, tend to diffuse in from the surrounding environment to balance the charge of the Fe$_{2}^{2+}$ and H$^{+}$ cations. Electrical neutrality must be maintained. This is achieved by anions diffusing in from the surrounding environment to balance the charge of the Fe$_{2}^{2+}$ and H$^{+}$ cations. Chloride ions, in particular, tend to react and precipitate in the concretion rather than on the surface of the object. Because of the acidity that develops beneath the concretion of marine iron, there may not be many corrosion products retained on the surface of wrought iron or cast iron. Wrought iron will have its characteristic fibrous structure while cast iron will usually have its original shape maintained by the remaining porous matrix of soft graphite filled with some iron corrosion products.

### 2.2 After Excavation

On-going corrosion problems occur on iron objects after excavation if they still contain an iron core and are contaminated with salts, especially an acidic iron(II) chloride solution (Selwyn et al. 1999). When a freshly excavated iron object is exposed to a new environment above ground, it generally experiences a lower relative humidity (RH) and a higher O$_2$ concentration relative to the burial environment. As the iron dries, the contaminating solution of acidic FeCl$_2$ plus other salts concentrate and the corrosion layers crack, allowing...
greater access of oxygen to remaining metal. Rapid drying of freshly excavated iron can also result in the
formation of yellow crystals of FeCl$_2$ (Costain 1984; Turgoose 1993).

Solids or dissolved ions that were stable in the burial environment may no longer be stable in air
and may oxidize to new corrosion products or to new ions in solution. When an acidic solution of iron(II) chloride is
exposed to air, the Fe$^{2+}$ ions can undergo hydrolysis and be oxidized to Fe$^{3+}$ ions and new compounds can form:

$$4\text{Fe}^{2+} \text{(aq)} + \text{O}_2 \text{(g)} + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}(\text{s}) + 8\text{H}^+ \text{(aq)} \quad (1)$$

This corrosion process causes physical damage to the shape of the object and chemical damage to any
remaining iron metal. Chemical damage is caused by the formation of hydrochloric acid (HCl). The following
acid regeneration cycle has been proposed for the cause of ongoing corrosion of iron contaminated with HCl
(Askey et al. 1993):

$$2\text{Fe(s)} + 4\text{H}^+ \text{(aq)} + 4\text{Cl}^- \text{(aq)} + \text{O}_2 \text{(g)} \rightarrow 2\text{Fe}^{2+} \text{(aq)} + 4\text{Cl}^- \text{(aq)} + 2\text{H}_2\text{O} \quad (2)$$
$$2\text{Fe}^{2+} \text{(aq)} + 4\text{Cl}^- \text{(aq)} + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \text{(g)} \rightarrow 2\text{FeO(OH)}(\text{s}) + 4\text{H}^+ \text{(aq)} + 4\text{Cl}^- \text{(aq)} \quad (3)$$

The crucial factor in this cycle is that the Cl$^-$ ions form a soluble salt with iron(II) ions and it is this
solubility that allows the cycle in Equations 2 and 3 to proceed.

Physical damage is caused by the formation of new solids (i.e. iron oxyhydroxides, FeO(OH)) within
the surface layers which causes stresses and cracks. The molar volumes of FeO(OH)$^-$s are about three times
greater than the molar volume of iron. Laboratory studies of the oxidation and hydrolysis of FeCl$_2$ found that at
low Cl$^-$ ion concentrations, goethite $\alpha$-FeO(OH) and/or lepidocrocite $\gamma$-FeO(OH) precipitate, and at high Cl$^-$ ion
concentrations, akaganéite $\beta$-FeO(OH) forms (Refait and Génin 1997). A representative chemical formula of
FeO$_{0.833}$(OH)$_{1.167}$Cl$_{0.167}$ for akaganéite (reflecting the presence of chlorine within the crystal structure) has
recently been suggested (Ståhl et al. 2003).

One visual symptom that there is a corrosion problem on excavated iron is the formation of either wet
bubbles of acidic liquid (weeping or sweating iron), or dry, hollow red spherical shells on an artefact’s surface.
Weeping is attributed to the hygroscopic nature of iron chloride salts. Iron(II) chloride and iron(III) chloride are
both hygroscopic and form a series of salts with different waters of hydration depending on the relative
humidity. Iron(II) chloride, for example, exists as yellow crystals (FeCl$_2$$ \cdot $2H$_2$O) below about 20% RH, as green
crystals (FeCl$_2$$ \cdot $4H$_2$O) between 20-55% RH, and deliquesces above 56% RH (Turgoose 1982). When the
relative humidity is high, these salts absorb water, dissolve, and form wet droplets of orange coloured liquid.
Iron oxyhydroxides precipitate around the outside of the droplets and generate a framework for the spherical
shells.

