

ANOTHER BASE, ANOTHER SOLVENT? DESALINATING IRON FINDS WITH TETRAMETHYLAMMONIUM HYDROXIDE SOLUTION

FULL PAPER

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The desalination processes commonly applied to improve the corrosion stability of archaeological iron artifacts are based on immersion treatments in aqueous sodium hydroxide solutions. Faster and more efficient chloride extraction in solutions based on organic solvents with a lower surface tension can be expected. Furthermore, the danger of new corrosion forming during the subsequent washing out of residual chemicals from the desalinating solution could be minimised, if organic solvents would replace the water, commonly used for this process.

Only alkali metal hydroxide (LiOH and NaOH) solutions in organic solvents have been tested so far. Their comparatively low chloride extraction efficiency was ascribed to the low solubility of the alkali metal hydroxides and the corresponding chlorides in the solvents used. Tetramethylammonium hydroxide (TMAH) is readily soluble in alcohols and has been tested in aqueous and/or methanolic solutions as an alternative. Neither improved overall chloride extraction efficiency, nor a higher chloride extraction rate could be observed using methanolic solutions. However, aqueous TMAH showed a trend towards higher overall chloride extraction efficiency than the common alkaline treatments. These results could be explained by the different solubility of corrosion products, in particular akaganéite, β -FeO(OH), in the tested solutions.

1 Introduction

Excavation of archaeological iron artifacts enables improved access of oxygen to their inner corrosion layers. This causes further oxidation of ferrous compounds and ions within the corrosion layers and the remaining iron core underneath. Typical damage phenomena are the flaking off of corrosion fragments and the formation of new, powdery corrosion products at the metal/corrosion interface. This post-excavation corrosion process is efficiently catalysed by chloride ions, which are attracted from the surrounding soil and accumulate inside the corrosion layers during burial.¹

Experience shows that the corrosion stability of iron artifacts after excavation can be significantly improved by extracting chloride ions from their corrosion layers². The common, so-called desalination methods, are based on immersion treatments in aqueous, basic solutions. Usually, sodium hydroxide (NaOH) is used, often with the addition of sodium sul-

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fite (Na_2SO_3) as an oxygen scavenger (well known as the alkaline sulfite method³).

Various studies show that these solutions are effective in extracting chloride ions.⁴ Yet, especially the disadvantage of long treatment periods of several months requires further improvements of the desalination process.

The use of organic solvents instead of water promises faster chloride extraction and better overall extraction efficiency due to the lower surface tension of such solutions, resulting in better penetration behaviour. However, earlier experiments to desalinate iron artifacts in sodium or lithium hydroxide (LiOH) solutions in organic solvents have not been particularly successful.⁵ This was thought to be due to the minor solubility of these alkali metal hydroxides and the corresponding chlorides in the organic solvents used.

To avoid the problems with low solubility of the commonly used alkali metal hydroxides in organic solvents, tetramethylammonium hydroxide (TMAH, $(\text{CH}_3)_4\text{N}^+\text{OH}^-$) which is readily soluble in diverse organic solvents was tested as an alternative desalinating agent. In the presented preliminary study the desalination efficiency in aqueous and/or methanolic TMAH solutions was tested on a limited number of iron artifacts and the synthetic corrosion product akaganéite ($\beta\text{-FeOOH}$) to see if further research into this topic is promising.

2 Experimental

The desalination efficiency of TMAH solutions in various concentrations and solvents – water and/or methanol (CH_3OH) – has been tested on Roman iron nails and compared to the desalination efficiency of aqueous sodium hydroxide and alkaline sulfite solution. In each solution, three test samples have been desalinated separately over a total period of 8 weeks at room temperature in closed containers. For each test, a solution volume of 50 mL was used, while the sample weight ranged from 1.36 g to 6.24 g.

During desalination, formation of precipitates, formation of new corrosion products on test samples, spalling of fragments and discolouration of the solutions has been observed systematically. After desalination, the test samples have been washed by immersion in fresh solvent, also used for desalination, for 60 h and dried at 80 °C for 48 h. After desalination in aqueous TMAH solution, washing in water as well as in methanol was tested.

