

# RESIDUES OF ALKALINE SULPHITE TREATMENT AND THEIR EFFECTS ON THE CORROSION OF ARCHAEOLOGICAL IRON OBJECTS

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## Abstract

*The formation of chemical residues on archaeological iron following its treatment in aqueous alkaline sulphite (NaOH/Na<sub>2</sub>SO<sub>3</sub>) is simulated by evaporating selected ion mixtures to dryness. The residues are identified by X-ray diffraction (XRD) and their influence on iron corrosion is investigated by mixing them with iron powder and dynamically recording the weight change of these powder mixtures at fixed temperature and relative humidity (RH) in a climatic chamber. Ferrous chloride was dissolved in Na<sub>2</sub>SO<sub>4</sub> to simulate Fe<sup>2+</sup>/Cl<sup>-</sup> contaminated Na<sub>2</sub>SO<sub>4</sub> solution. This formed FeSO<sub>4</sub>·4H<sub>2</sub>O/FeSO<sub>4</sub>·7H<sub>2</sub>O/NaCl upon evaporation. Evaporating a FeCl<sub>2</sub>/NaOH/Na<sub>2</sub>SO<sub>3</sub> solution produced either Na<sub>2</sub>SO<sub>4</sub>/NaCl/γ-FeOOH or Na<sub>6</sub>(CO<sub>3</sub>)(SO<sub>4</sub>)<sub>2</sub>/Na<sub>2</sub>SO<sub>4</sub>/NaCl/γFeOOH mixtures according to ion concentration in the initial solution. Iron powder and various residues were mixed and exposed at 75% RH and 20°C; Na<sub>2</sub>SO<sub>4</sub>/Fe did not corrode iron; FeSO<sub>4</sub>·7H<sub>2</sub>O/Fe produced minimal corrosion of iron; during the hydration phase of FeSO<sub>4</sub>·4H<sub>2</sub>O to FeSO<sub>4</sub>·7H<sub>2</sub>O iron corroded; a NaCl/FeSO<sub>4</sub>·7H<sub>2</sub>O/FeSO<sub>4</sub>·4H<sub>2</sub>O mixture corroded iron rapidly. Overall, at 75% RH, soluble chloride residues offer a more immediate and significant corrosion risk to iron than Na<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O and FeSO<sub>4</sub>·4H<sub>2</sub>O.*

**Keywords:** archaeological iron, desalination, residues, iron sulphate, sodium sulphate

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## Introduction

Archaeological iron objects often contain chlorides from their burial environment, which act as counter-ions in the electrochemical corrosion process (Turgoose 1985, Neff et al. 2005). Post-excavation corrosion delaminates objects and destroys their aesthetic, technological and heritage value. (Turgoose 1985, Selwyn et al. 1999). While desiccation can prevent this corrosion (Watkinson and Lewis 2005), an alternative is to attempt the removal of soluble chlorides using washing methods, such as aqueous alkaline sulphite (NaOH/Na<sub>2</sub>SO<sub>3</sub>) (North and Pearson 1975). Washing has been described as a stabilisation process, but this is an unproven and inaccurate statement, as the amount of chloride removed is unpredictable and residual chloride is unknown (Watkinson 1983, 1996, Watkinson and Al Zahrani 2008). Consequently, washing is better described as a stability enhancer, as it does not remove the need to control the storage environment (Watkinson 1996, Watkinson and Al Zahrani 2008). Nevertheless, quantitative data indicate that alkaline sulphite washing can remove a large percentage of the total chloride present in an object (Watkinson 1996, Al-Zahrani 1999, Watkinson and Al-Zahrani 2008) and qualitative studies indicate that such objects have increased longevity when compared with untreated objects (Keene and Orton 1985, Selwyn and Logan 1993, Keene 1994).

Despite these advantages, conservators in the UK now

rarely use alkaline sulphite washing because it is time consuming and imparts an unknown level of stability. Also, there is a concern that treatment chemicals remain in the iron and pose a corrosion threat. Although post-treatment rinsing has been employed to combat this threat (Selwyn and Logan 1993; Keene 1994), this increases treatment time, causes iron to corrode in oxygenated aqueous wash solutions and has an unknown efficiency. Barium hydroxide rinsing has been suggested for immobilising SO<sub>3</sub><sup>2-</sup>/SO<sub>4</sub><sup>2-</sup> ions as BaSO<sub>4</sub> (North and Pearson 1975), but this produces white residues and its effectiveness is unknown (Keene 1994).