2.3 Akaganéite, $\beta$-FeO(OH)

Akaganéite can form only in the presence of Cl$^-$ ions. It can be prepared in the laboratory from either
Fe(II) or Fe(III) chloride solutions; it cannot be prepared from solutions having a pH $>$5. Akaganéite is thought
to form on archaeological iron only after it has been excavated and exposed to air (Gilberg and Seeley 1981).
Exposure to air promotes the oxidation and hydrolysis of accumulated acidic Fe(II) chloride. Because
akaganéite only forms under conditions of relatively high concentrations of Cl$^-$ ions (e.g. 2M (Refait and Génin
1997)), the presence of akaganéite on archaeological iron is considered evidence that the object is heavily
contaminated with Cl$^-$ ions (Ståhl et al. 2003).

There is concern that the formation of akaganéite might be a threat because it might somehow release
chloride ions at high humidity, thereby stimulating further corrosion (Ståhl et al. 1998). In a study of synthetic
akaganéite, it was demonstrated that as long as it remains dry, it is stable and the chlorine remains locked inside
the tunnels (Ståhl et al. 2003). It was also demonstrated that heating could cause the release of the chlorine (but
only when heated above 200°C which transforms akaganéite to hematite ($\alpha$-Fe$_2$O$_3$)), and that the chlorine could
not be removed from inside the tunnels of akaganéite by washing with water (Ståhl et al. 1998; 2003).
Furthermore, past observations that Cl$^-$ ions could be washed from synthetic akaganéite with water was
attributed to the removal of adsorbed Cl$^-$ ions rather than chlorine from the tunnels.

Although the chlorine cannot be washed out of akaganéite, there are reactions that can occur which
promote the transformation of akaganéite to goethite or magnetite and therefore the release of chlorine as Cl$^-$
ions. At room temperature, these reactions involve water. When akaganéite, for example, is immersed in an
aqueous solution (including alkaline ones), it slowly transforms to goethite by a process of dissolution and
precipitation (Cornell and Schwertmann 1996). Furthermore, any of the iron oxyhydroxides can react with Fe$^{2+}$ ions (or with Fe(OH)$_2$) to form magnetite:

$$\text{Fe(OH)}_2(s) + 2\text{FeO(OH)}(s) \rightarrow \text{Fe}_3\text{O}_4(s) + 2\text{H}_2\text{O} \quad (4)$$

or

$$\text{Fe}^{2+}(\text{aq}) + 2\text{FeO(OH)}(s) \rightarrow \text{Fe}_3\text{O}_4(s) + 2\text{H}^+(\text{aq}) \quad (5)$$

Laboratory studies have shown that $\alpha$-FeO(OH), $\beta$-FeO(OH), and $\gamma$-FeO(OH) react with Fe(OH)$_2$ to produce Fe$_3$O$_4$ in the order $\beta$-FeO(OH) $>$ $\gamma$-FeO(OH) $>$ $\alpha$-FeO(OH) (Ishikawa et al. 1998).

The chlorine trapped within newly-formed akaganéite will be released when it is transformed into goethite or magnetite, but more research is needed to document the conditions under which this transformation takes place. If akaganéite transforms to goethite or magnetite during an immersion treatment, then the chlorine will be released into the solution as Cl$^-$ ions, which will be removed by successive changes of the treatment solution. If the rate of these transformations is slow, pre-existing akaganéite may still remain after treatment.

3. Conservation

3.1 Untreated Iron

It is difficult to prevent the on-going corrosion of excavated archaeological iron if it remains untreated. It is usually recommended that untreated archaeological iron be stored below 20% RH (Turgoose 1982). It has been shown, however, that untreated archaeological iron can continue to corrode even if stored under desiccated conditions (RH less than 15%) (Keene 1994). One factor is the rough surface of corroded iron; inhomogeneities promote water condensation in the pores. Another factor is contamination by hygroscopic salts which can pick up moisture and promote corrosion. Because continued corrosion requires both oxygen and water, attempts have been made to minimize iron corrosion during storage by creating a sealed microclimate that keeps the relative humidity low and removes oxygen gas. Consideration is now being made for storing untreated iron in a dry, oxygen-free environment created using a scavenger (e.g. RP-A) sealed inside a transparent barrier film (e.g. Escal) (Becker 1999; Carrió and Stevenson 2003; Mathias 2003). Both RP-A and Escal are made by Mitsubishi Gas Chemical Company; more information about these products is available at the Mitsubishi web site (www.mgc-a.com). The drawback of the latter approach is that it depends on a perfect seal and only lasts about 5 years.

