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The impact of chloride desalination on the corrosion rate of archaeological iron

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Abstract

Although desalination of archaeological iron reduces its chloride concentration and enhances object stability, the reduction in corrosion rate has never been quantified. This study measures post-treatment corrosion rates in accelerated corrosion environments using either weight change or oxygen consumption to identify how removing chloride ions affects corrosion rate. Archaeological iron nails, treated individually in either alkaline sulphite or nitrogen-deoxygenated sodium hydroxide, were exposed to 75°C and 75% relative humidity (RH) together with untreated objects from the same archaeological sites. Weight change of the objects was used to monitor corrosion. Iron nails treated for two weeks in alkaline sulphite to extract chloride were placed in individual sealed containers controlled to 80% RH and the oxygen consumption within the jars was measured. Digestion determined the chloride content of each object. 77% of the treated objects showed no weight gain and no visible signs of corrosion, whereas only 13% of the untreated objects displayed no signs of corrosion behaviour. There was a significant correlation between chloride content and weight gain; treated objects with <400 ppm chloride content showed no corrosion behaviour. Corrosion of treated objects was attributed to incomplete treatment: 93% of objects treated to <5 ppm in the final solution bath displayed no corrosion behaviour. The two-week alkaline sulphite treatment significantly reduced chloride content and corrosion rate, suggesting that removing the most soluble chloride has the largest impact on reducing corrosion rates. Based on these results, desalination of iron objects to enhance their stability offers a valuable option for reducing corrosion rates which should increase object lifespan.

Biographies

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Introduction [Heading]

Archaeological iron objects undergo corrosion after excavation through the action of chloride ions that have diffused into the object from the burial environment as counter-ions to the oxidation of the metal (Turgoose, 1985, 1993; Réguer *et al.*, 2007). Contact with atmospheric conditions after excavation produces rapid corrosion governed by relative humidity (RH) and oxygen to produce iron oxyhydroxides, including the chloride-bearing product β-FeOOH which is itself corrosive to iron. In the presence of β-FeOOH, iron begins to corrode at 15% RH (Watkinson & Lewis, 2005; Watkinson & Lewis, 2008) and increases rapidly above 35% RH (Thickett & Odlyha, 2010; Thickett, 2011). As a result, objects fragment and disintegrate (Loeper-Attia, 2007), with subsequent loss of archaeological value. Maintenance of sufficiently dry environmental conditions to prevent chloride-induced corrosion is a significant challenge for museums.

Desalination treatments aim to remove chloride ions, and thereby reduce the objects corrosion susceptibility. A previous paper (Rimmer *et al.*, 2012) showed that deoxygenated alkaline solutions typically extract 60-99% of chloride ions present in objects, and reduced chloride ion levels to less than 1000 ppm in 87% of cases. While this is a clear indication of treatment efficiency for removing chloride ions, it is more difficult to assess what effect this will have on the longevity of the objects, as the relationship between chloride ion content and corrosion rate has not been quantitatively defined. Although anecdotal evidence from collection surveys suggests that treated objects are at lower corrosion risk (Keene & Orton, 1985; Keene, 1994; Loeper-Attia & Weker, 1997), no study to date has measured the corrosion rate of archaeological iron objects and linked it to their chloride content. A quantified evaluation of the effect of removing chloride ions on the predicted longevity of objects would allow an evidence-based approach to the management of archaeological iron collections, based on the desired lifespan of the objects and the resources available to treat and store them.

This paper presents research into the chloride ion/corrosion rate relationship of both treated and untreated iron artefacts. The main part of the study was undertaken using an accelerated corrosion testing methodology, with the aim of identifying general differences and trends in a short period of time. A pilot study into how effectively a quick, but incomplete, desalination wash reduces corrosion rate trialled the use of oxygen consumption measurements to quantify corrosion rates more accurately.

Post-treatment assessment – a problem [sub-heading]

Assessing the behaviour of both treated and untreated iron objects requires measurement of their corrosion rate and the variables affecting it. This requires quantification of the corrosion rate in real time, at room temperature and controlled humidity, and measurement of chloride content. It must use real archaeological material, as modern samples cannot replicate the complex morphology of soil-based corrosion layers developed

over centuries (Neff *et al.*, 2005; Neff *et al.*, 2006; Réguer *et al.*, 2007). The uniqueness of each individual artefact requires that large samples be used to allow for statistical validity.

These parameters present a number of difficulties for a short-term study of corrosion rates. Measuring the corrosion rate of a large enough sample of objects covering a range of chloride levels, humidity levels and treatment patterns would be time-consuming. In order to take a 'first look' at corrosion rates within a manageable time frame, an accelerated corrosion testing method was developed. This was followed by trialling a room temperature test procedure based upon accurate measurement of oxygen consumption of individual objects to evaluate its usefulness for longer studies.

Accelerated aging studies at increased temperature are used in paper and textile degradation studies (Erhardt & Mecklenburg, 1995; Ding & Wang, 2007; Luxford & Thickett, 2011) and materials testing for conservation (Robinet & Thickett, 2003). They have been previously used to duplicate the corrosion of modern iron samples in soils (Angelini *et al.*, 1998) and laboratory testing of corrosion product development (Thickett, 2005; Thickett & Odlyha, 2005). Although in theory the increase in rate caused by elevated temperatures can be calculated using the Arrhenius equation (Luxford & Thickett, 2011), in reality, the physical and chemical changes governing the decay of archaeological iron objects are complex and poorly understood, and the constituent compounds present in corrosion layers too varied to permit easy calculation of the activation energies. Therefore, it was not possible to apply the Arrhenius equation to extrapolate directly from the corrosion rate at high temperature to the behaviour of objects under room conditions. This is a significant drawback of accelerated aging studies in this context.

To compare treated and untreated iron objects, a study under accelerating conditions can indicate the relative corrosion rate differences between them and in relation to their chloride content as determined by digestion. By corroding objects under the same conditions, overall trends can be determined, provided the sample size is large. Although this provides no measure of how the actual lifespan of an object is affected by treatment, it is possible to assess the extent to which extracting chloride ions reduces the susceptibility of the objects to corrosion under accelerated conditions.

Although the consumption of oxygen can be used to monitor corrosion rate reactions (Matthiesen, 2007; Thickett *et al.*, 2008; Matthiesen & Wonsyld, 2010) this was not available during the initial part of this study. Dynamic weight measurement has been used to measure corrosion reaction rates of powdered iron and iron compounds, as the metal reacts with oxygen and water to increase weight by forming iron oxides and adsorbing water (Watkinson & Lewis, 2005). This method can only measure one sample at a time, and is therefore not suitable for a short-term study seeking to produce enough data for statistical validity. Measuring the weight of corroding objects at regular intervals has a range of disadvantages, particularly in the lack of constant humidity control during weighing and the risk of losing material through handling, but it will indicate whether corrosion is

occurring overall. This method was the most practical available given the constraints of the study, but with the recognition that it is a relatively imprecise method that provides a general indication of corrosion trends and offers a comparator for objects.

Given that no extrapolation to real-time conditions is possible, test conditions can be increased to induce measurable corrosion in the time available. 75°C and 75% RH were chosen as the test conditions, maintained using a temperature and humidity controlled oven. 75% RH was chosen so that ferrous chloride ($FeCl_2 \cdot 4H_2O$) within the objects would become liquid through deliquescence and promote the most aggressive types of corrosion. Adsorbed surface chloride on β-FeOOH would also attract water and promote corrosion under these conditions (Watkinson & Lewis, 2005). Objects containing no soluble chloride should be easily distinguished. 75°C was chosen as a high enough temperature to accelerate corrosion reactions significantly to be measurable within the time available (3 months), without altering the corrosion products.

Methodology: Accelerated corrosion testing [Heading]

Archaeological iron nails from three sites with metal cores (determined by x-radiography) were used as sample material: Bornais, Outer Hebrides (BOR), Billingsgate, London (BIL) and Caerwent, South Wales (CAE). Nails were desalinated at room temperature (20°C ± 3) using either nitrogen-deoxygenated 0.1 M sodium hydroxide solution (dNaOH) or 0.1 M NaOH /0.05 M Na_2SO_3 alkaline sulphite solution (AS20) (Rimmer, 2010; Rimmer *et al.*, 2012). Nine nails from each of the two desalination treatments were used for accelerated corrosion testing, along with fourteen untreated nails from the same archaeological sites. Additionally, seventeen nails were cut in half using a diamond saw, and one half was treated; these samples were also included in the accelerated corrosion test. In total, 66 individual samples were tested, 31 untreated and 35 treated. The test took place over 63 days at 75°C ± 0.5 and 75% ± 3 RH in a Sanyo-Gallenkamp temperature/humidity controlled oven (model BR185H/RO). After the accelerated corrosion test was completed, the objects were digested in 5 M nitric acid (HNO_3) and residual chloride content measured using a Radiometer Analytical PHM250 specific ion meter with chloride-specific electrode and $Hg/HgSO_4$ reference electrode (Rimmer, 2010; Rimmer *et al.*, 2012).

