

Technical Report

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**Natural analogues for expansion
due to the anaerobic corrosion
of ferrous materials**

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Executive summary

In Sweden, spent nuclear fuel will be encapsulated in sealed cylindrical canisters, consisting of a cast iron insert and a copper outer container. The canisters will be placed in a deep geologic repository and surrounded by bentonite. If a breach of the outer copper container were to occur the cast iron insert would undergo anaerobic corrosion, forming a magnetite film whose volume would be greater than that of the base metal. In principle there is a possibility that accumulation of iron corrosion product could cause expansion of the copper canister. Anaerobic corrosion rates are very slow, so in the work described in this report reference was made to analogous materials that had been corroding for long periods in natural anoxic aqueous environments. The report considers the types of naturally occurring environments that may give rise to anoxic environments similar to deep geological groundwater and where ferrous materials may be found. Literature information regarding the corrosion of iron archaeological artefacts is summarised and a number of specific archaeological artefacts containing iron and copper corroding in constrained geometries in anoxic natural waters are discussed in detail. No evidence was obtained from natural analogues which would suggest that severe damage is likely to occur to the SKB waste canister design as a result of expansive corrosion of cast iron under repository conditions.

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1 Introduction

To ensure the safe encapsulation of spent nuclear fuel elements for geological disposal, SKB, Sweden, are considering using the Copper-Iron Canister, which consists of an outer copper canister and an inner cast iron container. After emplacement in the repository the canisters will be surrounded by bentonite clay to limit the release of radioactivity, if for any reason there is leakage from the canister. If failure of the copper overpack occurred, allowing water to enter, the cast iron insert would corrode anaerobically, liberating hydrogen and forming a solid corrosion product, which is likely to be predominantly magnetite. This corrosion product would have a greater volume than the base metal, to an extent defined by the Pilling-Bedworth ratio (i.e. the ratio between the volume of the oxide and the corresponding volume in the metallic state) and so the possibility of it causing deformation and expansion of the outer copper canister has been studied both experimentally /1–23/ and through modelling /4/.

In view of the very slow anaerobic corrosion rates of cast iron and carbon steel /5–7/ and the long timescales involved in the geological disposal of radioactive waste containers, a number of investigators in the field of radioactive waste disposal have studied the corrosion of materials that have been buried for long periods. This approach has been dubbed the ‘natural analogue’ concept /8–11/ and its aim is to obtain supporting evidence for the prediction of long-term behaviour in a radioactive waste repository, as a means of validating corrosion models for the failure of metallic waste containers /12/. The advantage of examining natural analogue materials is that they are likely to have been exposed to the corrosive environment for many years and will therefore have developed a thicker oxide film than can be achieved on a reasonable timescale in laboratory tests. In the case of SKB’s specific application, attention so far has concentrated on the corrosion of copper-based natural analogues (e.g. /13–20/).

Corrosion of ferrous natural analogues is of interest to SKB, particularly in relation to the effect of anaerobic corrosion product formation on the generation of stresses in neighbouring materials. The main natural analogues for the anaerobic corrosion of ferrous materials are archaeological artefacts (> 1,000 years) and material from modern industrial or domestic operations (< 1,000 years). Iron meteorites have also been viewed as natural analogues and there are a few examples of native iron in geological sites with a low redox potential and high pH /21/. The use of archaeological metal artefacts for predicting the long-term corrosion rates of metals for radioactive waste containers has been reviewed for NAGRA /22/ (the Swiss National Cooperative for the Disposal of Radioactive Waste) and other workers have also examined natural analogues for iron corrosion /23–26/ and the corrosion of other metals /27/ in the general context of radioactive waste disposal. Other related studies have considered naturally occurring analogues for nuclear reactors (e.g. at Oklo, Gabon /28/), cement deposits /29/ and other potential minerals for the encapsulation of radioactive waste /30–33/.

In the present work, natural analogues for the expansive anaerobic corrosion of iron were sought. The objective was to identify natural analogues for iron, or ideally combinations of iron and copper alloys, which had corroded anaerobically in constrained geometries over long periods of time, with the intention that if such items could be found, further detailed analysis would be undertaken. On the basis of such analogues it might be possible to demonstrate whether or not corrosion product formed on ferrous material under anoxic conditions can exert sufficient stress in enclosed areas to deform the surrounding metal. The results from such analysis could be compared with the results of experimental studies on the mechanical properties of oxides and corrosion-induced expansion /3/.

Although it is recognised that it is impossible to find natural analogues exposed to exactly the same conditions as in a geological repository, particularly in terms of temperature, radiation flux and microbial activity, natural analogues have the potential to provide valuable support

for predictions of the corrosion behaviour of waste container materials over long periods. One disadvantage of the natural analogues approach is that it is unlikely that detailed information about the environmental conditions during the exposure of the natural analogue will be available /34, 35/.

The approach taken during this work to draw conclusions about the mechanical stresses induced by corrosion of natural analogue ferrous materials under anoxic conditions was as follows:

1. Identify naturally occurring environments that may give rise to anoxic environments similar to deep geological groundwater.
2. Identify situations where ferrous materials may have been subjected to the conditions identified in 1.
3. Trace materials or artefacts that have been exposed to relevant conditions and analysed and described in the published literature.
4. Identify natural analogue samples that could be examined further.

The preliminary findings from this work are published as a recent conference paper /36/.