3.2 Immersion Treatments

Conservation treatments for archaeological iron are designed to remove as much of the salt contamination (especially Cl$^-$ ions) as possible. If enough Cl$^-$ ions are removed, then these objects can resist corrosion when stored or displayed in a controlled museum environment without special storage conditions. Archaeological iron has a significantly higher survival rate if it is treated by some form of desalination treatment (typically by immersion) compared to being left untreated (Keene 1994). In general, immersion treatments involve placing iron in an aqueous solution, usually a near-neutral or alkaline one, and waiting for the Cl$^-$ ions to diffuse out. Studies have now shown that immersion of archaeological iron in water (at room temperature, warm, or boiling) is generally not effective in removing Cl$^-$ ions (Watkinson 1996). One contributing factor may be that in neutral solutions, some fraction of the Cl$^-$ ions remain adsorbed on the surface of the iron corrosion products. One advantage of using alkaline treatment solutions is that they promote the desorption of Cl$^-$ ions because of the net negative charge induced on the surface of iron oxyhydroxides by excess OH$^-$ ions. Another advantage is iron passivation; this is discussed below in more detail in the section “Iron passivation”.

One approach to deciding if an immersion treatment has been successful is to expose the treated iron to high RH to find out if there are enough Cl$^-$ ions remaining to cause new weeping. Another approach is to dissolve the artefact in acid after treatment to determine the quantity of residual chlorine. This approach can also be used to determine the relative effectiveness of a treatment: the total amount of Cl$^-$ ions that have diffused into a treatment solution is measured; then the total amount of chlorine remaining in the artifact after treatment is determined (usually based on a destructive method, such as by completely dissolving the artefact in acid). A few such studies have been carried out to determine the relative effectiveness of various immersion treatments (Watkinson 1996; Al-Zahrani 1999; González et al. 2003). Further studies are needed to better understand the effectiveness of different immersion treatments when used on cast and wrought iron from both terrestrial and marine sites.
The length of time an object is immersed in a treatment solution is usually based on monitoring the Cl\textsuperscript{-} ion concentration in the treatment solution (North and Pearson 1978b). The treatment solution is changed either on a regular basis or after the Cl\textsuperscript{-} ion concentration has stopped increasing, and treatment is stopped when the Cl\textsuperscript{-} ion concentration in the solution stays low, usually below 20 parts per million (Watkinson 1983). One drawback with monitoring the Cl\textsuperscript{-} ion concentration in treatment solutions is that this doesn’t provide any information about whether there are still Cl\textsuperscript{-} ions remaining in the object. An advantage of this approach is that if the Cl\textsuperscript{-} ion concentration is measured as a function of time, then it may be possible to interpret the results using existing diffusion models developed for Cl\textsuperscript{-} ions diffusing out of archaeological iron.

North and Pearson, for example, developed a diffusion model for Cl\textsuperscript{-} ions diffusing from the corrosion layer of cast iron where the Cl\textsuperscript{-} ions are assumed to be evenly distributed (North and Pearson 1978b). Their model, which can be described as a ‘uniform’ model, provides a general expression for the diffusion of Cl\textsuperscript{-} ions from any shaped object for short times. The expression predicts that when the amount of Cl\textsuperscript{-} ions in solution is plotted against the square root of time (t\textsuperscript{1/2}), the resulting graph contains a straight line passing through the origin, and the slope of this line is proportional to the Cl\textsuperscript{-} ion diffusion constant. Their model predicts that Cl\textsuperscript{-} ions diffuse into a treatment solution immediately after an object is immersed because the Cl\textsuperscript{-} ions are assumed to be uniformly distributed in the solid.

Another diffusion model has been developed for Cl\textsuperscript{-} ions diffusing from iron that is corroding (at least when it is first placed in a treatment solution) (Selwyn et al. 2001). This model is based on Cl\textsuperscript{-} ions initially concentrated at the interface between the iron and the corrosion layer. This abrupt starting distribution (‘abrupt model’) can be viewed as the opposite limit of the uniform distribution of North and Pearson (‘uniform model’). The abrupt model predicts a delay before any Cl\textsuperscript{-} ions appear in the treatment solution and an S-shaped (sigmoidal shaped) variation of the Cl\textsuperscript{-} ions removed versus square root of time. The delay corresponds to the time needed for the Cl\textsuperscript{-} ions to diffuse from their initial position at the interface between the iron metal and the overlying corrosion layer, over the distance of the corrosion layer, and finally reach the outer surface where it can then diffuse into the solution.

