

Original research or treatment paper

# The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions

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Chloride-contaminated archaeological iron is unstable and problematic to store and display within museum collections. Reducing its chloride ion content using aqueous desalination followed by storage in controlled relative humidity offers one treatment option. This study reports a quantitative assessment of chloride extraction by aqueous deoxygenated alkaline desalination solutions from 120 individual archaeological iron nails. The three treatment methods comprised alkaline sulphite solution (0.1 M NaOH/0.05 M Na<sub>2</sub>SO<sub>3</sub>) at room temperature and at 60°C and sodium hydroxide solution (0.1 M) deoxygenated using a nitrogen gas positive pressure system at room temperature. Chloride extraction was monitored using a specific ion meter. The nails were digested after treatment to measure their residual chloride content. A wide range of extraction patterns emerged, with the majority of individual treatments extracting 60–99% of the chloride present. Residual chloride levels for 87% of the objects fell below 1000 ppm and 42% were below 200 ppm. Although no treatment extracted 100% of the chloride in the object, alkaline desalination produced very significant reductions in chloride content. The impact of this on future corrosion of the objects is discussed. This quantitative and statistically viable assessment of deoxygenated desalination treatments provides evidence to support their use in conservation practice, which will impact on procedures for the preservation and management of archaeological heritage.

**Keywords:** Archaeological iron, Chloride, Desalination, Alkaline sulphite, Sodium hydroxide

## Introduction

During burial, archaeological iron attracts chloride ions (Cl<sup>-</sup>), which contribute to the corrosion process as counter ions. They act as corrosion accelerators after excavation and exposure of iron objects to damp oxygenated atmospheres (Turgoose, 1982, 1985, 1993). Chloride-bearing akaganéite (β-FeOOH) is a post-excavation corrosion product (Zucchi *et al.*, 1977; Selwyn *et al.*, 1999; Réguer *et al.*, 2006, 2007a) that is capable of promoting iron corrosion at only 15% relative humidity (RH) (Watkinson & Lewis, 2005a, 2005b). The corrosion rate of chloride-contaminated excavated iron increases with rising RH (Watkinson & Lewis, 2005a, 2005b) with rapid corrosion above 60% RH when adsorbed water films thicken (Garverick, 1994, p. 5). This physically damages and ultimately destroys the iron object as an archaeological resource. It is possible to

maintain iron collections below 15% RH to prevent their corrosion, but irrespective of the technical requirements of the desiccation methodology, meeting low RH targets requires strict maintenance programmes and considerable expenditure (Watkinson & Tanner, 2008). Financial, staffing, and other pressures ensure that museums with large collections of archaeological iron will struggle to maintain consistently low RH over long periods. Any failure of the desiccation system allows corrosion to restart, as the objects still retain their chloride ions. Desiccation, although a proven method of both corrosion prevention and control, therefore also presents high risks if its failure goes undetected for long periods (Watkinson & Lewis, 2004, 2005a, 2005b).

## Removing chloride ions

Conservators have viewed the removal of chloride ions from objects to be a viable preservation option since washing methods were first reported (Krause, 1882). Resurgence of interest in desalination occurred in the

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1970s with the development of the alkaline sulphite method (North & Pearson, 1975), which offered corrosion protection to objects during their treatment (Gilberg & Seeley, 1982; Turgoose, 1985). However, there were concerns regarding the effectiveness of chloride ion removal (Beaudoin *et al.*, 1997) and the risk of damage to information-bearing corrosion layers from long-term immersion in alkaline solutions (Selwyn & Logan, 1993; Selwyn & Argyropoulos, 2005). A lack of quantitative evidence to support the use of desalination treatments and increased professional focus on preventive conservation reduced the use of desalination treatments in the UK (Knight, 1997; Ganiaris, 2009), whereas in Europe there continued to be a limited use of alkaline sulphite and other desalination methods (Scott & Eggert, 2009, p. 162).

The long-standing concept that desalination ‘stabilizes’ iron has rightly produced scepticism, which has distorted the possible value of desalination in preserving chloride-infested iron. A more accurate interpretation of desalination is that it *enhances* stability by reducing corrosion rates, rather than preventing corrosion and inducing stability, but this concept has only slowly become the focus for conservation research into desalination (Watkinson, 2010). To define and assess the worth of alkaline desalination treatments, it is essential to generate reliable, quantitative, and statistically valid data on the effectiveness of treatments as chloride ion extractors and to examine the degree of stability imparted to objects. It will then be possible to define the role of desalination within holistic treatment strategies for preserving archaeological iron. An increased stability in desalinated iron objects may mean post-treatment storage RH can be raised to higher values without endangering object longevity, reducing energy, and management burdens for long-term storage of iron. Without quantitative and robust data defining the outcome of treatments, such questions cannot be addressed.

It is assumed that removing some chloride ions from archaeological iron improves its stability, but there are no quantitative data to support this. Anecdotal evidence and information from collection surveys does appear to show that desalinated objects are more likely to survive longer, and in better condition, than untreated objects. A survey of 5000 objects treated in alkaline sulphite found a re-corrosion rate of only 0.02% (Loeper-Attia & Weker, 1997), and periodic collection surveys at the Museum of London found that overall object lifespan was increased by alkaline desalination treatments, although re-corrosion was not always prevented (Keene & Orton, 1985; Keene, 1994). Data from collection surveys must be viewed with caution, as the consistent measurement of existing condition in comparison with original condition is difficult and subjective, whereas other variables such as environmental

parameters may not be well controlled and a reliable control sample is not always available. Nevertheless, current knowledge with regard to the form, location, and action of chloride ions in iron supports this qualitative assessment that treatment imparts enhanced stability (Neff *et al.*, 2004, 2005; Réguer *et al.*, 2005, 2006, 2007a, 2007b, 2009; Guilminot *et al.*, 2008); quantitative data are required to prove this.

