

# QUANTIFYING EFFECTIVENESS OF CHLORIDE DESALINATION TREATMENTS FOR ARCHAEOLOGICAL IRON USING OXYGEN MEASUREMENT

D Watkinson, M Rimmer\*

Cardiff University  
Department of Archaeology and Conservation  
John Percival Building  
Colum Drive, Cardiff  
CF10 3EU  
UK

\*Corresponding author: rimmermb@cardiff.ac.uk

## Abstract

Alkaline deoxygenated aqueous treatments are employed to remove damaging chloride ions ( $\text{Cl}^-$ ) from excavated archaeological iron objects; however, their effectiveness is either qualitatively assessed or anecdotal. A novel oxygen measurement technique is used to assess pre- and post-treatment corrosion rates of individual archaeological iron objects; these rates are related to their  $\text{Cl}^-$  content before and after treatment. Ten archaeological iron nails were individually sealed in reaction vessels conditioned to 80% relative humidity (RH) at 20 °C. The oxygen partial pressure inside each vessel was measured remotely over the course of 37 days using an OxyMini fibre-optic meter and a sensor spot inside each vessel. Control vessels containing nitrogen gas revealed negligible leakage. Objects were removed and treated for two weeks in an alkaline sulphite (0.1 M NaOH / 0.05 M  $\text{Na}_2\text{SO}_3$ ) solution at 60 °C and the extracted  $\text{Cl}^-$  was recorded quantitatively and then the objects were placed back in the oxygen measurement vessels (80% RH and 20 °C). After recording oxygen consumption, nitric acid digestion was used to determine the residual  $\text{Cl}^-$  content.

Half of the ten objects that were treated had their oxygen consumption rate reduced by 91% or more, with the oxygen consumption rate of the remaining reducing by 49-71%. Object  $\text{Cl}^-$  contents reduced from between 336-3487 parts-per-million (ppm) before treatment to a maximum of 364 ppm after treatment. A linear correlation between pre-treatment  $\text{Cl}^-$  content and oxygen consumption rate existed but was not apparent post-treatment, suggesting that the readily accessible soluble  $\text{Cl}^-$ , which is removed by a single two-week bath, is the most significant driver for corrosion. Half of the objects were still measurably consuming oxygen after treatment but it is expected that this slower corrosion rate should significantly increase overall lifespan. A single, brief, alkaline deoxygenation treatment is a useful addition to preventive conservation strategies for vulnerable iron objects. Use of oxygen partial pressure measurement to assess corrosion rates provides a new insight into the effectiveness of treatments for quantifying corrosion risk, determining the success of conservation strategies, developing management procedures and cost benefit analysis.

## Keywords

Archaeological iron, treatment, desalination, alkaline sulphite, oxygen consumption, corrosion rate.

## Research aims

This study used a novel oxygen consumption measurement technique to determine the effect of removing  $\text{Cl}^-$  ions on the corrosion rate of individual archaeological iron objects. The aim of the research was two-fold: first, to show that quantifying the corrosion behaviour of objects before and after treatments is a successful method for assessing treatment effectiveness and outcomes, and second, to determine whether it is possible to use short, low-risk desalination to significantly decrease corrosion rates for iron objects. The objective is to fit this into a broader programme of research into corrosion rates and treatment of archaeological iron in order to develop quantified datasets for underpinning conservation strategies for iron. Ultimately this will form part of a model for designing evidence-based predictive conservation and long-term management of archaeological iron objects.

## Introduction

Chloride ions ( $\text{Cl}^-$ ) are a significant driver of post-excavation corrosion of archaeological iron, resulting in cracking, delamination and eventual fragmentation of the objects (Loeper-Attia, 2007; Turgoose, 1982). Various strategies are available for mitigating this problem; either desiccation of objects to less than 15% relative humidity (RH) (Watkinson and Lewis, 2005a, b; Watkinson and Lewis, 2008), or attempting removal of  $\text{Cl}^-$  from the corrosion layers by means of treatment. One of the most common treatments is aqueous washing in an alkaline sulphite solution (North and Pearson, 1975) comprising sodium hydroxide (NaOH) to flood the object with negative ions to replace adsorbed  $\text{Cl}^-$ , and sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), which deoxygenates the solution, stops the corrosion process and frees  $\text{Cl}^-$  from their attraction to positively charged anodes at the metal surface. Both desiccation and desalination treatments have advantages and disadvantages, particularly regarding the resources needed to apply them to large iron collections.