Diffusion models contain a diffusion constant. If the model accurately reflects experimental data, then it is often possible to extract the diffusion constant, the magnitude of which reflects the rate at which diffusing species (e.g. Cl\textsuperscript{-} ions) move. The ability of Cl\textsuperscript{-} ions to diffuse through a solution permeating a corrosion layer depends on the pore size, channel size, and their connectivity within the solid. Diffusion constants are smaller for ions diffusing through a solution within the pores of a solid (e.g. a corrosion layer) than for ions diffusing through an open solution. Further research, based on systematic monitoring the Cl\textsuperscript{-} ion concentration as a function of time for various treatment solutions (with each solution used to treat an individual artefact), is needed to help identify the most effective treatments. It may or may not be possible to interpret the results using a diffusion model, such models apply only if the conditions under which they were derived remain valid (i.e. the solid remains physically unchanged and the diffusion distance remains constant).

### 3.3 Key Factors Affecting Chloride Ion Removal

Two of the key factors that influence the ability of dissolved Cl\textsuperscript{-} ions to diffuse out of archaeological iron are whether the iron metal is corroding, and whether the corrosion layer is porous. The Cl\textsuperscript{-} ions will be released to diffuse into a treatment solution if the corrosion of the iron can be stopped, and will diffuse more easily if the porosity of the corrosion layer can be increased.

### 3.4 Stopping Corrosion

As long as archaeological iron is corroding during immersion, the Cl\textsuperscript{-} ions are prevented from diffusing out because they are attracted to the Fe\textsuperscript{2+} ions being generated by the corrosion process. If the corrosion can be stopped, then the potential gradient (generated by Fe\textsuperscript{2+} ions) is removed. When Cl\textsuperscript{-} ions no longer act as counter ions, they are able to diffuse out of the corrosion layer into the treatment solution. Iron corrosion can be slowed or stopped by: passivating the iron surface using an alkaline treatment solution; removing dissolved oxygen from the treatment solution; using electrochemical methods; or using corrosion inhibitors.

#### 3.4.1 Iron Passivation: The corrosion rate of iron is dramatically reduced if the surface is passivated by an adherent layer of insoluble corrosion products. When iron corrodes in an alkaline solution, Fe\textsuperscript{2+} ions precipitate as Fe(OH)\textsubscript{2}. Iron(II) hydroxide, once formed, is easily oxidized and hydrolyzed to an essentially insoluble film of Fe(OH)\textsubscript{3}. The corrosion film, if formed in direct contact with the iron surface, can prevent the transfer of Fe\textsuperscript{2+} ions from the iron metal to the solution. On clean (bare) iron, precipitation of Fe(OH)\textsubscript{3} starts to occur at about pH 8 in the presence of oxygen. In general, the iron corrosion rate slows as the pH is increased above 9 and...
In alkaline solutions, the formation of an adherent and passivating oxide film generally requires both dissolved O₂ gas and OH⁻ ions. The dissolved O₂ is necessary to support the corrosion process and generate Fe²⁺ ions at the metal surface. The OH⁻ ions are necessary to react with the Fe²⁺ ions to form Fe(OH)₂ as well as maintain the pH in a region where this hydroxide is insoluble. Precipitation of Fe(OH)₂ depletes the local concentration of OH⁻ ions and so there must always be sufficient OH⁻ ions at the metal surface to ensure direct precipitation of Fe(OH)₂. Laboratory studies have shown that bare iron can be passivated in alkaline solutions such as sodium borate (Na₂B₄O₇, pH 9.2), sodium sesquicarbonate (equimolar Na₂CO₃ and NaHCO₃, pH 10), sodium carbonate (Na₂CO₃, pH 11.2), and sodium hydroxide (NaOH, pH 12.6–13.5) (Mayne and Turgoose 1975; Hjelm-Hansen et al. 1993).

Conservators favour aqueous NaOH solutions (0.1M to 0.5M, pH 13–14) for treating archaeological iron because they are relatively cheap, readily available, and have a high pH (Mathias 1994; North and Pearson 1978b; North 1987). Furthermore, many studies have demonstrated the effectiveness of NaOH solutions in removing Cl⁻ ions from archaeological iron (Al-Zahrani 1999; González et al. 2003; Selwyn and Argyropoulos 1978b; North 1987). In particular, it has been shown that bare iron nails can be passivated in NaOH solutions because the negative component of the current is carried mainly by the OH⁻ ions rather than Cl⁻ ions (Hjelm-Hansen et al. 1992; 1993). After several months, they observed that the iron nails had not passivated in solutions of Na₂SO₃, pH 13.5) (North and Pearson 1979). An oxygen scavenger (e.g. sodium sulphite) can be used to remove dissolved oxygen (i.e. 2Na₂SO₃(aq) + O₂(g) → 2Na₂SO₄(aq)). A near-neutral solution of sodium sulphite has been used to treat marine cast iron (Gilberg 1987). Although dissolved O₂ was successfully removed, the iron corroded because of sulphate-reducing bacteria contamination. Sodium sulphite has also been used in alkaline solutions, in a treatment commonly known as alkaline sulphite (0.5M NaOH and 0.5M Na₂SO₃, pH 13.5) (North and Pearson 1975). Many conservators use this treatment (or have studied it), and find it to be reasonably effective, especially on archaeological iron that has not been allowed to dry (Keene 1994; Al-Zahrani 1999; Costain 2000).