Previous studies indicate that substantial amounts of chloride ions can be removed from iron using a wide range of desalination methods, but especially by aqueous alkaline systems (North & Pearson, 1978b; Watkinson, 1982, 1983, 1996). Although alkaline deoxygenated treatment has existed for nearly four decades, there remains uncertainty with regard to its true effectiveness in removing chloride ions from archaeological iron. To some extent, research has been limited by ethical considerations; quantitative measurement of extraction efficiency requires detecting the post-treatment bulk chloride ion content of objects. This is usually only possible through destructive analysis involving digestion, resulting in total loss of the object. The relatively small sample sizes of the few studies providing quantitative extraction data (Watkinson, 1982, 1983, 1996; Watkinson & Al-Zahrani, 2008) make statistical evaluation difficult. In the most recent study (Al-Zahrani, 1999; Watkinson & Al-Zahrani, 2008), the alkaline deoxygenated treatments extracted an average of 97–99% of the chloride ions present in objects. Such high extraction efficiencies have been questioned, as the potential exists for loss of chloride ions as HCl during the digestion phase of the experimental work (Scott & Eggert, 2009, p. 141; Schmutzler & Eggert, 2010). To address these potential problems, the study reported in this paper uses carefully controlled digestion and a large dataset to determine chloride ion extraction efficiency and post-treatment residues; a second paper will report the response of treated objects to corrosion-accelerating environmental conditions. These results will enable the re-evaluation of alkaline deoxygenated treatments in improving the stability of archaeological iron and how their use may contribute to more efficient management strategies.

### *Aims and objectives*

The primary aim of the study was to offer data on the effectiveness of chloride ion removal by alkaline deoxygenated methods, to facilitate their use in an evidence-based and predictive manner.

This was achieved by

- examining three deoxygenated desalination methods for treating archaeological iron nails: alkaline sulphite (0.1 M NaOH/0.05 M Na<sub>2</sub>SO<sub>3</sub>) at room temperature (AS20) and at 60°C (AS60) and 0.1 M sodium hydroxide deoxygenated with nitrogen gas (dNaOH);

- determining the amount of chloride removed during desalination treatment;
- determining residual chloride ion content in treated objects by digestion;
- determining chloride extraction efficiency for each object;
- examining relationships between the quantity of chloride ions removed, residual chloride content, and treatment method, and identifying other factors contributing to treatment outcome.

## Experimental

Archaeological wrought iron nails from three sites were donated for the experimental treatment and destructive analysis: Bornais, Outer Hebrides (BOR) (excavated 2003), Caerwent, South Wales (CAE) (excavated 1981–1984), and Billingsgate, London (BIL) (excavated 1983). None of the nails had been previously treated or had any of their corrosion products removed. Forty nails from each site were treated, divided among three treatment methods (shown in Table 1). This was a conscious choice to include a range of materials with different corrosion profiles and morphologies in each treatment, and to facilitate inter-treatment and inter-site comparison. The treatment methods were selected based on previous research into desalination methods, in particular the use of lower-concentration treatment solutions and nitrogen gas as an alternative deoxygenation method (Al-Zahrani, 1999; Schmidt-Ott & Oswald, 2006; Wang *et al.*, 2008).

Each nail was placed in an individual 125 ml high-density polyethylene (HDPE) flask; solutions were changed approximately every 14 days until two consecutive baths contained  $<10 \text{ mg/l Cl}^-$ . Owing to time constraints, some treatments had to be terminated before this criterion was met; the longest treatment time was 96 days (56 days for the heated treatment AS60). The maximum number of baths used was six; the solution pH was  $\sim 13$ . Nitrogen gas de-oxygenation was achieved using a positive pressure system that directed the gas into sealed Stewart Plastics™ boxes containing the individual treatment flasks (see Rimmer (2010) for further details). The oxygen concentration of all solutions was tested during treatment using a dissolved oxygen meter (Hach HQ40d with LDO® probe) and found to be no more than  $0.5 \text{ mg/l}$  in all cases, showing that the nitrogen-gas method is as efficient as sodium sulphite in removing oxygen.

Using 14-day immersion times speeds up the overall treatment by optimizing diffusion gradients: diffusion-controlled release of chloride ions reaches 60–70% completion within the first 14–21 days of immersion, after which decreasing concentration gradients slow down chloride ion diffusion (North & Pearson, 1978b; Watkinson, 1982; Selwyn *et al.*, 2001; Réguer *et al.*, 2007b; Liu & Li, 2008; Wang *et al.*, 2008). The mass of the nails fell within the range of 0.8–28.7 g, with 93% falling within the 2–20 g range and 75% in the 4–10 g range across all sites (see also Fig. 8). Solution volumes were  $100 \text{ cm}^3$  for dNaOH and  $120 \text{ cm}^3$  for AS20 and AS60, resulting in varying object weight-to-volume ratios. Provided the weight-to-volume ratio does not fall below 1:4, this does not have a significant effect on treatment outcome (Watkinson, 1982). This condition was maintained for all objects.

Chloride ion analysis was carried out using a Radiometer Analytical PHM250 specific ion meter with Hg/HgSO<sub>4</sub> reference electrode and a chloride-specific electrode. A four-point calibration using standard sodium chloride (NaCl) solutions was used and checked for accuracy every two hours during measurement periods using known standards. Treatment solutions were neutralized with 5 M nitric acid (HNO<sub>3</sub>) and a 0.5 M ammonium acetate/0.5 M acetic acid buffer was added in a 1:10 ratio. All solutions used deionized water, and blank solutions were checked for chloride contamination of the chemicals. The detection limit was 0.5 ppm and accuracy was around 10%.