Subsequently, chloride extracted into solution as well as chloride remaining in the test samples has been analysed quantitatively by the photometric thiocyanate method.⁶ In certain cases, chloride in the solution has been analysed after specific time periods during desalination as well to observe chloride extraction rates.

Sulfite ions in alkaline sulfite solutions have been oxidised by the addition of hydrogen peroxide solution and surplus hydrogen peroxide boiled out prior to analysis. Iron nails have been digested in hot sulfuric acid (20%) in covered vessels and the dissolved fer-

rous ions oxidised by the addition of hydrogen peroxide prior to analysis.⁷

Additionally, akaganéite has been synthesised⁸ and treated in TMAH solutions of varying concentrations in water and/or methanol as well as in aqueous sodium hydroxide and alkaline sulfite solutions over different time periods at room temperature. For each test, 100 mg akaganéite was treated in 5 mL solution. After treatment, the solids were separated from the solution by centrifugation, washed once in the solvent used during treatment, centrifuged again and dried at 40 °C.

For subsequent chloride analysis using the photometric thiocyanate method,⁶ the dried solids were digested in nitric acid (27%) in sealed glass ampoules⁹ at 100 °C.

Possible phase transformations have been studied by X-ray diffraction after treatment with a STADI-P diffractometer (STOE) using $\text{Cu} - \text{K}\alpha_1$ radiation.

All chemicals used were of analytical grade except TMAH (Sigma Aldrich no. 334901), which was tested to be free of chloride.

3 Results and Discussion

3.1 Desalination of Archaeological Artifacts

The desalination experiments on archaeological test samples clearly demonstrate that the overall chloride extraction efficiency increases with increasing TMAH concentration (Fig. 1).

Against primary expectations, the treatment in aqueous TMAH solution results in a slightly higher chloride extraction rate (Fig. 2). Furthermore, the overall extraction efficiency is significantly higher in a purely aqueous TMAH solution than in a partly methanolic TMAH solution of equal concentration. Comparing the pure solvents, water also extracts more chloride than methanol (Fig. 3).

Furthermore, aqueous TMAH solution showed a trend of higher extraction efficiency than sodium hydroxide and alkaline sulfite solutions of equal concentrations (Fig 4).

Archaeological test samples that had been desalinated in aqueous TMAH solutions of $[\text{OH}^-] > 0.5 \text{ mol L}^{-1}$ seemed to be mechanically less stable than all other objects desalinated differently. During desalination of these test samples, strong discolouration of the solutions and spalling of many small corrosion fragments was observed, which was ascribed to a partial dissolution of the corrosion products. After desalination and drying, the remaining corrosion layers appeared to be comparatively brittle. A lighter, yellowish surface of these test samples indicated that a re-precipitation of a part of the dissolved corrosion products had occurred during desalination.

No further corrosion of test samples that had been desalinated in aqueous TMAH solution could be observed during subsequent washing in methanol. When washed in water newly corroding areas on the test samples occurred.

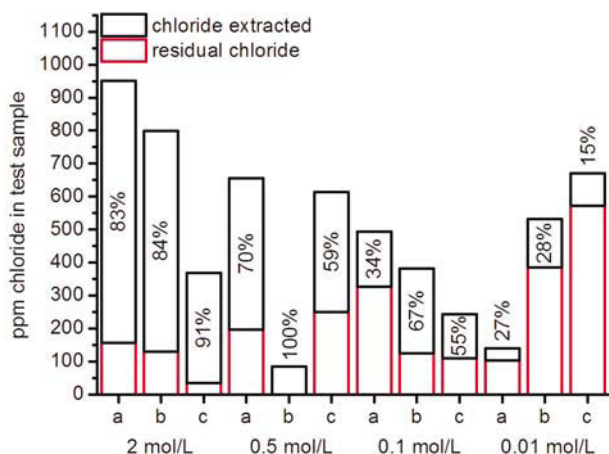


Figure 1: Chloride extraction efficiency in aqueous TMAH solution of different concentrations; a, b, c = three separately treated test samples for each solution; inscription in columns = extracted proportion of chloride.