2 Selection of natural analogues

2.1 Identification of naturally occurring anoxic environments

The aim of the investigation was to identify situations and environments where anaerobically corroding iron might be found and to identify objects containing restricted geometries which had been exposed to such conditions for long periods. Apart from iron-bearing meteorites, and rare examples of naturally occurring iron at geological sites with a low redox potential and high pH /21/, the earliest archaeological items of metallic iron originate from the iron age, which started ~ 1,000 years BC (reference /37/ provides a summary of metal working over the ages). Generally speaking the earliest artefacts consisted of single items of iron, such as jewellery, rather than multiple components, and therefore they did not contain the constrained geometries that are of interest here. Possible sources of analogues for anaerobically corroding iron in constrained geometries are:

- Objects lost at sea which have been encased in marine sediments or encrustation. For example, iron artefacts from Australian shipwrecks have been found embedded in coral concretions, which led to the development of anoxic conditions /38/ around the objects.
- Artefacts deposited in anoxic river sediments.
- Artefacts in land burial sites where oxygen has been excluded.
- Industrial environments where oxygen levels are low.

2.2 Identification of relevant ferrous materials

Literature searches were carried out for (i) previously published information about natural analogues for waste container materials, and (ii) information about the corrosion of iron and copper archaeological materials. These searches used bibliographic databases on corrosion, metallurgy and archaeology and also extensive use of the Internet to interrogate web sites for a number of institutions involved with the analysis of archaeological material. A list of the sources consulted is given in Appendix 1. The main aim of the searching was to identify examples of iron or ideally, iron-copper, artefacts containing constrained joints (e.g. rivets in plates or bolted devices) that had been exposed to anoxic, aqueous conditions for long periods. Having searched and reviewed the relevant literature a number of visits were carried out to institutions holding relevant artefacts, namely the Mary Rose Trust, Portsmouth, U.K., the British Museum and the London Museum (both in London), the Yorkshire Museum (York, U.K.), Bradford University Archaeology Department and Museo Arqueológico Nacional, Madrid.

There is a wealth of archaeological artefacts made from iron or copper based materials and in a few items both metals are present. No attempt was made to carry out an exhaustive analysis of all the available material, since it soon became apparent during the course of this work that there is an overwhelming volume of archaeological artefacts in existence. Instead, a few relevant items are described in detail, with the aim of illustrating how iron corrodes over long periods in natural low-oxygen environments in constrained geometries. It was not possible to obtain any freshly excavated archaeological items for examination; in future work this may be a useful approach that would enable preservation of corrosion products for immediate chemical and physical analysis.

2.3 Analysis of published literature

The literature on the conservation of iron artefacts contains detailed information about the composition of corrosion products and concretions formed on archaeological artefacts and methods of stabilising corroded objects (e.g. /39–55/). The main factors affecting the corrosion of metals from shipwrecks are:

1. Water composition (e.g. pH, salinity, oxygen concentration). Normal seawater has a pH of 7.5 to 8.2, but it can vary from 6.5 to 9.5 in stagnant waters and in the seabed sediments. Some pH changes may also be due to the activities of sulphate reducing bacteria (SRBs). Values below 6.5 are found in the concretions surrounding actively corroding metals. Low oxygen levels are encountered underneath marine concretions and below the seabed, even when the seawater above is well-oxygenated. In this case the low levels of oxygen are mainly the result of biological uptake of oxygen, combined with slow exchange with external seawater. In such situations the rate of corrosion may well be controlled by sulphate reducing bacteria.
2. Metal composition and treatment (e.g. cast or wrought iron).
3. Temperature, which affects both the corrosion rate and the extent of biological activity.
4. The presence of marine growth. Layers of marine growth have a large effect on corrosion rates because they provide a physical barrier to the external environment. This allows the development of a local micro-environment around the artefact, which may be low in oxygen.
5. Seabed composition (e.g. sediments, gravel, etc).
6. Location of object (e.g. in shallow sites the conditions can change during the exposure period for a number of man-related reasons, such as dredging).
7. Position of objects in relation to other shipwreck components (e.g. decomposing organic items).
8. Depth of burial beneath seabed, which determines the degree of microbial activity and concentration of oxygen.
9. The extent of water movement, which affects the rate of transport of oxygen to the metal surface and may also prevent the formation of corrosion products or prevent biological activity.
10. Microbial activity. The formation of acids by SRBs may accelerate the corrosion rate. The growth of SRBs requires the presence of organic material as a substrate, so the SRB activity falls off rapidly with increasing depth into the seabed sediment. At depths greater than 50 cm the bacterial activity should be very low; however the presence of buried wood from a shipwreck encourages the activity of SRBs.

If the oxygen content of the water immediately in contact with the metal becomes very low then the Eh can fall below the hydrogen evolution potential and the main cathodic reaction becomes the evolution of hydrogen. This occurs when (i) the seawater itself becomes anoxic due to pollution or high microbiological activity, (ii) the metal is buried beneath the seabed and oxygen diffusion from the overlying seawater is restricted, or (iii) the artefact becomes covered with a thick layer of marine growth, which restricts the oxygen supply. The hydrogen evolution reaction is faster on sulphide films formed by the activity of SRBs. The author has personally observed the release of gas from the surface of steel wreckage in a Scottish sea loch when it was rubbed by hand. This gas was probably hydrogen that formed at the surface of the steel. The black colour of the corrosion product beneath the red surface layer indicates that conditions at the surface of the steel were anoxic, due to the oxygen barrier formed by the upper surface of the corrosion product.