Our study examines the formation of chemical residues following alkaline sulphite treatment and investigates their influence on iron corrosion by:

- Modelling solutions to contain ions present during alkaline sulphite treatment of iron objects and evaporating these to dryness;
- Identifying the compounds formed upon drying using XRD;
- Mixing these compounds with iron powder and exposing them to controlled RH and temperature to determine if they corrode iron at selected RH values.

## Formation of alkaline sulphite residues

The original alkaline sulphite treatment sequentially washed iron in sealed containers of aqueous 0.5M NaOH/0.5M Na<sub>2</sub>SO<sub>3</sub> at 70°C (North and Pearson 1975). The SO<sub>3</sub><sup>2-</sup> deoxygenates the solution and prevents cathodic reduction of oxygen, which stops iron corrosion and frees chloride from its counter ion role allowing it to diffuse into solution. Treatment modifications have included lower NaOH (0.1M) and Na<sub>2</sub>SO<sub>3</sub> (0.05M) concentrations (Schmidt-Ott and Oswald 2006) and room temperature treatment (Al-Zahrani 1999). During treatment, Fe<sup>2+</sup> ions present in the object react with OH<sup>-</sup> ions to produce insoluble Fe(OH)<sub>2</sub> that later oxidises to rust. Therefore, upon completion of treatment, Cl<sup>-</sup> and Fe<sup>2+</sup> concentration within the NaOH/Na<sub>2</sub>SO<sub>3</sub> solution and the corroded iron matrix are expected to be low. Drying treated iron objects without first washing them to remove chemical residues from treatment allows them to retain substantial amounts of Na<sup>+</sup>, OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>. The interactions between these ions will form new compounds that may pose corrosion risks to the iron.

Atmospheric oxygen will react with SO<sub>3</sub><sup>2-</sup> to form SO<sub>4</sub><sup>2-</sup> or SO<sub>3</sub><sup>2-</sup> will adsorb onto corrosion products during drying (Kaneko 1993). Fe<sup>2+</sup> may form on objects if post-treatment corrosion occurs and hygroscopic iron sulphate could form and corrode archaeological iron above 60% RH (Turgoose 1993, Jones 1996). However, since Fe<sup>2+</sup> precipitates as insoluble hydroxide during treatment the Fe<sup>2+</sup> needed to form FeSO<sub>4</sub> must be supplied by renewed corrosion. This may not produce FeSO<sub>4</sub> as oxidation of Fe<sup>2+</sup> in SO<sub>4</sub><sup>2-</sup> containing solutions favors goethite (α-FeOOH) formation via an intermediate sulphate-containing Green Rust II (Refait and Genin 1994, Oh et al. 2002). Also, aggressive atmospheric corrosion of iron by iron sulphate (Schwarz 1965a, Schwarz 1965b, Stambolov 1985) has recently been questioned (Weissenrieder et al. 2004, Cai and Lyon 2005) and there is currently no evidence either that iron sulphate forms on alkaline sulphite treated iron or that it offers a corrosion risk. Additionally, post-treatment drying of objects may form sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), but this has not been confirmed nor has its potential for corroding iron been studied.

## Experimental

Table 1 details the solutions used to simulate ion mixtures occurring in alkaline sulphite treatment of archaeological iron and on object surfaces following their removal from the treatment bath. These were evaporated to dryness over several days in an open container in the laboratory (35%-60% RH approximately 20°C). Throughout the experiments Analar grade reagents were dissolved in deionised water and products were analysed by X-ray diffraction (PANalytical X'Pert PRO at 40 kV/30 mA). Panalytical X'Pert High Score was used to identify and calculate approximate quantities of the principal products. All solutions in these tests are likely to contain more Fe<sup>2+</sup> than occurs on iron treated in alkaline sulphite.

Potential reactions of iron with the residues identified from the solution evaporation tests were examined by mixing their powders with nitrogen-reduced iron

Solution composition (concentrations are the concentrations of each component in 200 mls of solution)	Products on drying	Approx. proportion (±10%)
1M Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub> Na <sub>2</sub> SO <sub>3</sub>	64 36
1M FeCl <sub>2</sub> ·4H <sub>2</sub> O 1M Na <sub>2</sub> SO <sub>4</sub>	FeSO <sub>4</sub> ·7H <sub>2</sub> O FeSO <sub>4</sub> ·4H <sub>2</sub> O NaCl	52 17 30
0.1M NaOH 0.05M Na <sub>2</sub> SO <sub>3</sub> 0.05M FeCl <sub>2</sub> ·4H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub> NaCl γ-FeOOH	49 47 4
1M NaOH 1M Na <sub>2</sub> SO <sub>3</sub> 0.1M FeCl <sub>2</sub> ·4H <sub>2</sub> O	Na <sub>6</sub> (CO <sub>3</sub> )(SO <sub>4</sub> ) <sub>2</sub> Na <sub>2</sub> SO <sub>4</sub> NaCl γ-FeOOH	56 29 13 2

Table 1. Compounds formed by evaporation identified by XRD analysis.