After treatment, objects were dried using oven-dry silica gel as a desiccant for at least two weeks. Objects were then placed in 5 M nitric acid and digested at room temperature in screw-top HDPE containers or in beakers covered with either watch glasses or a polyethylene wax film (Parafilm™). The resulting solutions were neutralized with 3 M NaOH solution, filtered to remove the ferrous hydroxide precipitate, and analysed using the specific ion meter. The experimental protocols for the digestion method and the measurement of chloride were checked for accuracy and reproducibility using known concentrations of dissolved ferrous chloride, and showed that no measurable chloride loss occurred either through evaporation of HCl during the digestion process or through adsorption of chloride ions by the ferrous precipitate. Residual chloride data are available for all but two of the treated objects; two objects (both CAE, one

**Table 1** Details of three experimental treatments carried out

Treatment	NaOH concentration	De-oxygenation method	Temperature ( $\pm 5^\circ\text{C}$ )	Number of objects treated	Maximum treatment time (days)
dNaOH	0.1 M	Nitrogen gas	20	48	96
AS20	0.1 M	0.05 M Na <sub>2</sub> SO <sub>3</sub>	20	48	96
AS60	0.1 M	0.05 M Na <sub>2</sub> SO <sub>3</sub>	60	24	56

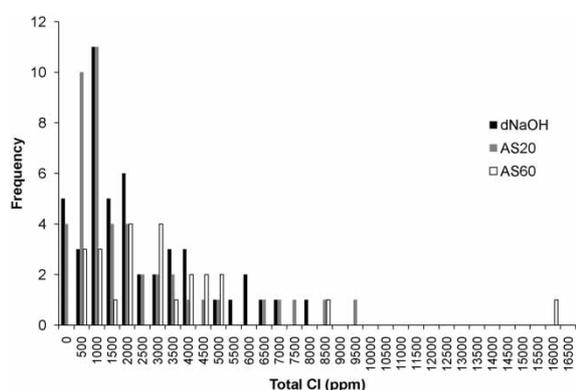
dNaOH and one AS20) did not complete the digestion process in the time available. The study data on residual chloride ions presented below, therefore, represents the analysis of 118 individual nails.

## Results

Chloride ion content in objects is expressed as parts-per-million related to the mass of each object (equivalent to microgram  $\text{Cl}^-$  per gram of object). Table 2 gives statistical data regarding the outcome of the three desalination treatments. Both mean and median have been calculated, as the data distributions are skewed and therefore the mean is not always representative of the central tendency of the data. Similarly, the interquartile range (IQR) has been calculated alongside standard deviation to represent the spread of the data. Total chloride is the sum of extracted and residual chloride for each object.

### Chloride content of samples

The treated samples had a wide range of total chloride content, up to 16 000 ppm but more typically in the range of 500–10 000 ppm (Fig. 1), which is remarkably similar to the range for 116 objects from three other archaeological sites reported elsewhere (Watkinson, 2010). There are some variations in the chloride content of the three object groups used for each treatment; AS20 contained more objects with total chloride in the 500–1000 ppm range, whereas AS60 contained no objects in the 0–500 ppm range and more in the



**Figure 1** Distribution of total chloride content of the objects in the three desalination treatments. Interval size is 500 ppm.

3000–5500 ppm range. However, the general pattern and distribution of the samples are similar (Fig. 1), and evaluation using the analysis of variance (ANOVA) test shows that the differences between the sample groups are not statistically significant ( $F = 2.26$ ,  $F_{\text{crit}} = 3.09$  at 0.05 confidence level), with the variation within each sample exceeding the variation between them. This means that the three groups of objects can be directly compared. (Although the ANOVA test is designed to work with normal rather than skewed distributions, in this case the sample size is robust enough to overcome this problem. The difference between the  $F$  value for the sample and the critical value is substantial enough to be confident that the result is valid, particularly as removing the outlier sample of 16 000 ppm reduces  $F$  to 0.68.)

**Table 2** Summary statistics for the three experimental treatments

	dNaOH 47	AS20 47	AS60 24
Number of samples			
Extracted Cl (ppm)			
Mean	1990	2028	3269
Median	1542	1095	2854
$\sigma$	1733	2283	3171
IQR	1936	2121	3244
Range	6884 (15–6899)	9335 (44–9379)	14 934 (130–15 064)
Median % Cl extracted in first bath	70	71	92
Number of objects not completing treatment	7 (15%)	4 (8%)	1 (4%)
Residual Cl (ppm)			
Mean	596	320	360
Median	300	196	218
$\sigma$	770	328	291
IQR	434	294	432
Range	3859 (32–3891)	1561 (37–1598)	1031 (109–1140)
Total Cl (ppm)			
Mean	2587	2348	3629
Median	1942	1293	3123
$\sigma$	2028	2318	3309
IQR	2517	2289	3261
Range	8077 (201–8278)	9310 (262–9572)	15 437 (768–16 205)
Extraction (%)			
Mean	74	77	84
Median	79	83	89
$\sigma$	22	23	19
IQR	28	24	10
Range	93 (6–99)	87 (12–99)	82 (16–98)

$\sigma$ , standard deviation.

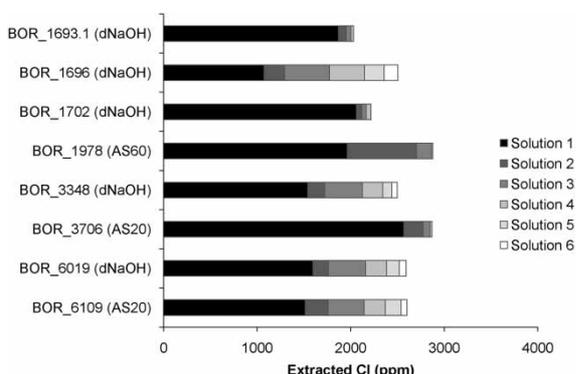
### Progress of treatment

In all three treatments, as might be expected, the majority of chloride was extracted in the first bath, from a median of 70% of total extracted chloride in dNaOH to a median of 92% of the extracted chloride in AS60 (Table 2). There was significant variation between objects in the progress of treatment: some objects extracted little chloride after the first bath, while significant quantities of chloride were still being removed from other objects in the later baths (for examples see Fig. 2). The speed and pattern of extraction could not be clearly related to the total chloride content of an object, although objects with low total chloride tended to show anomalous patterns. There was some variation by site; at room temperature, objects from BIL required no more than five baths to reach the 10 mg/l endpoint in all but two cases, whereas BOR and CAE objects were more likely to require the total treatment time using six baths, and BOR objects with the highest chloride content often show a smaller proportion of chloride extracted in the first bath.