The main corrosion products from marine corrosion of iron are α -, β - or γ -FeOOH, Fe_3O_4 , FeS, FeCO_3 and Fe-Cl containing compounds which have not been fully identified /56/. The pore solution may contain dissolved ferrous ions and chloride and on exposure to air the ferrous ions are oxidised to FeOOH, which results in a volume expansion and spallation of the corrosion product film and can be accompanied by the generation of sufficient heat to make artefacts glow red hot. Concretion is commonly formed around iron objects, by iron corrosion products mixing with material adjacent to the iron. It is predominantly composed of CaCO_3 , which undergoes ion exchange with the iron ions released by corrosion to form FeCO_3 and other iron compounds. The structure of the concretion is different depending on whether it is exposed to seawater or buried in sediment. In buried conditions the concretion contains predominantly Fe_3O_4 , compared to FeOOH and Fe_2O_3 in exposed situations. The conditions inside the concretion may be relatively acidic due to hydrolysis reactions (pH 4.8 /56/) and reducing. The cathodic reaction within the concretion is reduction of water and release of gas, assumed to be hydrogen, from concretions broken underwater has been reported /56/. Hydrocarbons, such as alkanes and alkenes, may also be released due to the decomposition of Fe_3C (cementite) in the iron matrix /56/.

The metal core of iron artefacts recovered from land burial, for example iron nails, which are common archaeological finds, are typically covered with a layer of corrosion products several millimetres thick. Analysis of iron nails from 17th century house sites in the US was reported by Nielsen /57/. In this case an impermeable surface layer of Fe_2O_3 , formed during a house fire, was found to have protected the iron nail against further corrosion. Van Orden /58/ reported the examination of a freshly excavated Roman nail that was buried in soil. Mössbauer analysis identified a mixture of FeOOH (lepidocrocite), Fe_3O_4 (magnetite) and γ - Fe_2O_3 . It was noted that the oxide structure suggested that there had been several changes in the environment, corresponding to more or less oxidising or reducing conditions. The corrosion products on a 12th Century iron nail buried in soil were also analysed by Mössbauer spectroscopy and other techniques by Novakova et al. /59, 60/ and found to be a mixture of magnetite and haematite, with little magnetite at the outer surface of the oxide. They also detected iron phosphate ($\text{Fe}_3(\text{PO}_4)_2$) and iron (II) sulphur compounds (e.g. FeS_2 , $\text{FeSO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) at the surface of the corrosion product layer, which they attributed to microbial activity, especially sulphate reducing bacteria (SRBs).

Neff et al. investigated the composition of the corrosion products formed on nine freshly excavated iron archaeological artefacts dating back to the 12th century AD /61/. The main crystalline phases identified in the corrosion products were α -FeOOH (goethite), Fe_3O_4 (magnetite) and in some cases FeCO_3 (siderite) and $\text{Fe}_2(\text{OH})_3\text{Cl}$. Some diffusion of iron from the corroded artefacts into the surrounding soil was observed. Estimated corrosion rates for the iron were generally less than 1 $\mu\text{m}/\text{yr}$. Pons et al. /62/ examined ferrous World War I artefacts that had been buried in clay and found from Raman analysis that the corrosion products were generally magnetite (Fe_3O_4) or maghemite (γ - Fe_2O_3) in the inner, dark grey layer of the corrosion product and α -, β - or γ -FeOOH in the outer orange-brown layer.

Dresselaers et al. /63/ examined the corrosion product on the surface of cast iron exposed to clay soil in a coal mine shaft for 60–90 years and detected mainly magnetite, which was formed at a corrosion rate calculated from the corrosion product thickness of 1–10 $\mu\text{m}/\text{yr}$.

The presence of SRBs leads to the formation of hydrogen sulphide and sulphide films on the surface of buried artefacts /64, 65/. Sulphide films can catalyse the hydrogen reduction reaction /66/. Some workers /67, 68/ have made electrochemical measurements on archaeological artefacts in situ. Most wrecks and artefacts exposed to oxygenated seawater corrode at a rate of 100–200 $\mu\text{m}/\text{yr}$.

3 Specific analogues for anaerobic corrosion-induced expansion

Previous natural analogue studies of iron have concentrated on deriving information about corrosion rates, in support of waste container assessments /23/, rather than on the possible effects of corrosion-induced expansion. There are no known reports in the literature regarding the mechanical properties of corrosion products formed on archaeological objects after long-term exposure to anoxic conditions, or about the effect of anaerobic corrosion on expansion damage in archaeological items. Johnson and Francis /23/ published an assessment of the corrosion rates of archaeological iron artefacts in relation to radioactive waste disposal. The samples they considered had been subjected to a wide range of environmental conditions and oxidising power; the most heavily corroded ferrous items were cannon balls removed from oxidising (i.e. aerated) seawater and the least corroded items were those exposed to dry atmospheres. The corroded items from environments expected to be anoxic typically exhibited corrosion rates of ca. 0.1 $\mu\text{m}/\text{yr}$, a value, which is consistent with long-term laboratory experiments on steel wire immersed in anoxic artificial groundwater /7/.

A number of specific artefacts were identified during the course of the study that are relevant to the corrosion of iron HLW containers and a selection of them is described below. They include artefacts from both land burial and shipwreck sites.

