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The stabilization of archaeological iron objects: Mössbauer and XRD studies

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Abstract Archaeological iron objects that were buried in the ground for long times often corrode rapidly once they have been excavated. We have used Mössbauer spectroscopy and X-ray diffraction to elucidate some specific problems of the corrosion of such objects and gain insights that may help to improve the methods of conservation.

Keywords Mössbauer spectroscopy · Archaeology · Iron objects · Corrosion · Conservation

1 Introduction

Archaeological iron objects that were buried in the ground for centuries or millennia often corrode rapidly once they have been excavated and come into contact with air. Their conservation poses severe problems, both for objects on exhibition in museums and for objects stored elsewhere. A variety of treatments and manners of storage have been proposed for the conservation of such objects [1, 2], but they do not always yield satisfactory results.

^{57}Fe Mössbauer spectroscopy has been used widely in studies of iron corrosion (e.g., [3–6]), and the corrosion processes of archaeological artefacts both during

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burial and after excavation have been investigated (e.g., [7–11]). The identification of the various iron oxide and oxyhydroxide phases formed during burial, after excavation and after various conservation treatments is an important application of Mössbauer spectroscopy. The oxides observed as corrosion products are mainly goethite, akaganéite, maghemite and hematite. Akaganéite ($FeO_{0.833}(OH)_{1.167}Cl_{0.167}$ according to Ståhl et al. [12]) in contact with the metallic surface is deemed to be particularly obnoxious [1], because it may release chloride ions and thus promote corrosion, though free chloride may often rather be the real culprit [12].

We have used Mössbauer spectroscopy and X-ray diffraction to elucidate specific questions arising in the analysis and conservation of archaeological iron artefacts from the heydays of the Celtic Culture in Central Europe (300–15 BC), e.g., nails, tools and weapons, many of them from the Celtic oppidum of Manching in Bavaria, Germany. Some objects had already been restored and subjected to conservation treatments decades ago, and with varying success. Their study allows an assessment of the long-time behaviour of restored material. In this paper we will report on some of the results obtained in this context.

2 Sensor for the efficiency of sealing methods for excavated objects

Since iron often begins to corrode rapidly on contact with air right after excavation, it is essential to protect the artefacts already at the site of excavation, for instance by sealing them into appropriate plastic foils. Mixtures of iron powder and ferrous chloride ($FeCl_2 \cdot 4H_2O$) have been suggested [13] as sensors to test such sealing methods. We have used 1:1 mixtures by mass of iron powder (grain size ca. 5 μm) and $FeCl_2 \cdot 4H_2O$ for this purpose. Experiments with such mixtures sealed into different plastic foils with or without drying agents and/or oxygen scavengers were performed as well as experiments in containers with controlled humidity and temperature. The reaction products were analyzed by Mössbauer spectroscopy and XRD.

At high humidity a complete reaction to akaganéite (called akaganéite M in the following) occurred, with no metallic iron or iron chloride left, as both the Mössbauer spectrum (Fig. 1) and the XRD pattern (Fig. 2) show. From the 1:1 mixing ratio of Fe and $FeCl_2 \cdot 4H_2O$, a Fe:Cl ratio of 1:0.278 results, which is higher than the ratio of 1:0.167 found by Ståhl et al. [12] for akaganéite. The mixing ratio of Fe and $FeCl_2 \cdot 4H_2O$ could, in fact, be varied between 1:0.6 and 1:1.2 and still a virtually complete reaction to akaganeite occurred, indicating that the akaganéite forms with widely different chlorine contents, either in its structure or adhering to the surface of crystallites. The RT Mössbauer spectrum of akaganéite M (Fig. 1) is different from that of akaganéite made by slow precipitation from a hydrous solution of $FeCl_3$ according to Schwertmann and Cornell [14] (akaganéite S, Fig. 1). While the latter is still all paramagnetic at 298 K, the former is largely magnetically ordered, though with a broad distribution of hyperfine fields around the mean value of 24 T, indicating that the ordering temperature is not far above ambient temperature. At 4.2 K the spectra of both akaganéites are virtually identical. The XRD patterns of the two akaganéites are also different: Akaganéite M exhibits a more pronounced monoclinic distortion than akaganéite S, which results in some of its diffraction peaks to split into two (Fig. 2). The different distortions may depend on the Cl content of the akaganéite.