Compound	RH (%)	Temp °C
Fe	75 and 90	20
Na <sub>2</sub> SO <sub>4</sub>	75 and 90	20
Na <sub>2</sub> SO <sub>4</sub> /Fe	75 and 90	20
FeSO <sub>4</sub> ·7H <sub>2</sub> O	75	20
FeSO <sub>4</sub> ·4H <sub>2</sub> O	75	20
FeSO <sub>4</sub> ·7H <sub>2</sub> O/Fe	75	20
FeSO <sub>4</sub> ·4H <sub>2</sub> O/Fe	75	20
FeSO <sub>4</sub> ·4H <sub>2</sub> O/FeSO <sub>4</sub> ·7H <sub>2</sub> O/NaCl/Fe	75	20

Table 2. Summary of climate chamber tests.

powder and exposing them at 20°C (±0.5°C) and fixed RH values (±1%) in a Vötsch VC4018 climatic chamber (Table 2). A Mettler AJ100 balance (±0.0001 g) recorded weight change to file every five minutes to offer hydration, dehydration and corrosion data. The instability of the balance from chamber vibration produces reproducible weight fluctuation. All powders were mixed in the ratio 1:1 by weight except the FeSO<sub>4</sub>·4H<sub>2</sub>O/Fe hydration experiment. They were spread out in Petri dishes to provide maximum surface area for reaction. Controls of Na<sub>2</sub>SO<sub>4</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O and Fe were run. Visual examination of the samples was used to check for any signs of corrosion occurring.

## Results

The nature and quantity of the compounds formed by the evaporation tests are shown in Table 1. After standing for several weeks in a closed volumetric flask in the laboratory a FeCl<sub>2</sub>/Na<sub>2</sub>SO<sub>4</sub> solution also formed natrojarosite (NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>).

In solid phase tests at 75% RH and 20°C, neither anhydrous Na<sub>2</sub>SO<sub>4</sub> nor iron powder showed detectable weight gain (see Figure 1a and b). A Na<sub>2</sub>SO<sub>4</sub>/Fe mixture showed a slight weight gain over a 16-day period with a few very small visible nodules of orange-brown corrosion products (see Figure 1c).

Anhydrous Na<sub>2</sub>SO<sub>4</sub> exposed to 90% RH hydrated rapidly (see Figure 2a) producing a mixture of liquid and solid Na<sub>2</sub>SO<sub>4</sub> in less than 24 hours. A Na<sub>2</sub>SO<sub>4</sub>/Fe mixture was slower to hydrate (see Figure 2b), but small quantities of iron corrosion product were observed within a day.

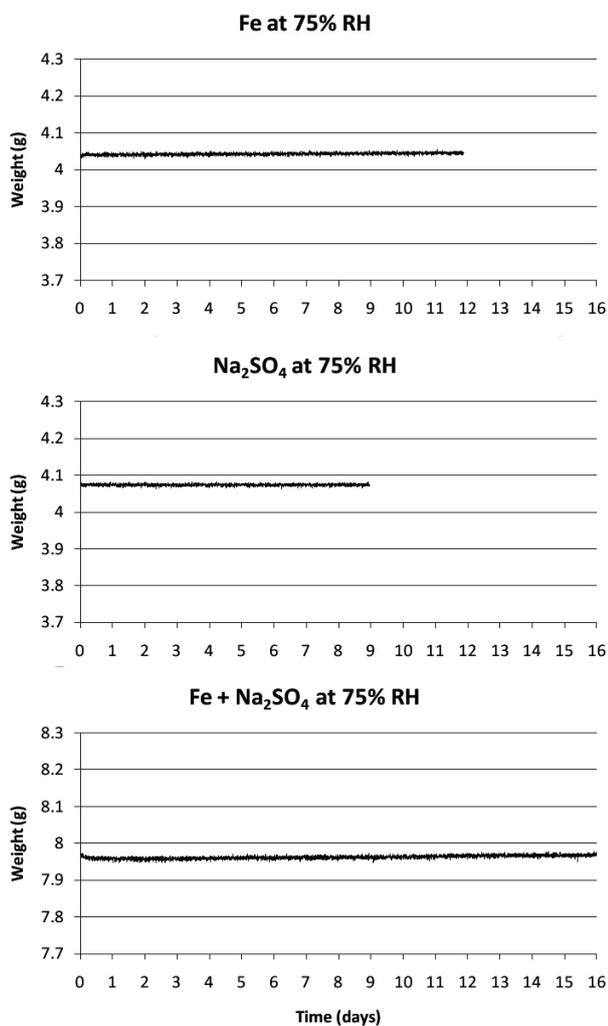


Figure 1. Iron powder and anhydrous Na<sub>2</sub>SO<sub>4</sub> at 75% RH at 20°C. From top: (a) iron powder, (b) Na<sub>2</sub>SO<sub>4</sub>, (c) Fe/Na<sub>2</sub>SO<sub>4</sub> mixture.