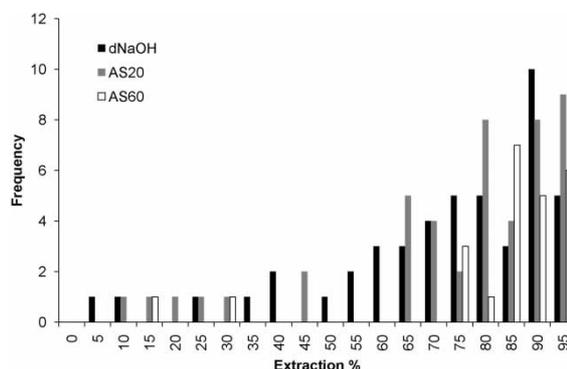
The intended completion point for treatment was designed to be a solution concentration of <10 mg/l Cl<sup>-</sup> in two successive baths. A few of the objects did not achieve this endpoint in the time available. Of the 120 objects treated, 12 did not complete: seven objects in dNaOH, four objects in AS20, and one object in AS60 (Table 2). By site, seven objects were from CAE, four objects from BOR, and one object from BIL. The maximum final solution concentration was 44 mg/l. Although this was an unintended outcome due to the limited time available for treatment, the variation in the endpoints provided useful data on the relationship between treatment completion and residual chloride content (see Discussion).

### Comparison of treatments

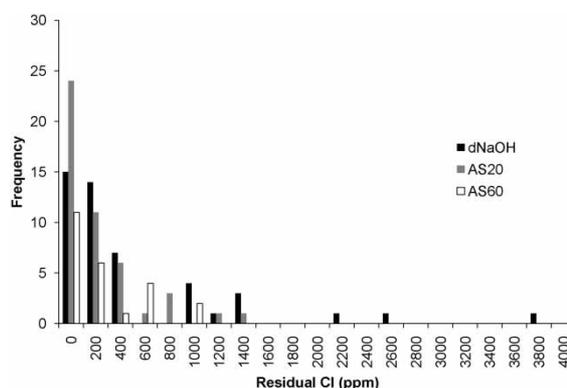
Two measures are used to compare the efficiency of the three treatments in extracting chloride ions from objects: the percentage efficiency of extracted chloride



**Figure 2** Extraction pathways for selected objects from BOR. For comparison, all of the examples selected have total extracted chloride between 2000 and 3000 ppm, and all reached <10 mg/l in the final treatment bath.



**Figure 3** Chloride extraction efficiency for objects from all treatments. Interval size 5%.



**Figure 4** Residual chloride concentration in objects after treatment as a function of treatment. Interval size 200 ppm.

as a proportion of total chloride present, and the post-treatment residual chloride content of the object. Figs. 3 and 4 show the distribution of percentage efficiency and residual chloride, respectively, and summary statistics are in Table 2.

A large majority of objects (85%) have extraction efficiency between 60 and 99% with a scatter of lower values (Fig. 3). This is the case for all three treatments, except that the main group of AS60 results begins at 75%, resulting in a higher median value of 89% and a smaller IQR of only 10% (Table 2). dNaOH performs least well, with a median efficiency of 79% and a larger IQR of 28% (Table 2). However, an ANOVA test shows that there is no statistically significant difference between the mean extraction percentage of the three treatments ( $F = 1.68$ ,  $F_{crit} = 3.09$  at 0.05 significance). Although it is still possible that the difference in extraction percentage is significant, the variation of the extraction results within each group exceeds the difference between the three treatment groups, and so statistically no treatment can be shown to be more effective from these samples. It seems that although there may be minor differences between the three treatments, all treatments are capable of extracting significant amounts of chloride ions.

Residual chloride levels are positively skewed, with 87% of objects retaining <1000 ppm chloride after

treatment (Fig. 4). All of the outliers in the higher regions of residual chloride stem from the dNaOH treatment, but otherwise there are no substantial differences between the three treatments in terms of residual chloride.

### Comparison of sites

Fig. 5 shows the distribution of the total chloride content of the objects from the three sites. BOR objects have a larger and higher-ranging distribution compared with CAE and BIL. The mean and median (Table 3) show that BOR objects have a much higher typical chloride content, about three times greater than the other two sites. This is not a surprising difference, as Bornais is located close to the sea

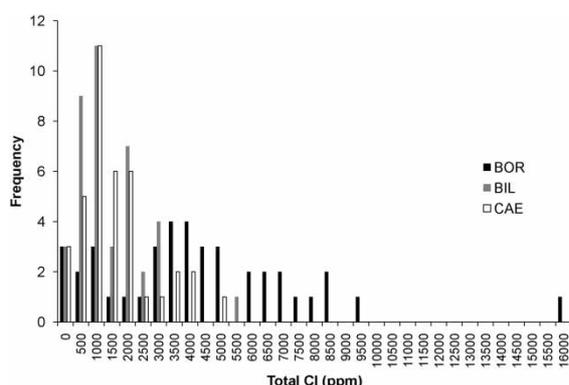


Figure 5 Total chloride concentration in all objects from BOR, BIL, and CAE. Interval size 500 ppm.

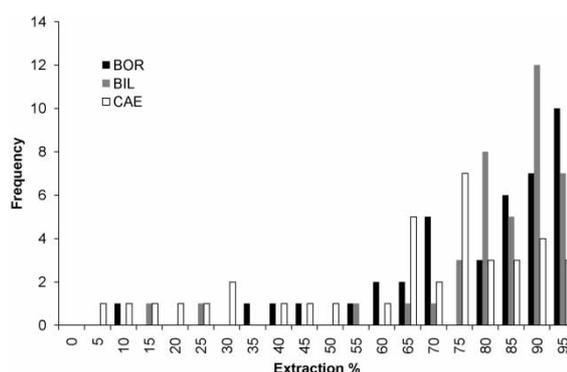


Figure 6 Chloride extraction percentage for all treated objects as a function of site. Interval size 5%.

and the soils in the area are therefore likely to contain high levels of chloride ions.