3.1 Iron nails

The deposit of two thousand year-old Roman nails at the Inchtuthil legionary site in Scotland is one of the best known archaeological finds of iron /69, 70/, where over a million nails were buried in a pit. In this case the nails at the centre of the find were hardly corroded, because they experienced low oxygen concentrations and less exposure to water due to the impermeable crust formed by corrosion of the nails at the edge of the mound. Some of the nails at the centre were covered with a smooth black closely adherent scale /70/.

3.2 The Wetwang chariot burial site, Yorkshire

In March 2001 an Iron Age grave was discovered on the top of a hill in the village of Wetwang in East Yorkshire, England during the construction of a small housing development. Excavation showed that the grave was that of a woman who had died over 2,300 years ago and was buried with a chariot. Since completion of the excavation, the finds have been conserved and studied at the British Museum. The grave contained various horse bridle parts, some of which consisted of iron components in close contact with bronze. They included horse bits and rein rings (Figure 3-1).

The chariot was buried in a pit approximately five feet deep, which was backfilled with clay or gravel and covered with a low mound, surrounded by a square ditch. Although the exact environmental conditions cannot be known with any certainty, it is likely that corrosion of the iron was occurring at low oxygen concentrations, because otherwise the iron items would have been completely corroded away, given the long time scales involved. It is probable that the conditions changed on a seasonal basis; for example the degree of wetting and oxygenation would have depended on the rainfall. The organic components of the chariot (i.e. the wood and leather) had completely decomposed indicating that some microbial activity occurred. This could also have resulted in consumption of oxygen.



Figure 3-1. Horse bit and rein ring from Wetwang chariot burial site (courtesy of British Museum).

The horse bits were made of iron and bronze. The central part was formed of cast bronze, and bronze sheet had been hammered over iron rings on either side of the central part. The bits were delicately made; even the part in the horses' mouths was decorated. It is noticeable that distortion of the bronze sheet on the rings had not occurred, even though water is likely to have penetrated into the crevice between the iron and the bronze, and caused corrosion of the iron.

British Iron Age chariots usually had five rein rings, or 'terrets', fixed along the top of the wooden yoke that spanned the horses. The rein rings consisted of a bronze section which was joined to an iron rod in the central region. The bronze section was decorated with pieces of embedded red coral or glass. It is clear that severe expansion damage had not been inflicted on the bronze components of the rein ring (Figure 3-1).

Two other artefacts of relevance from the same period of the Iron Age (200–300 BC) and area (East Yorkshire, U.K.) are a sword and a pair of linchpins from another chariot burial at Kirkburn. British Museum archaeologists excavated the sword in 1987. The handle of the sword is unusually elaborate, being made of thirty-seven different pieces of iron, bronze and horn (Figure 3-2).

The decorated linchpins supported the wheels of a cart or chariot on their axles. The main parts are made of iron, while both ends were decorated with a bronze cap, cast onto the iron bar. There are no indications of expansive damage to the bronze caps at the end of the iron rods.



Figure 3-2. Handle of sword and Linchpins from Kirkburn chariot burial site (courtesy of British Museum).

3.3 The Coppergate helmet

This helmet was found in May 1982 in a waterlogged pit at the Coppergate excavation site, when it was being levelled prior to the construction of the Jorvik Viking Centre in the city of York, U.K. /71/. The helmet was of Northumbrian origin and is estimated to have been crafted around 750 AD. The helmet was made from iron, brass, bronze and silver and contained riveted components (Figure 3-3). Brass was used to make edge bindings, cheek-piece bindings, rivets, some mail-loops and the decoration on the nose-piece. Bronze was used to make a few of the rivets. The cap consisted of eight separate iron plates riveted together. They varied in thickness from approximately 0.7 mm to 3 mm. Over 150 rivets were used in the construction of the helmet. The rivets attaching the mail suspension strip to the helmet were made from silver.

The brass bindings were made from strips that were bent into a U-shape and fitted round the edge of the helmet leaving a gap between the iron plate and the brass and were riveted near the ends of the strips. The edging on the cap covers the angular edges of the iron plates. There are four different types of edge bindings: (1) a plain binding around the nasal and eye cut-outs, (2) between the ends of each eyebrow and the cheek-piece hinges, (3) running from the back of the hinge to where the cheek-piece ends, and (4) the mail suspension strip. The mail suspension strip attaches the mail to the cap and is held in place by silver rivets.

3.3.1 Corrosion of the helmet

The whole site had been waterlogged since deposition so there was little oxygen available. Pieces of timber were preserved at the same site as the helmet, indicating that the site was permanently waterlogged and that microbial activity was low. The helmet was found in clay soil that formed a grey crust over the helmet and preserved it to some degree. The interior of the helmet had been filled with a thick clay. The local environment had the effect of greatly reducing the amount of oxygen available, leading to remarkable preservation of the helmet. If oxygen had not been excluded, the thin iron plates of the helmet would have been completely corroded away; at a typical aerobic corrosion rate of 10 $\mu\text{m}/\text{yr}$ the iron plate would have disintegrated



Figure 3-3. The Coppergate Helmet after conservation, (a) after conservation, and (b) after conservation and reconstruction (courtesy of Council for British Archaeology).

within 300 years of burial. Iron chain mail around the neck, made from 0.9–1.2 mm diameter wire, was also well preserved. It can be assumed that the iron components of the helmet suffered from slow anaerobic corrosion. Most of the damage to the helmet occurred during building works when the bucket of a mechanical excavator struck the helmet in the ground, causing some of the rivets to pop on the right side of the cap and distort the infill plate.