To measure the progression of corrosion, the objects were weighed at weekly or fortnightly intervals on a Sartorius A200s analytical balance (±0.0001 g). Removing the objects from the high RH of the accelerated corrosion test changes the weight of the object through hydration/dehydration, depending on the ambient conditions in the uncontrolled laboratory space. Objects were removed from the oven 24 hours before the weight was measured to allow them to acclimatise to the ambient RH and present a stable weight for measurement. By treating all the objects the same way for each measurement the relative fluctuations of ambient RH can be distinguished from the linear increase in weight due to corrosion, although very low weight increases from corrosion may not be detectable due to the uncertainty deriving from this method. Ambient RH was recorded using a Hanwell sensor

(RH ±2%). The effects of the accelerated corrosion were also recorded photographically at the end of the test and compared to pre-test images, as a guide to whether corrosion produced visible physical change.

Weight change is calculated as a percentage of the pre-test weight of the object, to compare objects which had a range of sizes and shapes. The objects weighed between 0.6 and 25.2 g, with a median weight of 5.6 g. 77% of the objects fell in the weight range 3 to 12 g. Ideally, corrosion rate would be related not just to the overall weight of the object but to the amount and surface area of the metal core where the corrosion reaction occurs. However, measuring this is not possible for archaeological objects where the metal surface is hidden by overlying corrosion products; therefore, weight is the only available comparator. For the same reasons, chloride content is given as ppm related to the weight of the object, equivalent to mg/kg. As all the objects were iron nails of roughly similar shape, the object weight may be a relatively good indicator of the varying amount of metal present.

Results and discussion [Heading]

The 66 objects subjected to accelerated corrosion conditions are divided into groups for discussion. Whole treated and untreated nails are discussed first followed by the halved nails. Data are given in Table 1.

Some objects lost weight during the accelerated corrosion test. Decreases in weight are normally correlated with measurements taken at low ambient RH. Some objects show a decrease in weight at the first measurement (after 14 days) despite a higher RH. The most likely reason is that the objects were not all acclimatised to the ambient RH before the pre-test weight measurement, which was carried out without allowing 24 hours for equilibration to the room conditions. As some objects were stored in polyethylene bags within a cardboard box in a closed cupboard, the storage RH may not have fully equilibrated to the very low ambient RH (30%) recorded in the room, allowing the corrosion products to retain more adsorbed water. Because of the uncertainty surrounding the role of humidity, corrosion of objects less than or very close to 0% change cannot be ruled out, but it is of a different order of magnitude to objects displaying clear linear weight gain.

Object	% Weight gain at 63 days	Chloride content (ppm)	Final solution chloride ion conc. (mg/l)	Object	% Weight gain at 63 days	Chloride content (ppm)
AS20				Untreated		
BOR_2975	-0.21	219	13.36	BOR_1690	-0.13	1034
BOR_6109	-0.41	410	3.55	BOR_1848	1.06	980
BOR_6750	-0.06	108	1.87	BOR_2021	4.43	2968
BIL_33	-0.16	37	1.81	BOR_4655	7.06	3742
BIL_35	-0.14	139	0.95	BOR_5330	5.81	4095
BIL_39	0.00	165	1.71	BOR_5615	3.89	1717
CAE_34	2.52	622	27.35	BOR_6151	4.35	3509
CAE_36	0.70	451	8.57	BOR_6748	2.24	2541
CAE_41	-0.65	527	0.87	BOR_6806	9.55	4229
BOR_1698.1	-0.11	158	0.61	BIL_46	2.50	1461
BOR_1708.1	-0.04	266	0.82	BIL_47	0.17	706
BOR_2706.1	-0.07	191	0.46	CAE_46	1.52	950
BIL_30.1	-0.01	110	1.65	CAE_47	1.63	1245
BIL_38.1	-0.03	77	1.19	CAE_48	16.01	1019
BIL_44.1	-0.14	61	2.98	BOR_1692.2	0.24	223
CAE_30.1	1.02	553	4.79	BOR_1693.2	2.01	1388
CAE_40.1	-0.17	216	2.23	BOR_1684.2	-0.04	466
CAE_45.1	0.41	950	3.97	BIL_19.2	-0.57	99
dNaOH				BIL_24.2	-0.13	565
BOR_1702	-0.20	388	1.29	BIL_28.2	0.23	495
BOR_6287	1.81	435	9.42	CAE_27.2	4.40	1652
BOR_6472	0.36	399	7.84	CAE_28.2	2.75	2507
BIL_16	-0.45	209	1.20	BOR_1698.2	0.49	208
BIL_20	0.21	82	14.01	BOR_1708.2	0.25	209
BIL_27	-0.02	300	1.05	BOR_2706.2	0.23	365
CAE_17	-0.69	198	1.28	BIL_30.2	0.17	177
CAE_18	-0.08	244	3.71	BIL_38.2	0.54	493
CAE_24	-0.22	263	2.95	BIL_44.2	-0.28	106
BOR_1692.1	-0.06	92	1.50	CAE_30.2	0.19	1049
BOR_1693.1	-0.11	195	1.53	CAE_40.2	-0.04	498
BOR_1684.1	-0.20	347	1.64	CAE_45.2	2.37	425
BIL_19.1	-0.19	97	0.94			
BIL_24.1	-0.07	80	1.77			
BIL_28.1	-0.01	86	1.41			
CAE_27.1	-0.50	467	13.17			
CAE_28.1	4.98	1112	7.01			

Table 1: Data for all objects subjected to accelerated corrosion testing. Total weight change at the end of the 63-day test is given as % of weight of object.

Whole nails [sub-heading]

Figures 1, 2 and 3 show the weight change of whole untreated objects and objects treated in dNaOH and AS20. Untreated objects do not strongly reflect the changing RH conditions

(Figure 1) but show approximately linear increases in weight. The maximum weight change is +16.0% (CAE_48) with other untreated objects ranging from -0.1 to +10.8%. All but two of the fourteen objects show a definite weight gain.
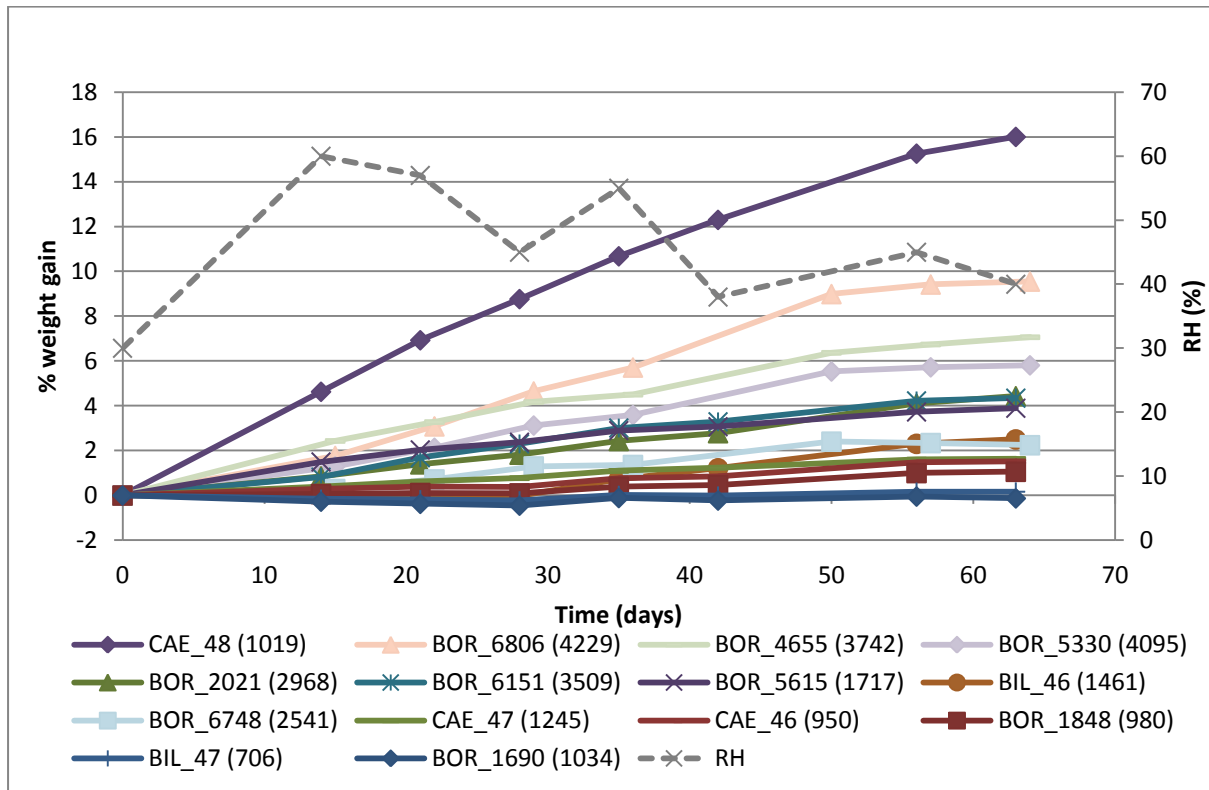

Figure 1: Weight gain of untreated nails. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample in ppm.

Of the objects treated in dNaOH (Figure 2), only three showed positive weight change (BOR_6472, BOR_6287 and BIL_20), ranging from +0.2 to +1.8% after 63 days. The other objects showed some fluctuation from humidity changes, but no overall weight gain could be detected.

