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LONG-TERM CORROSION OF IRON AND COPPER

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ABSTRACT

Analysis of long-term corrosion data for iron and copper shows that parabolic kinetics provide an adequate description of the corrosion behaviour in soil over thousands of years. When iron corrodes in free water however, the corrosion rate is approximately constant with time. The implications of these observations are discussed.

INTRODUCTION

The safety of long-lived radioactive waste disposal depends on containment, which needs to be maintained for long enough to allow the radioactivity to decay to acceptable levels. Disposal concepts are often designed to employ a durable, high integrity container, capable of providing absolute physical containment. Containers may be surrounded by a material that serves to protect them and provide chemical containment for the radionuclides if the physical containment should fail.

In assessing the performance of containers, an important issue is their possible failure by corrosion. Corrosion rates may be derived from laboratory tests that reproduce, so far as possible, the appropriate environmental conditions. But because the containers must retain their integrity for thousands of years, laboratory tests need to be accompanied by a level of understanding that allows the laboratory data to be extrapolated to the appropriate timescales. To provide confidence that the level of understanding is adequate to the task, natural, anthropogenic and archaeological analogues can be used. Because a perfect analogue is a practical impossibility, analogues cannot provide a complete validation of repository modeling; but they can be used to show that the understanding that is embedded in the modeling is capable of describing similar phenomena on similar timescales.

This paper draws together corrosion data for iron and copper from laboratory, field, in-service and archaeological sources. The purposes of the paper are to assess the level of consistency in the data and to draw out any conclusions about likely mechanisms.

NOMENCLATURE

W - *metal loss by corrosion* t – *time*
k_1 - *parabolic rate constant* k_2 - *linear rate constant*

LONG TERM CORROSION OF IRON

Iron is probably the most examined and the best documented of all engineering materials. Several studies of its corrosion behaviour are analysed here; all are concerned with corrosion in soil or free water of cast iron and plain carbon steel (including wrought iron). The studies may be conveniently classified into laboratory data extending to up to 10 years [1,2,3], field trials up to 18 years [4], in-service data up to 90 years [5,6,7,8] and archaeological data [9,10,11,12,13,14]. The use of iron by humans goes back 4000 years in some parts of the world but such finds are rare. In Europe, iron nails are frequently found during archaeological investigation of Roman structures (to the extent that, until recently, they were often discarded) and a typical example found in soil at Kingscote Roman Villa (Glos. UK), with metal loss between 1 and 5 mm, is included here. At 1700 years, it is the oldest iron object in the present study.

A particular problem with archaeological data is the difficulty of characterizing the environmental conditions experienced by an object: often these go unrecorded and there is the added complication that the conditions may have changed over the period of burial. Recognizing this, the present study begins by separating the iron corrosion data into (i) burial in soil and (ii) exposure to free water.

Corrosion of Iron in Soil

Figure 1 shows corrosion (expressed as metal loss) plotted against time for iron in soil. The time span ranges between 0.5 and about 1700 years. A significant fraction of the data comes from the work of Romanoff [4] (omitting data obtained from iron buried in cinders). Individual data series appear to approximately follow parabolic kinetics, i.e.