Previous work has shown that alkaline sulphite is an efficient extractor of  $\text{Cl}^-$  (Rimmer et al., 2012a), but no aqueous treatment has yet been shown to remove all of the  $\text{Cl}^-$  from an object. In order to reduce  $\text{Cl}^-$  contents as much as possible, treatment is normally continued until the solution contains less than 5  $\text{mgL}^{-1}$   $\text{Cl}^-$  (Rimmer et al., 2012b). However, there are concerns regarding long-term treatment of iron objects in alkaline solution since it may have a range of detrimental effects including unwanted transformation of corrosion products, weakening of the corrosion layers,

destruction of evidence of mineralised organics, and fragmentation and detachment of corrosion layers (Selwyn and Argyropoulos, 2005; Selwyn and Logan, 1993). The degree of risk for these outcomes is not known precisely but it remains a concern for conservators considering the application of alkaline sulphite treatment.

Measurement of  $\text{Cl}^-$  extraction processes from heated baths of alkaline sulphite has shown that the majority of  $\text{Cl}^-$  is extracted in the first two-week bath (Rimmer et al., 2012a; Rimmer, 2010). It was suggested that a treatment that used only a single bath of alkaline sulphite would reduce the risk of damage to the objects while still providing a significant reduction in  $\text{Cl}^-$  content. It has not been previously possible to quantitatively assess the risk that any remaining  $\text{Cl}^-$  residues do not pose a significant threat and corrosion is slowed down after a short period of treatment, it may be possible to utilise short treatments as part of conservation management strategies, allowing collections to be stored at higher RH without risk of exposing them to rapid corrosion. This would offer clear cost-saving in terms of staff input, resources and energy preservation.

As part of a Cardiff University based Arts and Humanities Research Council (AHRC)/Engineering and Physical Sciences Research Council (EPSRC) Science and Heritage Large Grants project examining the corrosion rates of large numbers of archaeological iron objects, it has been possible to test the effect of  $\text{Cl}^-$  removal on the rate of corrosion of objects. Based on the novel method of Matthiesen (Matthiesen, 2007; Matthiesen and Wonsyld, 2010), a methodology has been developed which uses oxygen consumption measurements of whole objects in controlled environments to determine corrosion risk, allowing direct assessment of the effect of removing  $\text{Cl}^-$  on the objects. This method measures all oxidation reactions occurring, not exclusively iron metal oxidation, but it is assumed that little oxidation of corrosion products occurs in objects that have been exposed long-term to an oxygenated storage environment and therefore the bulk of the oxygen consumption derives from metal oxidation. The oxygen consumption rate is therefore approximately proportional to the corrosion rate. A pilot study using a small number of objects was carried out to test the use of short-term alkaline sulphite treatments in reducing corrosion rates of iron.

### Methodology

Ten untreated archaeological iron nails, weighing between 1.95 and 10.97 g from a Roman/Medieval site at Billingsgate, London, were used in the study. The objects, which have a large metal core with thin and fragile corrosion layers, were stored with dry silica gel prior to the testing. Material from this site has been previously treated and analysed;  $\text{Cl}^-$  contents typically ranged between 200 and 6000 ppm, with high  $\text{Cl}^-$  extraction rates compared to objects with thicker corrosion layers (Rimmer et al., 2012a; Rimmer et al., 2012b; Rimmer, 2010).

In order to produce rapid corrosion of the iron, the nails were placed into 250 mL 'Mason Ball' glass food preservation jars, with brass sealing discs with a waterproof

plastic lining on their underside, and brass outer threaded sealing rings to deform a synthetic rubber seal, together with 160 g of silica gel conditioned to 80% RH (Fig. 1a). Temperature was maintained at  $20 \pm 0.5$  °C throughout the test by placing the jars in a Binder KBF240 climate chamber. Relative humidity in the jars was measured using Madgetech RHTemp101A data loggers and was found to be  $80 \pm 3\%$  RH during the period of the test. A sensor spot containing an oxygen-sensitive fluorescent compound (WPI part #503090) was adhered to the inner glass surface with silicon adhesive (Radio Spares RTV silicone rubber compound) (Fig. 1b), allowing oxygen partial pressure in the jar to be measured using a WPI OxyMini™ with fibre-optic cable (WPI OXY-MINI-AOT with cable #501644). The system is similar to that used by Matthiesen and Wonsyld (2010), and measures the amount of oxygen used up by oxidation reactions in the object through the glass and adhesive. Oxygen measurements have a precision of 2 mbar at atmospheric oxygen pressure (210 mbar); precision increases proportionally as oxygen pressure decreases. Control jars containing nitrogen gas were prepared by flushing jars with a continuous flow of nitrogen gas prior to sealing and these showed negligible ingress of oxygen during the test period. Further control jars containing all components of the test except an object (conditioned silica gel, sensor spot, adhesive and RH logger) were also prepared. These showed minor oxygen consumption over the period of the test ( $0.026$  mbar day<sup>-1</sup>) and this was subtracted from the test samples during data analysis. The oxygen pressure of each sample was measured at the start of the test and then every 3 or 4 days for a total of 37 days. No object used up all the oxygen contained in the test vessel.



