The desalination of archaeological iron objects with hydroxylamine

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Abstract

Compared to the alkaline sulphite method, the desalination of archaeological iron finds with hydroxylamine as reducing agent has promising advantages e.g. a short desalination time and no necessary post-treatment. Experiments with synthetic akaganeite showed that hydroxylamine removed more adsorbed chloride ions from it than common desalination methods in the same time, whereas archaeological iron objects desalinated with hydroxylamine were not stable at high humidity levels. During desalination of iron objects Fe^{2+} was oxidized to Fe^{3+} by hydroxylamine, which could lead to diffusion barriers by precipitating Fe(III) compounds in the corrosion layer. Experiments on synthetic magnetite showed that it is slowly oxidized by hydroxylamine. Hydroxylamine is therefore suspected to damage the original surface of archaeological iron objects and is not recommended as an alternative to the alkaline sulphite desalination.

Keywords: archaeology, iron, desalination, hydroxylamine, akaganeite, chloride

Introduction

In 1998, Wunderlich and Neubacher presented the desalination of archaeological iron objects with hydroxylamine (H_2NOH) at the ADR Conference 'Archaeological Iron' in Mainz, Germany. Two years later, Wunderlich (2000) published his results and claimed this reagent to be more advantageous compared to other methods like alkaline sulphite.

In this study at Landesamt für Denkmalpflege und Archäologie Sachsen-Anhalt/Landesmuseum für Vorgeschichte, Halle, some archaeological iron objects were treated with hydroxylamine. For this purpose objects were immersed in aqueous solutions containing 2.5 % (v/v) hydroxylamine. The solutions were changed once a week because of their chloride uptake and the decay of hydroxylamine into volatile compounds (see below). After complete chloride extraction[1] the desalinated objects were dried directly under infrared light.

The desalination with hydroxylamine is now a routine method for iron desalination at Landesamt für Denkmalpflege und Archäologie Sachsen-Anhalt/Landesmuseum für Vorgeschichte. Few others have tried the method, but no further experiences have been published. Discussions with users and own experiences showed results contradictory to Wunderlich´s report. This was the reason for a closer look into the desalination of iron finds with hydroxylamine. Especially the properties and behaviour of hydroxylamine in presence of iron are to be considered for a better understanding of processes taking place during desalination. By means of experiments the method is to be compared with better known methods like the alkaline sulphite reduction method (see below).

Properties of hydroxylamine

According to Cornell and Schwertmann (2003), the transformation of akaganeite (by which incorporated chloride ions are released) needs high pH level, because hydroxyl ions are necessary for the ion exchange of OH^- versus Cl^- from the akaganeite phase. A 50 % (v/v) hydroxylamine solution has a pH of 10.6, a 2.5 % (v/v) solution about 9, so it is able to supply hydroxyl ions. Besides hydroxylamine is a strong reducing agent (Jander and Blasius 2002). So it seems to protect metallic iron during desalination. This is an advantage compared to alkaline sulphite treatment designed by North and Pearson in 1975, where sodium sulphite was thought to act as reducing agent, and sodium hydroxide as desalinating component (North and Pearson 1975). As we know today, sodium sulphite is able to reduce the oxygen of treatment solution, but not iron (III) phases (Gilberg and Seeley 1982). Another positive property of hydroxylamine is its decay after several weeks into the volatile compounds ammonia and nitrogen, e.g. according to the gross chemical equation: $3\,H_2NOH \rightarrow NH_3 + N_2 + 3\,H_2O$ (Hollemann and Wiberg 1985). Therefore no post-washing of treated objects is required in contrast to alkaline sulphite method where finds have to be rinsed and washed thoroughly.

These properties give the impression that hydroxylamine is very suitable for conservation of archaeological iron finds. But as mentioned before, the experiences with desalination are inconsistent and not positive in every case regarding method's efficiency and visual appearance of the finds after treatment. Our research intended to understand how the desalination

Table 1: Washing solutions used to decompose akaganeite

desalinating agent	concentration	solvent
lithium hydroxide	0.12 %	ethanol
sodium sulphite sodium hydroxide	6.3 % 2 %	distilled water
hydroxylamine	2.5 %	distilled water
sodium hydroxide	2 %	distilled water
distilled water	100 %	distilled water

Table 2: Desalination efficiency of hydroxylamine solutions. The chloride content decreases clearly after the first change of solution

bath number	concentration in ppm
1	525
2	40
3	6
4	2

with hydroxylamine process really works and to determine the efficiency of the treatment.