3.4.2 Dissolved Oxygen Removal: At pH > 4, the corrosion of iron is usually caused by the presence of dissolved O₂ gas. The corrosion rate can be significantly reduced if dissolved O₂ is removed from the treatment solution. Laboratory studies on archaeological iron carried out by Al-Zahrani demonstrated that solutions without oxygen were more effective at removing Cl⁻ ions than similar solutions with oxygen present (Al-Zahrani 1999). Several conservation treatments are designed to remove dissolved O₂. Boiling the treatment solution removes dissolved oxygen because the solubility of oxygen gas decreases with increasing temperature. Bubbling an inert gas (e.g. nitrogen) through a solution also displaces dissolved oxygen (Scott and Seeley 1987; Al-Zahrani 1999). An oxygen scavenger (e.g. sodium sulphite) can be used to remove dissolved oxygen (i.e. 2Na₂SO₃(aq) + O₂(g) → 2Na₂SO₄(aq)). A near-neutral solution of sodium sulphite has been used to treat marine cast iron (Gilberg 1987). Although dissolved O₂ was successfully removed, the iron corroded because of sulphate-reducing bacteria contamination. Sodium sulphite has also been used in alkaline solutions, in a treatment commonly known as alkaline sulphite (0.5M NaOH and 0.5M Na₂SO₃, pH 13.5) (North and Pearson 1975). Many conservators use this treatment (or have studied it), and find it to be reasonably effective, especially on archaeological iron that has not been allowed to dry (Keene 1994; Al-Zahrani 1999; Costain 2000).

3.4.3 Electrochemical Methods: Another approach to stopping (or slowing) iron corrosion is to use an electrochemical approach (e.g. making the artefact the cathode in an electrochemical cell). (For electrochemical methods to work, the artefact must have a substantial core of metal left). If the corrosion rate of the iron can be slowed by using this approach, then any Cl⁻ ions that were being held as counter ions will be released. This effect is probably contributing to the release of Cl⁻ ions when iron is treated by electrolysis (North 1987), cathodic reduction at constant (or limiting) potentials (Beaudoin et al. 1997; Dalard et al. 2002), cathodic protection using sacrificial anodes (MacLeod 1996), and cathodic protection using an impressed current (Mardikian 2004). However, there is some question as to whether the presence of the electric field has any significant effect on the rate at which the Cl⁻ ions diffuse out. North and Pearson, for example, have suggested that the presence of the electric field has an insignificant effect on the rate of Cl⁻ ion removal in alkaline solutions because the negative component of the current is carried mainly by the OH⁻ ions rather than Cl⁻ ions (North and Pearson 1978a; North 1978).

3.4.4 Corrosion Inhibitors: It may be possible to use corrosion inhibitors to slow the corrosion rate of archaeological iron. Anodic inhibitors slow the anodic reaction (e.g. iron corrosion), and cathodic inhibitors slow the cathodic reaction (e.g. oxygen reduction). For an inhibitor to be effective, it must reach the region where either the anodic or cathodic reactions occur. As such, anodic inhibitors need to reach the metal surface...
and cathodic inhibitors need to reach the electronic conductors making contact with the corroding iron (e.g. graphite on cast iron or conducting corrosion products such as magnetite). Corrosion inhibitors have been developed for use on clean metal surfaces (typically covered by only a thin air-formed oxide film) and, because of the thickness of corrosion products on excavated material, it is difficult to determine how effective such corrosion inhibitors might be when used on archaeological iron (Turgoose 1985).