Figure 1: Set up of oxygen measurement system; a) the object and RH/temperature logger sit on a bed of conditioned silica gel to control humidity; b) the sensor spot (pink) adhered to the inside of the jar using transparent silicon adhesive allows measurement through the glass.

The objects were then placed into individual HDPE screw-top containers with 120 ml of 0.1 M NaOH / 0.05 M Na<sub>2</sub>SO<sub>3</sub> solution for two weeks, using an electric laboratory oven (SNOL 60/300 LFN) to maintain temperature at 60 °C. The solutions were prepared using Fisher AnaLar grade chemicals. There were no solution changes in that time and no further rinsing of any kind was undertaken. The objects were dried using oven-dry silica gel for three weeks and placed in the oxygen measurement system for a second time, under the same conditions as already described. The treatment solution was analysed for  $\text{Cl}^-$  content using

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a Radiometer Analytical PHM250 specific ion meter with a Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode (REF621) and a Cl<sup>-</sup> specific electrode (ISE25CL).

Upon completion of oxygen measurements the objects were digested in 5 M nitric acid at room temperature, neutralised with 3 M sodium hydroxide, filtered to remove the iron hydroxide precipitate and then analysed using the specific ion meter (Rimmer, 2010) using the measured volume of the solution to calculate the total mass (mg) of Cl<sup>-</sup> removed from the object. Cl<sup>-</sup> content for objects in ppm is reported in relation to the mass of the object (equivalent to mg kg<sup>-1</sup> or µg g<sup>-1</sup>).

Data processing and analysis was carried out using statistical software IBM SPSS v18. After subtraction of oxygen consumption in control samples (see above), the linear slope (oxygen consumption rate) was determined by regression, with the 95% confidence interval for the slope coefficient given as errors (Table 1). For the post-treatment rates (OCR<sub>a</sub> in Table 1) these errors are influenced by the oxygen meter error, which becomes more apparent when there is no or very little oxygen consumption; therefore the errors appear inflated compared to the size of the measurement. Errors in the chloride measurements are calculated from the standard deviation of repeated measurements.

The treatment efficiency (%) was calculated using:

$$\text{Treatment efficiency} = \frac{Cl_e}{Cl_e + Cl_r} \times 100$$

where Cl<sub>e</sub> is extracted Cl<sup>-</sup> and Cl<sub>r</sub> is residual Cl<sup>-</sup>, both in ppm related to mass of object.

The reduction in oxygen consumption rate (%) was calculated using:

$$\text{Reduction in OCR} = \frac{OCR_b - OCR_a}{OCR_b} \times 100$$

where OCR<sub>b</sub> is oxygen consumption rate before the treatment and OCR<sub>a</sub> is oxygen consumption rate after the treatment, both in mbar day<sup>-1</sup>.

## Results

Although a direct corrosion rate of metal cannot be calculated, as the surface area of the metal is not known, the oxygen consumption rate is proportional to the rate of oxidation reactions occurring, including corrosion of the metal surface and any oxidation of corrosion products. Direct comparison of the same object before and after a treatment is applied allows measurement of the effect of the treatment on the rate of oxidation, including the rate of corrosion and addresses the problem of local corrosion due to the almost certain occurrence of uneven Cl<sup>-</sup> distribution across the surface of the objects.

The results of the test are given in Table 1. All of the objects consumed oxygen before the treatment, with oxygen consumption rates varying between 0.47 and 1.79 mbar day<sup>-1</sup> (Table 1). After treatment, all of the oxygen consumption

rates slowed down to between 0.03 and 0.56 mbar day<sup>-1</sup>. For five out of the ten objects, the decrease in oxygen consumption rate was ≥ 91%, mean 94%, with the remaining objects between 49% and 71%, mean 59% (Fig. 2).