$$W \approx k_1 \, t^{0.5} \qquad (1)$$

Fig.1: Carbon steel and cast iron corrosion in soil

Legend:
- ◆ [9] CS/CI
- ■ [11]
- ▲ [10] CI
- ✕ [12] CS
- ● [13] CS
- ◇ [8] CI gen.
- + [8] CI internl
- ○ [4] CI Tab29
- △ [4] CI Tab27
- ▬ [3] low
- ▬ [3] high
- □ See text
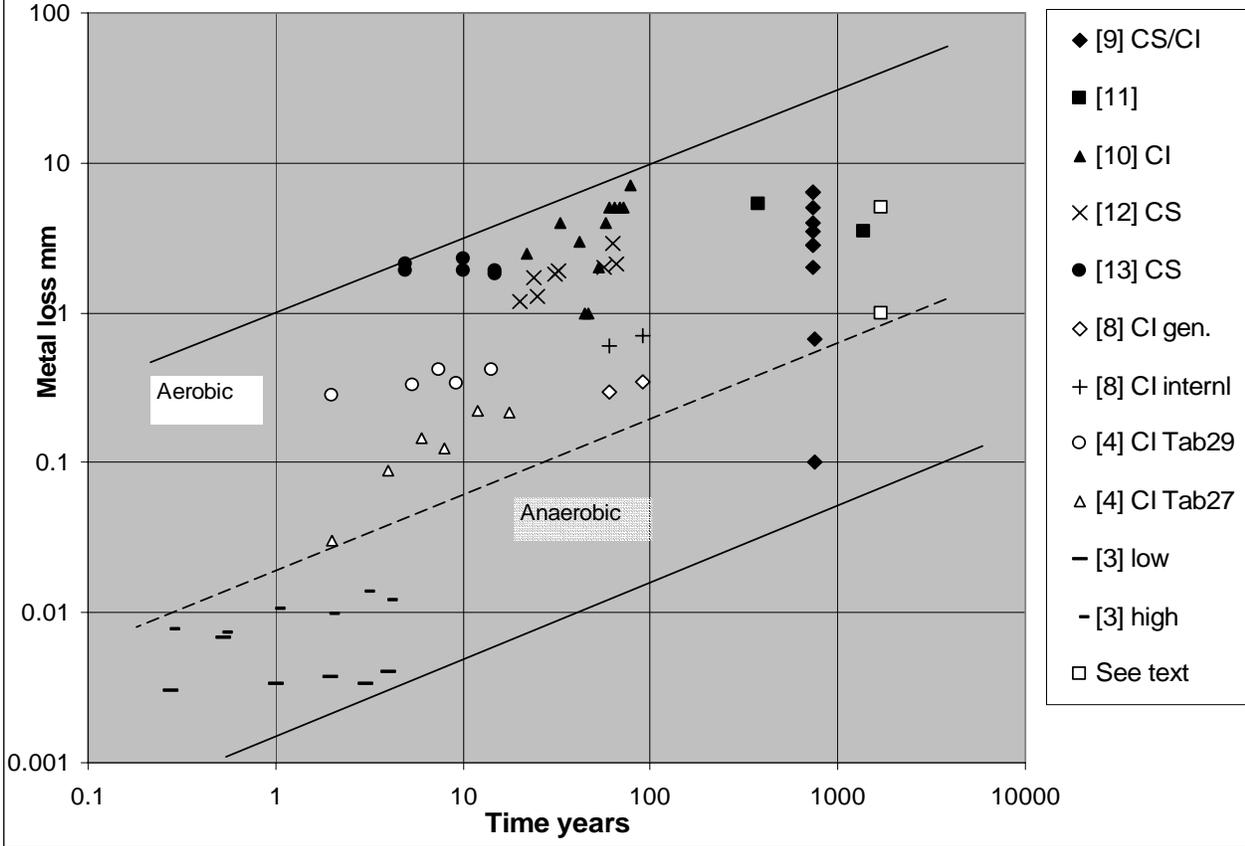
Fig.2: Carbon steel and cast iron corrosion in free water