The corrosion that occurred while the helmet was in the ground varied from a light surface coverage of a black corrosion layer to severe patches of attack on the right cheek-piece and the rear left of the brow band. The dense black deposit was identified as siderite (FeCO_3) and this had partially replaced the iron [72]. The formation of siderite probably resulted from reaction with carbonate in the groundwater derived from demolished Roman plaster and mortar buildings that were previously on the site.

The back left browband of the helmet had been virtually removed and it was unclear whether this attack had been before or during deposition. This was also the case with the left cheek-piece; half of it had shattered because it mainly consisted of brittle replacement corrosion. The parts of the helmet covered by the brass fittings or where the plates were riveted and overlapped were obviously free of crust. The inside of the helmet was dark and smooth and corrosion in the cap was clearly visible.

The brass fittings had been etched by groundwater corrosion and chalcopyrite (CuFeS_2), a lumpy yellow deposit, and bornite (Cu_5FeS_4), a thin, bright blue deposit, had formed a veneer; both were easily removed with a bristle brush.

Jim Spriggs, who worked on the conservation of the helmet, was of the opinion that there was insufficient volume of corrosion products from the anaerobic corrosion of the iron to cause any deformation of the brass edgings and bindings covering it. Rather than magnetite, the corrosion product was mostly siderite (FeCO_3), which had virtually replaced the iron and was

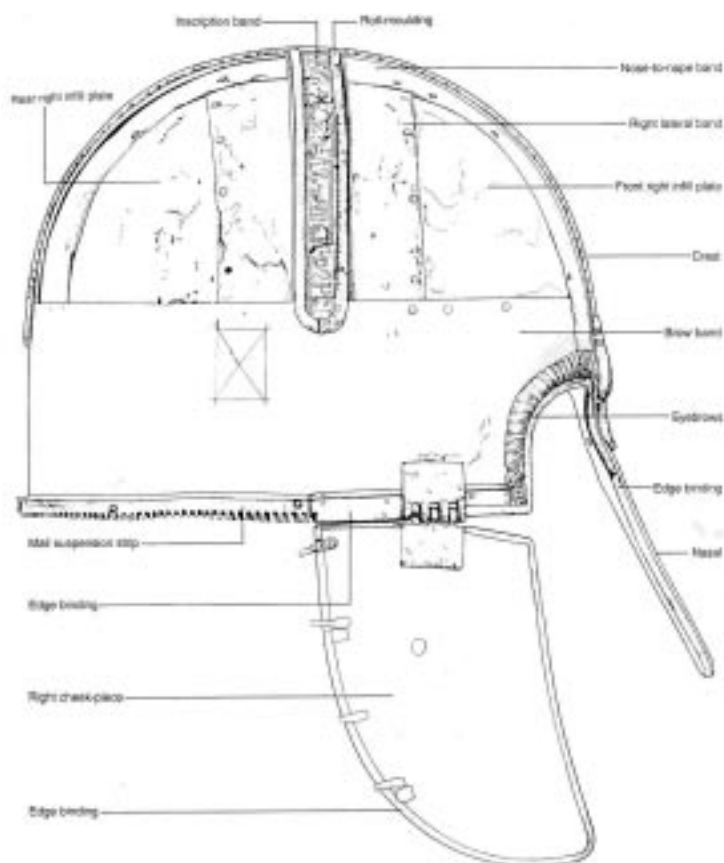


Figure 3-4. Construction of Coppergate Helmet.

brittle. There was no evidence of vivianite ($\text{Fe}_3(\text{PO}_4)_2$), which is commonly found at other Anglo-Scandinavian deposits at Coppergate. It is possible that organic molecules formed by the degradation of biological material (e.g. polyphenols from the breakdown of lignin) may have behaved as corrosion inhibitors.

The extent, in terms of depth, of the replacement corrosion depends on the thickness of the iron. Thin plate is fully penetrated and generally does not survive, especially in oxygenated conditions, but thicker pieces of metal were protected in the centre by a thick corrosion layer. The helmet survived, although being made from thin iron plate, because it was preserved in the anoxic, waterlogged environment.

Archaeologically, the Coppergate Helmet is a fascinating object, which has been rigorously studied /71/. For the purposes of the present discussion, the most interesting features of the helmet are those regions where constrained geometries were present between copper alloy and iron, and between the iron components, for example under the rivet heads, between plates of iron and in the chain mail hinge. In these regions there are no indications of gross distortion due to the formation of a voluminous corrosion products. The corrosion product was mostly siderite (FeCO_3). Based on considerations of theoretical density, formation of siderite would cause an expansion of 4.2 times compared to the base metal /61/.

Small quantities of arsenic were found in the iron that may have inhibited microbial corrosion of the helmet. Arsenic occurs naturally in iron ores and can become enhanced at the surface of metal artefacts. It is unusual that the helmet was preserved so well after deposition for so long even considering the waterlogged, deoxygenated environment of the pit, which, itself was possibly intended for cess or rubbish – ideal for microbes. It was suggested that the presence of arsenic on the helmet prevented microbial attack in this environment.

3.3.2 Sword beater

This object (Figure 3-5), used in weaving, measures approximately $\frac{3}{4}$ metre long with a wooden handle. It was found in the same pit as the helmet and therefore it was assumed that it was exposed to the same environment for the same amount of time. The sword beater had broken in two places, so that the iron core was visible and the exfoliating replacement corrosion of the iron was clear.



Figure 3-5. A broken part of the sword beater (courtesy of Council for British Archaeology).