Comparative treatment efficiencies on akaganeite (β-FeO(OH,Cl))

The first experimental series investigated the effectiveness of hydroxylamine compared to other desalination methods. By removing not only the adsorbed but also the structural bound chloride, akaganeite should be transformed dependent on temperature and pH into hematite (α-Fe$_2$O$_3$) or goethite (α-FeOOH) (Cornell and Schwertmann 2003). There is no chloride-free akaganeite: as long as this phase exists chloride ions incorporated in the channels of the crystal structure are present.

Akaganeite prepared by hydrolysis of a Fe(III)chloride solution[2] was used as test material. XRD analyses confirmed the precipitate to be akaganeite. Samples of 300 mg akaganeite powder were immersed in 25 g of five different washing solutions (see table 1) and left 14 days at room temperature (higher temperatures would have increased the decomposition rate especially of hydroxylamine). The result of the X-ray diffraction (XRD) analysis showed, that akaganeite was still present after desalination with every tested desalinating agent. The chloride extraction was determined by potentiometric titration. During the experimental period, hydroxylamine had the highest efficiency (see figure 1) of all tested solutions.

The second part of this experiment was to find out if there is residual chloride in the desalinated akaganeite which could be released under moist conditions (akaganeite is a precursor of post-excavation corrosion on iron finds). To test this, akaganeite powder was desalinated with a 2.5 % (v/v) aqueous hydroxylamine solution for four weeks with regular bath changes once a week. The first desalination solution showed the highest chloride content. In subsequent washing solutions hardly any chloride could be quantified (see table 2). XRD-measurements showed the presence of akaganeite, therefore hydroxylamine was not able to remove all structural bound chloride even after 4 weeks treatment.

The desalinated akaganeite powder samples were given onto steel plates in a climate chamber (at 98 % RH) for four weeks. The corrosion processes were evaluated visually. The steel plates covered with unwashed akaganeite corroded at a high degree. Akaganeite, which was washed with distilled water after production was corrosive, too. But the akaganeite desalinated with hydroxylamine did not cause corrosion of the steel plate at all!

Although after desalination akaganeite is still present, it is possible that the content of adsorbed and bound chloride fell below a critical value by desalination of this synthetic phase where no chloride can be mobilized and so no corrosion is caused by chloride ions.
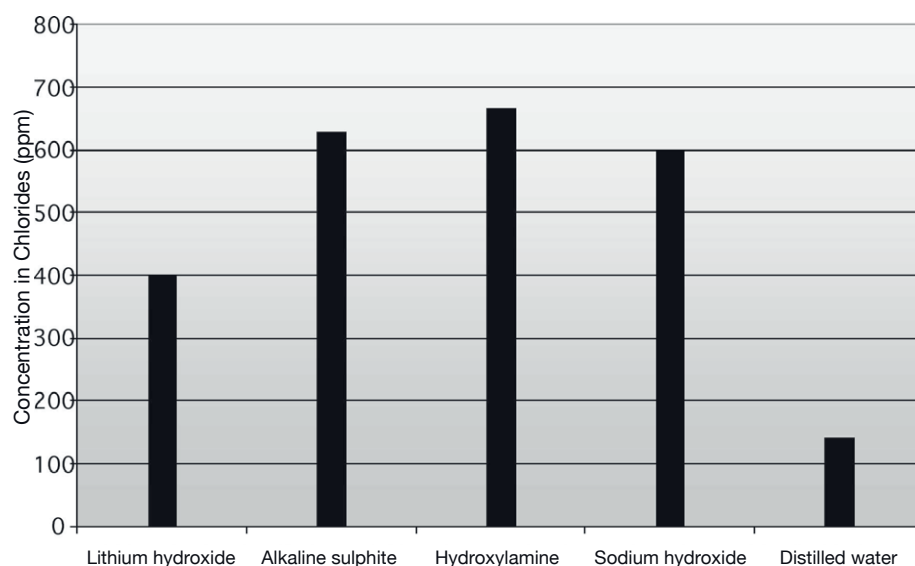

Figure 1: Comparison of the level of chloride extraction from akaganeite powder when immersed in different washing solutions