Legend:
- □ [5] CI/CS fresh
- ▲ [5] CI/CS sea
- ● [6] CS sea
- ■ [7] CS sea
- ◆ [14] CI sea
- △ [1] CS ground
- ◇ [2] CS ground
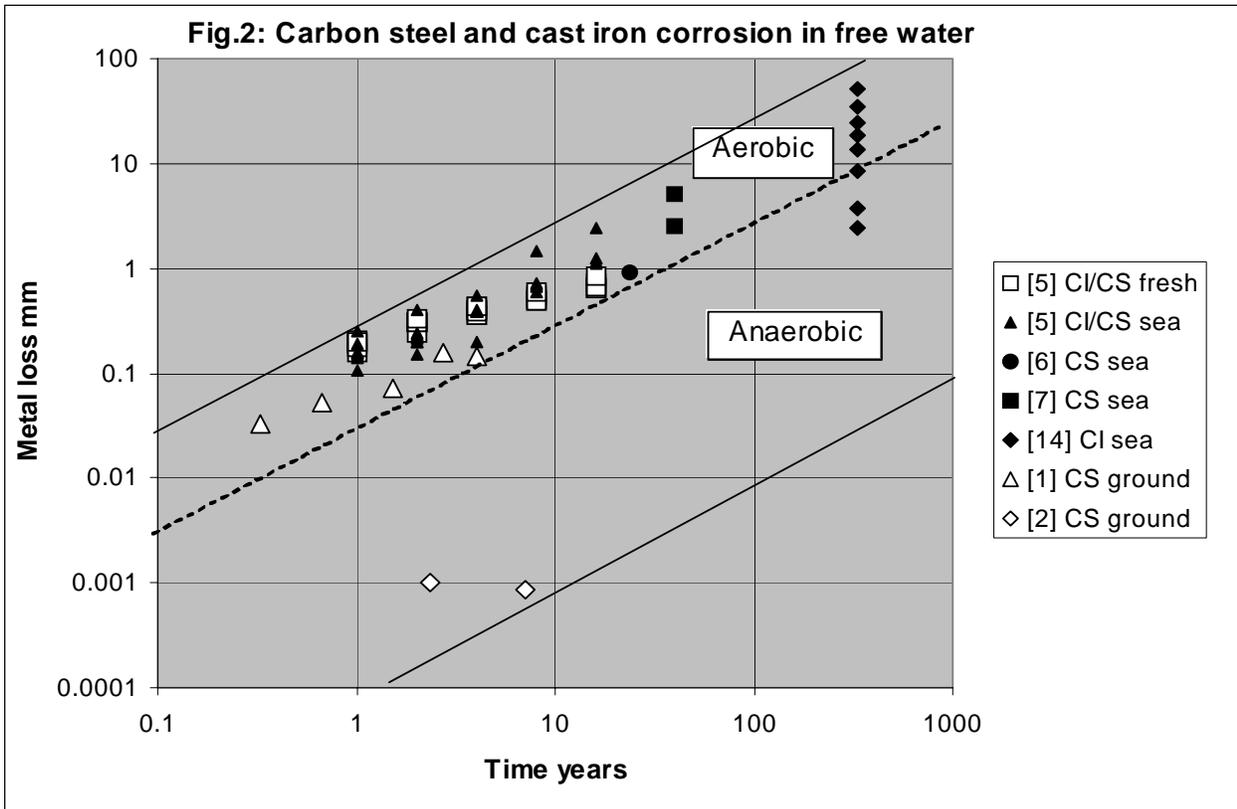
Furthermore, Figure 1 indicates that, not only is it possible to interpret the behaviour of individual data series as parabolic oxidation, but the complete dataset can be interpreted this way. With this interpretation, the effect of the different soil environments is to change the value of the parabolic rate constant (k1) in equation (1). It is well known that very low rates of corrosion result when iron corrodes under anaerobic conditions [15] and, for this reason the data are (somewhat arbitrarily) separated into aerobic and anaerobic regimes. For the aerobic corrosion data (i.e. points lying above the broken line) there is a variability of about times/divide ten.

For iron objects corroding in soil, a common observation is that the effect of the corrosion is to cement the soil around the object so that, when removed from the soil, the object may be completely unrecognizable until an X-ray photograph is taken or the soil/oxide concretion is removed. Once corrosion has progressed to this extent, it is difficult to distinguish between pitting and general corrosion and, for that reason, these forms of corrosion are not separately identified in Figure 1. In most cases the main corrosion product is goethite ($Fe_2O_3.H_2O$), sometimes with an inner layer of magnetite (Fe_3O_4). Occasionally there can also be an outer layer of magnetite but this is likely to be a transitional phase caused by a change from aerobic to anaerobic conditions. Under fully anaerobic conditions, magnetite is the main corrosion product. See, for instance, Pourbaix diagrams for the iron-water system in [16].

Corrosion of Iron in water

Figure 2 shows similar data for the corrosion of iron in water. Because the data show little difference between fresh water and seawater results, the figure includes data for both. The in-service data (≤40 year exposure) show results for cast iron and carbon steel that has been completely immersed in free water i.e. not exposed by tides nor covered by sediments. The archaeological data refer to cast iron cannon balls found in the C17 wreck of the *Wasa*. Figure 2 shows the spread of corrosion values presented by Barkman [14], who notes that the cannon balls were found in two stores in the hold. The most corroded were 'the outermost balls and those not covered by a thick layer of mud'. This suggests that the most corroded balls are likely to be most typical of free seawater. The two points at the bottom left of Figure 2 show laboratory data collected under anaerobic conditions at near-neutral pH where iron corrodes by the reduction of water to hydrogen [2]. Here, corrosion was measured from the amount hydrogen gas that was produced.

The upper and lower lines in Figure 2 have been drawn to bound the highest and lowest corrosion rates. The central broken line indicates the possible separation between aerobic and anaerobic conditions. The separation between the top and middle lines is less than an order of magnitude, suggesting a variability of about times/divide three for these data. The slope of the lines suggests that

$$W \approx k_2\, t$$
(2)

i.e. that metal loss increases approximately linearly with time.