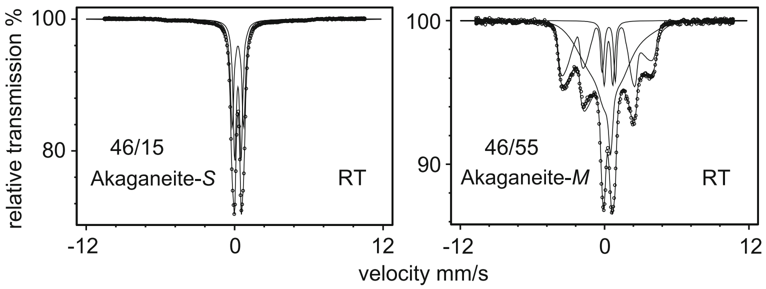

Fig. 1 ^{57}Fe Mössbauer spectra recorded at 298 K of akaganéite S (*left*) and of akaganéite M (*right*)

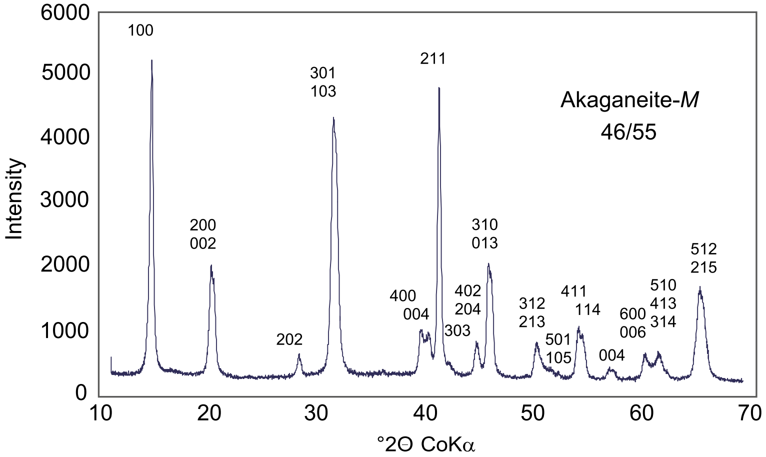

Fig. 2 X-ray diffraction pattern of akaganéite M made by the solid state reaction of a 1:1 mixture by mass of iron powder and $FeCl_2{\cdot}4H_2O$

3 Removal of akaganéite from iron objects by leaching methods

Akaganéite or free chloride ions present in the corrosion layer close to the metallic iron are believed to promote further corrosion [11]. It is therefore a major goal in the conservation of iron artefacts to remove chloride and akaganéite. For this, desalination by leaching in water or in solutions of NaOH or NaOH/Na_2SO_3 mixtures is often used [1]. The conversion of akaganéite into chlorine-free compounds can be monitored by Mössbauer spectroscopy. It turned out that solutions containing both NaOH and Na_2SO_3 are quite effective in converting akaganéite into goethite and hematite already at ambient temperature, while pure water or NaOH solutions do not affect the akaganéite (Fig. 3), though they may remove free chloride [15].

4 Studies on Celtic nails

As examples of corrosion studies on archaeological artefacts we report on two rather well preserved Celtic nails from the oppidum of Manching. Nail 46/43 was excavated

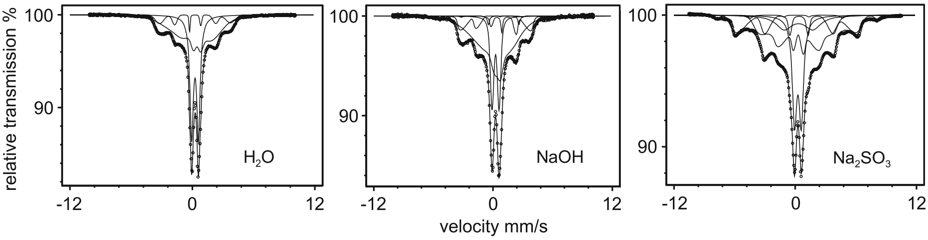

Fig. 3 Mössbauer spectra recorded at 298 K of akaganéite M after 7 days leaching in pure H_2O at 55°C, in a 4 g/l solution of NaOH at 55°C and in a solution of 6.3 g/l Na_2SO_3 plus 4 g/l NaOH at 25°C