AS20-treated objects also show a range of positive and negative weight change, but only two objects (CAE_34 and CAE_36) show a definite increase in weight, up to +2.5% (Figure 3). The other seven objects present only RH-linked fluctuations.
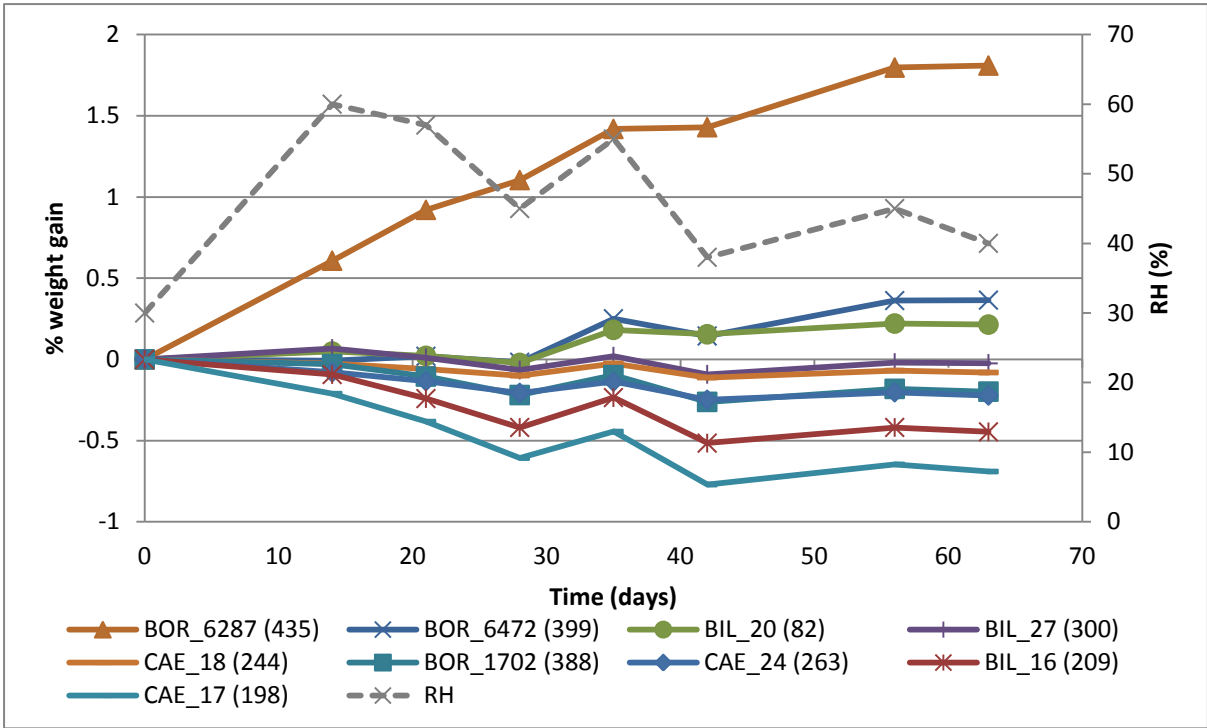
Figure 2: Weight gain of objects treated in dNaOH. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample after the treatment in ppm.
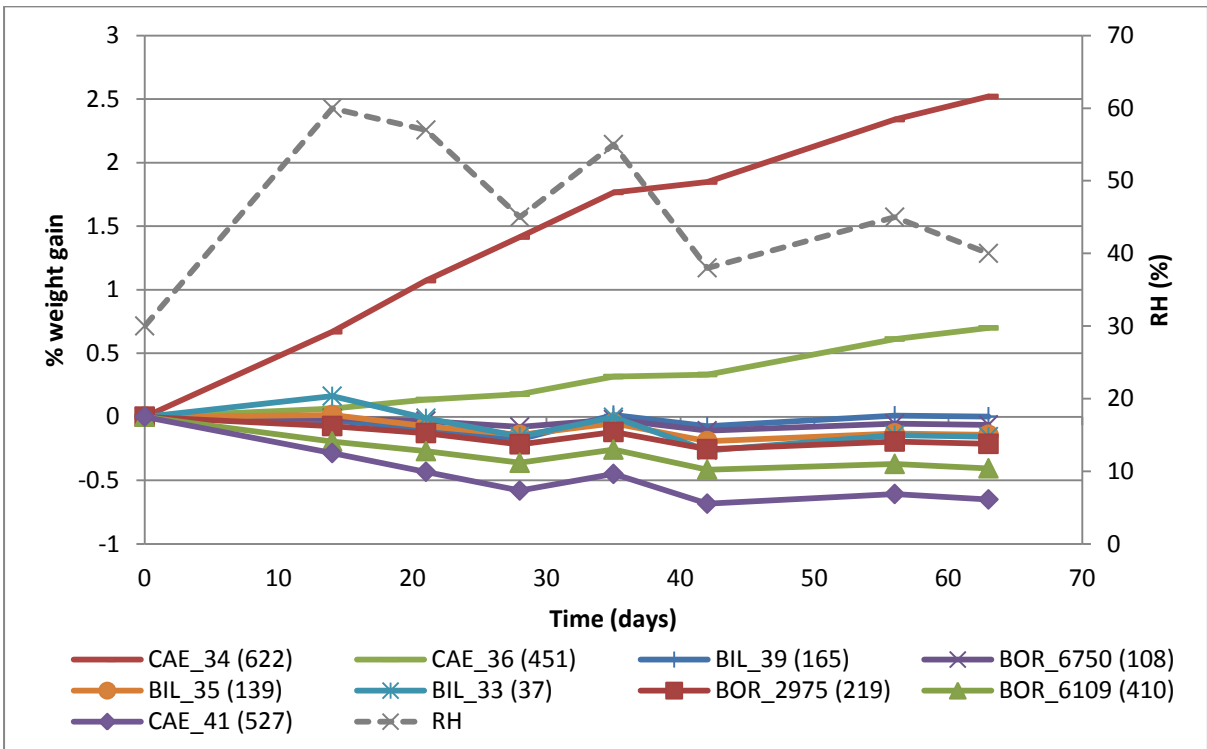

Figure 3: Weight gain of objects treated in AS20. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample after the treatment in ppm.

Half nails [sub-heading]

The nails cut in half before treatment were also exposed to accelerated corrosion conditions. It is assumed that the corrosion morphology of the two halves is similar, but the chloride concentration of the two halves is not exactly the same (Table 1). Their behaviour is discussed grouped by the three sites from which the nails came. Samples with the suffix .1 were treated, those with .2 are untreated.
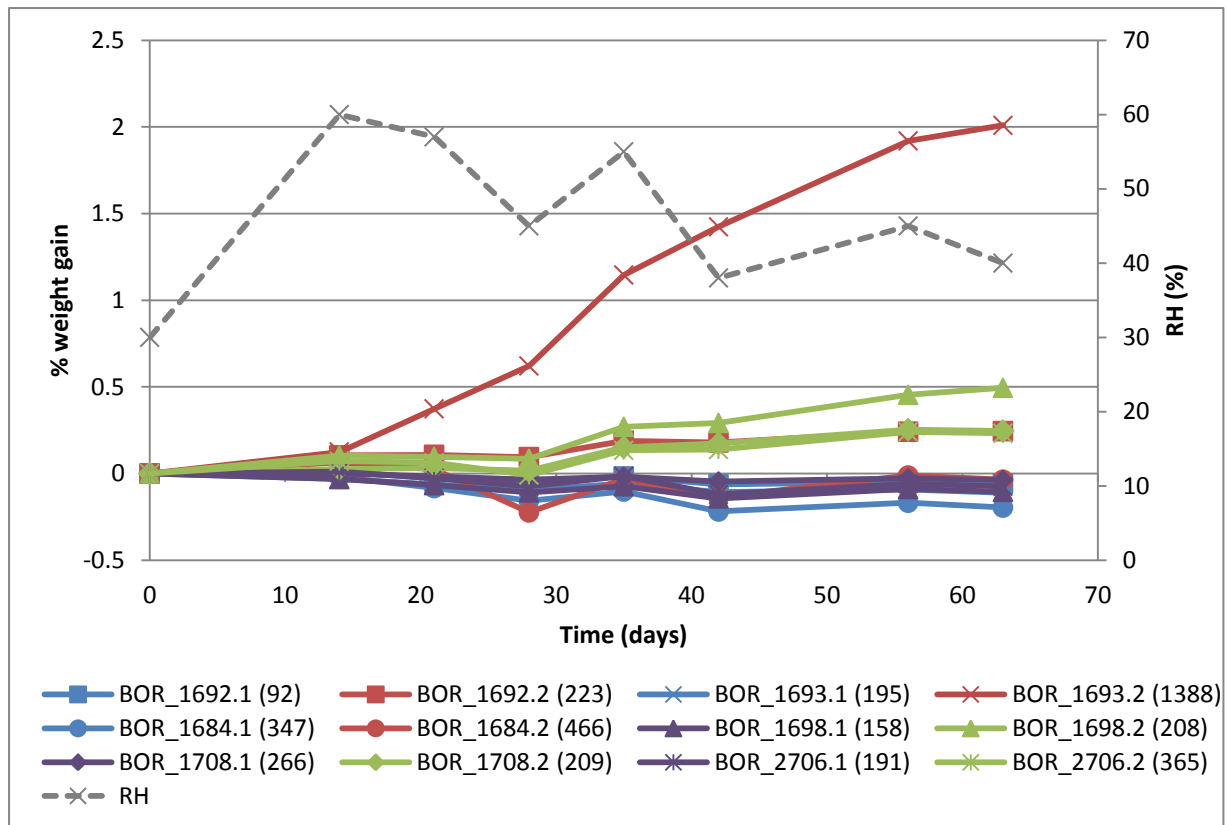

Figure 4: Weight gain of Bornais nails – treated (blue - dNaOH; purple - AS20) and untreated (red and green) halves. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample in ppm.