Figure 2: Immersion of archaeological iron objects in hydroxylamine. A reddish brown precipitate appeared on the bottom of the beaker after the first desalination bath

Experiments with archaeological iron objects

The desalination treatment with hydroxylamine was also tested on four archaeological iron objects from the Moritzburg, Halle. Crystals of akaganeite on the surface of the objects indicated a heavy chloride contamination. Following Wunderlich, the objects were desalinated four weeks in an aqueous 2.5 % (v/v) solution of hydroxylamine, whereby every week the solution was changed. After immersion of the objects into the hydroxylamine solution gas evolved spontaneously, which indicates the decomposition of hydroxylamine[3]. A reddish brown precipitate was visible at the bottom of the beaker (see figure 2). In following baths the reaction was less vigorous. The chloride extraction was determined by potentiometric titration. Particularly in the first washing solution the extraction was very high (see table 3). After treatment, on the surface of the desalinated artefacts fresh orange corrosion products were visible. It seemed that the objects corroded in the solution. In the cross sections of three objects residual chloride could be detected by energy dispersive X-ray spectroscopy (EDX). As in the case of the akaganeite samples, the efficiency of the desalination treatment

Table 3: Chloride extraction rate of an archaeological terrestrial iron found, which is desalinated in an aqueous hydroxylamine solution (2.5 % v/v)

bath number	concentration in ppm
1	3513
2	455
3	115
4	108

was further tested in a climate chamber by visual evaluation. The three desalinated objects showed, like the not desalinated ones, many fresh orange corrosion spots on their surface which is interpreted as unsuccessful conservation by hydroxylamine. No new corrosion product could be detected on the fourth artefact.

Chemical behaviour of hydroxylamine, iron and iron oxides
The colour change of the iron objects caused by hydroxylamine treatment indicated that the iron was not immune during desalination despite its postulated inhibitive effect. To explain this phenomenon the chemical behaviour of hydroxylamine needs a closer examination.

Hydroxylamine behaves as reducing agent for iron(III) in a sulphuric acid solution, where Fe^{3+} ions are reduced to Fe^{2+} ions (Jander and Blasius 2002). The redox capability of Fe^{2+}/Fe^{3+} is independent of pH in strong acid solutions, because $Fe(OH)_2$ and $Fe(OH)_3$ are both soluble. By raising up pH, Fe^{3+} will precipitate more readily than Fe^{2+} because $Fe(OH)_2$ is more soluble than $Fe(OH)_3$ in alkaline environment.

On account of the larger solubility product of Fe^{2+} in alkaline environments the oxidation of Fe^{2+} to Fe^{3+} is favoured. This is why the redox capability of Fe^{2+} in alkaline conditions raises and why it represents one of the strongest reducing agents (Jander and Blasius 2002). Hence, hydroxylamine becomes an oxidant, and is not able to reduce Fe^{3+} anymore. Instead, freshly precipitated $Fe(OH)_2$ will be oxidized to $Fe(OH)_3$, whereby hydroxylamine is reduced to ammonia (Gmelin 1936; Haber 1896; Hofmann and Rüdorff 1963; Knorre 1899): $2Fe(OH)_2 + NH_2OH + H_2O \rightarrow 2Fe(OH)_3 + NH_3$. This precipitate will dehydrate to FeO(OH) and would have the effect of a diffusion barrier.

The chemical behaviour of hydroxylamine in connection with metallic iron is not clear. According to Gmelin (1936), "ferrum reductum"[4] is oxidized and hydroxylamine is reduced to ammonia. These reactions were reproduced in test tubes. Figure 3 shows, that iron(II) reacts immediately with hydroxylamine to iron(III), but iron powder being less reactive than 'ferrum reductum' seems not to be oxidized by hydroxylamine directly.

As reported above objects seem to corrode in the desalination solution containing hydroxylamine because the original surface consisting of magnetite (Fe_3O_4) seemed to change from black to orange appearance. Because magnetite is an iron(II/III) compound, there was suspicion of its stability in the hydroxylamine solution. In a test tube artificially synthesized magnetite was immersed into a hydroxylamine solution (25 %, v/v). Spontaneous gas evolution indicated the decomposition of hydroxylamine by magnetite powder. The reaction rate was much stronger than in a control tube, where glass bead was immersed in a hydroxylamine solution (25 %, v/v). After two weeks the solution was reddish brown, and a chemical test with ammonium thiocyanate indicated that iron(III) ions were present in the solution. So magnetite seems to be slowly oxidized by hydroxylamine which would explain the observations regarding colour change of desalinated finds.