One corrosion inhibitor that has been studied for use in treating archaeological iron is ethylenediamine (H₂N-CH₂-CH₂-NH₂, abbreviated EN) (Argyropoulos et al. 1997). This organic compound readily dissolves in water to form an alkaline solution. Laboratory studies have shown that EN solutions are effective as a corrosion inhibitor on non-archaeological iron because the EN molecule can be adsorbed onto oxide-free (Incorvia 1985) or oxide-covered (Incorvia and Contarini 1989) iron surfaces. Duprat et al., for example, have compared the effectiveness of EN with NaOH (each solution at pH 11 and containing 3% NaCl) for inhibiting non-archaeological iron corrosion (Duprat et al. 1986). They observed that (at the same pH) an EN solution was more effective than an NaOH solution in slowing iron corrosion. They attributed the overall effectiveness of these two solutions to their alkalinity (a source of OH⁻ ions) and their ability to form a passivating film on iron. They ascribed the increased effectiveness of EN over NaOH at the same pH to the EN molecule contributing an additional inhibiting effect by being adsorbed onto the metal surface (Duprat and Dabosi 1981).

Unfortunately, in a quantitative study involving EN solutions (5% v/v, 0.75M, pH 11.5) to treat archaeological iron, the Cl⁻ ions were not removed effectively (Selwyn and Argyropoulos 2004). Furthermore, relatively high levels of iron were detected in the treatment solution. This observation was attributed to the formation of soluble complexes between the EN molecule and Fe²⁺ ions and suggested the possibility that iron corrosion was being stimulated. There have, in fact, been several reports in the conservation literature about rapid corrosion of archaeological iron immersed in EN solutions (Brown 1985; Busse 1997; Costain 2000). Ethylenediamine is well known for its ability to form complexes with transition metal ions in the +2 oxidation state (Paoletti 1984). Both nitrogen atoms on an EN molecule are capable of simultaneously interacting with the same metal ion and forming a five-membered ring. Iron(II) ions can form three different [Fe(EN)ₓ⁺] complexes with ethylenediamine, with metal: EN ratios of 1:1, 1:2, or 1:3 (Paoletti 1984). As a consequence of the toxicity of EN, and its ability to stimulate corrosion, there has only been limited use of EN solutions to treat archaeological iron.

### 3.5 Increasing Porosity

The main driving force for the removal of Cl⁻ ions from archaeological iron is their diffusion from a region of higher concentration (in the corrosion layer) to a region of lower concentration (in the treatment solution). The ability of Cl⁻ ions to diffuse away from the metal surface into the treatment solution depends on the porosity of the solid material (e.g. corrosion layer, concretion) through which they must move. Because the Cl⁻ ions are dissolved in solution, they must diffuse through the solution filling the cracks, fissures, interconnecting pores, and tiny channels inside the solid material before they can reach the treatment solution. The rate at which Cl⁻ ions diffuse out depends on the size of the open spaces within the solid, how well they are linked together, and if continuous pathways exist from the metal to the outer surface of the object. It is the porosity within the solid material that allows the treatment solution to diffuse in and the Cl⁻ ions to diffuse out. If the Cl⁻ ions are trapped in discrete areas under relatively impermeable material, then the treatment solution will be unable to diffuse in and the Cl⁻ ions will be unable to diffuse out. If Cl⁻ ions are still trapped after treatment, then in the future, they may cause problems, especially if a channel opens up, water and oxygen enter, and corrosion is stimulated.

The porosity of the corrosion products may be increased by dissolving extraneous material in alkaline solutions. Many inorganic and organic materials are more soluble in alkaline solutions than neutral ones. The solubility of quartz, for example, increases above pH 9. Greasy dirt, fatty compounds, oils, and other organic material (e.g. cellulose, protein) are broken down in alkaline solutions into water-soluble compounds.

The porosity of the corrosion products may also be increased by heating the treatment solutions. It is recommended, for example, that alkaline sulphite treatment solutions be heated (50–70°C). Higher temperatures significantly increase the solubility of surface materials. In alkaline solutions, the solubility of iron oxyhydroxides increases with increasing temperature (Blesa et al. 1994). For iron in alkaline solutions (pH greater than ~ 12), there is a region of active corrosion that becomes larger at higher temperatures (and lower pH) because of the increased solubility (Townsend 1972).