3.4 The Mary Rose

The Mary Rose, King Henry VIII's wooden flagship, sank in the Solent in July 1545 /73/. The seabed in the area is covered in sediment into which half the ship's hull was embedded. The wreck was excavated during the 1970s and in 1982 the remaining timbers of the wreck (approximately half the hull) were removed from the water, after 437 years' immersion. The sediments excluded oxygen and this accounts for the extremely good state of preservation of both organic and inorganic materials. A number of relevant metallic artefacts (i.e. iron with constrained geometries) were found on the wreck and there are a number of copper items that were of interest. These are either on display in the Mary Rose museum or in the dry store. All the items are carefully catalogued and some have been X-rayed to clarify the internal structure. These included chain shot, consisting of iron embedded in lead, and cannon barrels, made from strips of iron surrounded by bands of the same material. None of these items had suffered from expansive damage from the formation of corrosion products in the tight geometries, in contrast to items that have mistakenly been allowed to corrode aerobically after recovery from the seabed and have suffered from catastrophic breakaway corrosion.

Concretion is concentrated around ferrous items. An item the size of a cannon ball may be encased in concretion the size of a basket ball. Could this be because some of the marine fauna metabolise the dissolved iron ions (e.g. iron oxidisers)? Bronze items are usually clean, due to the biocide properties of the copper ions.

If iron artefacts are not conserved, severe corrosion will occur due to the residual chlorides in the corrosion products and the presence of air. The chlorides are extracted by immersion in a sesquicarbonate solution (mixed carbonate/bicarbonate) or sodium hydroxide /74/. The alkaline conditions prevent corrosion but leach out the trapped chloride ions. The artefacts may also be treated electrolytically, where the artefact is set up as the cathode and a stainless steel anode is used. Chloride ions migrate out of the item and the surface oxide is reduced, making it more porous and it is therefore easier to release chloride. After treatment the items are coated with wax. "Bronze cancer" was occurring on one of the cannons in the museum due to incomplete extraction of all the chlorides from the surface. The green coloration was probably due to a mixture of chlorides and sulphates.

The following items were of most interest:

Chain shot

The item consisted of a piece of iron that was embedded in a piece of lead. The iron would have been placed in the molten lead and allowed to cool. In this situation there would have been a very tight fit of the lead around the iron, although the lead would have been able to creep to a certain extent and so accommodate some expansion caused by corrosion of the iron. The item had been X-rayed and this would be available for examination. There was a layer of concretion around the item.

Corroded cannon ball

This cannon ball had an iron core but was surrounded by a lead casing. It had been mistaken for a completely lead cannon ball and so had not been conserved. The iron core had corroded aerobically forming a more voluminous corrosion product, which had led to severe damage to the lead casing. This is an illustration of the damage that can be caused by expansion due to corrosion. The staff at the museum had not observed any damage to items with constrained geometries due to expansive corrosion products.

Iron cannons

There were a number of iron cannons in the dry store. These were made from strips of iron, which were held together to form the gun barrel using iron bands. They therefore constituted a tight constrained geometry around the central barrel. Cast iron contains high concentrations of carbon and when it corrodes the anodic iron is dissolved leaving the residual cathodic graphite, a process known as graphitisation.

Copper bowl

Residues of bitumen were present in the bottom of the dish. The bowl itself was in good condition.

Copper coins

The possibility that these coins would represent samples of copper containing residual tensile stresses was considered; however, XRD analysis performed by SKB on similar artefacts has shown that the residual stresses in such items are always compressive and they are not therefore a useful analogue for stress corrosion cracking of copper. A gold coin was also in the collection.

Bronze pulley wheel

This was in very good condition and the composition of the copper had been determined.

Museum exhibits

The following items were on display in the Mary Rose exhibition, which contains a number of metal artefacts. Of particular interest were the following:

Bronze cannons

These were in very good condition. The decorative features were clearly visible.

Copper spring

This may be of interest, because it is likely that the copper strip contained residual stresses, but no SCC was apparent.

Other items

The following items had survived immersion in the sea after the sinking of the Mary Rose:

- Iron chain – still intact, but no constrained geometries.
- Copper weights.
- Iron nail preserved in lump of bitumen.
- Brass dividers, sundial and lid.
- Bronze watch bell – iron clanger did not survive.
- Various metal buckles.

Some items had been treated in a hydrogen furnace to reduce any residual iron oxides on the surface. This process resulted in a shiny black surface finish. From the point of view of atmospheric corrosion it is interesting to note that the exhibits are kept in display cabinets which have dehumidifiers attached to reduce the humidity to 40% RH.

3.5 Other shipwrecks

It is estimated that there may be 0.5 million wrecks around UK /75/. Tylecote /27/ has summarised the availability of metal archaeological artefacts from pre-20th Century Shipwrecks and they are broadly classified into two main categories:

- Material recovered from Greek and Roman cargoes sunk in the Mediterranean.
- Armada and later ships sunk off the coasts of the British Isles and Western Europe.

