

Chapter 7

Erosion bacteria and sulphur

(by Huisman)

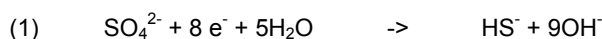
7.1 Introduction

The presence of reduced sulphur compounds in archaeological wood poses great problems with respect to long-term *ex situ* conservation. In an oxidising atmosphere, the compounds tend to oxidise. As a result the wood becomes covered with yellow, orange and sometimes white mineral blooms. Moreover, the oxidation of the sulphur compounds produces sulphuric acid, which causes major damage to the wood structure. The most well-known example where such problems occur is the Swedish Warship Vasa, where this problem occurs on a major scale (Sandström et al., 2002). It is, however, not unknown in other places, e.g. Roskilde (Jensen, *pers. comm.*) and Lelystad (the Ventjager; *unpublished data*). Presently, a large research effort is being put into developing methods of protecting archaeological wood - i.c. the Vasa - against the oxidation of reduced sulfur species in the wood.

7.2 Sulphur in BACPOLES

For the BACPOLES project, the problem of reduced sulphur species in wood is relevant as long as it is connected to erosion bacteria. In this section, an overview will be given of what is known from literature and of the interaction of reduced sulphur species formation with erosion bacteria. The origin of the reduced sulphur species and the oxidation processes that occur under oxic conditions are well known from the fields of soils science ("acid sulphate soils"), geochemistry (pyrite formation and "acid mine drainage") and conservation of marine iron artefacts. The processes leading to the accumulation of reduced sulphur species in wood can be subdivided into two types: The first type are the processes that cause the formation of iron-sulphur (Fe-S) corrosion scales on iron objects (including nails) in or next to the wood. The second type are the processes of formation of sulphur compounds that occur naturally on the sea floor sediments, and that may also occur in buried wood:

Metallic iron oxidises very easily. In the presence of oxygen it will react with it to form Fe^{3+} (precipitating as Fe_2O_3 and FeOOH). In the absence of oxygen, other electron acceptors are needed to oxidise the iron. In reduced marine settings, the sulphate (SO_4^{2-}) that is abundantly available from seawater usually takes on this role. It is reduced to sulphide according to:



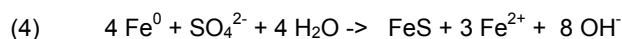
However, it is not able to oxidise Fe further than Fe^{2+} :



Fe^{2+} and HS^- subsequently precipitate as ironmonosulfides:



Combining half reactions (1) and (2) with the precipitation reaction (3) gives the overall reaction:



This reaction results in the formation of a scale of black iron sulphides with sediment particles that surrounds the iron object (fig 1), or - if the corrosion has progressed far enough - a cavity in the shape of the original object. If the iron object is surrounded by wood, the precipitating iron sulphides will precipitate inside the wood (fig 2).

When no elementary iron is present, the formation of iron sulphides and other reduced sulphur species is triggered by the reduction of sulphate through organic matter, which is traditionally described as:



The reaction of organic matter here represented as CH_2O however, is in fact more complex: It involves fermentation processes that produce hydrogen gas (H_2), methane (CH_4), and short-chain organic molecules like acetate (CH_3COOH). These components then react with the sulphate forming HS^- . The sulphide formed in this way can react with Fe^{III} minerals like goethite (FeOOH) and magnetite (Fe_2O_3) that are present in the sediment according to the overall reaction:

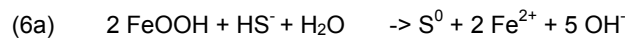


Figure 1: Example of iron object - two iron chain rings - with a scale of FeS-encrusted sand. (De Meern 1)

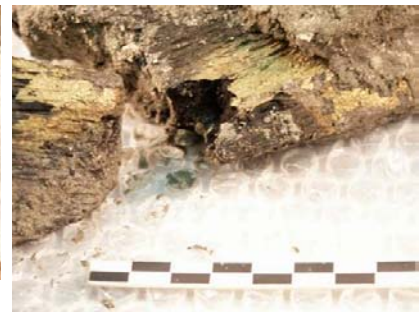


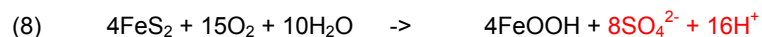
Figure 2. Fragment of wood with iron nails; iron sulfides - a lustrous gold color - have formed in a crack inside the wood.

The Fe^{2+} that is formed in this way reacts with the HS^- present (see reaction 5) to form an iron monosulphide (reaction 3). Part of the iron may also be formed by direct reduction with organic matter analogous with reaction (5) but this is not necessary. This monosulphide is usually relatively unstable. In most environments, it reacts with the elementary sulphur formed in equation (6) to form pyrite:



Pyrite is a relatively stable mineral, and will only be attacked under reducing conditions. It is often present in a so-called framboidal shape; it then consists of groups of spheres each of which is built-up of a large number of separate pyrite crystals. However other shapes (large crystals, massive concretions) sometimes occur also.

If exposed to oxygen, reduced sulphur species will react with it to produce iron oxides and sulphuric acid according to (sulphuric acid in red):



The oxidation reactions for FeS and S^0 are similar and also produce sulphuric acid. While this reaction goes on, intermediate products may be formed including Fe(II,III) sulphates (e.g. FeSO_4) Sulfur (S^0 or S_8) and Jarosite $(\text{K,Na,H})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$. In the presence of lime, gypsum (CaSO_4) may be formed also. Mineral "blooms" of yellow jarosite accompanied by orange-red iron oxyhydroxides and sometimes white gypsum are indicators for the occurrence of these reactions.

7.3 Conclusions

Pyrite seems to occur quite frequent in wood from both piles and archaeological sites (Klaassen and Nilsson, pers. comm). This indicates that the environment inside the wood has become sulfidic (i.e. anoxic) at some point up to the moment of sampling. It also indicates that sulphate was available inside the wood. Assuming that erosion bacteria were active during the formation of the pyrite, this suggests that erosion bacteria are at least facultative anaerobes, as oxygen is not present in sulfidic environments.

The formation of sulphides like H_2S (or HS^-) and FeS_x during wood decay by erosion bacteria - as observed in chapter 3 - indicates that erosion bacteria facilitate the activity of sulfur reducing bacteria; probably by providing CH_4 or other short-chain organic molecules. Erosion bacteria could function as the basis of the food chain of large bacterial communities. It also strengthens the suggestion that erosion bacteria are (at least facultative) anaerobes. There is not enough information to make a correlation between the degree of attack by erosion bacteria and the S-content in the wood.

The potential toxicity of sulphides towards erosion bacteria may be the basis for a potential method of inhibition of degradation; injection of sulphate in wood would potentially reduce the speed of erosion bacteria degradation. However, it would not be able to completely halt this degradation mechanism.