On the other hand, the porosity of the corrosion products may be decreased when freshly excavated iron is exposed to air. Turgoose predicted that placing archaeological iron into an alkaline solution would cause any dissolved Fe²⁺ ions to precipitate within the corrosion layer, decreasing the porosity, restricting the Cl⁻ ion diffusion, and possibly trapping them (Turgoose 1993). More recently, González et al. demonstrated that if
3.6.1 Sodium Hydroxide: Turgoose et al. demonstrated that when archaeological iron is placed in alkaline NaOH solutions, there is an increase in the porosity of the corrosion products (Turgoose et al. 1996). They attributed this beneficial effect to rapid electrochemical reactions occurring at the iron/corrosion interface, causing fissures and cracks to develop in the corrosion layer, and resulting in a more open, fragile structure. The rapid processes are thought to be oxidation-reduction reactions involving iron metal, magnetite, and iron(II) species (Hjelm-Hansen et al. 1993). They may also involve the precipitation of small amounts of solids within the corrosion layer. These reactions occur on electronically-conducting surfaces (e.g. magnetite) and cause irreversible changes and softening of the corrosion product layer (Hjelm-Hansen et al. 1993). Two other reactions that might also contribute to this process are the interactions between Fe$^{2+}$ and FeO(OH) (see Equations 4 and 5). Recent laboratory studies of non-archaeological iron in NaOH solutions (pH 11–13) have detected the electrochemical activity of the passive film on iron and confirmed that oxidation-reduction reactions easily occur between the iron(II) and iron(III) oxidation states (Schmuki et al. 1998; 1999). These studies have also shown that there is little or no dissolution of the iron corrosion products making up the passive layer (e.g. FeO(OH), Fe$_2$O$_3$, Fe(OH)$_2$) in these alkaline NaOH solutions under oxidizing or reducing conditions. Under reducing conditions, the passive film does not dissolve but instead undergoes a solid-state conversion from Fe(III) compounds to lower oxidation-state compounds (e.g. probably with a structure related to Fe(OH)$_2$) having a porous structure (Schmuki et al. 1999). Based on electrochemical studies of archaeological nails in 0.5M NaOH or in 0.5M sodium sesquicarbonate, it was concluded that iron undergoes rapid electrochemical processes in NaOH, but not in sodium sesquicarbonate (Hjelm-Hansen et al. 1992; 1993). It is not known if rapid electrochemical processes occur when archaeological iron is placed in any other alkaline solutions besides NaOH. Further research is needed to better understand the conditions under which these processes occur.

3.6.2 Alkaline Sulphite: When freshly excavated iron is placed in an alkaline sulphite solution, some of the iron oxyhydroxides may be converted to magnetite, thereby opening up the pore structure and allowing faster diffusion of the Cl$^-$ ions into the treatment solution. The formation of magnetite takes place only if there are excess Fe$^{2+}$ ions present, such as in freshly excavated iron that has not been allowed to dry (Gilberg and Seeley 1982). The formation of magnetite is probably the result of the reaction between Fe$^{2+}$ ions (or precipitated Fe(OH)$_2$) and FeO(OH) (see Equations 4 and 5). An alkaline sulphite solution is reported to be more aggressive to the corrosion layers on archaeological iron than a NaOH solution (Keene 1994). Further research is needed to better understand and quantify exactly what the difference is between treating iron in an alkaline solution containing dissolved oxygen (e.g. NaOH) and without dissolved oxygen (e.g. alkaline sulphite), and to determine the role, if any, of the sulphite ion on the reduction or transformation of iron corrosion products.

3.6.3 Electrochemical Methods: Electrochemical methods, either electrolysis (North 1987), or more controlled cathodic reduction at constant or limiting potential (Beaudoin et al. 1997; Dalard et al. 2002), are thought to increase the diffusion rate of Cl$^-$, possibly by reducing the iron oxyhydroxides to magnetite, thus increasing the porosity of the corrosion layers. Electrolysis involves immersing an artefact (containing remaining metal) in an alkaline electrolyte and applying a voltage between it and another electrode. The artefact is made the cathode (i.e. polarized cathodically) and another electrode is made the anode (i.e. polarized anodically) (Dalard et al. 2002). If the potential of the artefact is not too negative, then the main species that are said to be reduced are dissolved oxygen or iron(III) oxyhydroxides. The iron(III) oxyhydroxides may be reduced to magnetite (3FeO(OH)(s) + e$^-$ → Fe$_3$O$_4$(s) + H$_2$O + OH$^-$ (aq)) or to iron(II) hydroxide (FeO(OH)(s) + H$^+$ (aq) + e$^-$ → Fe(OH)$_2$(s)). Electrochemical studies of iron corrosion have noted that lepidocrocite is more electrochemically active than goethite and so it is usually lepidocrocite that is reduced, either to magnetite or Fe(OH)$_2$ (Stratmann...
If the cathodic potential of the artefact is made even lower, then hydrogen gas may be produced by the electrolysis (i.e. reduction) of water ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$). The formation of bubbles of hydrogen gas at the metal surface (or some other conducting surface) can damage the overlying corrosion layers. For this reason, electrolysis is sometimes intentionally used to generate bubbles that knock off concretion and/or the corrosion crust. Hydrogen bubble formation may slow Cl$^-$ ion diffusion (Carlin et al. 2001). Laboratory studies on non-archaeological iron have shown that once iron becomes covered with iron corrosion products, it is then not possible to electrochemically reduce the corrosion products back to metallic iron (Schmuki et al. 1999).