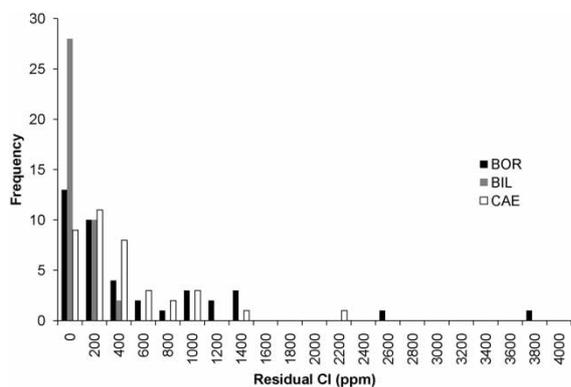
Extraction percentage is evaluated on a site-by-site basis using data from all three treatments together, on the assumption, as shown above, that the differences between the treatments are not statistically significant. As objects from each site were treated by each method, any systematic differences between treatments should apply to all the sites equally.

BOR and BIL have more objects at higher extraction percentage than CAE (Fig. 6), which spreads more across the range of extraction percentage and has a significantly lower mean and median percentage (Table 3). The median residual chloride level of CAE objects is at par with BOR objects (Table 3). Their distribution is also very similar (Fig. 7), while the

Table 3 Summary statistics for treated objects by site origin

	Bornais 40	Billingsgate 40	Caerwent 38
Number of samples			
Extracted Cl (ppm)			
Mean	3946	1490	1313
Median	3298	1227	952
σ	3086	1126	1130
IQR	3111	1532	1063
Range	14 934 (130–15 064)	5653 (44–5696)	5083 (15–5098)
Residual Cl (ppm)			
Mean	656	171	490
Median	359	152	361
σ	770	98	459
IQR	757	123	401
Range	3810 (81–3891)	399 (32–431)	2224 (50–2274)
Total Cl (ppm)			
Mean	4602	1661	1803
Median	4247	1389	1422
σ	3186	1142	1165
IQR	3923	1432	1013
Range	15 825 (380–16 205)	5750 (201–5951)	5053 (254–5307)
Extraction (%)			
Mean	80	84	67
Median	86	89	77
σ	20	17	26
IQR	23	13	29
Range	86 (12–99)	82 (17–99)	93 (6–99)

The data from all three treatments have been combined for the objects from each site. σ, standard deviation.



**Figure 7** Distribution of residual chloride arranged by site. Interval size 200 ppm.

distribution of BIL objects is more sharply skewed towards the lower end of residual chloride values. As total chloride values for BOR are statistically higher than those of CAE (Table 3), this suggests that CAE nails are retaining a higher percentage of their chloride than would otherwise be expected from their typical total chloride ion content, which is more similar to BIL nails. The nails from BIL have the most encouraging results, with no object retaining >450 ppm and a median residual chloride value of only 152 ppm (Table 3).

## Discussion

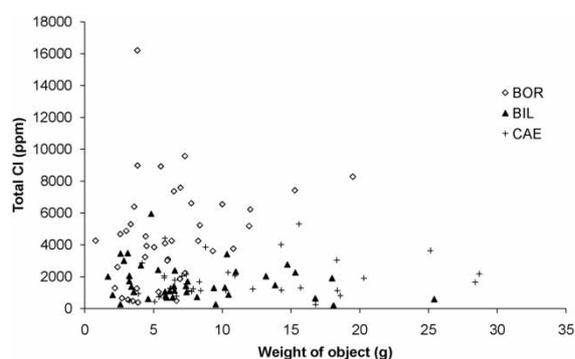
### *Extraction performance of treatments*

The objects treated in this study displayed a wide range of extraction patterns. There is no doubt that high extraction values are attainable by deoxygenated alkaline treatments: 36% of the chloride extractions recorded in the tests reported here were in the 90–99% range and 48% within the 85–99% range. The mean values of treatments in this study are significantly lower than the mean extraction of 97% for alkaline sulphite and 99% for nitrogen-deoxygenated sodium hydroxide reported by Al-Zahrani (1999). It is possible that the smaller statistical population of Al-Zahrani can account for this difference, but such an extensive statistical bias towards high extraction seems unlikely, particularly as over half of the objects treated in that study reported 100% chloride extraction, which was not achieved for any object for those papers or in any previous study of desalination (Watkinson, 1982, 1983, 1996). The difference may be due to chloride loss as volatile HCl during heated object dissolution (Scott & Eggert, 2009: 141; Schmutzler & Eggert, 2010) or relate to the lower concentration of NaOH used in this study, although 0.1 M NaOH has been previously suggested to have the same extraction power as 0.5 M (Schmidt-Ott & Oswald, 2006; Wang *et al.*, 2008). Whatever the cause, the high treatment efficiency reported by Al-Zahrani

was not reproducible here. The results of this study compare favourably with previous small-scale treatment studies that measured residual chloride content (Watkinson, 1982, 1996). The 60°C alkaline sulphite washing here returned a mean of 84%, whereas Watkinson (1996) recorded an 87% mean, suggesting that the lower treatment concentration used here (0.1 M compared with 0.5 M in Watkinson, 1996) produced results very similar to the more standard treatment concentration. The range of chloride contents of the objects in this study also compares well with that of other sites that have been tested (Watkinson, 2010), which further supports the representative nature of the samples used in this study.

There was no observable difference in the treatment effectiveness of the two deoxygenation methods (nitrogen gas and sodium sulphite). The time needed for nitrogen gas to deoxygenate the solution via positive pressure was not detrimental to the overall performance of the treatment. Although the heated treatment (AS60) completed more quickly, statistical analysis could not demonstrate a significant difference in the extraction percentage of the three treatments or in their average residual chloride content, although the mean and median extraction percentage of AS60 were somewhat higher (Table 2). This suggests that there is no major advantage in heating treatments to increase chloride extraction, but there are benefits in reducing treatment time by increasing the chloride diffusion rate, allowing a greater proportion of the objects in the heated treatment to reach the completion criteria within the allotted period. The faster diffusion of ions at 60°C may be releasing a larger proportion of the soluble chloride in the first bath, and this significantly speeds up extraction and reduces the chloride content of the object more rapidly. As a percentage of the total chloride present in the object, the first AS60 bath extracted a mean of 74% (median 79%), close to the total extraction efficiency of the room temperature baths over 96 days. It appears, therefore, that even a short bath of two weeks at 60°C is sufficient to achieve a significant chloride release.

