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# Assessing the effects of alkaline desalination treatments for archaeological iron using scanning electron microscopy

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**Summary** Archaeological iron objects are often vulnerable to severe post-excavation corrosion induced by chloride ions, a corrosion accelerator. To reduce this problem, alkaline deoxygenated desalination treatments may be used to remove chloride ions. There is very little information on the mechanisms and efficacy of such treatments and they are not in general use by British conservators. As part of a larger study, some iron objects were desalinated and a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometry (EDX) was used to analyse eight polished cross-sections of treated and untreated archaeological iron nails to investigate whether differences between treated and untreated nails could be detected with this method.

The analysis showed clear differences between the treated and untreated halves of the iron nails. Untreated nails showed regions of high chlorine content that appeared to be mobile and caused corrosion on the polished surfaces of the samples, despite storage at low humidity. Chlorine-containing corrosion products were identified as akaganéite using Raman spectroscopy. The majority of the treated samples showed no fresh corrosion or areas of very high chlorine content except near slag inclusions surrounded by metal. These caused fresh corrosion, presumably due to the inability of the treatment solution to reach these deep-seated areas.

The use of SEM-EDX showed that desalination of the objects had a positive impact on the stability of archaeological iron. It also showed some of the limitations of desalination, such as its inability to remove deep-seated chloride ions. Although not an extensive study, this information is useful in understanding the effects of treatment on a detailed level and will complement existing data on the effectiveness of treatments.

## INTRODUCTION

Archaeological iron objects often suffer from deterioration after excavation. This results in loss of corrosion products that contain important archaeological information, loss of the shape of the object and loss of its original surface as the object breaks up. In severe cases the object may become completely fragmented. This type of rapid corrosion is caused by chloride ions that diffuse into the object during burial as a counter-ion to the positive ferrous ( $\text{Fe}^{2+}$ ) ions produced by the corrosion process. After excavation, chloride ions promote corrosion by reacting with  $\text{Fe}^{2+}$  in the presence of oxygen and moisture to form the corrosion product  $\beta\text{-FeOOH}$  (akaganéite), which expands inside the corrosion layers and causes cracking and spalling of the outer surface. Although the exact processes by which chloride ions promote this rapid and damaging corrosion continue to be investigated, the role of chloride ions was

identified by Turgoose in 1982 [1]. Since then their removal has become one of the biggest challenges faced by conservators. Many methods have been used, including electrolysis [2], hot washing [3, 4], Soxhlet extraction [5], plasma treatment [6], and chemical desalination using alkaline solutions. The last method has most often consisted of the alkaline sulphite treatment developed by North and Pearson in 1975 [7, 8]. Subsequent research on this treatment showed that procedures using alkaline deoxygenated solutions were among the most successful methods for removing chloride ions and reducing the iron corrosion rate [3, 4, 9–15]. This is due to hydroxide ions displacing chloride ions from the object, while deoxygenation of the solution prevents corrosion occurring during desalination and helps release chloride ions from their role as the counter-ion.

As part of a wider research project between Cardiff University and the British Museum, iron nails from three British sites were treated with two alkaline deoxygenated

solutions: an alkaline sulphite solution based on the original method, but altered according to the suggestions made by Schmidt-Ott and Oswald [16]; and a sodium hydroxide solution deoxygenated using nitrogen gas in a sealed positive pressure system [17, 18]. The majority of the nails treated were then dissolved in nitric acid to analyse the residual chloride ion content, but a small number were retained and prepared for analysis under a scanning electron microscope (SEM). The aim was to investigate the differences between treated and untreated objects using this instrument and to look in detail at the presence and distribution of chlorine (Cl) in treated and untreated nails as an indication of the effect of desalination treatment on the location and concentration of chloride ions. This would help to contextualize the information on residual chloride ion content as determined by digestion of the objects, which will be reported elsewhere in due course.