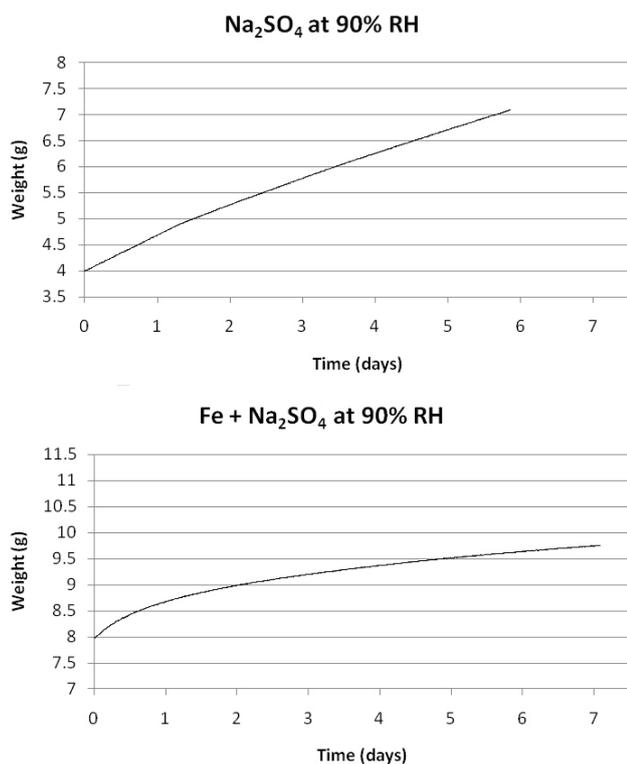


Figure 2. Iron powder and anhydrous Na<sub>2</sub>SO<sub>4</sub> at 90% RH at 20°C. From top: (a) Na<sub>2</sub>SO<sub>4</sub>, (b) Fe/Na<sub>2</sub>SO<sub>4</sub> mixture.

Exposing FeSO<sub>4</sub>·7H<sub>2</sub>O to 75% RH showed no weight gain over seven days (see Figure 3a). In the same conditions, a FeSO<sub>4</sub>·7H<sub>2</sub>O/Fe mixture gradually gained a very small amount of weight (see Figure 3b), although after eight days a visual inspection could not identify iron corrosion products. Close inspection of the slope reveals a very slight continuous weight gain over a four-day period (see Figure 3c).