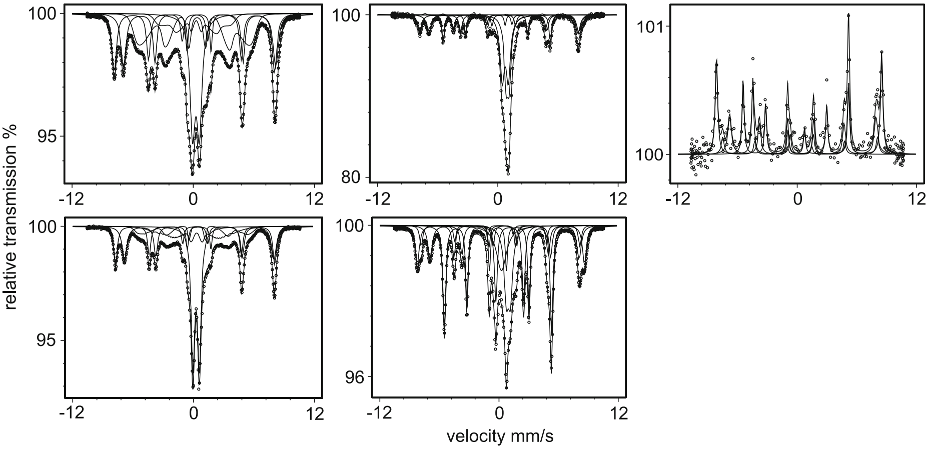

Fig. 4 RT Mössbauer spectra of the Celtic nails 46/43 (*upper row*) and 46/155 (*bottom row*). The spectra of samples from the corrosion layer are shown on the left. For the spectra in the middle these samples were reduced for 1 h with charcoal in a closed vessel at 900°C. On the right the CEMS spectrum of the thin oxide film formed by the same treatment on a freshly cut section through the metallic part of nail 46/43 is shown

in 1964 and then cleaned and covered with epoxy resin. It had developed a new corrosion layer under the epoxy film. Nail 46/155 was excavated in 1999 and hence stored untreated. Figure 4 shows that the Mössbauer spectra of the corrosion layers of both nails are very similar and show mainly magnetite and fine-grained goethite. The epoxy cover may have slowed corrosion, but did not affect the nature of the corrosion products. Small amounts of akaganéite are difficult to detect by Mössbauer spectroscopy in the presence of goethite. XRD is clearly superior in this respect and showed the presence of small amounts of akaganéite in both corrosion layers.

Thermal treatments of corroded iron artefacts may destroy akaganéite and drive off chloride. In agreement with previous observations [12, 16–18] we observed, by both XRD and Mössbauer spectroscopy, that akaganéite M and akaganéite S both convert into hematite when heated to about 400°C, though there are differences in the detailed behaviour.

Thermal treatments in reducing atmospheres above about 700°C convert the corrosion layers into mixtures of metallic iron, magnetite, wüstite and hematite. The metallic surface becomes covered by a thin film of magnetite, wüstite and hematite that may prevent further oxidation. A Celtic nail treated at 850°C in a N_2+5% H_2 gas mixture 15 years ago and kept in air ever since shows no signs of new corrosion. The disadvantage of high temperature heat treatments is, however, that they will wipe out the microstructure of the metal that bears information on the production of the iron artefacts [1].

Figure 4 shows the effect of heat treatments on the two studied Celtic nails. When the nails were reduced with charcoal in a closed vessel at 900°C, the corrosion products were converted into magnetite, wüstite and metallic iron, though with different relative amounts that were also found to depend on the time of reduction: After 2 h more metallic iron was found than after only 1 h. A thin film consisting of hematite and magnetite formed on the surface of the metallic iron, as is shown by the CEMS spectrum of Fig. 4, which reveals 41% hematite, 33% magnetite and 26% metallic iron, the latter probably representing the iron substrate seen through the thin surface coating. Such surface coatings provide a good protection against further corrosion [3].

5 Conclusions

The aim of the present paper is to show that Mössbauer spectroscopy can be used in various ways to study questions related to the conservation of archaeological iron artefacts. In the future, more and more systematic work is expected to contribute to the solution of some of the pending problems of iron conservation.

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