In addition there are a few wrecks off the Australian coast. Most of the artefacts from early shipwrecks analysed by archaeologists have been copper-based alloys rather than iron, because in most conditions the iron from shipwrecks corrodes away relatively rapidly, unless it happens to be protected by marine sediments, as in the case of the *Mary Rose*. Iron cannons are found extensively in post-medieval wrecks. It is not possible to carry out a thorough review of the material retrieved from all these wrecks within the scope of the present report; reference /76/ provides a useful overview of the wrecks that have been of most archaeological significance to date, although there are doubtless many to be fully investigated and this reference highlights wrecks that could be pursued further for suitable material for analysis. Some of the wrecks that may be worthy of further investigation to identify relevant artefacts are:

- The *Holland I*. This was the Royal Navy's first submarine, with an underwater displacement of 122 tons, which was launched in 1901 and sank while being towed to the scrap yard in 1913. It was recovered almost intact from the seabed in 1982 and conserved by hydroblasting to clean it and treating with Ferton rust converter. This treatment was not entirely successful and she had to be retreated later by soaking in sodium carbonate solution to reduce the concentration of chloride. It is now on display in Gosport /77/. It is understood that this wreck mainly suffered from aerobic corrosion and it has since been painted.
- The *H.L. Hunley* was an American submarine that sank in 1864 into seabed sediments where it was preserved by the low-oxygen environment until it was raised in 2000. It has been the subject of extensive corrosion analysis and conservation /78/ studies and is currently protected by the concretion that was left in place after it was raised and the application of cathodic protection while it is immersed in a tank of water, pending further analysis of the submarine's contents /79/.
- *Pandora* sunk off the Great Barrier Reef, Australia in 1791 and excavated between 1983 and 1999. It was well preserved in soft seabed sediments /80/. Articles retrieved include a telescope.
- *Uluburun* wreck sunk off the southern coast of Turkey in the late 14th Century BC and excavated 1984–1994, contained ten tonnes of copper and 1 tonne of tin ingots /81/, but no iron artefacts. The copper ingots may be a useful analogue for the corrosion of copper.
- *Machault* wreck, a French frigate scuttled in 1760 in the Restigouche river estuary in Canada, which was excavated 1969–1972. It contained many well-preserved artefacts including armaments such as rifles and cast iron grenades.
- *Vasa*, sunk near Stockholm in 1628 and raised in 1961. It was well preserved due to the low-oxygen conditions and lack of wood boring worms in the prevailing conditions. It has since been catalogued and restored /82/. Iron nails had completely corroded away, but metal items recovered included firearms and tools.
- *Kronan*, /83/ sunk in 1676, contained over 22,000 objects, including 44 bronze cannons. These items were preserved by the compact, glacial clay which maintained anoxic conditions.

The London Museum possesses a wide range of artefacts retrieved from the sediments bordering the River Thames in London. Many items are well preserved due to the low oxygen concentration within riverbed sediments. However, during a visit there it was not possible to identify specific artefacts that suited the requirements of the present study (i.e. iron or iron-copper items with constrained geometries).

3.6 Industrial analogues

There are a number of situations in modern industrial applications where anoxic water is present in contact with iron and/or copper, such as

- Hot water systems where copper pipes and steel radiators are exposed to near neutral waters, and black magnetite is commonly found as a deposit in the heating systems;
- Corrosion of seabed pipelines. For example experience with seabed installations, such as chains embedded in Norwegian seabed clay below the upper 10–20 cm of sediment, shows that the corrosion rates are in the range 1–10 $\mu\text{m}/\text{yr}$ /84/.
- Steel corroding in old concrete, where the rate of diffusion of oxygen through the concrete is so slow that anaerobic conditions pertain at the surface of the reinforcement bars. The fact that spallation of concrete cover occurs due to corrosion of the rebar is an illustration of the expansive force which can be generated through corrosion processes; however, in this situation the water supply is restricted and it is likely that the corrosion product is harder than in a fully immersed system.
- Oxide jacking, for example in civil engineering structures (e.g. the railings around St Paul's cathedral and the Acropolis in Greece /85/), in heat exchangers in nuclear plant /86/ and in atmospheric corrosion situations, where atmospheric corrosion of mild steel can lead to splitting of the surrounding materials (e.g. copper /87/).
- First World War copper munitions, which are found in the water logged clays of battle sites may offer potential natural analogues.

4 Discussion

In the stress cell experiments with carbon steel /3/, no expansion occurred, even though corrosion product analysis identified the presence of both hydrogen and magnetite, confirming that anaerobic corrosion was taking place. In the stainless steel-copper control cell some contraction of the stack took place. The contraction may have been due to creep of the copper at asperity tips on the roughened copper surface. No expansion was observed with cast iron specimens, where a thicker more voluminous oxide would be expected /3/, or even under aerated conditions, where much more rapid corrosion (ca 100 $\mu\text{m}/\text{yr}$ cf. 1 $\mu\text{m}/\text{yr}$) would have occurred. The reason for the lack of any detectable expansion in the stress cell experiments is probably because the corrosion product was easily compressed or extruded from the copper-steel interface and it was not capable of withstanding the applied loads. Scanning electron microscopy showed that the anaerobic corrosion product was finely divided and it had deformed to fit into the available spaces between the discs in the stack of specimens, rather than forcing them apart. It is probable that the surface roughness and the grooves in the copper discs were filled with corrosion product from the anaerobic corrosion of the steel. This situation is in contrast to that experienced in concrete or in heat exchangers where jacking effects can cause severe mechanical disruption of the surrounding structures.

One possible reason for the low mechanical strength of the corrosion product formed at low temperature under anaerobic conditions is the higher proportion of water, in contrast to the situation in concrete where the supply of water is limited, or to the oxide films formed at high temperature which have a much higher hardness and a lower water content.

