FACTORS INFLUENCING THE CORROSION RATE OF METAL OBJECTS

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Introduction

It is a basic principle that all metals (excluding the noble ones) are chemically unstable in ordinary air, but this can hardly be said to be part of common knowledge. In spite of this fact many metals appear quite permanent in many everyday surroundings. The reason for this and the reasons why metal corrosion occurs under other circumstances are fundamental questions of corrosion science.

When metal comes in contact with oxygen a chemically unstable state is created. The corresponding stable state is metal oxide. A metal can, for obvious geometrical reasons, only react with oxygen where it is in contact with it (ie on the metal's surface). That is why all non-noble metals are covered with a layer of metal oxide (although this layer often is so thin that it is invisible).

Metals which are covered with a protective oxide have such properties that they can form a barrier against surrounding oxygen and are potentially useful for making metal objects. Other properties such as hardness, ductility etc are of course also determinants of their usefulness.

The nobility of the metal (ie its tendency to chemically convert into an oxidized state) is of importance for the development of corrosion reactions. For example, zinc is less noble than iron. That means that it has a greater electrochemical tendency to convert into chemical compounds than iron has. If an object made partly of zinc and partly of iron is placed in an aerated water solution, the zinc will corrode first and leave the iron practically uncorroded as long as the zinc remains in contact with the iron.

In another situation the relatively less protective properties of corrosion products on surfaces determine the corrosion rate. A practical application of this is the common practice of covering iron with zinc ("galvanizing"). This treatment is useful because zinc corrodes slower in outdoor environments than iron, since the zinc corrosion products in the atmosphere are more protective for the metal compared to porous iron corrosion products.

Wet and dry corrosion

The occurrences of corrosion are usually divided into two main categories: dry and wet corrosion. Limiting the discussion to archaeological metal objects, one could say that dry corrosion is typically found in two situations.

Objects from, for example, cremation graves, have been oxidized in fire before they were deposited in the soil. As a result of these heat treatments, the objects were covered with oxide layers. Such oxide layers often withstand millennia of exposure in soil. This is the case for magnetite layers on iron objects. The other important type of dry oxidation for archaeological metal objects is often found in museums. Polished copper and silver surfaces are stained in atmospheres containing sulphur compounds with sulphur in the oxidation state -II. The sulfide containing corrosion products of copper and silver are less protective since matter can be transported through them at marked rates by diffusion. Usually the diffusion rates in oxides are very slow at ordinary temperatures and therefore oxides normally constitute very effective barriers against the surrounding atmosphere.

The majority of important corrosion phenomena is wet corrosion. The presence of liquid water on metal surfaces (even with very thin layers) allows the possibility for electrochemical reactions. These reactions are of two kinds, cathodical and anodical. They can occur spatially separated from each other but must then be connected via an electrical conductor in which electrons can flow. The reason for this is that the anodic reactions produce electrons which are used for the cathodic reactions. The two kinds of reactions balance each other so that all produced electrons must be consumed and vice versa. Electrochemical corrosion can therefore be limited or controlled by introducing restrictions in one of three phenomena:

- the anodic reaction
- the cathodic reaction or
- the electrical current which unite the reactions

The anodic reactions convert the metals from elements to metal ions and electrons. The most important cathodic reaction, for corrosion processes, is the reduction of oxygen dissolved in water to form hydroxide ions by taking up the electrons generated by the anodic reactions.

The soil environments from which archaeological objects are excavated are more or less wet. In the temperate climatic zone the prerequisites for wet corrosion are almost always fulfilled in unfrozen soils. In spite of this, corrosion rates vary a great deal between different soil environments. Corrosion problems with technical equipment such as steel pipes and poles have necessitated the development of a field of soil corrosion technology.

Soil corrosion technology

Corrosion research can be divided into the scientific and technological areas. There is no clear distinction between these two fields.

Corrosion technology usually avoids complicated theoretical models and is mainly based on experience and evaluations of relatively simple experiments and standard measurements.

In corrosion science theories and hypotheses are formulated and tested. For these purposes corrosion conditions in liquids or atmospheres are easier to work with than soil conditions (which are difficult to define and reproduce). This is probably the reason for the relatively little work done on soil corrosion science compared to soil corrosion technology. Another reason for this situation is that the need for knowledge concerning soil corrosion emanates from technology. Corrosion rates in soils of the magnitude 0.1 millimeter per decade or more are considered to be of technical importance and require countermeasures.