## METHODOLOGY

Wrought iron nails were obtained from three archaeological sites – Bornais in the Outer Hebrides (Norse period, excavated 2003), Caerwent in South Wales (Medieval and later contexts, excavated in the 1980s) and Billingsgate in London (Roman/Medieval, excavated 1983). The nails had been in storage with silica gel since excavation. Nails from each site were selected and cut in half using a diamond saw. One half of each nail was treated in either alkaline sulphite, consisting of 0.1 M sodium hydroxide (NaOH) and 0.05 M sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), or in 0.1 M NaOH deoxygenated using nitrogen gas via a positive pressure system. Both treatments were carried out at room temperature, with solutions changed approximately every 14 days and treatment halted after measurements on two successive changes of solution produced chloride ion concentrations less than 10 ppm, or after a maximum of five changes of solution. Chloride ion content in each treatment solution was measured using a Radiometer Analytical PHM250 specific ion meter with a mercury/mercury sulphate reference electrode. This was calibrated using standard sodium chloride solutions. The objects were not rinsed after treatment but were dried in a chamber containing silica gel then stored in ambient conditions (temperature 18–25°C; relative humidity (RH) 35–75%) together with the untreated halves for between three and nine months.

As chloride ions are very soluble in water, no aqueous lubricants could be used during sample preparation for SEM analysis. A small transverse section was cut from both halves of each nail using an Isomet diamond saw and an oil-based lubricant (Buehler ISOCUT), and set in epoxy resin. The surface was ground and polished to a finish of 1  $\mu\text{m}$  using white spirits as the lubricating agent and a few drops of industrial methylated spirit (IMS) were used to clean the surface of any residual white spirits after polishing. The samples were then carbon coated.

TABLE 1. Samples of archaeological iron examined. Nails were cut in half before treatment and samples for SEM examination and EDX analysis were taken from near the cut face

Sample	Treatment	Total chloride removed during treatment (mg)	Chloride removed relative to the weight of nail (ppm)
BOR_1693.1	dNaOH	14.8	2029
BOR_1693.2	Untreated	–	–
CAE_27.1	dNaOH	49.1	1709
CAE_27.2	Untreated	–	–
CAE_45.1	AS	7.9	1902
CAE_45.2	Untreated	–	–
BWB83_44.1	AS	24.8	2255
BWB83_44.2	Untreated	–	–

Note. dNaOH indicates sodium hydroxide deoxygenated with nitrogen gas while AS indicates alkaline sulphite.

SEM analysis was carried out at the British Museum using a Hitachi S-4800 field emission (FE) scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDX). The SEM was run at an accelerating voltage of 20 kV, using either a positive diode back-scattered electron detector or a mixed signal of upper and lower secondary electron detectors. Eight samples were analysed in total; two halves of each of four nails. Two nails (BOR\_1693 and CAE\_27) were treated in deoxygenated sodium hydroxide and the other two (CAE\_45 and BWB83\_44) were treated in alkaline sulphite, Table 1. Both spot identification and area mapping were used to locate and map chlorine in images with magnifications ranging from  $\times 60$  to  $\times 4500$ . The detection limit for chlorine was  $c.0.2\%$  and the relative precision was 10% in the concentration range 5–20%, deteriorating as the detection limit was approached.

Once chlorine-containing corrosion products had been located, Raman spectroscopy was carried out on the polished sections using a Jobin Yvon Infinity spectrometer with a green laser (532 nm with a maximum power of 1.2 mW at the sample) to identify the compounds present. The analytical spot size was  $c.5 \mu\text{m}$  in diameter and the analysis was run with a laser power of 0.3 mW to avoid burning the corrosion products. The resulting Raman spectra were identified by comparison with a British Museum in-house reference database and published data [19, 20]. Due to time constraints the analysis was restricted to a very small number of samples.

## RESULTS

Between polishing and the completion of analysis, the samples were kept in a desiccator with silica gel at a RH of  $10 \pm 2\%$ . However, even at this low humidity, fresh orange-brown corrosion appeared on some of the polished surfaces

and is noted below for those samples on which it occurred. Table 1 indicates the total quantity of chloride ions extracted from the treated half of each nail. In the SEM images, the embedding resin appears black, solid metal as white or off-white and the corrosion products, slag and mineral inclusions as shades of grey.

*Sample BOR\_1693*

This sample had a thin layer of corrosion products surrounding a substantial metal core. Corrosion product growth appeared on the polished surface of the untreated half of this nail, BOR\_1693.2. EDX analysis showed that these new corrosion products contained chlorine and originated from areas where chlorine-containing corrosion products were present in the structure, Figure 1. The chlorine-containing growths on the surface appear to be associated with a deep crack in the corrosion product structure. Chlorine was also identified along the metal–corrosion interface and as a thin band at the edge of the sample.