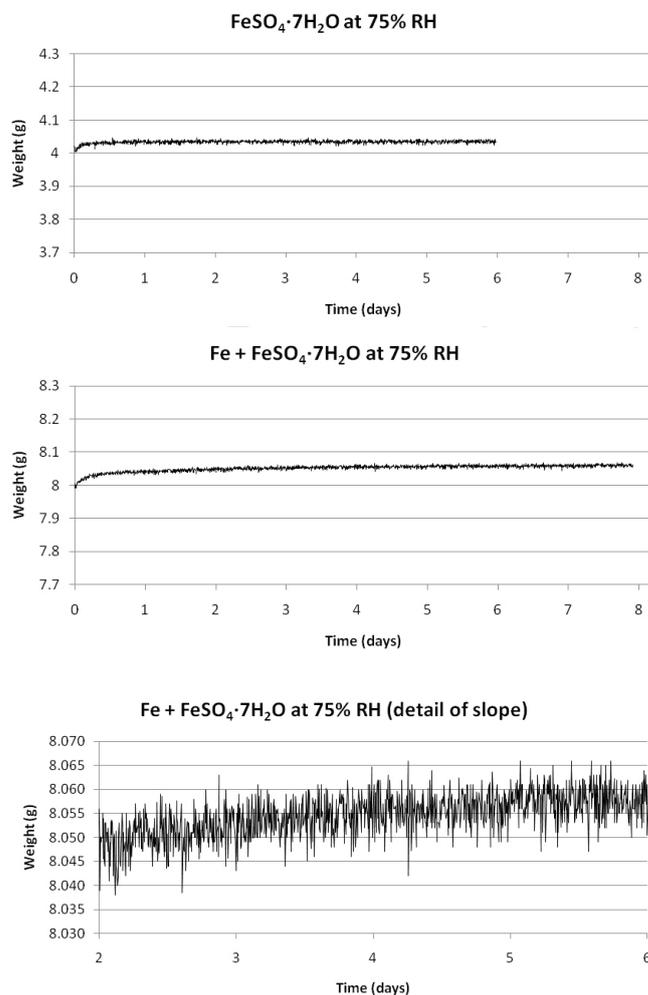


Figure 3. FeSO<sub>4</sub>·7H<sub>2</sub>O and iron powder and at 75% RH at 20°C. From top: (a) FeSO<sub>4</sub>·7H<sub>2</sub>O, (b) FeSO<sub>4</sub>·7H<sub>2</sub>O/Fe mixture, (c) FeSO<sub>4</sub>·7H<sub>2</sub>O/Fe mixture- detail days 2-6; approximately 0.005g weight gain.

Since exposure of FeSO<sub>4</sub>·7H<sub>2</sub>O/Fe at 75% RH had not caused detectable corrosion of iron, it was determined whether the hydration phase for FeSO<sub>4</sub>·4H<sub>2</sub>O to FeSO<sub>4</sub>·7H<sub>2</sub>O corroded associated iron. A sample of FeSO<sub>4</sub>·7H<sub>2</sub>O was dehydrated to constant weight at 40% RH to form FeSO<sub>4</sub>·4H<sub>2</sub>O, this was then mixed with Fe and exposed at 75% RH and 20°C.

FeSO<sub>4</sub>·4H<sub>2</sub>O hydrated much more quickly than the FeSO<sub>4</sub>·4H<sub>2</sub>O/Fe mixture (see Figure 4a and b). The FeSO<sub>4</sub>·4H<sub>2</sub>O/Fe sample comprised 1.118g FeSO<sub>4</sub>·4H<sub>2</sub>O and 1.1505g of Fe. Consequently, the expected weight gain from hydrating 1.118g (0.005 moles) of FeSO<sub>4</sub>·4H<sub>2</sub>O to FeSO<sub>4</sub>·7H<sub>2</sub>O is 0.2668g of H<sub>2</sub>O. In 43 days the overall weight gain was 0.4574g; therefore 0.1906g (0.4574g - 0.2668g) is attributable to the formation of new products from corrosion of iron. Figure 4b records most corrosion occurring during the hydration phase of FeSO<sub>4</sub>·4H<sub>2</sub>O, which was completed at approximately 28 days. Examining the period from 28 days to termination at 43

days reveals a regular, but slow, weight gain indicating very slow ongoing corrosion of the iron (see Figure 4c). (In Figure 4b, connection between the balance and the computer was briefly lost at 20 days and from 23-28 days it was intermittent, due to software problems.)

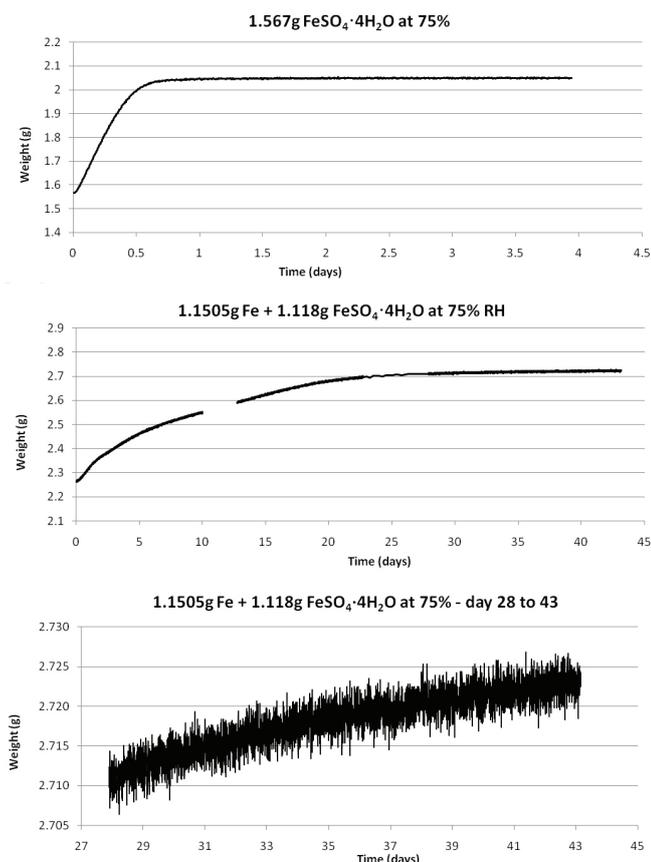


Figure 4.  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  and iron powder and at 75% RH at 20°C. From top: (a)  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  hydration, (b)  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}/\text{Fe}$  mixture (c)  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}/\text{Fe}$  mixture- detail days 28-43; approximately 0.012g weight gain.