Both chloride extraction percentage and residual chloride ion content as measures of treatment success relate chloride ion content to the object weight. Recording chloride extraction per unit area of metallic iron in the object would be a more realistic way to compare the removal of chloride ions from iron objects (Watkinson, 2010), as most chloride ions are held there either as the counter-ion at anodes or within  $\beta$ -FeOOH and its precursor  $\text{Fe}(\text{OH})_3\text{Cl}$  (Turgoose, 1985; Réguer *et al.*, 2007a). Using surface area as a comparator would account for objects of similar weight with differing shapes and surface areas influencing chloride concentration. Larger

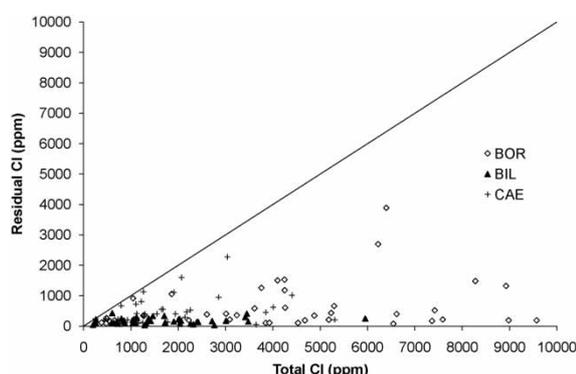


**Figure 8** Distribution of chloride content of objects as a function of the object weight. No clear relationship exists between the object weight and its chloride content for any of the sites tested.

surface areas offer a more extensive area for corrosion and therefore chloride retention. Unfortunately, measuring the metallic surface area of a corroded iron object is prevented by the overlying corrosion layers; estimation from the radiograph of objects is also problematic due to the intrinsic unevenness of the corroded metal. Choosing iron nails as test samples in this experiment offered objects of broadly similar shape, so that to some extent weight differences will reflect differences in the metal surface area present. Comparing extraction efficiency as a function of object weight offers a comparison between differing objects and is the only easy measure available (Watkinson, 2010).

Using chloride extraction percentage as a guide to treatment success has been used in previous treatment studies (Watkinson, 1983, 1996; Al-Zahrani, 1999), but the extent of its usefulness is limited (Watkinson, 2010). Objects of similar weight can have very different total chloride content (Fig. 8). A 900 ppm extraction for an object containing 1000 ppm chloride and a 9000 ppm extraction for a 10 000 ppm object would both record a 90% extraction efficiency, but the resulting residual chloride content of the objects is very different. Most conservators would be intrinsically happier with a 9000 ppm extraction in a treatment than 900 ppm, yet the chloride residue in the former is ten times higher than in the latter.

The quantity of chloride ions retained within objects after treatment is more likely to be of significance in determining post-treatment corrosion performance than extraction percentage, and is therefore of more interest in describing treatment success. An object starting out at 700 ppm total chloride and ending up in the 200–400 ppm residual chloride range records a significantly worse extraction efficiency than an object starting out with 3000 ppm chloride, yet both objects have had their chloride content reduced to similar final concentrations. In this study, 68% of objects retain <400 ppm chloride after washing,

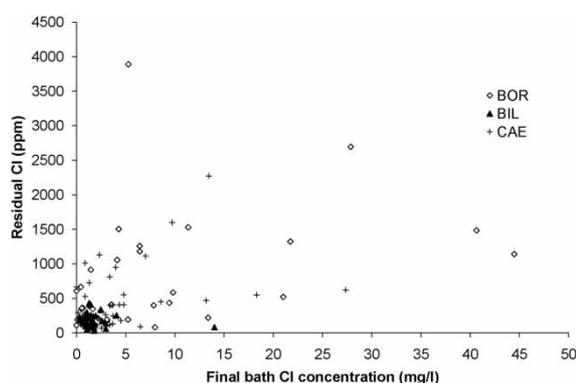


**Figure 9** Total chloride content of objects plotted against their residual chloride content after treatment, grouped by site. The black line shows where total Cl = residual Cl, i.e. if no treatment had occurred. The further a data point is away from the black line, the more successful the treatment has been in reducing chloride content. The outlier at 16 000 ppm has been excluded to improve legibility.

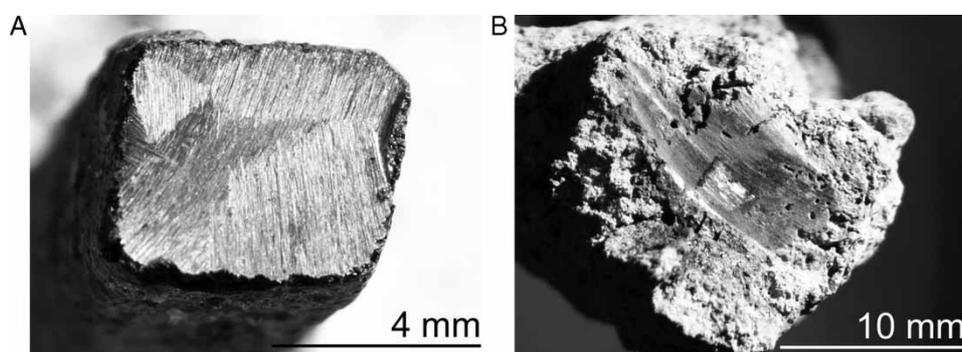
irrespective of their total chloride content (Fig. 9) and 81% of objects retain <600 ppm chloride. There is no clear relationship between the total chloride and residual chloride, particularly for objects above 2000 ppm total chloride where chloride contents are significantly reduced by treatment (Fig. 9).