The technological aims of corrosion research in soil can be taken up in one of two fields. The first one concerns the construction of a set of reliable criteria for determination of whether there is high potential corrosivity in a given soil or not. The second one concerns development of cheap and reliable corrosion countermeasures, such as coatings or cathodic protection. Therefore soil corrosion technology is mainly concerned with problems in environments where only relatively young iron artifacts are not completely corroded.

The technological criteria used in estimating soil corrosivity are based on measurements of electrical resistivity, pH and concentration of some ions such as hydrogen carbonate and chloride (German Standard DIN 50 929) in the soil. Sulphur content of the soil is also considered to have a great influence on corrosion rates in soil. The most important factor for the corrosion rate of iron in soil is, however, whether the corroding object in question is above or below the ground water table. Below the ground water table the transport rate of oxygen is the step that determines the rate for the corrosion of iron (Iversen 1988, Camitz and Vinka 1989).

Archaeological metals in soil

The conditions which are prevalent at the time of the excavation may often be very different from the ones that prevailed some time after the deposition of the material. The objects may have been placed in containers made of organic materials which created a microclimate. This should have resulted in corrosivity similar to a den in the earth rather than soil conditions. In other cases, the environment might have been dominated by organic material from, for example, a decaying body in a grave or waste materials in a compost heap. In order to gain knowledge about the possible changes in the environment over time and their nature, archaeological evidence from excavations should provide valuable information. Physical conditions, such as particle size of the soil and factors influencing the water flow around the object can be expected to influence the corrosion rate. As well, as various chemical factors such as the chemical composition of the soil constituents, the pore water composition and the pH levels can also affect corrosion rates.

It might be assumed that biological processes can also have an important influence on corrosion processes in soil. There are at least two kinds of processes which seem to have great potential influence. The first is oxygen-consuming and carbon dioxide-producing fermentation of organic materials. This can on one hand lower the availability of oxygen so that the corrosion processes are slowed. On the other hand carbon dioxide dissolved in water increases the solubility of certain corrosion products. The second kind of processes are caused by sulphur bacteria of different kinds which promotes transformation of sulphur between the oxidation states -II and +VI which may have influence on corrosion mechanisms.

Bronze corrosion

Archaeological bronze objects are attacked to a lesser degree by corrosion than iron objects. The corrosion products usually consist almost entirely of cuprite, malachite and stannic oxide (Nöggerath 1825, Becquerel 1832, Fink and Polushkin 1936, Gettens 1951, Geilmann 1956, Otto 1961, Walker 1980, Ullrich 1985, Tylecote 1979, Grauer 1980). Malachite is typically expected to form a protective layer under appropriate conditions. This can also be true of cuprite. The stannic oxide is amorphous and can probably be described as a hydrogel. It should therefore not be expected to act as a protective barrier.

The stannic oxide is precipitated within the boundaries of the original shape of the object. This often allows even completely corroded bronze objects to keep their original shape.

According to the classical article by Geilmann (Geilmann 1956) bronze artifacts can be completely corroded in sand with high organic content. They can even be transformed so extensively that they become white objects of tin oxide. This shows that leaching - or using the pedological term "eluviation" - of soluble copper compounds from bronze objects, is an important factor for the deterioration mechanisms of bronze in soil. Low pH from carbonic acid and substantial water transport are bound to promote this process. These circumstances are also known from the field of corrosion technology. Conditions which lead to dense coatings of corrosion products on copper alloys lead to low corrosion rates (Linder 1984). Unsuitable pH values ie below pH 7 lead to relatively rapid corrosion attacks.

It can therefore be concluded that the most detrimental factors for copper alloys in soil seem to be those which promote eluviation of inter alia malachite and cuprite. These processes include lowering the carbonate activity (eg by lowering the pH) and lowering the copper(II) ion activity (by reactions such as complexation). Ion exchange with clay minerals can also play a role.

The literature describes several cases of bronze artifacts with banded structures of malachite and cuprite in the stannic oxide layer. These have been found covering the remaining metal core. The mechanisms of formation of these banded structures does not seem to be completely understood, but the interpretation of the so called Liesegang type patterns indicate influence of diffusion in the tin hydroxide gel (Scott 1985, Robbiola et al 1988).

In soils with high chloride content, copper(I) chloride (nantokite) is often formed in the inner parts of the corrosion product layer.