Comparison of Pourbaix diagrams for the iron-water system in the absence and presence of chloride [16] shows that the main effect of the chloride it to extend the field of stability of goethite to lower pH values and, to a lesser extent, to lower Eh values also. This suggests that the corrosion products resulting from exposure to soil, fresh water and sea water will, to a first approximation, be the same.

LONG-TERM CORROSION OF COPPER AND BRONZE

The use of copper by humans stretches back about 6500 years. At first, native copper would have been used, followed by copper smelted from its ores. The chief impurities are iron and, especially, arsenic so that Early Bronze Age artifacts are mostly arsenical copper. Harder material (for cutting edges for example) was produced by cold working. Alloying of copper with tin produces bronze, which has superior mechanical properties while retaining good casting properties. In the Late Bronze Age, lead was added to further improve the ability to make high quality castings. Lead is normally absent from wrought material. Most ancient bronze is a single phase alloy, having a tin content of less than about 15% [17] and it is assumed here that this behaves similarly to copper.

Figure 3 shows corrosion versus time data for copper and bronze. Exposure times range from 2 to 8000 years, the latter referring to a bronze chisel from Jericho [18]. The environments are limited to burial in soil and burial in sea sediments and, because there is no obvious difference between them, all the results have all been plotted on the same graph. The data at less than 20 years all come from the work of Romanoff on pure copper [4]; the data at more than 2000 years are extracted from Tylecote [17,19] and Johnson and Francis [18] and refer to both copper and bronze; in between these dates is data from the *Kronan* cannon which, as reported by Hallberg et al. [20], is composed of 96.3% copper with 3.3% tin and minor amounts zinc and iron.

The two lines shown in Figure 3 are drawn with a slope of 0.5 (equation (1) above) and positioned to capture Romanoff's data (including pitting corrosion). It is remarkable that, when extrapolated, they enclose almost all of the 'ancient data'. The median parabolic rate constant in this case is about an order of magnitude less than that for iron. It is notable that the single data point for the *Kronan* cannon falls below the lower line. In their analysis of the cannon and the surrounding clay, Hallberg et al. concluded that there was insufficient oxygen in the surrounding clay to produce the observed quantity of corrosion products. Consequently, they argued that the corrosion products had mostly formed from the decomposition of tenorite (CuO), present as inclusions in the metal that were formed from slag during casting. They therefore estimated the depth of corrosion from observations of copper depletion seen just below the surface and this is the value shown in Figure 3. This result reflects the anaerobic conditions in the sediments surrounding the cannon.

Copper is insufficiently reactive to reduce water to produce hydrogen at neutral pH: examination of the Pourbaix diagram for the copper water system [21] shows that at low Eh values, metallic copper is stable. At higher Eh values, cuprite (Cu_2O) is the dominant phase; and at higher Eh values still and pH>6 tenorite (CuO) is stable. The presence of bicarbonate causes limited replacement of tenorite by malachite ($Cu_2CO_3(OH)_2$ [22]. Sulphide has a profound effect on the thermodynamics

Fig.3: Long term corrosion of copper and bronze in different environments

Legend:
- ◆ [19] soil
- ■ [20] sea
- ◇ [17] sea
- — [18] soil min
- - [18] soil max
- ✕ [4] soil mean
- + [4] soil pits
- ○ [4] soil lwr qtl
- ● [4] soil upr qtl