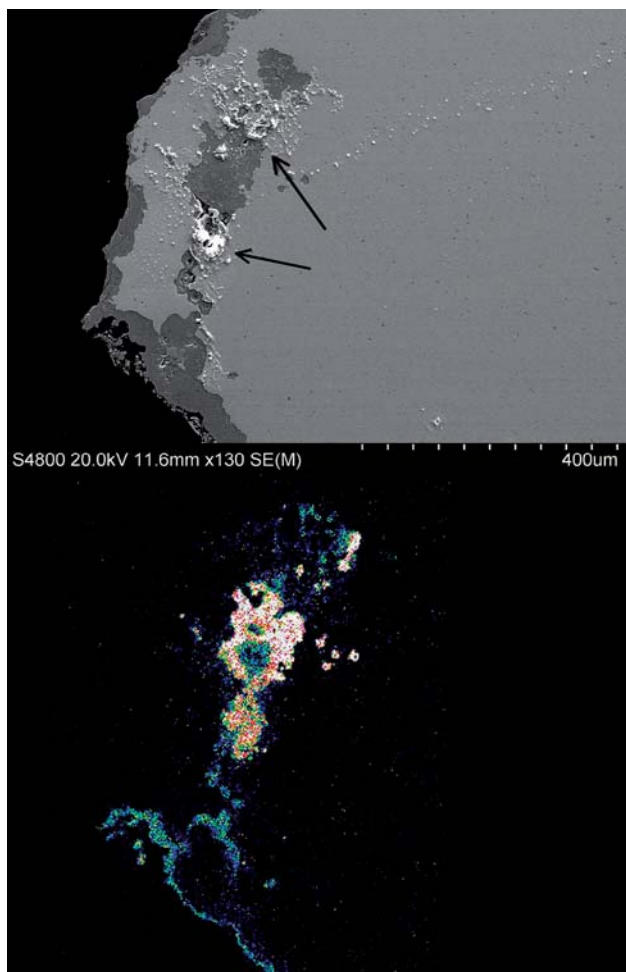


FIGURE 1. Sample BOR\_1693.2: (top) secondary electron image showing fresh corrosion on the polished surface located near cracks in the corrosion structure (marked by arrows); (bottom) EDX map for chlorine, showing very high levels in the areas of new corrosion. Chlorine is also located on the metal–corrosion interface and along the outer edge of the sample

Sample BOR\_1693.1, treated in deoxygenated sodium hydroxide, showed no sign of fresh corrosion product growth on the surface. Although chlorine was identified in three places, only low levels were found compared to the untreated half. Chlorine was not detected along the metal–corrosion product interface, but within patches of corrosion product. Sodium was also detected in low quantities in many places in the treated half, but was not seen in the untreated half. The most likely origin of sodium is residual traces of the treatment solution, which was not rinsed from the objects after treatment, although it was not detected in any other treated nail. It was not possible to determine the form of the sodium, but it is likely to be sodium carbonate, which forms when sodium hydroxide reacts with carbon dioxide during drying.