#### Factors affecting treatment performance

Several factors seemed to contribute to the likelihood of objects retaining higher chloride levels after treatment. Incomplete treatment was an obvious factor. Although in this study treatment was defined complete with <10 mg/l  $\text{Cl}^-$  in the final solution, Fig. 10 shows that where the final solution contained less than <5 mg/l, residual chloride levels were almost always less than <500 ppm. Of the 94 objects with final solution concentration <5 mg/l, only 13 (14%) objects had a residual chloride concentration of more than 500 ppm, and only four (4%) had a residual chloride content of >1000 ppm. Incomplete treatment was



**Figure 10** Residual chloride in objects versus the concentration of chloride in the final treatment bath related to object origin. Failing to achieve <5 mg/l in the final bath increases the likelihood of high residual chloride.



**Figure 11** Two objects showing varying corrosion morphologies. (A) BIL\_19.1 has only thin overlying corrosion products, whereas (B) CAE\_29.1 shows thicker corrosion with a significant dense product layer and outer adhering soil products.

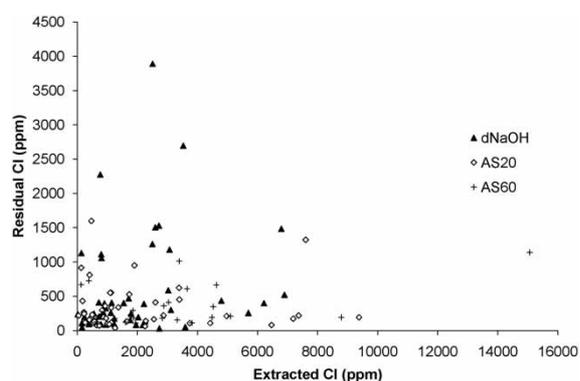
associated most strongly with objects from CAE (Table 2). This may point to a role of object morphology in affecting the residual chloride levels. CAE objects had the bulkiest, thickest corrosion products (Fig. 11), and also seem to have had the poorest extraction performance (Fig. 6, Table 3), whereas BIL objects, from a partially anaerobic site with much thinner corrosion products (Fig. 11), had the best, with no object retaining more than 450 ppm (Fig. 7). A small study of objects from these sites using scanning electron microscopy coupled with energy-dispersive X-ray spectrometry showed that treated CAE objects also continued to harbour chloride ions along slag inclusions within the metal, which may account for their poorer extraction performance and higher residual chloride levels (Rimmer & Wang, 2010). The effectiveness of treatment therefore depends at least partly on factors related to the object, its provenance and morphology, rather than being dependent on the mechanism of the treatment alone.

A further reason for poor extraction performance may be the form of the chloride in the objects (Watkinson, 2010), which will relate to the initial concentration of chloride, its location, the post-excavation environment, and time since excavation. The formation of chloride-bearing  $\beta$ -FeOOH is symptomatic of iron corrosion in the presence of high concentrations of chloride and oxygen (Turgoose, 1985, 1993; Stahl *et al.*, 2003).  $\beta$ -FeOOH contains chloride ions in its hollandite structure and adsorbed onto its surface (Stahl *et al.*, 2003; Guilminot *et al.*, 2008; Réguer *et al.*, 2009). The latter are mobile and readily washed away by water and alkaline solutions (Al-Zahrani, 1999; Stahl *et al.*, 2003; Watkinson and Lewis, 2005a), which may explain the high extraction of chloride ions in the first two weeks of heated treatment. The chloride ions trapped in the tunnel structure of  $\beta$ -FeOOH have been found to be difficult to remove below 2–3 mass% (North, 1982), although a recent study lowered this to 1 mass% for  $\beta$ -FeOOH synthesized by ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) hydrolysis

(Réguer *et al.*, 2009). Unless  $\beta$ -FeOOH transforms during treatment, it will continue to retain chloride ions within its crystal structure, which will be detected by digestion. The quantity of chloride ions retained in this form is unknown, as it is not possible to distinguish whether residual chloride is in a bound or soluble form using the digestion method. If most residual chloride is present as bound chloride inside  $\beta$ -FeOOH crystals, this may not be significant for future corrosion, as  $\beta$ -FeOOH washed free of its mobile surface-adsorbed chloride ions has been shown to offer a negligible corrosion threat to iron (Watkinson & Lewis, 2005a; Wiesner *et al.*, 2007). Thus, removing the majority of the soluble and surface-adsorbed chloride ions with a short bath at 60°C should have a disproportionately high effect on reducing corrosion rates. The differences in corrosion-causing behaviour between bound and soluble chloride also mean that two objects containing the same amount of residual chloride may not have the same stability: one may contain only bound chloride whereas the other retains soluble chloride ions and so remains more susceptible to corrosion. This requires further testing.

### *Predicting treatment outcomes*

Predicting the outcome of desalination treatments is obviously of significant interest to conservators. The best method must be to determine residual chloride contents of objects, but this measure is not typically available to conservators; the amount of chloride extracted during a treatment can be measured, but the residual chloride cannot usually be detected without destroying objects. Nuclear activation analysis has been shown to be capable of non-destructive bulk chloride determination of archaeological iron objects (Selwyn & Argyropoulos, 2006), but the method is not commonly available for routine analysis. The only information available to conservators regarding the chloride content of their objects is how much chloride has been extracted, and as Fig. 12 shows



**Figure 12 Relationship of extracted and residual chloride. None of the treatments show any definable relationship between extracted chloride and the amount of residual chloride, showing that extraction data alone is a poor guide to the outcome of treatment.**

there is no significant relationship between extracted and residual chloride.

Although the range of extraction efficiency for any one treatment offers best- and worst-case scenarios for chloride extraction, it is too large to be of any predictive use (Table 2). Using the median extraction percentage with IQR providing limits may offer a better guide to how the majority of objects will perform during treatment, but exceptions to the statistic remain and it is not possible to know whether the object being treated is an exception. Furthermore, as already discussed, extraction percentage is a limited measure of treatment outcome. It is residual chloride values that offer the most robust and encouraging indication of the outcomes of desalination, irrespective of what extraction is recorded during treatment.

As the relationship between chloride content, location, and form and corrosion rate of objects has not been quantified, assessing the impact of treatment on the stability of objects is difficult. Bulk chloride data do not accurately represent the localized nature of chloride ions, which may concentrate in pits and cause localized corrosion that is extremely destructive to object morphology without bulk chloride levels being particularly high. No studies have examined how the all-important physical changes associated with corrosion of iron and loss of heritage value relate to chloride content, location, and form. Given these unanswered questions, it can only be assumed that low overall chloride levels are better for objects.