Although scientific studies of non-archaeological iron have shown that it is possible to reduce newly formed iron corrosion products (e.g. iron(III) oxyhydroxides) to magnetite or Fe(OH)$_2$, the conservation literature contains little scientific evidence that such reduction processes are possible on archaeological material covered with a relatively thick, well-aged corrosion crust. It has been noted, however, that archaeological iron artefacts change colour from rust red to black during electrolysis (Pearson 1972; North 1978). Furthermore, Pearson provides a graph of the Cl$^-$ ion concentration plotted against the square root of time for an iron artefact undergoing electrolysis (Pearson 1981). The increase in the slope after a period of electrolysis suggests that the chloride ions are diffusing faster into solution, possibly by an increase in porosity. Further research is needed to better understand what happens to the corrosion layer on archaeological iron during electrolysis or when other electrochemical techniques are applied.

3.6.4 Plasma Treatment: A hydrogen plasma (a highly reactive gas containing partially ionized hydrogen molecules and atoms) can be used to treat archaeological iron (Schmidt-Ott and Boissonnas 2002). The reactive hydrogen plasma reacts with the iron corrosion products, reducing them to lower oxidation state compounds. If the plasma is used for a short period, some of the outer iron oxyhydroxides can be reduced to magnetite which increases the porosity of the corrosion crust. During exposure to the plasma, the temperature of the artifact is kept well below 400°C to avoid altering the metallurgical structure of any remaining metal. Use of the plasma at this low temperature has not proven to be effective in removing Cl$^-$ ions (Schmidt-Ott 1997). The application of hydrogen plasma as a pretreatment, however, does create small cracks and fissures that improve the subsequent removal of the remaining Cl$^-$ ions by immersion, such as in an alkaline sulphite solution (Schmidt-Ott and Boissonnas 2002).

4. Conclusions

The net result of iron corroding during burial is the filling of cracks, pores, and open spaces within the corrosion layer with an acidic iron(II) chloride solution, with the Cl$^-$ ions concentrated at the metal surface. Exposure of this acidic iron(II) chloride solution to air after excavation leads to on-going corrosion of any remaining metal as well as mechanical damage to the corrosion layer by the formation of iron oxyhydroxides, including akaganéite. The presence of akaganéite on archaeological iron is considered evidence that the object is heavily contaminated with Cl$^-$ ions.

Further research is needed to characterize the stability of akaganéite to better determine when, under storage conditions, it can transform into goethite or magnetite, release its chlorine as chloride ions, and stimulate on-going corrosion.

Immersion treatments for archaeological iron remove salt contamination when the Cl$^-$ ions diffuse through the corrosion layer into the treatment solution. As long as archaeological iron is corroding during immersion, the Cl$^-$ ions are prevented from diffusing out because they are attracted to Fe$^{2+}$ ions generated by the corrosion process. If the corrosion can be stopped, then the Cl$^-$ ions no longer act as counter ions and they are able to diffuse through the corrosion layer into the treatment solution. Four approaches to slowing iron corrosion during immersion treatments are: (1) passivating the iron surface in an alkaline treatment solution, (2) removing dissolved oxygen, (3) using electrochemical methods, or (4) using corrosion inhibitors.

Further research is needed to better understand treatments that help slow iron corrosion and to identify the most effective ones. It would be interesting to compare the effectiveness of an alkaline solution with and without oxygen (e.g. sodium hydroxide versus alkaline sulphite).

The Cl$^-$ ions can diffuse out faster if immersion treatments contribute to an increased porosity (void space) in the corrosion layers.
Further research is needed to study how treatments affect the porosity of the corrosion layer. Rapid electrochemical reactions contribute to an increased porosity of archaeological iron in sodium hydroxide solutions, but it is not known if similar processes occur in other alkaline solutions. Furthermore, it is claimed that several treatments (e.g. alkaline sulphite, electrochemical reduction) result in the reduction of solid corrosion products (e.g. reduce iron oxyhydroxides to magnetite) and an increase in porosity. These claims need to be studied in more detail.

Acknowledgements

The author gratefully acknowledges the contributions made to this paper by Vasilike Argyropoulos, Paul Begin, Judy Logan, Ross McKinnon, and Jane Sirois.

References


Mathias, C., (2003) Archaeological Conservator, Memorial University of Newfoundland, private communication


Selwyn, L. S. and Argyropoulos, V., (2004) Removal of chloride and iron ions from archaeological iron with sodium hydroxide and ethylenediamine solutions. Studies in Conservation, accepted for publication


© Published by the National Museum of Australia www.nma.gov.au