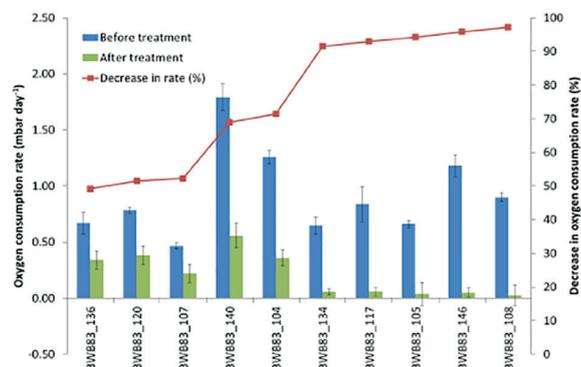


Figure 2: Change in oxygen consumption rate due to treatment in alkaline sulphite at 60 °C for two weeks. The data is presented in order of increasing reduction in oxygen consumption rate (secondary Y axis).

The group of five objects that had a ≥ 91% reduction in oxygen consumption rate contained two objects whose oxygen consumption rate was not statistically different from zero and the remaining three had very low rates (≤ 0.06 mbar day<sup>-1</sup>) which represent virtually no corrosion (Table 1, Fig. 2). The objects in this group can therefore be confidently assumed to be either not corroding or corroding only imperceptibly.

Cl<sup>-</sup> removal from the objects was highly variable, ranging between 172 and 3344 ppm with a mean of 1337 ppm (Table 1). The range of total Cl<sup>-</sup> was 336 to 3487 ppm with a mean of 1525 ppm. Residual Cl<sup>-</sup> content was between 86 and 364 ppm with a mean of 188 ppm (Table 1). The treatment efficiency was between 51 and 96% with a mean of 78%. Fig. 3 shows that objects with lower treatment efficiency (≤ 65%) have lower Cl<sup>-</sup> content (≤ 574 ppm), whereas objects with > 1000 ppm total Cl<sup>-</sup> have extraction efficiency of ≥ 84%. Regardless of the treatment efficiency and starting Cl<sup>-</sup> content, all of the objects fell into a similar Cl<sup>-</sup> range after treatment (Fig. 3).

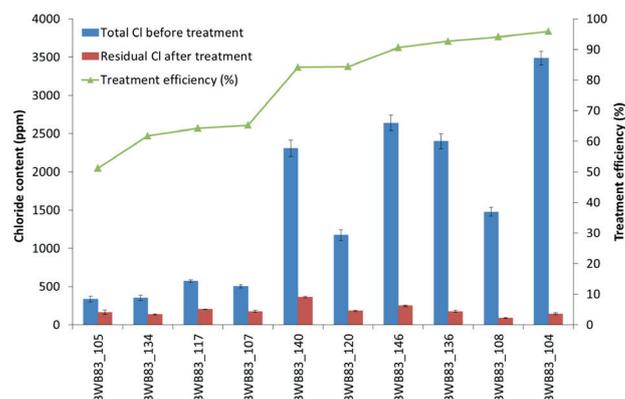


Figure 3: Change in chloride content due to alkaline sulphite treatment for two weeks at 60 °C. The data is presented in order of increasing treatment efficiency (secondary vertical axis).

Figure 4 shows the relationship between  $\text{Cl}^-$  content and oxygen consumption rate before and after treatment. Correlations between  $\text{Cl}^-$  content and oxygen consumption rate were calculated to determine the type and significance of relationship between the two variables. Due to the small number of samples a non-parametric test, Spearman's rho, was used (Table 2). The correlation between oxygen consumption rate and  $\text{Cl}^-$  content is significant before treatment, and represents a large effect ( $r_s > .5$ ) (Field, 2009). The correlation between  $\text{Cl}^-$  content and oxygen consumption rate after treatment represents a medium size effect ( $r_s$  between 0.3 and 0.5) but the correlation is not statistically significant (Table 2). This may be related to the small number of samples; therefore this relationship requires further investigation. The highest  $\text{Cl}^-$  content after treatment has the highest oxygen consumption rate by a large margin (Fig. 4b).

## Discussion

### Treatment performance

The single two-week extraction of  $\text{Cl}^-$  using alkaline sulphite at 60 °C performed well compared to previous tests using longer-term treatment on objects from the same site (Table 3) (Rimmer et al., 2012a; Rimmer, 2010). While treatment efficiency was lower and less consistent for the objects in this study, the range of residual  $\text{Cl}^-$  is comparable to the longer treatment (Table 3). As predicted, the initial immersion in the solution extracts the largest proportion of  $\text{Cl}^-$ , with very little  $\text{Cl}^-$  being removed in subsequent baths (Rimmer et al., 2012a). This fits in well with the concept of diffusion control of  $\text{Cl}^-$  removal (Gilberg and Seeley, 1982; North and Pearson, 1978; Watkinson, 1982).