Y-axis: Metal loss mm
X-axis: Time years

Corrosion limited by availability of oxgen
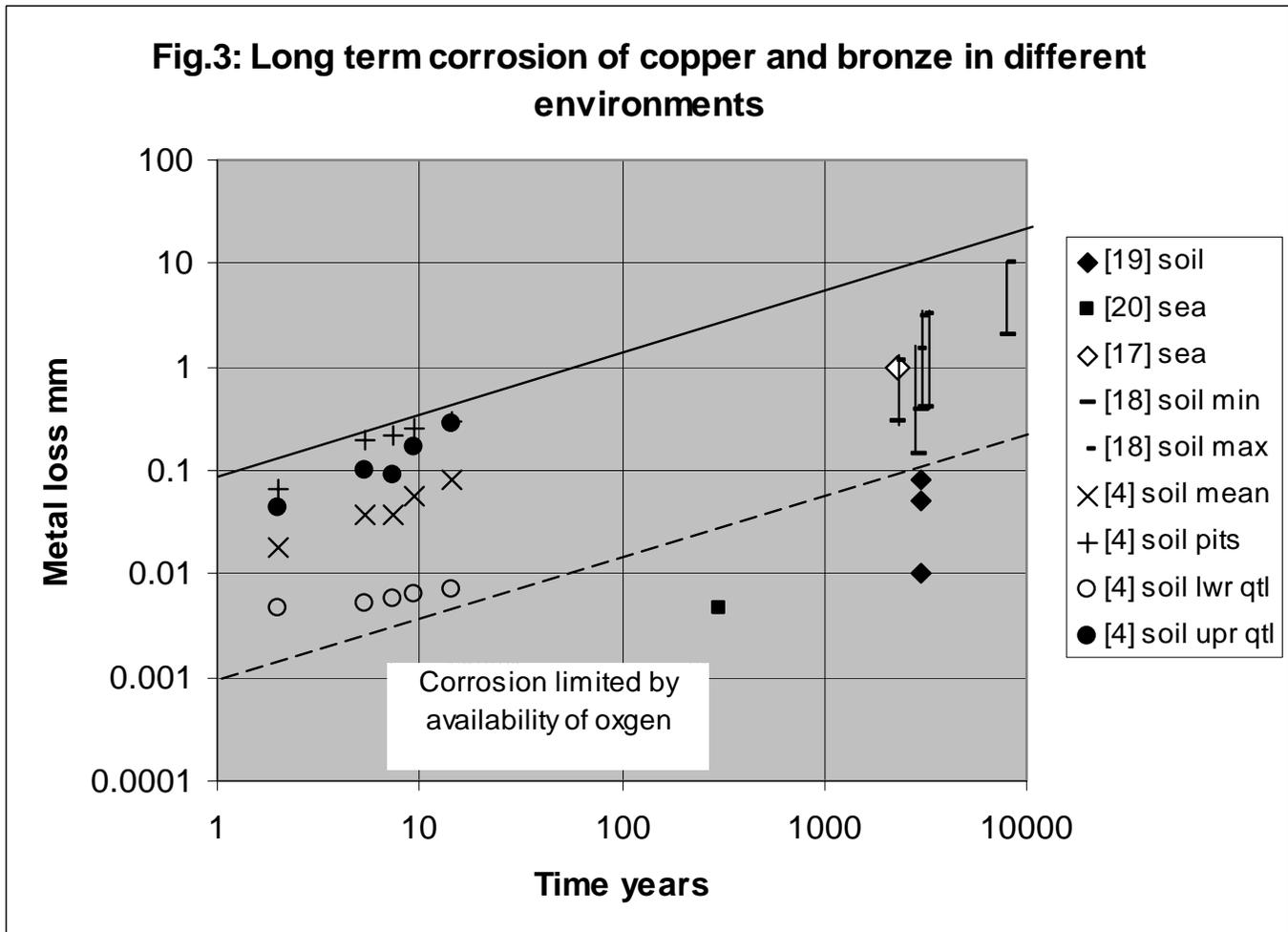
because copper sulphides can form even under reducing conditions. Hence, the effect of sulphide on the Pourbaix diagram is to reduce the size of the field of stability of metallic copper. Corrosion then proceeds with the formation of a layer of chalcosite (Cu_2S) covered by a layer of covellite (CuS).

In the presence of chloride ions (the chloride concentration of sea water is roughly half molar) cuprite and tenorite are replaced, at lower Eh and pH values, by the $CuCl_2^-$ ion. At higher Eh and near-neutral pH values, cuprite and tenorite are replaced by atacamite ($CuCl_2.3Cu(OH)_2$).

These thermodynamic predictions broadly agree with what is observed in practice. For instance, Hallberg et al [20] report the presence of cuprite and malachite corrosion products on the *Kronan* cannon. Detailed laboratory investigations of copper corrosion in bentonite clay saturated with saline groundwater indicate the presence of atacamite, possibly overlying cuprite [23]. However, while it is known that commercially available bentonite clays may contain sulphide (as iron pyrite) up to about 0.1%, corrosion of copper in bentonite clay appears not to produce copper sulphides unless additional sulphide is added. Given the effect – both predicted and observed - of chloride on copper corrosion (particularly its ability to promote

pitting) [21], it is surprising that the datasets for corrosion in soil and seawater in Figure 3 appear so similar.