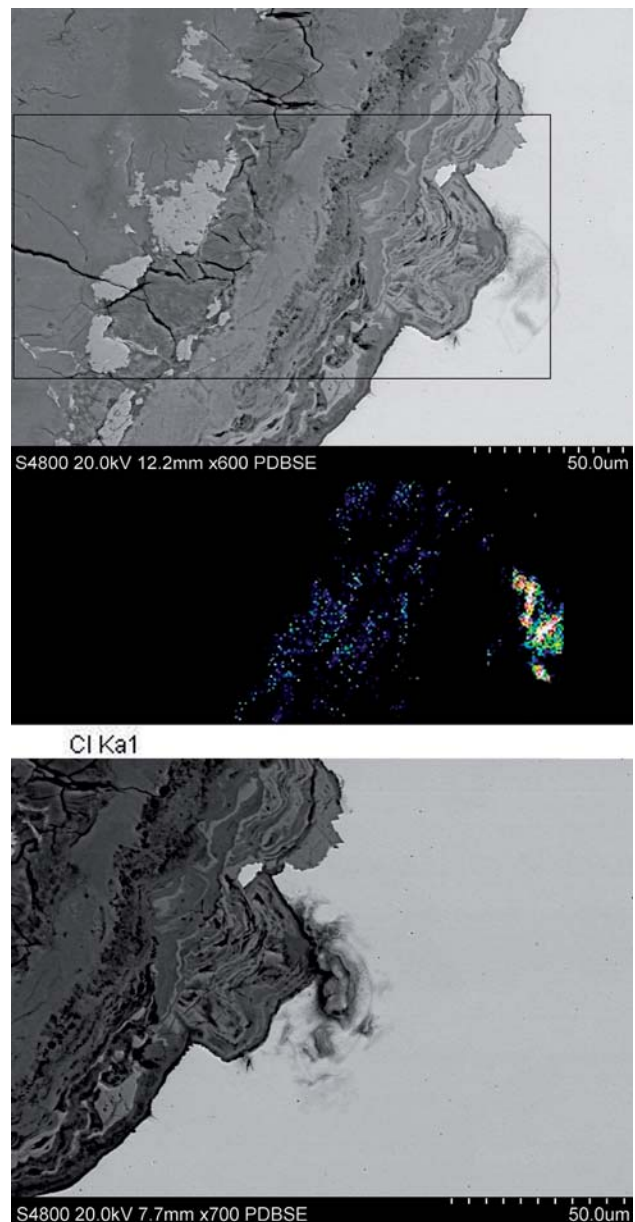


FIGURE 2. Sample CAE\_27.2: (top) backscattered electron image of the freshly prepared sample; (middle) EDX map of the chlorine distribution in the area marked by the rectangle; and (bottom) the same area imaged several weeks after the top image was made, showing the development of chlorine-containing corrosion product on the metal surface over time



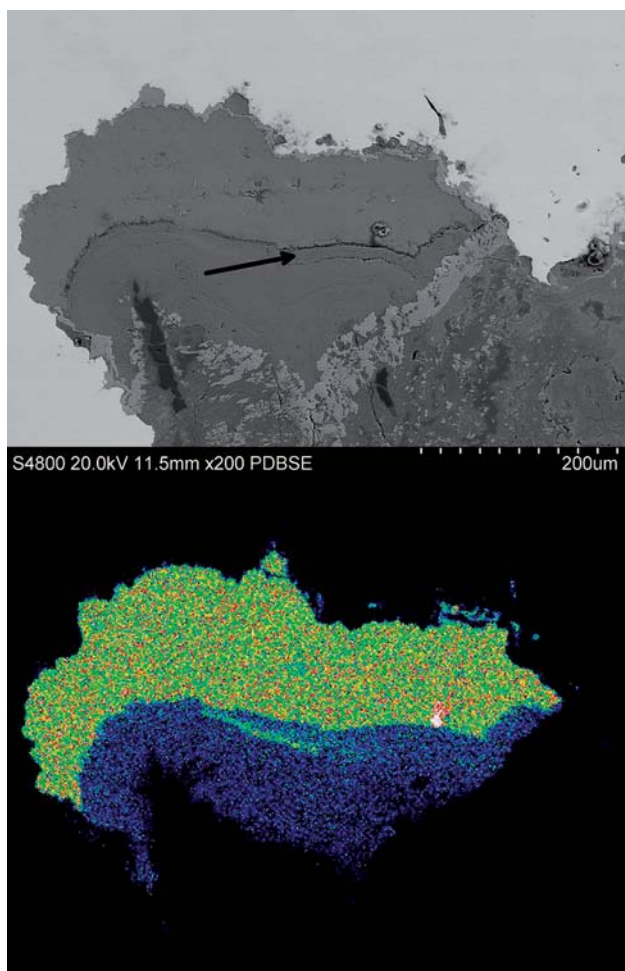


FIGURE 3. Sample CAE\_27.2: (top) backscattered electron image of an area located at the base of a deep sequence of corrosion layers; and (bottom) the corresponding EDX map showing that chlorine is present at two different concentrations, although both areas were identified as akaganéite by Raman spectroscopy. The arrow in the top image indicates the location of the banded structure at the boundary

#### Sample CAE\_27

This sample had thicker corrosion products than the other nails, particularly in one corner of the untreated half, CAE\_27.2. Chlorine was detected in several areas by EDX analysis. At the base of a sequence of deep corrosion products a small quantity of chlorine was found and imaged twice several weeks apart. The small patch in which chlorine was distributed expanded and became fresh corrosion product extending onto the metal surface (Figure 2), in a manner similar to that found on BOR\_1693.2, Figure 1. In another area a patch of corrosion product was detected, also deep in the corrosion structure and located next to the metal–corrosion interface. When mapped, it was found that this area contained corrosion products with two different concentrations of chlorine, Figure 3. There was a sharp interface between the two areas of corrosion product, with a banded structure (arrowed in Figure 3), suggesting that the front may have moved over time. Small patches of fresh corrosion products containing very high levels of chlorine grew on this sample over a period of weeks.