Bornais (Figure 4): All the treated halves had negative overall weight change and showed only RH-linked weight fluctuation. None showed visual signs of corrosion. Weight gain for the untreated halves other than BOR_1693.2 was quite low, up to +0.49% (BOR_1698.2), but the positive trend is easily distinguishable from the treated halves. All of the untreated halves showed visual signs of corrosion, including cracking, flaking, formation of fresh corrosion products and fragmentation of the object.
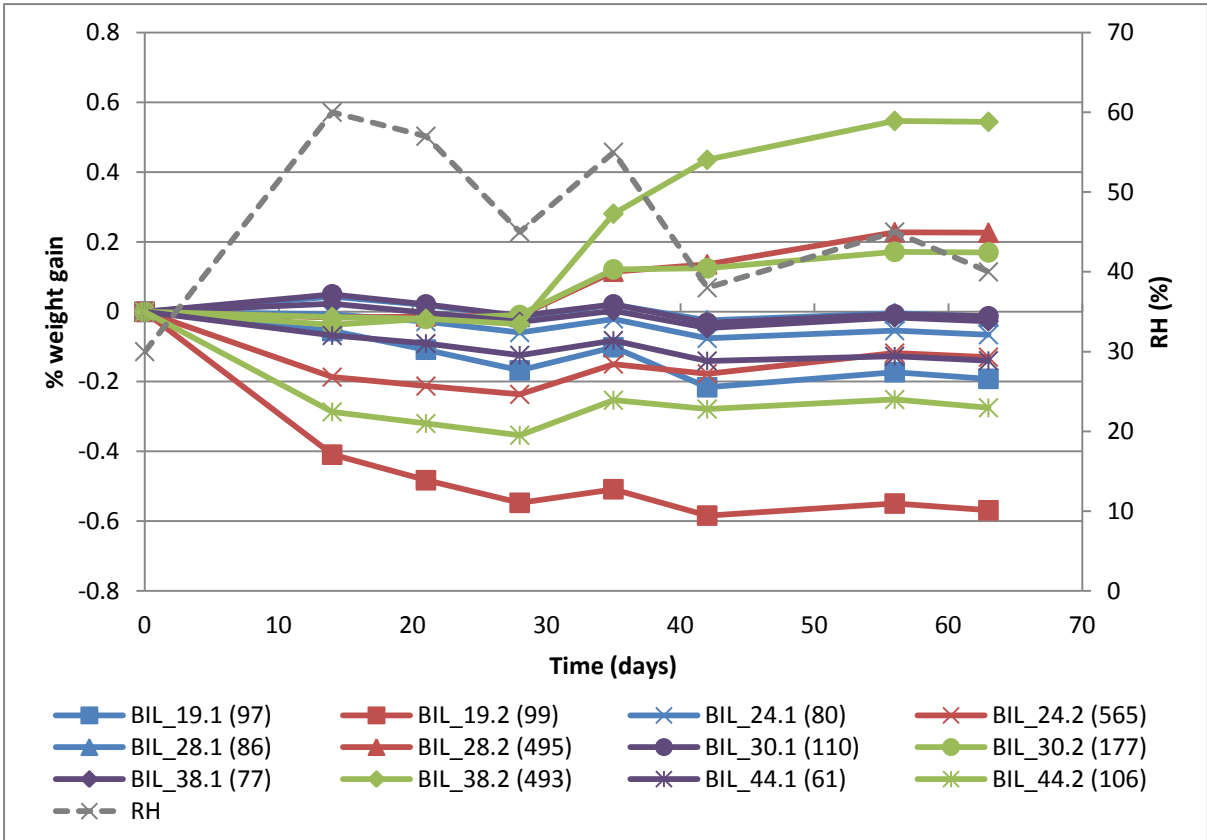
Figure 5: Weight gain of Billingsgate nails – treated (blue - dNaOH; purple - AS20) and untreated (red and green) halves. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample in ppm.

Billingsgate (Figure 5): these nails did not generally react strongly to the accelerated conditions. None of the treated halves show detectable weight increase or visual corrosion. Three of the untreated halves also show no weight gain, although two of these experienced some minor fragmentation (BIL_44.2, BIL_19.2). The remaining three untreated halves show a small positive weight increase up to +0.5%. The behaviour of BIL_38.2 was somewhat unusual; initially it lost weight with ambient RH decreases, but after 28 days it began to gain weight rapidly. This may be the result of initial slow corrosion opening up a crack which then allowed rapid ingress of water and oxygen towards the centre of the object, increasing the corrosion rate.
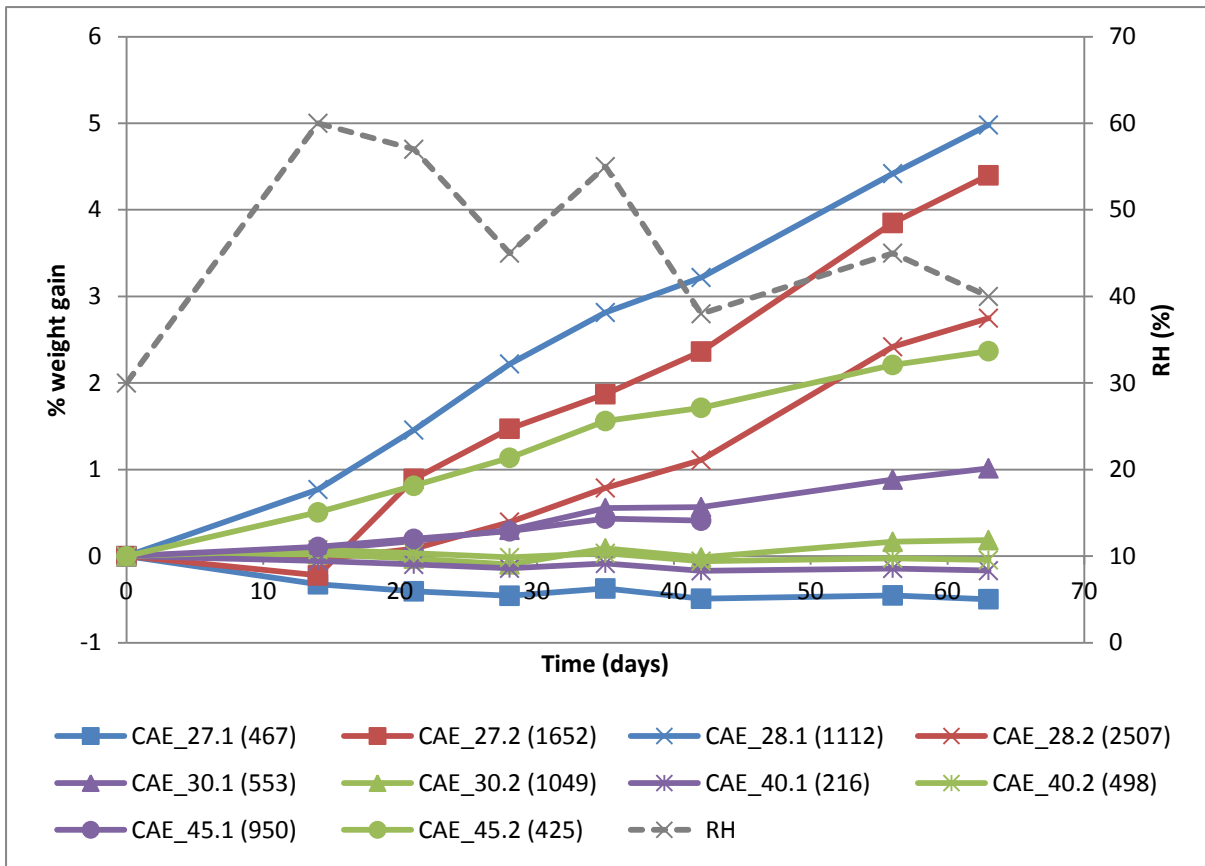
Figure 6: Weight gain of Caerwent nails – treated (blue - dNaOH; purple - AS20) and untreated (red and green) halves. Ambient RH at the time of measurement is given on the secondary axis. The number in brackets gives the chloride ion content of each sample in ppm.

Caerwent (Figure 6): Of the five untreated halves, three showed significant linear increases, while CAE_40.2 showed no weight gain and CAE_30.2 gained only 0.2%. Of the treated halves, only two showed no weight gain, with the remainder showing weight gains up to +5.0% (CAE_28.1). This is in contrast to both of the other sites, where treated halves showed no measurable weight gain, although among the whole nails both BOR and BIL have isolated treated objects showing weight gain (Figure 2).

Relationship with physical change [sub-heading]

As a full condition survey was not possible, the objects were simply assessed on a determination of whether any change, of any magnitude, was visible in the before and after photographs (Table 2). The results clearly show that untreated objects were highly likely to suffer from some sort of physical change during the test; 87% suffered damage, including flaking and widespread fragmentation, and weeping of a dark orange-brown solution. A number disintegrated completely during the period of the test, e.g. BOR_6151 (Figure 7). CAE_48, which had the highest weight gain, was almost completely covered with small

orange crystals before the test, and experienced massive fragmentation and flaking over the whole object during exposure.