Conclusion

The experiments showed that hydroxylamine was more effective than other desalination methods in removing adsorbed chloride in the given experimental time. But structural bound chloride ions in akaganeite could not be removed by any desalination method tested during two weeks at room temperature. After desalination with hydroxylamine akaganeite is still detectable by XRD analysis.

Furthermore, the reddish brown precipitate in the hydroxylamine solution during desalination and in the test tube with Fe^{2+} indicates the oxidation of iron(II) to iron(III) by hydroxylamine in alkaline environment in opposite to alkaline sulphite where this oxidation is prevented by sodium sulphite. Fresh $Fe(OH)_3$/FeOOH is visibly precipitating in the hydroxylamine solutions and most likely in the micropores of the object preventing effective desalination. Accordingly, most objects which were desalinated with hydroxylamine seemed not to be stable at high humidity conditions. In addition, hydroxylamine seems to react with magnetite phases of the original surface, which could be confirmed by oxidation of pure magnetite in hydroxylamine solution.

Therefore the desalination of archaeological iron with hydroxylamine cannot be recommended. The search for an eagerly needed method better suited for the mass treatment of all uncovered archaeological iron objects is not finished yet. Still too much of our ferrous heritage is simply rusting away!

Notes

[1] The desalination needed 2-4 baths. Wunderlich measured the chloride concentration in the washing solution with a photometer using mercury(II)thiocyanat ($Hg(SCN)_2$) reagent. The chloride content of the last treatment solutions was between 90 and 210 ppm.

[2] 108.12 g $FeCl_3$ x 6 H_2O were immersed in 4 L twice distilled water and left at 40 °C. After two weeks the precipitate was
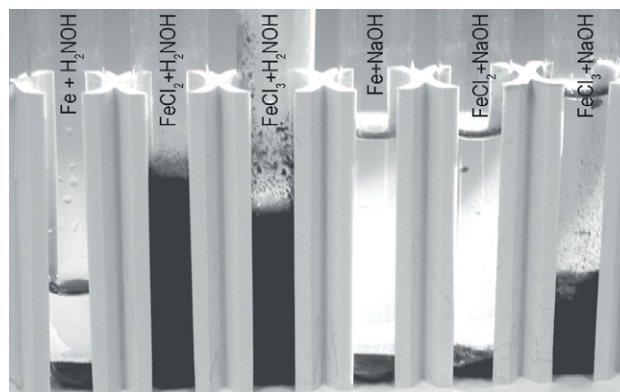

Figure 3: Reaction of iron, iron(II) and iron(III) with hydroxylamine and sodium hydroxide. In a hydroxylamine solution iron(II) is oxidized to iron(III), which is visible as characteristic reddish brown precipitate in comparison to sodium hydroxide

washed, centrifuged, and dried under vacuum (Schwertmann and Cornell 2003).

[3] In contrast to finds immersed in hydroxylamine, gas evolution was not observed when iron objects were immersed in pure water.

[4] "Ferrum reductum" is a highly dispersed and, therefore, very reactive iron powder, which is produced by reduction of ironoxyhydroxides with hydrogen.

Materials list

- VWR International GmbH

Hilpertstraße 20a, 64295 Darmstadt, Germany, 06151 / 39 72 – 0, 06151 / 39 72 – 450, info@de.vwr.com, www.vwr.de
Hydroxylamine (NH2OH), no. 8.14441.0500
Iron powder (Fe), no. 1.03819.0100
Iron(II)chloride tetrahydrate (FeCl2 x 4H2O), no. 1.03861.0250
Iron(III)chloride hexahydrate (FeCl3 x 6H2O), no. 1.03943.0250
Lithium hydroxide (LiOH), no. 1.05691.0100
Sodium hydroxide (NaOH), no. 1.06498.1000
Ammoniumthiocyanate (NH4SCN), no. 21344.237

- Carl Roth GmbH & Co.KG , Schoemperlenstr. 1-5, 76185 Karlsruhe, Germany

Tel +49 (0)721/5606-0, +49 (0)7 21/56 06 – 149
info@carlroth.de, www.carlroth.de
Sodium sulphite (Na2SO3), no. PO332

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