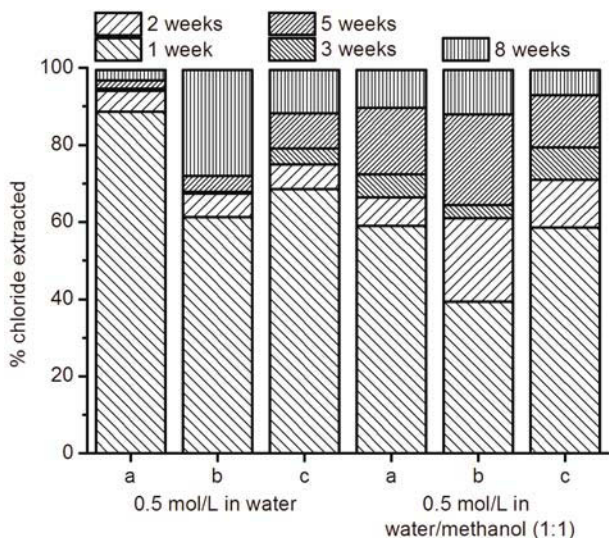


Figure 2: Chloride extraction rates in TMAH solution in water and a water/methanol mixture (1:1); 100 % extracted = amount of chloride extracted after 8 weeks.

3.2 Treatment of Akaganéite

In all tested solutions with $[OH^-] \geq 0.05 \text{ mol L}^{-1}$, the chloride content of akaganéite could be reduced to 2-3% within 4 days or less, independently from the hydroxide salt or solvent used, if no phase transformation had occurred (Fig. 5, 8).

In less concentrated solutions or pure water or methanol, higher chloride contents remained in the solid, while the residual chloride content was significantly higher after treatment in methanol than after treatment in water (Figs. 6, 8).

Phase transformations via dissolution and re-precipitation as goethite, $\alpha\text{-FeO(OH)}$, could only be observed in aqueous TMAH solutions. The transformation rate increased with an increasing TMAH concentration (Fig. 7). After 4 days, a minimal transformation could be observed in 0.5 mol/L TMAH solution, while the transformation in 2 mol/L solution was almost complete. The chloride content of the solid

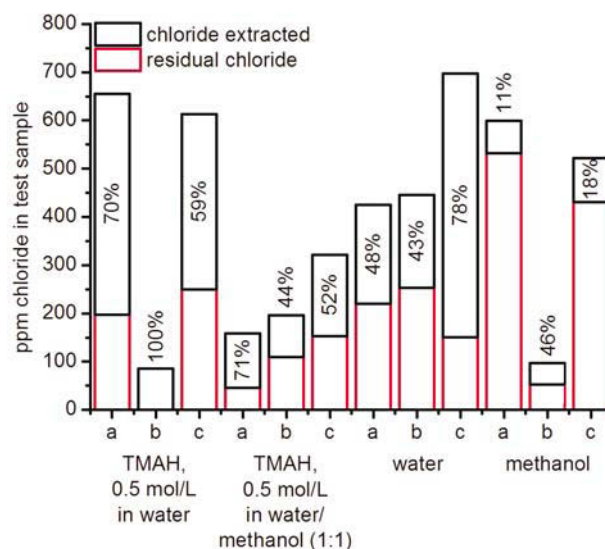


Figure 3: Chloride extraction efficiency in TMAH solution in water and a water/methanol mixture (1:1) and the pure solvents; a, b, c = three separately treated test samples for each solution; inscription in columns = extracted proportion of chloride.