Upon terminating the experiment the sample was dehydrated at 35% RH until it reached a constant weight (Figure 5). Dehydration was fast and recorded weight loss from conversion of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , as well as any dehydration of hydrated iron oxides produced by corrosion of the iron. The weight loss was 0.2868g, which means 0.1706g (0.4574g - 0.2868g) could be attributed to the new corrosion products. This is in good agreement with the 0.1906g weight gain that can be theoretically attributed to corrosion on the 75% RH hydration graph (see Figure 4b). The slight discrepancy of 0.0200g between theoretical (0.1906g) and recorded (0.1706g) corrosion can be attributed to the loss of 0.0200g of water from the new corrosion products during their dehydration at 35% RH.

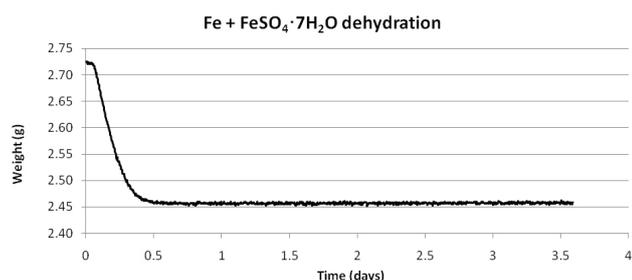


Figure 5. Dehydration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{Fe}$  mixture at 35% RH at 20°C.

$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaCl}$ , produced by solution evaporation from 1M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/1\text{M Na}_2\text{SO}_4$ , was mixed with an equal weight of iron powder and exposed at 75% RH. Corrosion was readily visible within hours and weight gain was rapid and continuous (Figure 6). Corrosion was ongoing and greater than for any of the sulphate-containing compounds studied in these experiments.

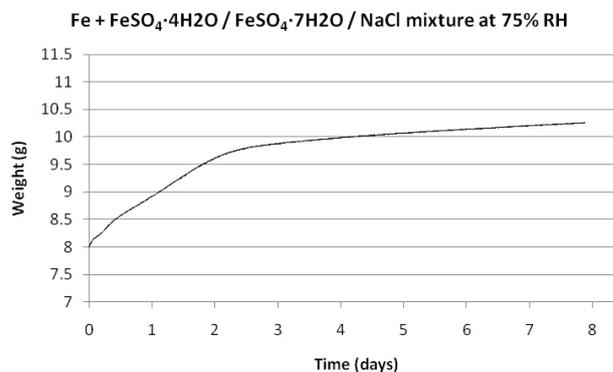


Figure 6. The powder residue from evaporating 200mls of a 1M NaOH/1M  $\text{Na}_2\text{SO}_4/0.1\text{M FeCl}_2$  solution mixed with equal weight of Fe and then exposed to 75% RH at 20°C.

## Discussion

Incomplete oxidation of  $\text{Na}_2\text{SO}_3$  upon drying probably results from high  $\text{SO}_3^{2-}$  concentration and speedy evaporation. Formation of both  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  from the evaporating  $\text{FeCl}_2/\text{Na}_2\text{SO}_4$  solution likely resulted from partial dehydration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  during storage. Many of the compounds formed by evaporation are hygroscopic (see Table 3). NaCl is very hygroscopic and the  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaCl}$  formed from evaporating  $\text{FeCl}_2/\text{Na}_2\text{SO}_4$  caused significantly greater and faster iron corrosion than either  $\text{Na}_2\text{SO}_4$  or  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  or hydration of  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  at 75% RH (see Figure 6), although it should be noted that the quantity of chloride in this test was high. Interestingly, evaporation of NaOH/ $\text{Na}_2\text{SO}_3/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  at two differing concentrations did not produce any NaOH (Table 2).

Compound	Transition RH	Hydrated form	Deliquescence RH
$\text{Na}_2\text{SO}_4$ (thenardite)	76.4% <sup>1</sup>	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite)	95.6% <sup>1</sup>
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite)	approx. 60% <sup>2</sup>	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite)	approx. 95% <sup>3</sup>
NaCl (halite)	N/A	N/A	75.4% <sup>4</sup>

<sup>1</sup>Steiger and Asmussen 2008, <sup>2</sup>Chou et al. 2002, <sup>3</sup>Ehlers and Stiles 1965, <sup>4</sup>Linnow et al. 2007

Table 3. Transition RH and deliquescence RH for the compounds in this study. RH values are given for 20°C.