Raman analysis was carried out on the chlorine-containing areas shown in Figure 3, and on the fresh corrosion products formed on the surface. The two areas in Figure 3 were both identified as akaganéite ( $\beta$ -FeOOH), which is the most common corrosion product containing chloride ions and can contain levels of chlorine that vary from 2 to 7 mol% [21]. The analysis of the fresh corrosion products on the surface produced a spectrum with a broad peak at  $710\text{ cm}^{-1}$ , suggesting that these corrosion products are a form of iron hydroxide or oxyhydroxide, but from the spectrum alone it was not possible to determine which particular compound was present [22].

Sample CAE\_27.1, treated in deoxygenated sodium hydroxide, was found to contain chlorine in only one area, where spot analysis detected chlorine in a deep pit associated with a slag inclusion, Figure 4. There was no new corrosion product growth and no chlorine was found within the corrosion structure.

#### Sample CAE\_45

The untreated half of this nail, CAE\_45.2, showed significant development of fresh corrosion products on the polished surface. Under magnification, these were seen to be localized at both the metal–corrosion interface and around slag inclusions in the centre of the metal.

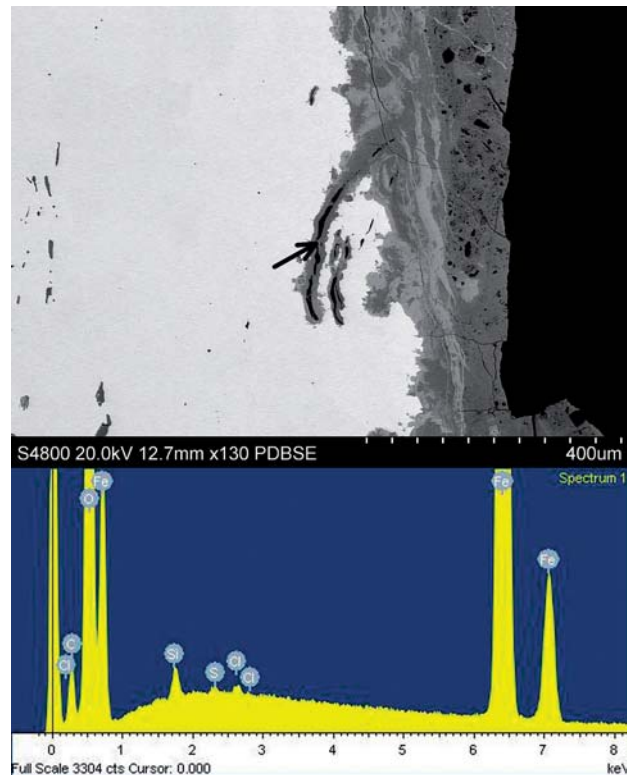


FIGURE 4. Sample CAE\_27.1: (top) backscattered electron image of a polished cross-section showing an area of slag inclusions; and (bottom) EDX spectrum of the area marked by the arrow in the top image, showing that chlorine is present in very small quantity in slag inclusions