	Untreated	AS20	dNaOH
BIL	6/8 (75%)	0/6 (0%)	0/6 (0%)
BOR	15/15 (100%)	1/6 (16%)	2/6 (33%)
CAE	6/8 (75%)	3/6 (50%)	1/5 (20%)
Total	**27/31 (87%)**	**4/18 (22%)**	**3/17 (18%)**

Table 2: Number of objects showing any kind of physical change during the course of the accelerated corrosion test. Fragmentation and weight gain are correlated in 91% of cases (6 out of 66 are not correlated).

Figure 7: BOR_6151 before and after accelerated corrosion testing. This untreated object was completely fragmented during the test.
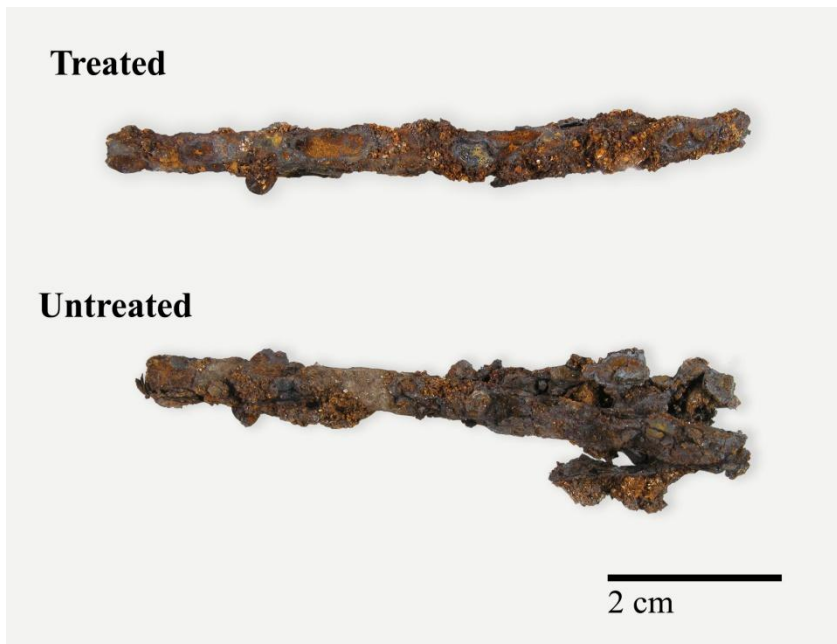
Figure 8: The treated and untreated halves of BOR_1693 after the corrosion test. The treated half showed no sign of damage, while the untreated half began to fragment, indicating active corrosion.

In comparison, the treated objects had much lower overall likelihood of damage, with only 22% (AS20) and 18% (dNaOH) showing any change (Table 2). Untreated objects were always less damaged than treated objects, which in most cases showed no signs of physical change (Figure 8). BIL objects that were treated showed no physical damage during the period of the test. Given that the accelerated conditions were significantly more corrosive than normal room conditions, it is expected that objects not damaged during the accelerated test would also be stable for a significant period of time under non-accelerated conditions.

The imprecision of the weight gain method means that in some cases, weight gain and visual change were not correlated. For example, BOR_1684.2 fragmented into pieces, despite showing no significant weight gain (Figure 4). This occurred in 9% of cases. Although not perfect, the weight gain of an object appears to be a reasonable indication of the likelihood of physical change and damage. Physical damage could also result from purely physical events such as differential expansion of corrosion product layers and the metal core at the 75°C test temperature, and this could explain the cases where physical damage was not correlated with weight gain. It should be remembered that although generic profiles of objects have been identified (Neff *et al.*, 2005), each object is unique in terms of its corrosion profile, porosity, cracking and fit to the metal core, and that differential behaviour is therefore to be expected.

Relationship with chloride content [sub-heading]

Figure 9 shows that there is a positive correlation between chloride levels and weight gain for untreated objects. CAE_48, which had the highest weight gain of 16%, is an anomalous result. Excluding it, the Pearson correlation coefficient (r) of chloride content and weight

gain is 0.908, with the coefficient of determination (r^2) 0.8251. This represents a very strong linear correlation between chloride content and weight gain.
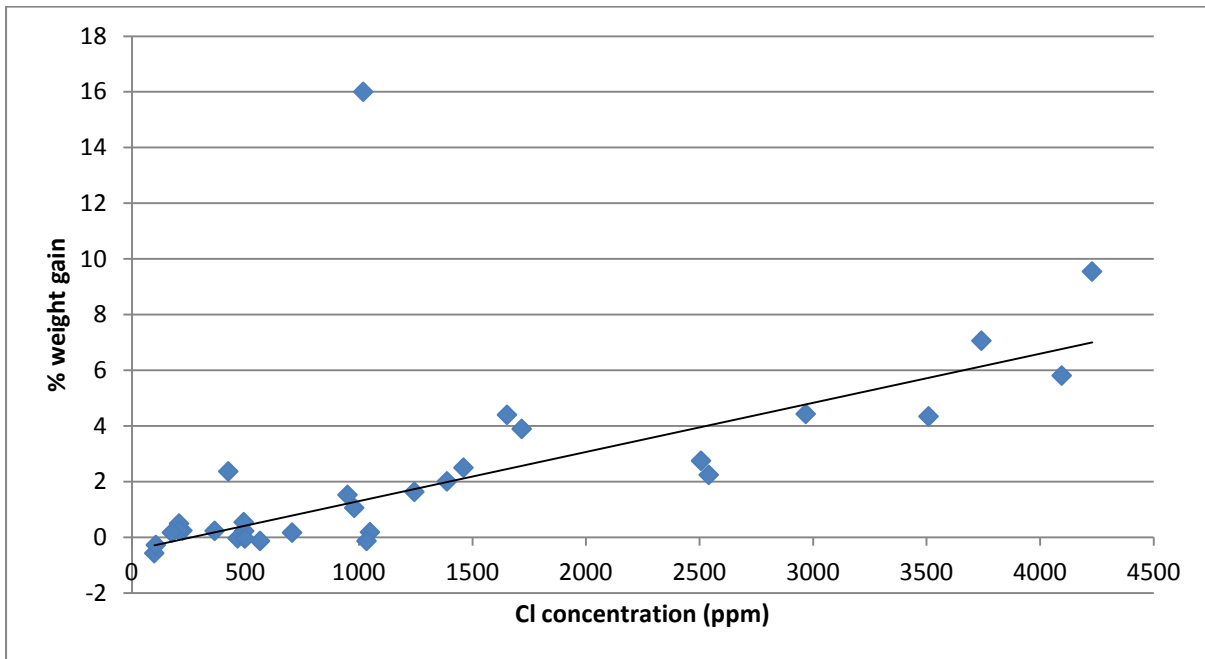

Figure 9: Relationship between concentration of Cl and % weight gain for untreated objects.

The relationship between chloride content and corrosion rate of objects has not previously been quantitatively evaluated on this scale. North and Pearson (1978) suggested that objects with a chloride content of < 200 ppm would be stable, while those above 1000 ppm are at 'high risk'. The data on untreated objects suggest a more linear relationship than these boundary values suggest. All but one of the 15 untreated objects with chloride content greater than 1000 ppm show positive weight gain, although this varies between 0.2 and 16%. Below 200 ppm there are only three objects: two show weight loss and one minor weight gain (0.17%), but all three experienced minor fragmentation suggesting that they may not be entirely 'stable'. Between 200 and 1000 ppm the majority of objects (10 out of 13) show some weight gain, but this is never higher than 2.4%.
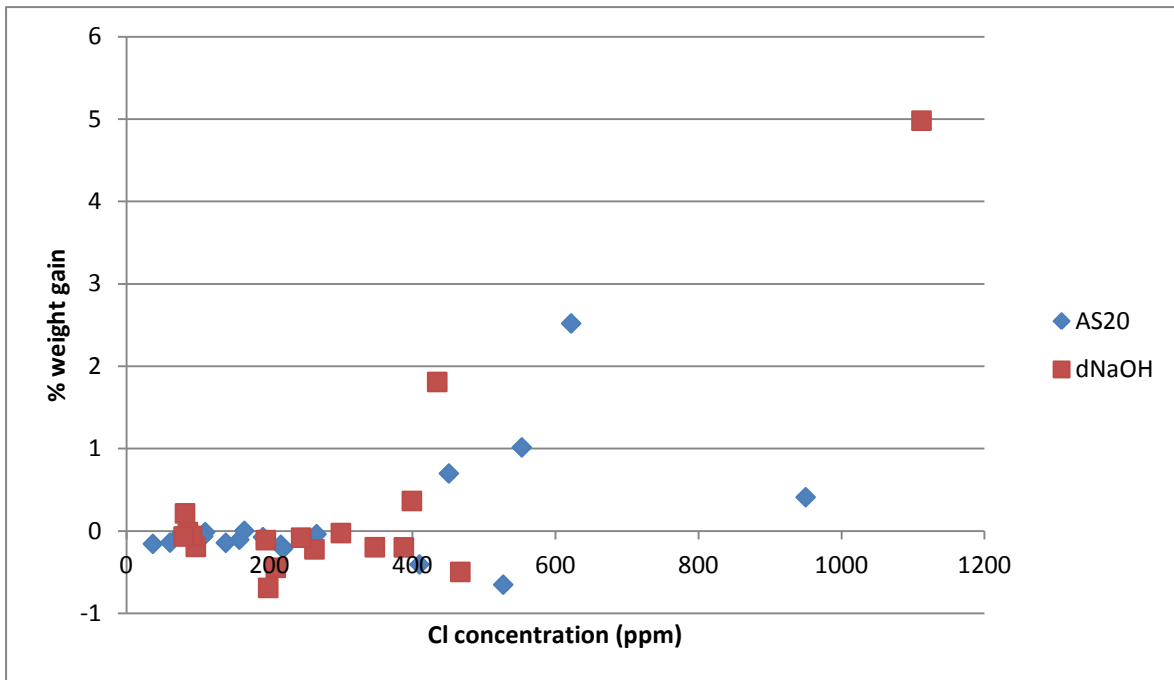
Figure 10: Relationship between chloride concentration and % weight gain for treated objects.