$\text{Cl}^-$  concentrations of less than 5 mg l<sup>-1</sup> in the final treatment bath have been noted as offering good post-treatment stability (Rimmer et al., 2012b). This is true for BWB83\_105 (4.9 mg l<sup>-1</sup>) (Table 1) whose oxygen consumption was reduced by 94% (Fig. 2). However, two other objects, BWB83\_108 and BWB83\_146, had greater reduction in their oxygen consumption rate but returned treatment solution concentrations of 38.9 mg l<sup>-1</sup> and 59.2 mg l<sup>-1</sup>  $\text{Cl}^-$ , respectively (Table 1), indicating that very significant reductions in corrosion can occur without excessive washing to a predetermined end point.

### Effect on corrosion rate

The reduction in oxygen consumption rates after treatment for all objects shows that a short period of treatment has significant impact in reducing corrosion risk. Half of the objects had no significant oxygen consumption occurring after the treatment, while the remaining half had oxygen consumption rates reduced by over 49%. These measurements were made at 80% RH, when corrosion is extremely rapid; evidence from other AHRC/EPSRC Science and Heritage research at Cardiff indicates that corrosion rates would be expected to be further reduced at lower humidity (publication in preparation). Even a 50% reduction in corrosion rates overall should significantly increase the lifespan of the objects. Additionally, by linking quantified corrosion measurements to changes in the physical state of the object, which is being researched at Cardiff University, it will be possible to link loss in heritage value with corrosion risk.

Due to the small number of objects in this study, it is not possible to determine particular factors which cause some objects to continue to corrode after the treatment. There were no significant correlations with object mass, treatment efficiency, residual or total  $\text{Cl}^-$ , or the starting corrosion rate. The most likely explanation is that the short treatment was not able to remove all of the soluble  $\text{Cl}^-$  from these objects, whereas in other objects only insoluble  $\text{Cl}^-$  occluded in the akaganéite crystal structure remains, which is unable to contribute further to corrosion (Watkinson and Lewis, 2005a, b). Two objects containing the same amount of  $\text{Cl}^-$  can corrode at very different rates depending on whether  $\text{Cl}^-$  is soluble and available to act as an electrolyte. This relates to how much akaganéite is present and how effectively it has been washed to remove its surface adsorbed  $\text{Cl}^-$  (Watkinson, 2010) but it may also be influenced by other

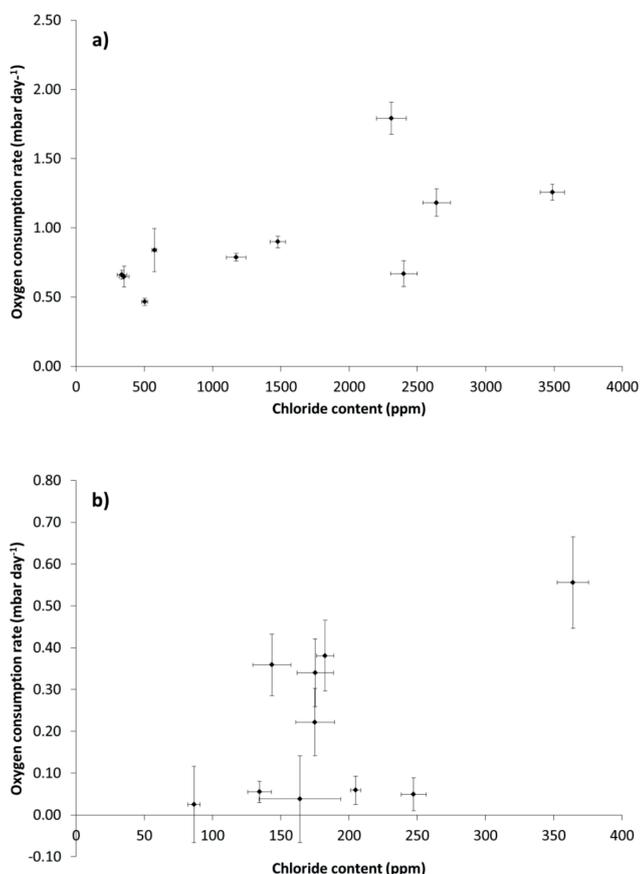


Figure 4:  $\text{Cl}^-$  content and oxygen consumption rate a) before treatment, b) after treatment.

variables including the thickness and morphology of the corrosion layers and metallurgy. It will be important to ascertain whether continuing treatment beyond two weeks until no more  $\text{Cl}^-$  can be extracted from objects would lead all objects to have their corrosion reduced by 90% or more; this requires further experimental study.