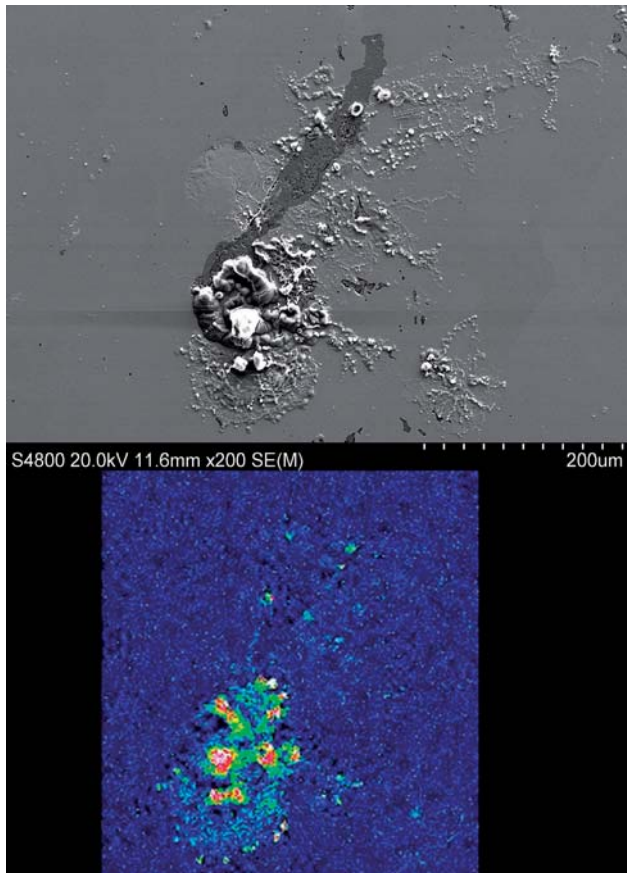


FIGURE 5. Sample CAE\_45.1: (top) secondary electron image of a polished cross-section of a treated nail; and (bottom) the corresponding EDX map for chlorine, showing fresh surface corrosion caused by chlorine located around internal slag inclusions

Chlorine-containing corrosion products were found associated with these slag inclusions and fresh corrosion had also formed near cracks in the corrosion products. Chlorine-containing corrosion products and fresh corrosion growths were also found near the outer edge of the sample.

Sample CAE\_45.1, which was treated in alkaline sulphite, showed the appearance of corrosion on the polished surface near internal slag inclusions (in the centre of Figure 5), similar to those in the untreated half. EDX analysis showed that the corrosion products associated with the slag inclusions contained high levels of chlorine, as did the fresh corrosion on the surface. The metal-corrosion interface and the outer layer of corrosion products were free of chlorine, and no fresh corrosion products formed here. This suggests that the treatment was effective in the outer layers of corrosion and on the metal-corrosion interface, but could not access chloride ions in the internal structure surrounded by metal.

#### Sample BWB83\_44

This nail showed thin and coherent corrosion products around a substantial metal core. BWB83\_44.2 was the

only untreated sample not to display fresh corrosion product growth on its surface. Although small quantities of chlorine were found as part of corrosion products in the structure of the nail, no areas with high chlorine or renewed corrosion could be identified. This is somewhat surprising, as the level of chloride ions extracted from its treated counterpart was similar to those for other samples, Table 1. It is possible that the part of the surface that was sampled was not representative as it did not include any chlorine-containing areas, which might be located elsewhere in the structure.

Sample BWB83\_44.1, which was treated in alkaline sulphite, showed no fresh surface corrosion products. Areas of chlorine-containing corrosion product were found, but none showed any renewed corrosion or growth of new corrosion products and all were located away from the metal-corrosion interface, Figure 6. Chlorine was also identified on the outermost edge of the cross-section. When imaged at  $\times 4500$ , a very thin band about  $1\text{--}2\ \mu\text{m}$  thick of blade-like crystals containing chlorine was located at the very edge of the sample, Figure 7. The corrosion products