Treated objects, apart from one exception, have chloride content less than 1000 ppm, and of these, objects with less than 400 ppm show no significant weight gain (Figure 10). Of the ten objects with chloride content after treatment of > 400 ppm, 7 show some weight gain, with the higher weight gain correlating with the higher chloride levels. This suggests that chloride remaining after treatment does not induce weight gain if the concentration is below 400 ppm, while above 400 ppm there is a 70% chance that the object will experience some corrosion.

Figure 11 shows the same data as Figure 10, but the treated objects are divided according to the chloride concentration of the final treatment solution. Objects where the concentration of the final treatment bath was less than 5 mg/l cluster around 0 to -0.5% weight change, and usually have chloride content less than 400 ppm. Of the seven treated objects that show weight gain, five have a final bath concentration of > 5 mg/l, and the remaining two have final bath concentrations of 3.97 and 4.79 mg/l. The relationship between final bath concentration and weight gain of all treated objects is also statistically significant at the .05 significance level ($r = 0.472$, $r_{crit} = 0.3246$). Although there is no clear linear relationship between final bath concentration and weight gain ($r^2 = 0.223$) (Figure 12), all but two of the objects with final bath concentration above 5 mg/l show some weight gain. This supports the hypothesis that incomplete treatment leads to continued susceptibility to corrosion.

Figure 11: Relationship between chloride concentration and % weight gain for treated objects, arranged according to the final solution concentration.

Figure 12: Relationship of final solution concentration for treated objects and weight gain.

Reasons for weight gain in fully treated objects (CAE_30.1 and CAE_45.1) are unclear, but may be related to incomplete extraction due to inaccessible chloride located deep within the object. A small study of some of the objects before the accelerated corrosion test used scanning electron microscopy and energy-dispersive X-ray analysis to locate chlorine in cross-sections of some of the halved nails (Rimmer & Wang, 2010). CAE_45.1, which showed weight gain behaviour despite being treated to < 5 mg/l in the final solution, had chloride ions located deep within the metal along slag inclusions. This may be responsible for its

apparent corrosion after treatment. As these two objects represent only 7% of the fully treated objects in the test (out of 27 objects that had a final solution concentration less than 5 mg/l) it seems that for most objects (93%), a properly completed treatment does reduce corrosion susceptibility.

The correlation of final solution concentration and weight gain may indicate the different effects of bound and soluble chloride. The residual chloride in objects (up to 400 ppm) that complete treatment does not appear to have a strong effect on corrosion behaviour, and may therefore represent bound chloride in β-FeOOH tunnels (Stahl *et al.*, 2003; Réguer *et al.*, 2009). β-FeOOH which is washed to remove its surface-adsorbed chloride does not cause corrosion of iron in contact with it (Watkinson & Lewis, 2005). Flooding β-FeOOH with hydroxide ions during washing removes surface-adsorbed chloride, leaving the bound chloride which is detected during post-treatment digestion of the object. Objects that do not complete the treatment are likely to still contain some soluble chloride in addition to this bound chloride, and it is probable that the soluble chloride fraction leads to weight gain compared to objects that did complete the treatment.

Quantifying treatment success using oxygen measurements: a pilot study [Heading]

As part of a Cardiff University based AHRC/EPSRC Science and Heritage Large Grants project examining the corrosion rates of large numbers of archaeological iron objects, it has been possible to further test the effect of chloride removal on the rate of corrosion of objects. This pilot study is reported here to support the preliminary conclusions that were reached in the accelerated corrosion study. Rimmer *et al.* (2012) suggested that, based on the chloride removal data, a short alkaline sulphite treatment of only two weeks at 60°C could remove sufficient chloride ions to significantly reduce the corrosion rate. This hypothesis was tested by sealing ten untreated iron nails from BIL into 250 ml food preservation jars with metal sealing discs ('Kilner'-type) together with a standard quantity of silica gel conditioned to 80% RH. The RH in the jars was measured using RHTemp101A data loggers, and found to be within 3% of 80% RH during the period of the test. A sensor spot containing an oxygen-sensitive fluorescent compound was adhered to the inner glass surface, allowing oxygen partial pressure in the jar to be measured using a WPI OxyMini™ fibre-optic meter. 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. Oxygen measurements are accurate to within c. 2 mbar or 1% and control jars containing nitrogen gas showed negligible ingress of oxygen during the test period. The oxygen consumption of the objects at 80% RH was measured for 37 days. The objects were then placed into a 0.1 M NaOH / 0.05 M Na_2SO_3 solution for two weeks at 60°C. There were no solution changes in that time, and no further rinsing of any kind was undertaken. The objects were then dried using oven-dry silica gel for three weeks, and placed in the oxygen measurement system for a second time, under the same conditions. The treatment solution was analysed for chloride content using the

specific ion meter. Upon completion of oxygen measurements the objects were digested in nitric acid and analysed for residual chloride content as above.

Results [sub-heading]

The results of the test are given in Table 3. The rate (R) is the slope of the line of oxygen consumption, as shown in the example in Figure 13.
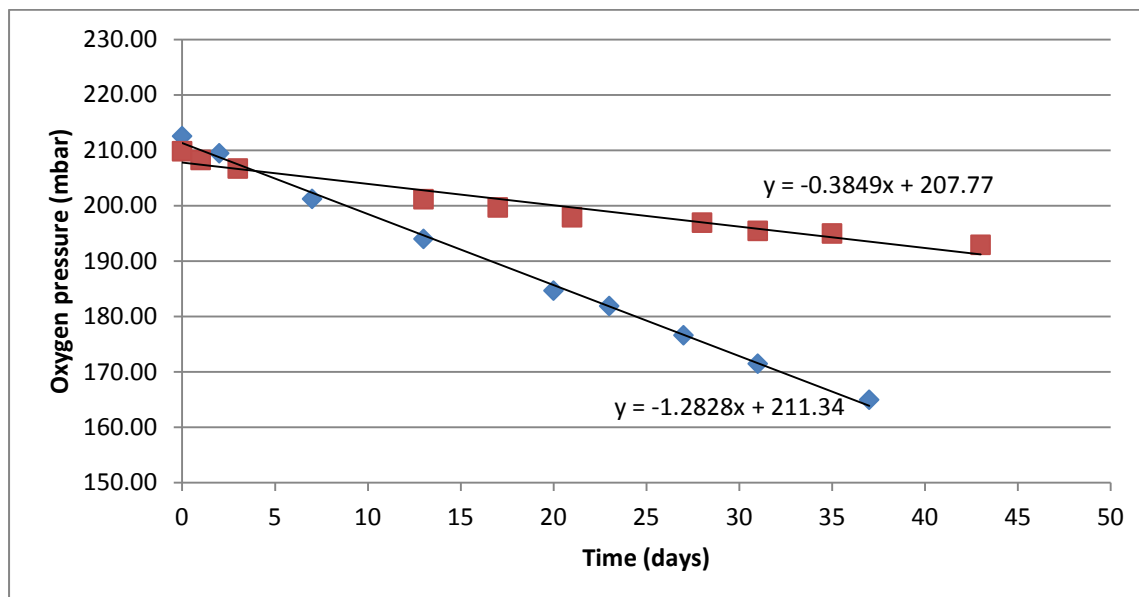

Figure 13: Oxygen consumption of BIL_104 from AS60 2-week test; blue – before treatment, red – after treatment. The equation for the straight line drawn through each set of points provides the rate R.

Sample	Weight nail (g)	R before	R after	% change in R	Extracted Cl (ppm)	Residual Cl (ppm)	Total Cl (ppm)	Treatment efficiency %
BIL_104	4.24	1.28	0.38	70	3344	143	3487	96
BIL_105	3.45	0.69	0.06	91	172	164	336	51
BIL_107	10.79	0.43	0.25	43	328	175	503	65
BIL_108	5.10	0.85	0.05	94	1391	86	1478	94
BIL_117	4.49	0.87	0.08	90	369	205	574	64
BIL_120	5.69	0.81	0.41	50	990	183	1172	84
BIL_134	4.57	0.67	0.08	88	218	134	352	62
BIL_136	2.99	0.96	0.37	62	2224	175	2399	93
BIL_140	9.29	1.82	0.58	68	1944	364	2308	84
BIL_146	1.95	1.21	0.07	94	2393	247	2640	91

Table 3: Results of oxygen measurement and chloride content of ten objects treated for 2 weeks in alkaline sulphite.