It should be remembered that archaeological brass objects are often referred to as bronze. The corrosion of brass objects is similar to that of bronze objects with the main difference being that no tin oxide hydrogel layer can then be formed. There seems to be very little known regarding details of influence by humic and fulvic acids or other soil components with high ion exchange capacities on corrosion mechanisms.

Iron corrosion

The details of the corrosion process of iron objects in soil seem to be more complicated than those of bronze. According to Stambolov (1985), who quotes many publications, the most commonly found corrosion products in soil are magnetite and goethite. The reason for this is explained by Turgoose (1982), who also proposes a model for corrosion of iron in soil. This model includes the anodic reaction of iron oxidation to ferrous ions and the cathodic reduction of oxygen to hydroxide ions. These two reactions are assumed to occur spatially separated by a layer of "largely magnetite and goethite with perhaps some other stable ferrous-compounds". A water solution which may contain high concentrations of ferrous ions is assumed to be contained in pores of the deposited corrosion products. The counter ion is usually chloride. The accumulation of chloride ions is explained by the flow of ionic current between anodes on the metal surface and cathodes on the surface of the deposited corrosion products. These are assumed to possess electronic conductivity.

The corrosion model described above is in accordance with established corrosion theory and seems to give a reasonable explanation in qualitative terms. However, a semiquantitative treatment of the accumulation of ferrous chloride raises some questions. Corrosion rates on archaeological iron objects with chloride enrichments are usually on the order of millimeters per millennium. The corrosion current density for a corrosion rate of 1 mm/millennium can be calculated by considering 1 cm^2 of an iron surface.

- 1 mm penetration corresponds to 0.786/55.847 = 0.014 moles of iron.
- In the corrosion reaction electrons are delivered to generate the charge 2x0.014x96500= 2700 As.
- Division by the number of seconds in 1000 years, 31536000000,gives as a result that it is equivalent to a current density of 0.1 $\mu A/cm^2$.

This is a very low current density. From the above we can also calculate the case if all anionic charge transfer is accomplished by chloride ions. There would then be a flow of:

$$2x0.014/1000 = 28x10^{-6} \text{ mole}$$

chloride ions towards 1 cm^2 of anodic surface per year.

In the opposite direction there must be a diffusion of ferrous chloride from a concentration on the metal surface of the magnitude 1 molar compared to the magnitude of some millimolars in chloride (and much lower in iron(II) ions) in the pore water solution of the surrounding soil. This is assumed to have a composition in the normal range for ground waters.

Diffusion coefficients for salts are of the magnitude 10-5 cm^2/s. Approximating the rust layer to a thickness of ca 10 mm, there is a concentration gradient of 10^{-3} $mole/cm^2$.year. Based on these data Fick's first law gives a diffusion flux equivalent to 0.3 $mole.cm^{-2}.year^{-1}$. This is four orders of magnitude larger than the assumed flux of chloride ions which serve as charge carriers. Even with very small pore sizes it seems unlikely that electrophoresis alone could counteract diffusion to such an extent, and that this could lead to substantial accumulations of ferrous chloride between the layer of solid corrosion products and the metal surface. With small pores in the layer, ion selective properties should be expected in ferric hydroxide membranes. This has been investigated by N. Sato and co-workers (eg Sakashita et al 1984). In these studies it was found that ferric hydroxide membranes are anion selective below a pH of about 10. This property leads to an electro-osmotic flow of chloride ions. Sato et al concluded that these play a significant role in the corrosion of metals. Perhaps these matters deserve additional attention in research regarding corrosion in soils.

There has so far been limited interest in these questions among those who work with corrosion problems in soil. This is in contrast to the great development in similar fields described in modern literature on surface and soil science (Lindsay 1979, Stumm 1987). Many examples can be found of fruitful approaches to phenomena in soil that also should be possible to apply on questions regarding corrosion in soil.

Conclusions

The above discussion gives a somewhat simplified survey of the most important factors for metal corrosion, with special emphasis on soil corrosion of archaeological metal objects. The following conclusions can be drawn:

- The principle inorganic chemical equilibria and thermodynamic data for virtually all corrosion products formed by corrosion of metal artifacts in soils seem to be known today.
- There are, however, important gaps of knowledge regarding details in reaction mechanisms.
- For an understanding of these questions more cooperation between corrosion science and modern soil chemistry may contribute to greater understanding of the problems addressed in this paper. Of course the close cooperation of archaeologists will be necessary to the success of such work.

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