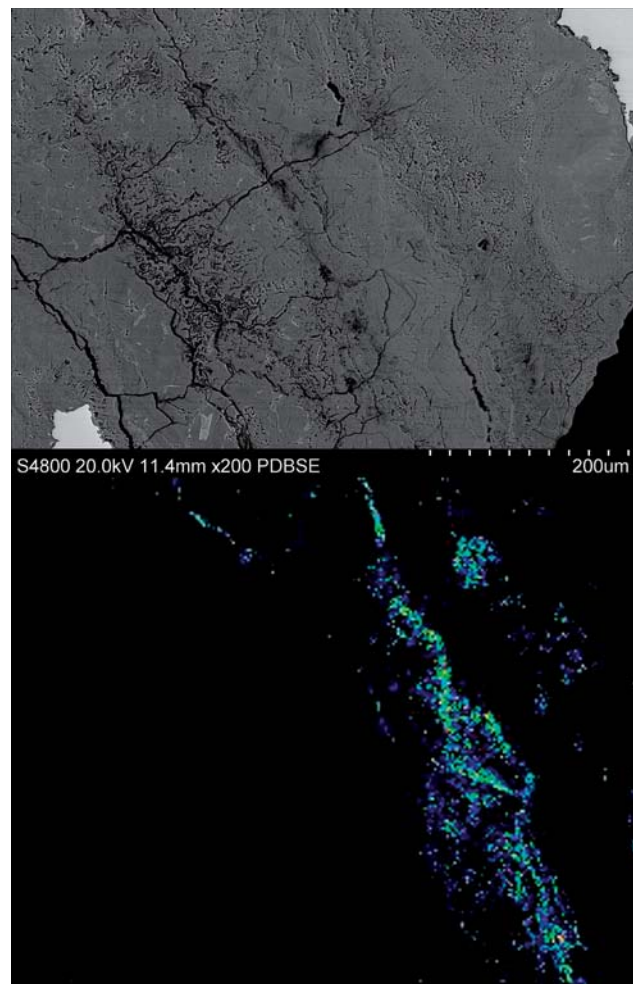


FIGURE 6. Sample BWB83\_44.1: (top) backscattered electron image of a polished cross-section of a treated nail; and (bottom) the corresponding EDX map for chlorine, showing that although low levels of chlorine were located within the corrosion structure there were no associated fresh corrosion growths



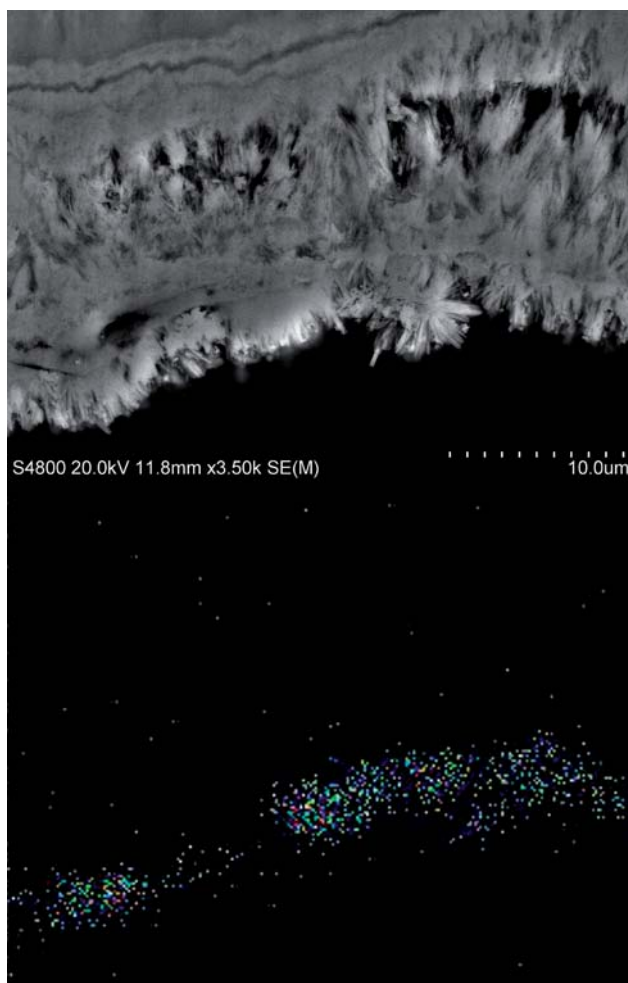


FIGURE 7. Sample BWB83\_44.1: (top) secondary electron image; and (bottom) corresponding EDX map for chlorine, showing a band of crystals containing chlorine at the edge of the sample

below contained very little chlorine. This thin band was also seen in BOR\_1693.1 and CAE\_27.2. An attempt was made to identify these crystals using Raman spectroscopy, but the adjacent resin at the edge of the sample interfered with the measurements and prevented a spectrum from being acquired.

## DISCUSSION

The SEM-EDX analysis showed clear differences between treated and untreated samples of archaeological iron nails. All but one of the untreated samples developed fresh corrosion products containing high chlorine levels on the polished surface. Their formation on the untreated objects suggests that there were free chloride ions in cracks and pores within the corrosion product matrix, which on contact with oxygen formed corrosion products. This may be similar to the process that leads to ‘weeping’ on iron objects, where an acidic solution of iron and chloride ions dries and reacts with oxygen to form bubbles or shells of akaganéite [23]. Many of the fresh products were found

near cracks in the structure or at the interface between the metal and the corrosion products, both areas where solutions containing iron and chloride ions are likely to be present in an actively corroding object.