All of the objects consumed oxygen before the treatment, with R between 0.4 and 1.8 (Table 3). After treatment, all of the object corrosion rates slowed down, with R between 0.05 and 0.58. For 5 out of 10 objects, the decrease in R was 85% or greater, with the remaining objects in the range 42% to 70% (Figure 14). The mean reduction in R was 73% and the median 78%. After treatment, half of the objects had R indistinguishable from that of control samples, suggesting that the oxygen consumption was so low as to be undetectable.
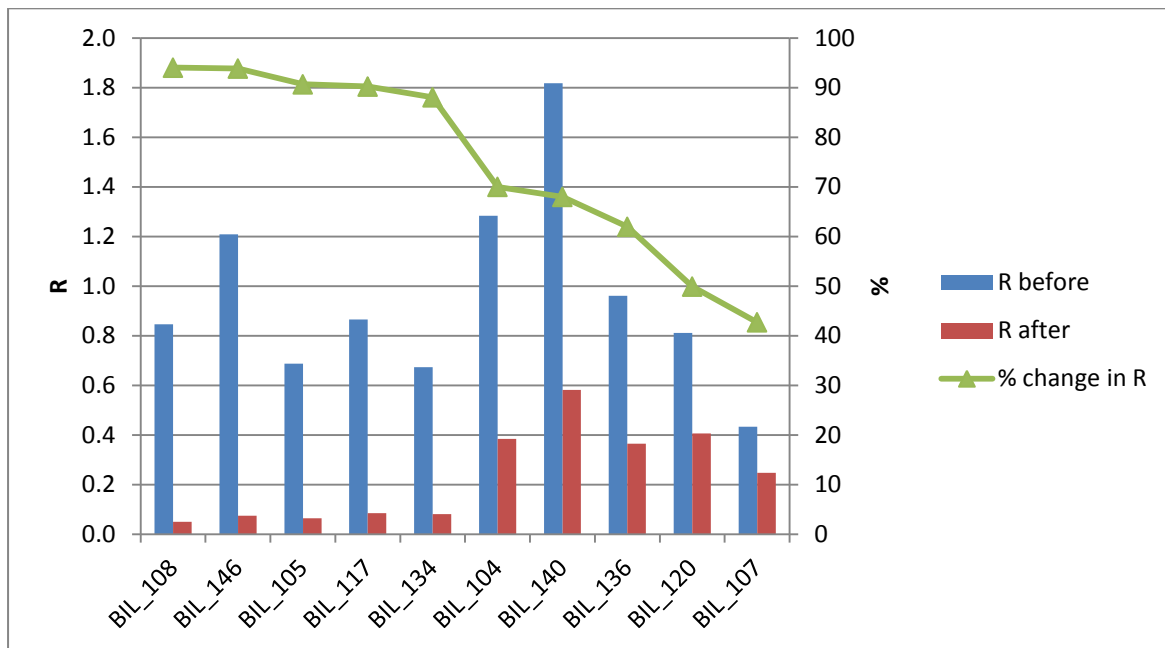

Figure 14: Change in rate (R) of oxygen consumption due to treatment in alkaline sulphite at 60°C for 2 weeks. The data is in order of % change in R (secondary Y axis).

Chloride removal from the objects was highly variable, ranging between 218 and 3344 ppm (Table 3). The range of total chloride was 300 to 3500 ppm, with the mean total chloride 1500 ppm. The mean residual chloride content was 188 ppm, and no object retained more than 364 ppm after the treatment, despite the treatment lasting only two weeks. As a proportion of the total chloride in the object, the extraction of chloride was between 51 and 96%, with a median of 84%.

Figure 15 shows that there is a linear correlation between chloride content and R before treatment. There is no apparent correlation between chloride content and R after treatment. This clearly shows the impact of removing chloride from the objects in reducing the corrosion rates.
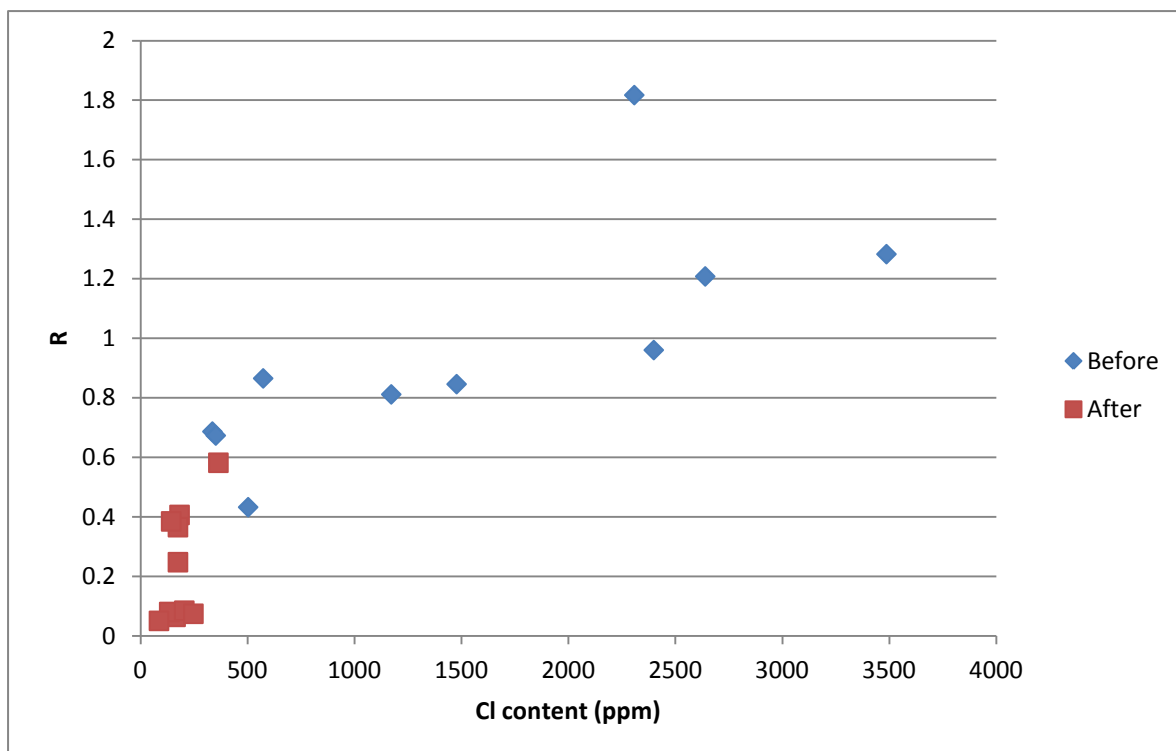
Figure 15: Effect of two weeks treatment in alkaline sulphite solution on chloride content and corrosion rate (R).

Discussion [sub-heading]

The results of the preliminary study show that a short treatment which removes some of the soluble chloride ions does have a significant impact in reducing corrosion rates. A statistically significant correlation exists between the amount of chloride removed and R before treatment (r = 0.704, r_{crit} = 0.632 at .05 significance), suggesting that it is the most soluble chloride, removed at the beginning of treatment, that acts as the most significant driver for the corrosion rate. Although half of the objects were still corroding at a measurable rate after treatment, these measurements relate to 80% RH, a humidity which is severely damaging to objects. At lower RH, it is likely that the corrosion rate after treatment would be extremely slow after this short treatment. The residual chloride content of the objects and the treatment efficiency are very similar to those obtained in longer treatments for objects from this site (Rimmer *et al.*, 2012). The data from the oxygen consumption test also substantiates the accelerated corrosion study finding that a linear relationship exists between chloride content and corrosion rate before treatment, and that treated objects typically corrode much more slowly than untreated objects. While the small number of samples means that drawing conclusions from these correlations must be done with caution it is clear that a measurable relationship does exist between chloride and corrosion rate, and that removing chloride has a significant impact on the rate. This is as expected, but has

not been previously shown quantitatively in conservation. Larger sample sizes must be used to test this further.

Further work in using oxygen consumption to measure the effectiveness of treatment is underway. 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 overall loss of object lifespan. The improvement in corrosion behaviour after a short treatment will be measured against that produced by a full treatment achieving the lowest possible residual chloride content. Residual chloride data will be obtained to determine its influence on corrosion; in particular, to investigate what post-treatment levels of chloride are not damaging to objects. The results of this study will be published in due course.

Conclusion [Heading]

This study has shown that objects treated in alkaline deoxygenated solutions are much less susceptible to corrosion than untreated objects. A linear correlation has been established between chloride ion content and the weight gain of untreated objects due to corrosion at accelerated conditions, supporting the hypothesis that chloride levels correlate to increased corrosion rate, even in archaeological iron objects with complicated morphology and unevenly distributed chloride in the structure.

Although the accelerated corrosion methodology used was subject to some imprecision, clear patterns have emerged regarding the successful stabilisation of iron objects using treatment solutions. Fully treated objects containing less than 400 ppm chloride appear to be stable under the test conditions. Untreated objects containing similar amounts of chloride were not stable, indicating that treatment is removing the soluble chloride which causes corrosion, and that residual chloride after treatment may be bound in the structure of akaganeite without causing damaging corrosion. It is possible that later decay of the akaganeite crystal structure could release this bound chloride fraction to cause corrosion, but it is not known at what rate this occurs or how damaging its influence might be.

The most significant factor in determining the success of a treatment appears to be the final solution concentration and the distribution of chloride within objects. Objects with incomplete treatment (> 5 mg/l in final solution) are likely to be unstable, whereas 93% of the objects treated to < 5 mg/l were stable in the test. This underlines the importance of measuring chloride extraction during treatment and continuing treatment until chloride levels in solution are low.