Although chloride remaining after alkaline sulphite treatment should mostly be at anodes on the metal surface, adsorbed onto  $\alpha\text{-FeOOH}$  and contained in  $\beta\text{-FeOOH}$ , evidence here suggests that small amounts of NaCl may occur as solutions concentrate during drying. No ferrous chloride was detected after evaporation of  $\text{FeCl}_2/\text{Na}_2\text{SO}_4$  solution, which is a welcome outcome as  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  corrodes iron at very low humidity (Watkinson and Lewis 2005).

Although natrojarosite ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) formed from  $\text{FeCl}_2/\text{Na}_2\text{SO}_4$  solution after several weeks, formation of

jarosite minerals requires acidic conditions (Baron and Palmer 1996), making them unlikely products of alkaline sulphite treatment. Also, they are stable (Navrotsky et al. 2005) and non-hygroscopic, so do not pose a corrosion risk (Vaniman et al. 2008).

Sodium sulphate offers a limited corrosion threat. It exists mainly as anhydrous  $\text{Na}_2\text{SO}_4$ , (thenardite) and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (mirabilite) (see Table 3). The phase transition RH for  $\text{Na}_2\text{SO}_4/\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is now reported as 76.4% RH at 20°C rather than 71% (Steiger and Asmussen 2008). Our results agree with this, as anhydrous  $\text{Na}_2\text{SO}_4$  was stable at 75% RH (Figure 1). While it did produce very minor corrosion of iron over a 17-day period at 75% RH (Figure 1), this may reflect the chamber RH fluctuation of  $\pm 1\%$  facilitating a very small amount of corrosion as the phase transition point to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is approached. Although the corrosion risk appears low, longer test periods may reveal continuous slow corrosion that poses a threat during long term storage.

High humidity may cause a corrosion problem with  $\text{Na}_2\text{SO}_4$ , as it deliquesces at 95.6% RH (Steiger and Asmussen 2008). The  $\text{Na}_2\text{SO}_4$  hydrated quickly at 90% RH (Figure 2a) and corroded iron (Figure 2b). Slow hydration of the  $\text{Na}_2\text{SO}_4/\text{Fe}$  mixture is likely due to adhesion of iron powder and  $\text{Na}_2\text{SO}_4$  reducing diffusion of water to the crystal (Linnow et al. 2006) (Figure 2b). Pragmatically considered, corrosion risks from  $\text{Na}_2\text{SO}_4$  residues will be limited below 75% RH, and although they increase as 90% RH is approached, the contribution of residual chloride to corrosion will outstrip the threat from  $\text{Na}_2\text{SO}_4$  hydration (see Figures, 1,2 and 6).

Formation of either  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  depends on environmental RH and temperature (Steiger and Asmussen 2008). At RH > 40%,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  crystallizes and then dehydrates to  $\text{Na}_2\text{SO}_4$ . At RH < 15% only anhydrous  $\text{Na}_2\text{SO}_4$  forms and between 15%-40% RH both phases occur simultaneously. Above 32.4°C, only anhydrous  $\text{Na}_2\text{SO}_4$  forms (Rodriguez-Navarro et al. 2000). This suggests that drying objects at low RH will ensure immediate formation of safe  $\text{Na}_2\text{SO}_4$  and above this the  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  initially formed will convert to safe  $\text{Na}_2\text{SO}_4$ , unless RH approaches 95%.

Crystallization pressures may cause physical damage in lamellar and porous substrates like corrosion matrices.  $\text{Na}_2\text{SO}_4$  crystallisation pressures at low RH can be high (Steiger and Asmussen 2008) as formation of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  produces large volume increases (Rodriguez-Navarro et al. 2000; Steiger and Asmussen 2008). Solution supersaturation and pore morphology determine which compounds will form and the damage they can produce. Unfortunately, in the absence of quantitative data about corrosion product porosity and geometry in archaeological iron, it is difficult to determine whether drying a  $\text{Na}_2\text{SO}_4$  solution within it will cause physical damage.

Iron sulphates can occur as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  forms, whose state is controlled by  $\text{H}_2\text{O}$  and  $\text{O}_2$  fractions and pH. This study examined reaction of the initial product of iron oxidation in the atmosphere ( $\text{Fe}^{2+}$ ) with alkaline sulphite and chloride, identifying only  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in evaporation residues (see Table 1).

Consequently, the impact of the less common ferrous sulphates and the various ferric sulphates on corrosion were not assessed, although they may offer potential problems (Table 4).