By contrast, none of the treated objects showed this substantial development of fresh corrosion and in general the polished surfaces remained very close to their clean condition. The exception was in the treated half of CAE\_45, where fresh corrosion developed near internal slag inclusions and their associated corrosion products. It is likely that the treatment solution was not able to penetrate into these areas, which are deep inside the object and surrounded by very dense metal. This suggests one reason why objects may re-corrode after treatment; if chloride ions remain deep in the structure where the solution cannot diffuse they may subsequently stimulate renewed corrosion [15]. In this case, the structure of the metal may play an important role in how effective a treatment can be; iron with a large number of slag inclusions may be more susceptible to recurring corrosion from deep within the structure than iron that has few slag inclusions. Chlorine was also still present at low levels in the outer corrosion layers, presumably as part of corrosion products such as akaganéite. However, as there was no fresh development of corrosion products in these areas, and the levels were very low, it is likely that these do not pose a significant risk. If akaganéite subsequently transforms into goethite, chloride ions within its structure may pose a risk as they are released. The most recent evidence suggests that although some of the chloride ions in the structure of akaganéite can be released by desalination treatment, around one mass percent remains [24]. This remaining low level of chloride ions is considered a low risk compared to free chloride ions found in untreated objects [10, 24]. A second chlorine-containing corrosion product,  $\text{Fe}_2(\text{OH})_3\text{Cl}$ , has recently been identified in terrestrial and marine corrosion products [25, 26], but its role in the post-excavation corrosion of iron, and its response to desalination treatment, require further investigation.

Although, as observed in this study, desalination treatment may not remove chloride ions in sealed areas such as slag inclusions, it seems to have been successful in removing chloride ions present at the metal–corrosion interface and free chloride ions present in cracks in the corrosion structure. As chloride ions usually concentrate at the metal–corrosion interface [27, 28], their removal will reduce the risk of deterioration of archaeological iron. This was clearly shown by the rapid development of fresh corrosion on the untreated samples compared to the treated samples. The SEM data suggest that desalination treatment significantly reduces the risk of new corrosion occurring, even if some chloride ions remain in the structure of the corrosion products. Striving to remove 100% of the chloride ions present in an object may not be a realistic goal, but enough can be removed in most cases to make a clear difference to the object’s vulnerability to fresh corrosion.

## CONCLUSIONS

The analysis of cross-sections of treated and untreated iron objects using SEM-EDX analysis has proved an effective method of contributing to treatment assessment. The formation of fresh corrosion products on nearly all the untreated samples, compared to almost none on the treated samples, showed that treatment has a positive impact on the stability of iron. Some of the factors affecting treatment success were also identified:

- Free chloride ions can be removed from the outer layers of corrosion and the metal–corrosion interface and this seems to reduce the risk of further corrosion significantly;
- Chloride ions may remain within the corrosion layers of treated objects, albeit at much lower concentration than in untreated objects, but they were not associated with the development of fresh corrosion;
- Chloride ions located deep within the metal, such as those associated with slag inclusions, are unlikely to be accessible to the treatment solution and may cause further corrosion of the object.

Further confirmation of these points might be gained by taking an untreated sample, locating areas of chlorine and akaganéite in the structure using SEM-EDX and Raman spectroscopy as demonstrated in this study, treating this section and then reanalysing the same areas to note any change. SEM-EDX imaging and analysis might also shed light on the effect of treatments on corrosion product structure, for example its coherence and porosity, issues that are often discussed by conservators but have rarely been analysed in detail. This was not attempted in this limited study, but it too would need to be carried out on the same sample before and after treatment rather than on matched halves.

Although SEM-EDX analysis is limited to elemental analysis of the corrosion products, the changed distribution and concentration of chlorine in the treated and untreated sections has provided an insight into the effects and limitations of desalination treatment. Despite the small scale of this study, the detailed analysis provided by SEM-EDX has been beneficial in understanding desalination treatment and its effectiveness on a qualitative basis. This information will be used alongside quantitative data on treatment efficiency to provide a more rounded picture of desalination and inform conservators about its limitations and the factors that contribute to successful treatment.

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