On the other hand, the pilot study of a 2-week single-bath alkaline sulphite treatment showed that corrosion rates can be successfully reduced by removing the most soluble chloride in a short treatment. Although half of the objects continued to corrode after this short treatment, corrosion rates were reduced by more than 50% in all cases. Ongoing and

more expansive study of corrosion rates using quantitative oxygen consumption measurements will allow predictions to be made as to the likely increase in the lifespan of objects from removing chloride ions. On the basis of the evidence currently available, desalination treatments are normally successful in reducing corrosion rates, and therefore in increasing the lifespan of objects.

Acknowledgements [Heading]

Equipment and supplies [Heading]

BDH AnaLar Sodium sulphite, Na_2SO_3, anhydrous
BDH AnaLar Sodium hydroxide, NaOH
VWR International Ltd, Poole, BH15 1TD, UK. http://uk.vwr.com

AnaLar Nitric acid, HNO_3
Fisher Scientific UK Ltd, Bishop Meadow, Loughborough, Leicestershire, LE11 5RG, UK.
http://www.fisher.co.uk

Silica gel, self-indicating orange to green, 2-5 mm beads
GeeJay Chemicals Ltd, 1 Beamish Close, Sandy, Bedfordshire, SG19 1SD, UK.
http://www.geejaychemicals.co.uk

Deluxe Preserving Wide Mouth Jars (250 ml) with two-part lids
Crown Supplies Ltd, Unit 10, Hellesdon Hall Industrial Park, Norwich, Norfolk, NR6 5DR.
http://www.justpreserving.co.uk

OxyMini Fiber Optic Oxygen Meter
Planar Oxygen Sensor Spots
World Precision Instruments Ltd, Astonbury Farm Business Centre, Aston, Stevenage, Hertfordshire, SG2 7EG, UK. http://www.wpi-europe.com

Radiometer Analytical PHM250 specific ion meter, ISE25CL chloride-specific electrode, REF621 chloride-free Hg/HgSO$_4$ reference electrode
Radiometer Analytical, 72 rue d'Alsace, 69627 Villeurbanne CEDEX, Lyon, France.
http://www.radiometer-analytical.com

Hanwell ML4106 wireless temperature/relative humidity sensor
Hanwell Instruments Ltd, Pendle House, Jubilee Road, Letchworth, Hertfordshire, SG6 1SP, UK. http://www.hanwell.com

Madgetech RHTemp101A Humidity and Temperature Datalogger
Loggershop Technology, 189 Ashley Road, Poole, Dorset, BH14 9DL, UK.
http://www.loggershop.co.uk

References [Heading]

Angelini, E., Barberis, E., Bianco, P., Rosalbino, F. & Ruatta, L. 1998. Effect of burial in different soils on the decay of iron artifacts: Laboratory investigation. In: W. Mourey & L. Robbiola, eds. *Metal 98 : proceedings of the international conference on metals conservation, Draguignan-Figanières, France, 27-29 May 1998*. London: James & James, pp. 106-10.

Ding, H. Z. & Wang, Z. D. 2007. Time-temperature superposition method for predicting the permanence of paper by extrapolating accelerated aging data to ambient conditions. *Cellulose,* 14: 171-81.

Erhardt, D. & Mecklenburg, M. F. 1995. Accelerated vs Natural Aging: Effect of Aging Conditions on the Aging Process of Cellulose. In: P. B. Vandiver, J. R. Druzik, G. Madrid, J. Luis, I. C. Freestone & G. S. Wheeler, eds. *Materials Issues in Art and Archaeology IV*. Warrendale, P.A: Materials Research Society, pp. 247-70.

Keene, S. & Orton, C. 1985. Stability of treated archaeological iron: an assessment. *Studies in Conservation,* 30: 136-42.

Keene, S. 1994. Real-time survival rates for treatments of archaeological iron. In: D. A. Scott, J. Podany & B. Considine, eds. *Ancient & Historic Metals: Conservation and Scientific Research*. Marina del Rey: Getty Conservation Institute, pp. 249-64.

Loeper-Attia, M.-A. & Weker, W. 1997. Déchloruration d'objets archéologiques en fer par la méthode du sulfite alcalin a l'IRRAP. In: I. D. MacLeod, S. L. Pennec & L. Robbiola, eds. *Metal 95: Proceedings of the International Conference on Metals Conservation, Semur en Auxois, 25-28 Sept 1995*. London: James & James, pp. 162-66.

Loeper-Attia, M.-A. 2007. A proposal to describe reactivated corrosion of archaeological iron objects. In: P. Dillmann, C. Béranger, P. Piccardo & H. Matthiesen, eds. *Corrosion of metallic heritage artefacts: Investigation, conservation and prediction for long-term behaviour*. Cambridge: Woodhead Publishing, pp. 190-202.

Luxford, N. & Thickett, D. 2011. Designing accelerated ageing experiments to study silk deterioration in historic houses. *Journal of the Institute of Conservation,* 34: 115-27.

Matthiesen, H. 2007. A novel method to determine oxidation rates of heritage materials in vitro and in situ. *Studies in Conservation,* 52(4): 271-80.

Matthiesen, H. & Wonsyld, K. 2010. In situ measurement of oxygen consumption to estimate corrosion rates. *Corrosion Engineering, Science and Technology,* 45: 350-56.

Neff, D., Dillmann, P., Bellot-Gurlet, L. & Beranger, G. 2005. Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system. *Corrosion Science,* 47(2): 515-35.

Neff, D., Dillmann, P., Descostes, M. & Beranger, G. 2006. Corrosion of iron archaeological artefacts in soil: Estimation of the average corrosion rates involving analytical techniques and thermodynamic calculations. *Corrosion Science,* 48(10): 2947-70.

North, N. A. & Pearson, C. 1978. Methods for treating marine iron. In: eds. *ICOM Committee for Conservation 5th Triennial Meeting, Zagreb.* Paris: International Council of Museums. 78/23/3, pp. 1-10.

Réguer, S., Dillmann, P. & Mirambet, F. 2007. Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases. *Corrosion Science,* 49(6): 2726-44.

Réguer, S., Mirambet, F., Dooryhee, E., Hodeau, J.-L., Dillmann, P. & Lagarde, P. 2009. Structural evidence for the desalination of akaganeite in the preservation of iron archaeological objects, using synchrotron X-ray powder diffraction and absorption spectroscopy. *Corrosion Science,* 51: 2795-802.

Rimmer, M. & Wang, Q. 2010. Assessing the effects of alkaline desalination treatments for archaeological iron using scanning electron microscopy. *The British Museum Technical Research Bulletin,* 4: 79-86.

Rimmer, M., Watkinson, D. & Wang, Q. 2012. The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions. *Studies in Conservation,* 57(1): 29-41.

Rimmer, M. B. 2010. Investigating the treatment of chloride-infested archaeological iron objects. PhD Thesis, Cardiff University.

Robinet, L. & Thickett, D. 2003. A new methodology for accelerated corrosion testing. *Studies in Conservation,* 48(4): 263-68.

Stahl, K., Nielsen, K., Jiang, J. Z., Lebech, B., Hanson, J. C., Norby, P. & van Lanschot, J. 2003. On the akaganeite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts. *Corrosion Science,* 45(11): 2563-75.

Thickett, D. 2005. Analysis of iron corrosion products with Fourier transform infra-red and Raman spectroscopies. In: M. Picollo, ed. *Proceedings of the Sixth Infra-Red and Raman Users Group Conference (IRUG6), Florence, Italy, March 29th - April 1st 2004*. Padua: Il Prato, pp. 86-93.

Thickett, D. & Odlyha, M. 2005. Application of thermomagnetometry to corrosion studies of archaeological iron. *Journal of Thermal Analysis and Calorimetry,* 80(3): 565-71.

Thickett, D., Lambarth, S. & Wyeth, P. 2008. Determining the stability and durability of archaeological materials. In: *9th International Conference on Non-Destructive Testing of Art, Jerusalem, Israel, 25-30 May 2008*. [accessed 23 Feb 2012] Available at <http://www.ndt.net/search/docs.php3?MainSource=65>

Thickett, D. & Odlyha, M. 2010. Assessment of dry storage microenvironments for archaeological iron. In: E. Williams & C. Peachey, eds. *The Conservation of*

Archaeological Materials - Current trends and future directions. London: Archaeopress, pp. 187-99.

Thickett, D. 2011. Post Excavation Changes and Preventive Conservation of Archaeological Iron. PhD Thesis, Birkbeck College, University of London.

Turgoose, S. 1985. The corrosion of archaeological iron during burial and treatment. *Studies in Conservation,* 30: 13-18.

Turgoose, S. 1993. Structure, composition and deterioration of unearthed iron objects. In: S. Aoki, ed. *Current Problems in the Conservation of Metal Antiquities*. Tokyo: Tokyo National Research Institute of Cultural Properties, pp. 35-52.

Watkinson, D. & Lewis, M. R. T. 2005. The Role of beta-FeOOH in the Corrosion of Archaeological Iron. In: P. B. Vandiver, J. L. Mass & A. Murray, eds. *Materials Issues in Art and Archaeology VII*. Warrendale, PA: Materials Research Society of America Symposium, pp. 103-14.

Watkinson, D. & Lewis, M. R. T. 2008. Desiccated storage of chloride contaminated iron: A study of the effects of loss of environmental control. In: E. May, M. Jones & J. Mitchell, eds. *Heritage Microbiology and Science: Microbes, Monuments and Maritime Materials (Special Publication 315)*. Cambridge: Royal Society of Chemistry, pp. 279-89.