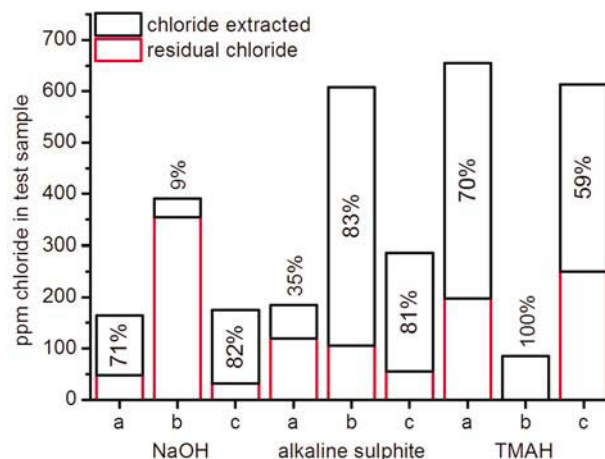


Figure 4: Chloride extraction efficiency in aqueous TMAH, NaOH and alkaline sulfite solution, c = 0.5 mol/L for each solution; a, b, c = three separately treated test samples for each solution; inscription in columns = extracted proportion of chloride.

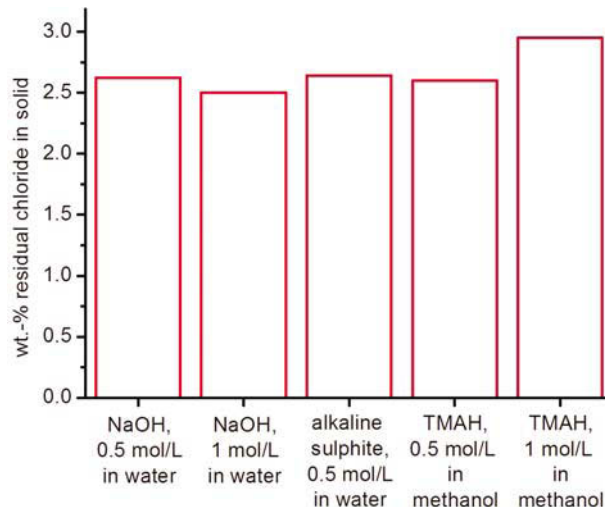


Figure 5: Residual chloride content in akaganéite after 4 days treatment in different basic solutions, initial chloride content = 7%.

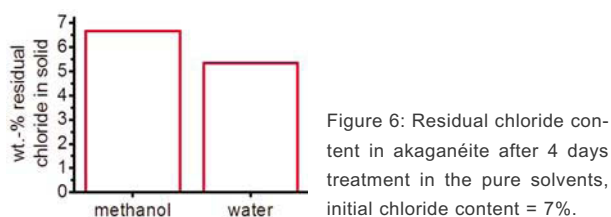


Figure 6: Residual chloride content in akaganéite after 4 days treatment in the pure solvents, initial chloride content = 7%.

samples which transformed partly into goethite could be further reduced below 2%, depending on the degree of transformation (Fig. 8). Only a complete phase transformation resulted in chloride free solids. A transformation in aqueous sodium hydroxide solutions of the same concentrations (0.5, 1.0, 1.5 and 2 mol/L have been tested) could not be observed over a period of 4 days, showing that akaganéite has a higher solubility in aqueous TMAH solutions.

These observations suggest that the akaganéite used in this study, holds about 4 - 5% chloride ions adsorbed onto the particle surfaces. The deprotonation of the surface hydroxyl groups of akaganéite in basic solutions, resulting in a negative surface charge, releases these anions. Another 2-3% chloride seems to be incorporated in the hollandite-type tunnel structure of akaganéite and can only be released by the decomposition of the compound.

4 Conclusions

The results demonstrate that solutions, which promote the dissolution of akaganéite, enable higher desalination efficiency of archaeological iron finds, typically containing this corrosion product. If akaganéite is not decomposed during treatment, chloride ions bound in the akaganéite structure remain inside the corrosion layers. As akaganéite is described to be meta-stable and tends to decompose into hematite, α -Fe₂O₃, or a chloride free modification of FeO(OH) over periods of several years,^{10,11} these chloride ions might be set free in the future and again have a catalytic effect on the corrosion of an artifact. Additionally, the solubility of other iron corrosion products can be expected to be higher in such solutions, which promote the dissolution of akaganéite.