Despite this problem, some attempt to assess the improvement in stability due to chloride removal may be useful. North and Pearson (1978a) proposed boundary values for corrosion risk; they consider <200 ppm to be 'safe', whereas >1000 ppm is 'definitely damaging'. These values have not been tested on archaeological iron in a systematic manner. Rinuy & Schweizer (1981) performed some

informative experiments relating corrosion of chloride-contaminated modern iron at 95% RH to both the chloride content and the corrosion behaviour of archaeological samples. Unfortunately, given the wide range of unmeasured variables involved and the difficulties of comparing modern polished surfaces with the complex corrosion and localized chloride distribution on archaeological iron, it is not possible to draw wider conclusions from this work. Until the boundary values are tested on archaeological iron, they cannot be taken to be meaningful in understanding the level of 'stability' which deoxygenated alkaline treatment imparts. Nevertheless, they offer the only published guide to the relationship between residual chloride content and corrosion rate, so it is worth considering the results of the tests reported here in relation to these concepts of safe and damaging chloride levels.

All three desalination treatments made significant reductions in chloride levels for the majority of objects. Only 13% of objects retained chloride levels >1000 ppm and 42% of objects completed treatment retaining <200 ppm (Figs. 4 and 7). If the boundary levels mentioned in the study of North & Pearson (1978a) are accurate, this suggests that alkaline deoxygenated desalination treatments are capable of reducing corrosion rates out of the high-risk zone for 87% of objects, and that 42% can be made 'safe' by removing almost all the chloride present. If all objects are treated to <5 mg/l  $\text{Cl}^-$  in the final solution, these figures rise to 96% of objects retaining <1000 ppm and 49% retaining <200 ppm. A three-year research project at Cardiff University is currently investigating the chloride–corrosion relationship and the validity of these boundary values.

As post-treatment bulk chloride content of an object is not usually available, it is not possible to determine how successful treatment has been in an individual case. Therefore, all objects may still be at risk after a desalination treatment, but removing at least some of the chloride present must reduce that risk, in many cases significantly. The question of risk from chemical residues of the treatment solution has been raised (North & Pearson, 1975; Turgoose, 1993; Watkinson, 1996) but a recent experimental study showed this to be negligible in comparison with the risk from chloride ions (Rimmer & Watkinson, 2010). The future challenge is to determine the level of the risk remaining from chloride residues in comparison with untreated objects, and compare this to the short-term risks occurring to objects from immersion in alkaline solutions. By determining the relative costs and benefits of desalination treatment in reducing corrosion rates, it will be possible to build treatment and storage protocols that offer more cost-effective and long-term low-corrosion management strategies for

archaeological iron, based on a more comprehensive understanding of corrosion control.

## Conclusion

Deoxygenated alkaline desalination methods extract significant amounts of soluble chloride ions from archaeological iron objects. Rather than judging their effectiveness by the percentage of the total chloride within an object removed by treatment, it is suggested that it is the concentration of chloride remaining in the object that is of primary importance in determining the impact of treatment on corrosion rates. Desalination significantly reduces chloride ion content, with 42% of the treated objects having their chloride content reduced to <200 ppm and 81% reduced to <600 ppm. This can be improved by continuing treatments until chloride concentrations in the treatment solutions are as low as possible, and not exceeding 5 mg/l. At the same time, the successful extraction of around three-quarters of total chloride in a single 60°C alkaline sulphite bath of two weeks duration suggests that even short treatment can have a significant impact for many objects, removing much of the soluble chloride which poses the greatest risk. Deoxygenated alkaline desalination treatments are clearly a useful tool for reducing chloride levels in archaeological iron, which will slow down future corrosion and increase the stability of objects even if not all chloride ions present can be removed. As iron that is desalinated before being deposited in controlled storage is at lower risk when environmental parameters exceed the set humidity levels, treatment can be recommended as a method of improving the long-term preservation of iron which is at risk of damage from high chloride contents. Further work to examine the corrosion rates of treated and untreated iron is underway to determine how much the stability of iron objects is improved by desalination, with the aim of developing more relaxed RH storage parameters for desalinated archaeological iron. The results of that work pending, it is clear that de-oxygenated alkaline treatments are a successful method of significantly reducing the chloride content and the potential for damaging corrosion, and have an important role to play in contributing to the future preservation of archaeological iron collections.

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## Materials and suppliers

### Materials

BDH AnaLar sodium sulphite, Na<sub>2</sub>SO<sub>3</sub>, anhydrous

BDH AnaLar sodium hydroxide, NaOH

BDH AnaLar ammonium acetate, CH<sub>3</sub>COONH<sub>4</sub>

BDH AnaLar acetic acid, CH<sub>3</sub>COOH

All from VWR International Ltd, Poole, BH15 1TD, UK. <http://uk.vwr.com>, accessed 6 December 2011.

AnaLar Nitric acid, HNO<sub>3</sub>

Solutrate sodium chloride 0.1 M ampoule Parafilm™

All from Fisher Scientific UK Ltd, Bishop Meadow, Loughborough, Leicestershire, LE11 5RG. <http://www.fisher.co.uk>, accessed 6 December 2011.

### Stewart Boxes

Stewart Plastics Ltd, Stewart House, Waddon Marsh Way, Purley Way, Croydon, Surrey CR9 4HS, UK.

### Equipment

Radiometer Analytical PHM250 specific ion meter, ISE25CL chloride-specific electrode, REF621 chloride-free Hg/HgSO<sub>4</sub> reference electrode: Radiometer Analytical, 72 rue d'Alsace, 69627 Villeurbanne CEDEX, Lyon, France, <http://www.radiometer-analytical.com>, accessed 6 December 2011.

Hach Lange HQ40d meter

Hach Lange LDO® dissolved oxygen probe

Both from Hach Lange Ltd, Pacific Way, Salford, Manchester M50 1DL, <http://www.hach-lange.co.uk>, accessed 6 December 2011.

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