Although in this case short treatment proved to be effective, further work is needed to determine whether this is the case for objects from other sites. The thin corrosion layers of BWB83 objects may aid rapid diffusion of  $\text{Cl}^-$  during the initial stages of treatment and the influence of thicker corrosion layers on the extraction rates requires investigation. Absence of post-treatment washing may mean that small amounts of  $\text{Na}_2\text{SO}_3$  and  $\text{NaOH}$  remain in the objects and it is possible that these might convert to  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  (Rimmer and Watkinson, 2010); this would use atmospheric oxygen, which would increase the apparent oxygen consumption rate. In this case, actual post-treatment corrosion rates may be slightly slower than the recorded oxygen consumption rate, making treatment more effective than recorded. Any impact is expected to be negligible due to the low solution concentrations and object sizes.

The oxygen consumption methodology used here can be applied to assess groups of objects with thicker corrosion layers from other sites in order to compare their performance in alkaline sulphite treatments. Longer treatments may be necessary for objects with thicker corrosion layers. In keeping with the results from this pilot study, however, it is to be expected that any reduction in  $\text{Cl}^-$  content achieved by treatment will be beneficial in reducing corrosion rates for iron objects.

The study also substantiates the existence of a linear relationship between  $\text{Cl}^-$  content and corrosion rate before treatment, as noted by Rimmer et al. (2012b). While the small number of samples means that drawing conclusions from this study must be done with caution, it is clear that a measurable relationship does exist between  $\text{Cl}^-$  and corrosion rate, and that removing  $\text{Cl}^-$  has a significant impact on the rate. The use of oxygen consumption rate to assess corrosion rates allows further investigation of the factors which influence corrosion risk to objects and also allows refinement of treatment methodologies to produce the best outcome. The use of shorter treatments to remove the majority of soluble  $\text{Cl}^-$  can be a useful tool for conservators and may minimise the risk of damage to objects that may result from long immersion in alkaline solutions, although the level of risk from this requires further study.

Experimental work in measuring the oxygen consumption rate of objects across a range of RH is currently underway at Cardiff University and this will be supplemented by further studies of treatments using the technique in this study. Potential exists for examining whether a short washing treatment prior to desiccated storage will significantly reduce risk to objects, or whether less stringent RH storage parameters can be used for treated objects with no decrease in object lifespan. Improvements in corrosion behaviour after a short treatment will be measured against that produced by a full treatment achieving

the lowest possible residual  $\text{Cl}^-$  content, contributing to the development of best-practice guidelines for the management of large iron collections.

## Conclusions

Measuring the oxygen consumption of an archaeological iron object in an enclosed environment controlled at 80% RH and 20 °C, followed by a two-week desalination treatment in alkaline sulphite solution before repeating the oxygen measurement procedure, revealed that ten objects undergoing testing had significantly reduced oxygen consumption rates post-treatment. Recording the oxidation of iron in this way offers comparative corrosion rates for recording the impact of treatments on the corrosion susceptibility of objects. Half of the objects had their oxygen consumption rate reduced by over 91%, and the remainder by over 49%. Quantitative determination of chloride content of each object identified a significant correlation between high  $\text{Cl}^-$  content and high oxygen consumption rates before treatment. The amount of  $\text{Cl}^-$  removed during treatment varied considerably among the ten objects. Despite the shorter treatment time than that normally used for aqueous alkaline sulphite and no uniform end point for  $\text{Cl}^-$  concentration in the treatment bath, residual  $\text{Cl}^-$  remaining in the objects after treatment was similar between all objects tested.

Short immersions in alkaline sulphite remove sufficient  $\text{Cl}^-$  to significantly reduce corrosion risk for iron objects with reasonably thin corrosion layers similar to the objects tested here. Since not all corrosion risk is removed any strategies for corrosion control would need to take this into account but the enhanced stability of the treated objects offers greater scope in design and management of any corrosion control system. In terms of cost benefit, a simple two-week immersion in alkaline sulphite appears to offer a good return, measured as reduction in corrosion of individual objects, for a relatively small outlay in time and resources.