DISCUSSION

Oxidation of iron in soil

Parabolic oxidation results from some form of diffusion control. In the present context this could be diffusion of a species through the oxide layer or alternatively, for iron oxidising in low porosity soil, diffusion through the soil. It needs to be remembered, however, that the data shown in Figure 1 relate to both saturated and unsaturated conditions and to a wide range of soil permeabilities. Because humid, unsaturated conditions will allow rapid movement of air and moisture through the soil, this effectively disallows the second possibility for most of the environments relevant to Figure 1. We also note (i) that rusting iron objects often form a concretion with the surrounding soil, and (ii) that duplex scales can form with magnetite adjacent to the metal surface and goethite further away. These observations are consistent with the outward diffusion of Fe^{++} ions from the magnetite-goethite interface to the goethite-soil interface, and with the precipitation of fresh goethite within the soil porosity to form a concretion (Figure 4). The process of concretion is promoted by

4

the high molar volume of goethite (about three times that of iron).

The effect of the surrounding soil on the kinetics is twofold: it promotes access of water and dissolved oxygen to the goethite/soil interface through capillary flow, and it serves as a substrate that fixes the oxide in position and prevents its being dislodged by gravity and/or internal stress. If the oxide does separate from the metal due to internal stresses, this will open a new, rapid transport path for oxygenated water that will eventually be filled by newly formed goethite. We note, however, that some voidage must remain in the goethite-soil concretion to allow Fe^{++} ions to diffuse through it in solution. The presence of the soil and, in particular, sorption of Fe^{3+} to the soil, will also limit the rate of dissolution of the scale by reducing the mobility of Fe^{3+} in infiltrating groundwater.

At low oxidation potentials, iron can corrode by the direct reduction of water to form gaseous hydrogen. It is suggested that these conditions apply to the lowest corrosion rate data shown in Figure 1. For objects buried in the near-surface environment, this situation is most likely to arise when the combination of corrosion and microbial action reduces the oxygen concentration and, simultaneously, the porosity of the medium surrounding the metal object is too low to allow the oxygen to be replenished. Such conditions may have been present in the steel-in-bentonite experiments of [3]. In situations like this, we can imagine that, with oxygen present initially, a duplex magnetite-goethite scale will form. Then, as the oxygen concentration falls, the goethite will be reduced to magnetite. Again, the soil serves to prevent the corrosion product from being dislodged or dissolved.

Figure 1 suggests that under these anaerobic conditions corrosion is again diffusion controlled. Depending on the magnitude of the various diffusion coefficients, the rate of scale thickening may depend on diffusion of any of several species through the magnetite scale; alternatively it may be diffusion through the low permeability soil that is rate limiting. This is discussed further at the end of the next sub-section.

Iron corrosion in water

In contrast to its behaviour in soil, when iron corrodes in aerobic free water, it does so at an approximately constant rate (about 0.1 mm y^{-1}). We also note that the corrosion products formed in soil and water are essentially the same. In terms of the mechanical stability argument offered for corrosion in soil, it is clear that, when iron corrodes in water, there is no porous material adjacent to the corroding object that would fix the corrosion products into position. A possible exception to this is the formation of biological growths on iron in seawater. These growths include calcareous fauna such as barnacles and limpets and microbial membranes. It has been variously claimed that these both increase and decrease corrosion and, certainly, they do promote crevice corrosion in stainless steel. But the indistinguishability (in Figure 2) of the fresh and sea water data, as well as laboratory data collected under (presumably) sterile conditions, suggests that this is not a dominant effect. Instead, the most likely explanation is that dissolution of the oxide, or cracking and spalling under the action of internal stresses, maintains the scale at a roughly constant thickness.

Fig 4: Formation of soil-oxide concretion through outward diffusion of Fe^{++} ions
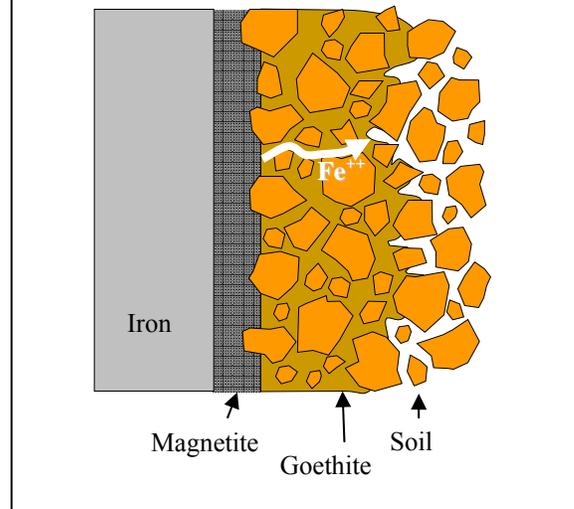
The observation of linear oxidation kinetics at long times in free water is consistent with earlier observations from laboratory studies [2,24]. In this earlier work it was concluded that the early stages of corrosion (times less than about one year) are diffusion controlled but that, eventually, a steady rate is achieved when the rate of oxide dissolution equals the rate of formation.