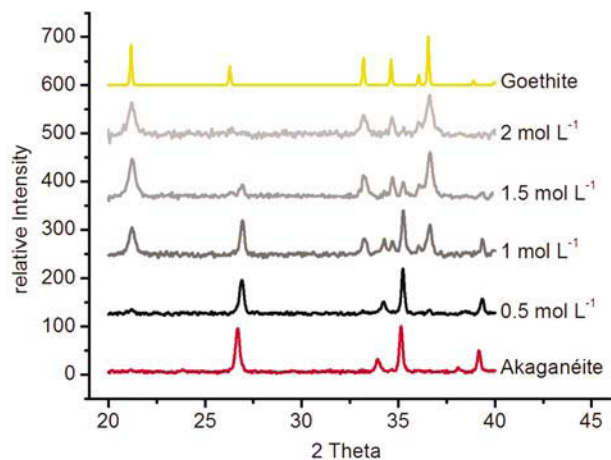


Figure 7: Observed X-ray powder diffraction patterns of synthetic akaganéite, the solid after 4 days treatment in aqueous TMAH solutions of different concentrations, calculated X-ray powder diffraction pattern of goethite (ICSD #159966).

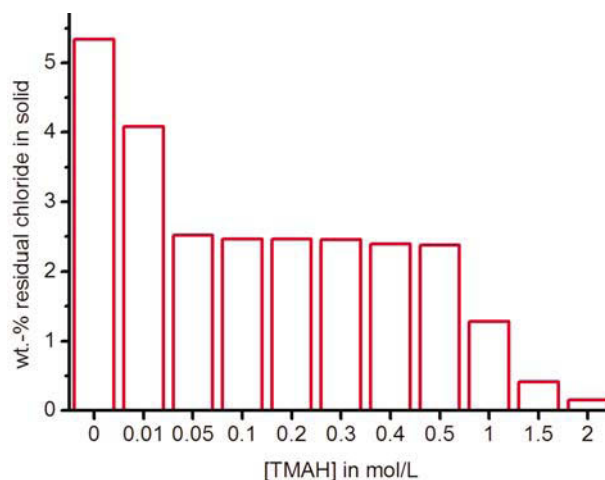


Figure 8: Residual chloride content in solids after 4 days treatment in aqueous TMAH solutions of different concentrations, initial chloride content = 7%.

This will lead to the partial dissolution of the corrosion layers during treatment, as could be observed during the desalination of iron artifacts in aqueous TMAH solutions with $[\text{OH}^-] > 0.5 \text{ mol L}^{-1}$. On the one hand, this will facilitate the diffusion of desalinating agents and chloride ions within the corrosion layers, hereby accelerating chloride extraction. On the other hand, the dissolution of corrosion products during treatment poses the risk to degrade the physical stability of the artifact, as it was also observed during the desalination of iron artifacts in aqueous TMAH solutions with $[\text{OH}^-] > 0.5 \text{ mol L}^{-1}$. Although not considered in conventional Pourbaix diagrams for the iron/water system, the dissolution of FeO(OH) phases as $[\text{Fe}(\text{OH})_4]^-$ rises linear with the concentration of OH^- and cannot be neglected in strongly alkaline solutions.⁸ This has so far not been addressed in desalination research.

Accordingly, the desalination process will always be a compromise between partially dissolving corrosion products to enhance the diffusion process and to decompose akaganéite, and trying to preserve as much of the corrosion products as possible, as they contain valuable information about the object's original shape and composition. To avoid this compromise, a desalinating procedure, which allows the selective decomposition of akaganéite, would have to be developed.

The most critical step in common alkaline desalination practice is the final removal of the residues of the washing solution with water as new corrosion can occur. The use of aqueous TMAH solution for desalination might be advantageous as its residues could be removed with subsequent washing in methanol, thus avoiding corrosive water.

The results of this preliminary study show that a desalination of iron finds in aqueous TMAH solution is generally possible and might offer several advantages compared to the common alkaline treatments. However, before recommending this method, it will have to be tested on a larger amount of samples to obtain statistically significant values about its efficiency. Using TMAH for mass treatment of objects would require the development of a recovery protocol for used solutions to reduce the expenses of the

treatment. Further research is clearly needed and warranted.

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