## Acknowledgements

We are grateful to Helen Ganiaris and the Museum of London for providing sample material for this study. This work was carried out as part of an Arts and Humanities Research Council (AHRC) and Engineering and Physical Sciences Research Council (EPSRC) jointly-funded Science and Heritage Programme Large Grant (AH/H032754/1).

## References

- Field A. , 2009 Discovering statistics using SPSS. Third edition, London: Sage Publications, pp.56-57
- Gilberg M. R., Seeley N.J.,1982 The alkaline sodium sulphite reduction process for archaeological iron: A closer look. *Studies in Conservation*, 27, pp.180-184.
- Loeper-Attia M.-A. , 2007 A proposal to describe reactivated corrosion of archaeological iron objects, in *Corrosion of metallic heritage artefacts: Investigation, conservation and prediction for long-term behaviour*, pp. 190-202, eds. P. Dillmann, C. Béranger, P. Piccardo and H. Matthiesen, Cambridge: Woodhead Publishing.
- Matthiesen H., 2007. A novel method to determine oxidation rates of heritage materials in vitro and in situ. *Studies in Conservation* 52, pp.271-280.
- Matthiesen H., Wonsyld K., 2010. In situ measurement of oxygen consumption to estimate corrosion rates. *Corrosion Engineering, Science and Technology* 45, pp.350-356.
- North N. A., Pearson C., 1975. Alkaline sulfite reduction treatment of marine iron. In *ICOM Committee for Conservation, 4th Triennial Meeting Venice.*, pp.1-14, Paris: International Council of Museums.
- North N. A., Pearson C., 1978. Methods for treating marine iron. In *ICOM Committee for Conservation 5th Triennial Meeting, Zagreb.*, pp.1-10, Paris: International Council of Museums.
- Rimmer M., Watkinson D. , 2010. Residues of alkaline sulphite treatment and their effects on the corrosion of archaeological iron objects. In *Metal 2010: Interim Meeting of the International Council of Museums Committee for Conservation Metal Working Group, October 11-15 2010, Charleston, South Carolina, USA*, pp. 16-23, eds. P. Mardikian, C. Chemello, C. Watters and P. Hull, Charleston, SC: Clemson University.
- Rimmer M., Watkinson D., Wang Q., 2012a. The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions. *Studies in Conservation* 57(1), pp.29-41.
- Rimmer M., Watkinson D., Wang Q., 2012b. The impact of chloride desalination on the corrosion rate of archaeological iron. In *Studies in Conservation*, published online 26/09/2012, DOI: <http://dx.doi.org/10.1179/2047058412Y.0000000068>
- Rimmer M. B., 2010. Investigating the treatment of chloride-infested archaeological iron objects, PhD Thesis, Cardiff University.
- Selwyn L. S., Argyropoulos V., 2005. Removal of chloride and iron ions from archaeological wrought iron with sodium hydroxide and ethylenediamine solutions. *Studies in Conservation* 50(2), pp.81-100.
- Selwyn L. S., Logan J.A., 1993. Stability of Treated Iron: A Comparison of Treatment Methods. In *International Council for Museums Committee for Conservation 10th Triennial Meeting, Washington DC*, pp.803-807, ed. J. Bridgland, Paris: James and James.
- Turgoose, S., 1982. Post-Excavation Changes in Iron Antiquities. *Studies in Conservation* 27, pp.97-101.
- Watkinson D., 1982. An assessment of lithium hydroxide and sodium hydroxide treatments for archaeological ironwork. In *Conservation of Iron: Maritime Monographs and Reports No. 53*, pp.28-40, eds. R. W. Clarke, and S. M. Blackshaw, London: National Maritime Museum.
- Watkinson D., 2010. Measuring effectiveness of washing methods for corrosion control of archaeological iron: problems and challenges. *Corrosion Engineering, Science and Technology* 45, pp.400-406.
- Watkinson D., Lewis M.R.T., 2005a. Desiccated storage of chloride-contaminated archaeological iron objects. *Studies in Conservation* 50, pp.241-252.
- Watkinson D., Lewis M.R.T. , 2005b. The role of beta-FeOOH in the corrosion of archaeological iron. In *Materials Issues in Art and Archaeology VII*, pp.103-114, eds. P. B. Vandiver, J. L. Mass, and A. Murray, Warrendale, PA: Materials Research Society of America.
- Watkinson D., Lewis M.R.T., 2008. Desiccated storage of chloride contaminated iron: A study of the effects of loss of environmental control. In *Heritage Microbiology and Science: Microbes, Monuments and Maritime Materials (Special Publication 315)*, pp.279-289, eds. E. May, M. Jones, and J. Mitchell, Cambridge: Royal Society of Chemistry.