Ferrous sulphate ( $\text{FeSO}_4$ ) is not reported naturally in its anhydrous form and, although  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  (szomolnokite) does occur in nature (Hemingway et al. 2002), it is not possible to convert  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  into  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  even in completely dry air (Ehlers and Stiles 1965).  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  are not thought to be stable (Hemingway et al. 2002).  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  (rozenite) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (melanterite) readily occur (Hemingway et al. 2002) and their phase transition RH is reported as ranging from 15% to 95% RH (25°C) (Hemingway et al. 2002), with most values around 60% RH (20°C) (Chou et al. 2002). Above 60% RH iron sulphate is said to be hygroscopic and to significantly increase corrosion risk (Jones 1996); it deliquesces around 95% RH (See Table 3).

Compound	Name	Occurrence
$\text{FeSO}_4$		rare
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	szomolnokite	
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	rozenite	common
$\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$	siderotil	rare
$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$	ferrohexahydrate	rare
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	melanterite	common
$\text{Fe}_2(\text{SO}_4)_3$		
$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	Enneahydrate nat. coquimbite	

Table 4. Iron sulphates.

Ferric sulphates have not been considered because they were not detected in tests reported here. Ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3$ ) offers a corrosion threat as it is water soluble and hygroscopic. The thermodynamic properties of various ferric sulphates at differing RH values have been reported (Wang et al. 2010), and the phase transition boundary between ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ ) has been examined (Wang et al. 2010). An amorphous ferric sulphate containing 4.5 to 11 structural water molecules per  $\text{Fe}_2(\text{SO}_4)_3$  has been found to precipitate from  $\text{Fe-SO}_4$  bearing aqueous solution in extremely arid conditions. Clearly, differing drying environments, pH and solution conditions may form different products than those observed in this paper. Consequently this study must be seen as an insight into one potential room temperature and RH drying route for alkaline sulphite solutions containing chloride and fairly high concentrations of ferrous ions. Examining differing concentrations of solutions at various temperatures, over a range of time periods, would offer additional insight into the compounds that may form and expand our understanding of the potential for further corrosion of iron.

Tests here showed that over a 12-day period at 75% RH,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  did not significantly corrode iron (see Figure 3b and c), but the hydration phase of a  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}/\text{Fe}$  mixture corroded the iron significantly, then slowed once hydration was complete (see Figures 4b and c). Hydration of  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  to  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  may proceed via a dissolution-precipitation pathway rather than a solid state transformation, with the dissolution phase providing enough dissolved ions to form an

electrolyte to support corrosion. Consequently, humidity fluctuations around the 60% RH boundary will cause corrosion during transition between the  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  hydrates. However, the presence of any residual chloride ions and compounds (see Figure 6) and their significant corrosive ability at low humidity is of much greater concern (Watkinson and Lewis 2005).

## Conclusion

This is the first study to investigate the occurrence and corrosion impact of residues from alkaline sulphite treatment for archaeological iron. The ferrous sulphate and sodium sulphate residues identified in this paper offered minor corrosion risks to iron below 75% RH. In the conditions examined here, sodium sulphate was the most abundant residue, but it did not significantly increase iron corrosion below 75% RH. The only iron sulphates detected were ferrous sulphates, and these did not cause significant corrosion of iron at 75% RH, but during the hydration of  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  to  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  corrosion of iron did occur. This may be less of a risk than first appears as the powdered iron was intimately mixed with the  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , which is a situation that will not occur on objects. It would be wise to avoid regular hydration/dehydration phases for ferrous sulphate, as it is during the hydration phase that it appears to be most aggressive to iron. As might be expected, the biggest corrosion accelerator was chloride. It produced rapid and continuous corrosion of iron at 75% RH. Further study is merited, but based on the laboratory models studied here, chemical residues from alkaline sulphite treatment appear to offer minimal corrosion risks for iron in the short term. The influence of the small amounts of corrosion from residues on the structural integrity of iron objects in the long term is less easy to predict and may be significant. Whether attempts to wash out treatment residues are necessary, or are more damaging than beneficial for the long-term survival of archaeological iron treated by alkaline sulphite, should be investigated.

## Materials

BDH GPR Iron powder, reduced by nitrogen,  
BDH AnaLar Sodium sulphite, anhydrous,  
BDH AnaLar Iron (II) chloride 4-hydrate,  
BDH AnaLar Sodium sulphate  
BDH AnaLar Sodium hydroxide  
all from  
VWR International Ltd,  
Poole, BH15 1TD, England  
<http://uk.vwr.com>

AnaLar Iron (II) sulphate  
Fisher Chemicals, Fisher Scientific UK Ltd,  
Bishop Meadow Road  
Loughborough, Leicestershire  
LE11 5RG, <http://www.fisher.co.uk>

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