If water were to penetrate the outer canister wall and enter the annulus it is likely that any anaerobic corrosion product formed would deform and spread around the annulus, rather than expand to force the copper outer canister away from the iron insert. Eventually the annulus may fill up with corrosion product, which would gradually be compressed by the confining walls of the canister. Subsequent corrosion would depend on whether water could penetrate the corrosion product in the annulus and reach the surface of the iron insert. It is possible that natural analogues may be found that will support this hypothesis, but the evidence is not available in the current body of literature and further careful work on industrial or archaeological objects is required involving fresh samples, with full environmental characterisation.

Analysis of the literature shows that magnetite is commonly formed on archaeological iron objects under reducing conditions, or where the artefact is protected by the formation of an outer scale, although FeOOH and Fe_2O_3 are formed under more oxidising conditions. The point is that other archaeological objects are covered with a corrosion product layer that is of similar composition to that expected to develop on the cast iron insert of the SKB canister design, although the detailed morphology of the corrosion product layer may be different. Furthermore the corrosion product formed on archaeological items normally shows the effect of local microbial activity (e.g. iron-phosphate or iron-sulphur compounds), which is expected to be lacking in the SKB canister situation. Nevertheless, some parallels can be drawn between the corrosion behaviour of the archaeological items and the probable behaviour of the SKB canister.

The good preservation of the Coppergate Helmet, which had been buried for over 1,200 years, and the iron age relics at the Wetwang site, which had been buried for ca. 2,300 years, confirms that in poorly oxygenated, naturally occurring, reducing conditions, iron will suffer from a very low anaerobic corrosion rate. Relatively short-term laboratory experiments /5/ have measured corrosion rates of $\sim 0.1 \mu\text{m}/\text{yr}$ with the formation of hydrogen and magnetite (Fe_3O_4), rather than siderite as was observed on the Coppergate helmet. The archaeological items described here have also demonstrated that the formation of iron anaerobic corrosion product does not cause expansive damage, even in tight crevices such as those present underneath the rivet heads or between the iron cap sheets of the Coppergate Helmet, or between copper sheet and

iron on the Iron Age artefacts described above. Items recovered from the wreck of the *Mary Rose* exhibit similar features, although the exposure time in this case was considerably less (437 years). This lack of expansion damage is probably due to the very low anaerobic corrosion rates for iron and the ease with which the corrosion product can deform /1/. Other workers have recorded corrosion rates in the region of 0.1–1 $\mu\text{m}/\text{yr}$ based on studies of buried archaeological artefacts /23/. The items described in this paper also demonstrate that in reducing conditions, galvanic coupling between iron and copper alloy does not cause highly accelerated corrosion rates of the iron. This is in agreement with recent experimental studies of galvanic corrosion in relation to the Swedish waste disposal concept /88, 89/ and with other investigations of archaeological items containing both iron and copper /16/.

5 Conclusions

1. Although it is recognised that it is impossible to find natural analogues exposed to exactly the same conditions as expected in a geological repository, study of archaeological items can provide information about the corrosion behaviour of iron under naturally occurring, reducing aqueous conditions which are relevant to the behaviour of waste container materials in a geological repository of the type proposed by SKB.
2. On the basis of the evidence from iron-copper artefacts exposed to reducing conditions for up to 2,300 years it appears that anaerobic corrosion product formation on iron does not lead to gross deformation when in contact with copper-based materials in constrained geometries. This is in agreement with the results of experimental work using a 'stress cell' apparatus, which did not detect any expansion from the anaerobic corrosion of carbon steel or cast iron after more than 900 days' exposure.

6 Recommendations

The following recommendations are made:

1. It is quite likely that other relevant objects containing iron and copper in close proximity exist in museums and other archaeological collections, which it was not possible to gain access to within the scope of this project. If further supporting evidence is required for the conclusions given above, the work started in this project could be continued by developing contacts with relevant organisations and institutions, such as those listed in Appendix 1 and by interrogating in-house catalogues in more detail.
2. If closer collaboration could be set up with archaeological groups that are actively obtaining fresh artefacts it may be possible to collaborate to obtain detailed information about the environmental conditions around them before carrying out thorough chemical and physical analyses of the corrosion products. To address the issue of corrosion product expansion, items are required where constrained geometries have been established, for example in crevices between two components of an object. The ideal situation would be to inform a range of archaeological groups of SKB's requirements, so that they can alert SKB when relevant items become available.

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- Bristol University
- Oxford University Materials Science-Based Archaeology Group
- Centre for Maritime Archaeology, Southampton University
- Institute of Nautical Archaeology / Texas A&M University (<http://nautarch.tamu.edu/index.htm>)

Museums

- Ashmolean Museum, Oxford
- Australian Maritime Museum
- British Museum (<http://www.thebritishmuseum.ac.uk/compass/index.html>)
- Museum of London
- National Maritime Museum (<http://www.nmm.ac.uk/>)

Archaeological institutions and societies

Anglo-Danish Maritime Archaeological Team (ADMAT) (includes Oxford University Maritime Archaeology Research and Excavation (MARE) Unit)

Australian Institute for Maritime Archaeology

Council for British Archaeology (<http://www.britarch.ac.uk/>)

European Institute of Underwater Archaeology

Nautical Archaeology Society (<http://www.nasportsmouth.org.uk/>)

Databases

Conservation Information Network (CIN) (http://www.bcin.ca/English/home_english.html)

British Museum (Compass database, <http://www.thebritishmuseum.ac.uk/compass/index.html>)

NACE Corrosion Abstracts

Energy Technology Data Exchange (<http://www.etde.org/>)