For corrosion in free water under truly anaerobic conditions, Figure 2 has very little data so that any interpretation must be tentative. At t≈330 years the corrosion data [14] come from cannon balls retrieved from the wreck of the *Wasa*. As noted above, the lowest corrosion rates correspond to cannon balls that were either in the middle of a heap or covered by a thick layer of mud. It seems reasonable, therefore to attribute these lower rates to anaerobicity. The two points at bottom left show results at 2 and 7 years for a plain carbon steel in groundwater of pH 7 (buffered and unbuffered) with the metal loss derived from the amount of hydrogen generated. The corrosion rates are low, about 0.1 μm y^{-1}, which is 10-100 times lower than rates suggested by other data in Figure 2 and lower, even, that the steel-in-bentonite data [3] in Figure 1. If the data derived from hydrogen generation [2] are correct, they imply that diffusioin through magnetite may be more rate-limiting than diffusion through the bentonite. It would be helpful if the use of hydrogen generation measurements to estimate very low rates of corrosion could be corroberated by another technique.

Corrosion of Copper

Unlike the data for iron, the data on copper corrosion (Figure 3) contain little or no information on corrosion in free water. The *Kronan* cannon [20] was buried in sediment and the other data point relating to corrosion in sea water [17] is described as having formed a concretion. These results do not, therefore, provide any information about the long-term kinetics of copper corrosion in free water.

Figure 3 does show, however, that parabolic oxidation provides a reasonable description of the kinetics of copper oxidation in soil. As with iron, concretion of copper in soil is commonly observed [17] and suggests that corrosion is accomplished by the outward diffusion of copper (as opposed to the inward diffusion of oxygen), a conclusion previously reached by [23] in relation to experiments performed on the corrosion of copper in bentonite. In the absence of sulphide, copper does not corrode under anaerobic conditions. Although Tylecote [19] maintains that there was 'little evidence of anaerobic conditions operating in the case of most of the finds referred to', some of the better preserved finds (for example a 3000 year old spear head found in tidal muds and a palstave found in peat) were, given the presence of organic matter, almost certainly exposed to anaerobic conditions. These objects are described as having a 'patina' – implying, perhaps, a surface layer of a few tens of microns – but they have not been plotted on Figure 3. To indicate the possibility of near-zero corrosion rates under these conditions, the label 'corrosion limited by availability of oxygen' has been placed at the bottom of Figure 3. Nevertheless, the warning of Puigdomenech and Taxen [25] that the 'concept of redox potential, Eh, has been found to be inadequate to describe copper corrosion in a nuclear repository' should alert the reader to the importance of other geochemical variables such as sulphide content.

CONCLUSIONS

A comparison of corrosion data on iron and copper from laboratory, field, in-service and archaeological information allows some conclusions to be drawn about the kinetics and the rate-determining mechanisms over timescales extending from less than a year to up to a few thousand years:

1. The kinetics of the corrosion of iron and copper in soil are adequately described by the parabolic rate equation. The main effect of soil/environmental conditions is to change the parabolic rate constant. In contrast, the rate of iron corrosion in aerobic free water is constant with time with a value of about 0.1 mm y^{-1}.

2. When iron and copper corrode in soil it is common for the corrosion products to form a concretion with the surrounding soil. This suggests that corrosion proceeds by the outward movement of metal ions and the formation of the corrosion products within the soil porosity.

3. Combining these two observations, it is suggested that, when iron or copper objects corrode in soil, the soil influences the kinetics in two ways: (a) it provides, through capillary action, oxygenated water to take part in the corrosion reaction; and (b) it acts as a substrate that stabilizes the corrosion product by preventing spalling and reducing dissolution. The presence of the surrounding soil thus brings about the conditions that lead to parabolic kinetics.

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