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TABLES

Sample	Mass (g)	OCR <sub>b</sub> (mbar day <sup>-1</sup> )	OCR <sub>a</sub> (mbar day <sup>-1</sup> )	ΔOCR (mbar day <sup>-1</sup> )	Reduction in OCR (%)	Extracted Cl <sup>-</sup> (ppm)	Residual Cl <sup>-</sup> (ppm)	Total Cl <sup>-</sup> (ppm)	Cl <sup>-</sup> solution conc. (mg l <sup>-1</sup> )	Treatment efficiency (%)
<b>BWB83_104</b>	4.24	1.26 ±0.06	0.36 ±0.07	0.90 ±0.13	71	3344 ±74	143 ±14	3487 ±89	118.2 ±2.6	96
<b>BWB83_105</b>	3.45	0.66 ±0.03	0.04 ±0.10*	0.62 ±0.14	94	172 ±6	164 ±30	336 ±36	4.9 ±0.2	51
<b>BWB83_107</b>	10.79	0.47 ±0.03	0.22 ±0.08	0.24 ±0.11	52	328 ±7	175 ±14	503 ±21	29.5 ±0.6	65
<b>BWB83_108</b>	5.10	0.90 ±0.04	0.03 ±0.09*	0.87 ±0.13	97	1391 ±51	86 ±4	1478 ±55	59.2 ±2.2	94
<b>BWB83_117</b>	4.49	0.84 ±0.16	0.06 ±0.03	0.78 ±0.19	93	369 ±14	205 ±4	574 ±18	13.8 ±0.5	64
<b>BWB83_120</b>	5.69	0.79 ±0.03	0.38 ±0.08	0.41 ±0.11	52	990 ±65	183 ±7	1172 ±72	46.9 ±3.1	84
<b>BWB83_134</b>	4.57	0.65 ±0.08	0.06 ±0.03	0.59 ±0.10	91	218 ±26	134 ±9	352 ±35	8.3 ±1.0	62
<b>BWB83_136</b>	2.99	0.67 ±0.09	0.34 ±0.08	0.33 ±0.18	49	2224 ±85	175 ±13	2399 ±98	55.4 ±2.1	93
<b>BWB83_140</b>	9.29	1.79 ±0.12	0.56 ±0.11	1.24 ±0.22	69	1944 ±98	364 ±12	2308 ±109	150.6 ±7.6	84
<b>BWB83_146</b>	1.95	1.18 ±0.10	0.05 ±0.04	1.13 ±0.14	96	2393 ±92	247 ±9	2640 ±101	38.9 ±1.5	91

Table 1: Results of oxygen measurement and Cl<sup>-</sup> content of ten objects treated for two weeks in alkaline sulphite. \* = linear rate not statistically different from zero. OCR<sub>b</sub> = oxygen consumption rate before treatment; OCR<sub>a</sub> = oxygen consumption rate after treatment; ΔOCR = difference in rates before and after treatment

Correlation between oxygen consumption rate and Cl <sup>-</sup> content	Correlation coefficient, r <sub>s</sub>	Significance value, p	Sample number, n
Before treatment	0.758	0.011	10
After treatment	0.486	0.154	10

Table 2: Correlation coefficient and significance for the relationship between Cl<sup>-</sup> content and oxygen consumption rate before and after treatment. Spearman's rho was calculated using SPSS. The larger the correlation coefficient, the more substantial the effect (Field 2009). p values less than 0.05 are normally considered statistically significant.

	Two-week 60°C alkaline sulphite treatment (this paper)	Eight-week 60°C alkaline sulphite treatment (data from Rimmer 2010)
Number of objects	10	8
Treatment baths	1 x 14 days	4 x 14 days
Mean total Cl <sup>-</sup> (standard deviation) (ppm)	1525 (1122)	2250 (967)
Mean extracted Cl <sup>-</sup> (standard deviation) (ppm)	1337 (1105)	2046 (931)
Mean residual Cl <sup>-</sup> (standard deviation) (ppm)	188 (75)	204 (90)
Maximum residual Cl <sup>-</sup> (ppm)	364	413
Treatment efficiency range	51-96%	79-96%
Mean treatment efficiency (standard deviation)	78% (16%)	90% (5%)

Table 3: Comparison of treatment outcomes between the two-week treatment (this paper) and eight objects treated for eight weeks, reported in Rimmer (2010). The objects were from the same site at Billingsgate, London.

