

# THE ROLE OF $\beta$ FeOOH IN THE CORROSION OF ARCHAEOLOGICAL IRON

David Watkinson<sup>1</sup> and Mark R. T. Lewis

<sup>1</sup>Conservation Section, HISAR, Cardiff University, Cardiff, CF10 3EU, UK

[watkinson@cf.ac.uk](mailto:watkinson@cf.ac.uk) Roman Legionary Museum, National Museums of Wales, Caerleon, UK

[mark.lewis@nmgw.ac.uk](mailto:mark.lewis@nmgw.ac.uk)

## ABSTRACT

The chloride bearing corrosion product akaganéite ( $\beta$ FeOOH) can form during post-excavation corrosion of chloride infested archaeological iron and is able to corrode iron in contact with it. Its action on iron is examined using  $\beta$ FeOOH synthesized from ferrous chloride and iron powder. Using weight measurements the hygroscopicity of  $\beta$ FeOOH is established. The influence of relative humidity on the corrosion of iron powder mixed with  $\beta$ FeOOH is examined by dynamic weight change within a climatic chamber. At 20°C and 12% relative humidity, iron in contact with  $\beta$ FeOOH did not corrode. At 15% relative humidity slight iron corrosion was detected after 160 hours but at 35% relative humidity rapid corrosion was recorded after a few hours. Surface adsorbed chloride was removed from  $\beta$ FeOOH by aqueous washing and this reduced its hygroscopicity. The reported metastability of  $\beta$ FeOOH was examined via xrd of a 23 year old sample, which was found to be still entirely composed of  $\beta$ FeOOH. These results provide better understanding of  $\beta$ FeOOH corrosion of iron, corrosion control of chloride infested iron using dry storage and the effect of aqueous washing on archaeological iron.

## INTRODUCTION

The metal core of archaeological wrought iron objects is normally covered by a dense corrosion layer, which predominantly comprises magnetite and maghemite strips in a matrix of goethite [1]. These corrosion layers contain information on the original shape of the object. Anodic sites on the metal core are infested with chloride ions drawn in from the surrounding damp soil as counter ions to the metal ions at anodes [2, 3]. This produces a ferrous chloride solution at the metal surface and within pits.

Post-excavation drying enriches the chloride (electrolyte) concentration at anode sites. Further corrosion produces  $\text{Fe}^{2+}$  ions that hydrolyse, produce a lower pH at anodes and then oxidise, predominantly to chloride bearing  $\beta$ FeOOH in the chloride-rich environment [4,5,6]. In low humidity storage high chloride concentration and low surface pH may favour formation of solid ferrous chloride, which can corrode iron in its  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  form [4]. At higher humidities, cited as being around 55% relative humidity @25°C,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  can either dissolve or hydrolyse to  $\beta$ FeOOH [4,6,7] and acidic, hygroscopic moisture droplets containing  $\text{Fe}^{2+}$  and Cl ions with  $\beta$ FeOOH skins may form [8,9]. The loss of metallic iron and formation of voluminous  $\beta$ FeOOH at metal anodes causes separation between the hard, dense corrosion layer and the iron

core [8,9]. The resulting cracked, spalling, acid-ridden chloride-rich object is of no use for interpretative purposes and is highly unstable.

Archaeological conservators seek to arrest corrosion of iron and often use aqueous washing methods in attempts to remove chloride ions and other soluble corrosion accelerators from iron objects [2,10,11]. The chloride extraction efficiency of the various wash methods is difficult to predict and they are rarely 100% efficient [10]. Turgoose [4] hypothesised that  $\beta$ FeOOH formed on archaeological objects could cause the corrosion of iron in contact with it. The influence of atmospheric humidity on this corrosion process is important for conservators who wish to control corrosion of archaeological iron by the use of desiccated storage environments. It is also important to know what effect aqueous wash treatments have on the chloride contained by  $\beta$ FeOOH and to assess how this influences its corrosion capacity. This paper reveals information about the hygroscopic nature of  $\beta$ FeOOH, its stability and its effect on the corrosion of iron as a function of relative humidity.

### **$\beta$ FeOOH: formation, structure and chloride content**

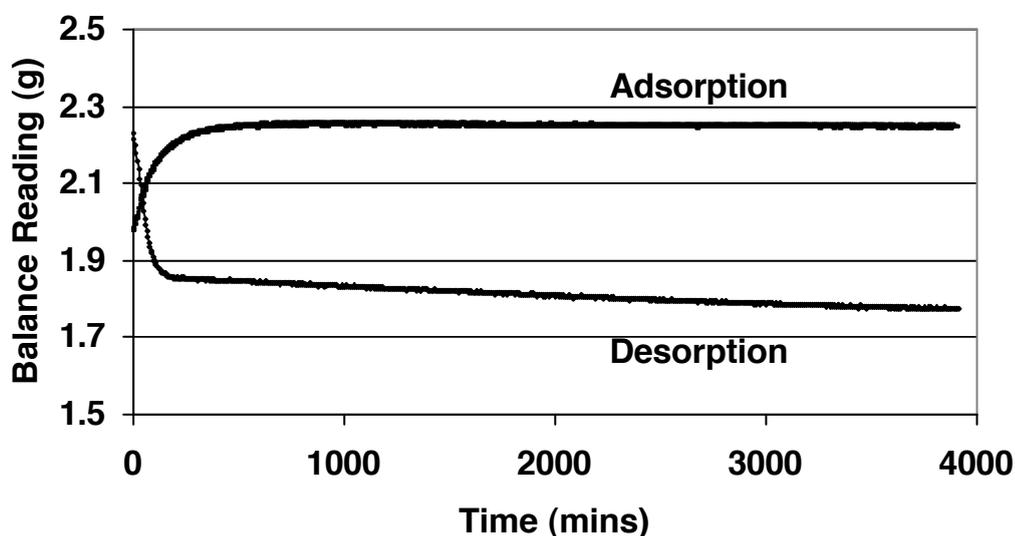
$\beta$ FeOOH forms in chloride rich environments and has chloride ions adsorbed onto its surface and within the tunnels of its hollandite ( $\text{BaMnO}_{16}$ ) structure [12,13,14,15]. The synthesis method controls particle size and determines the  $\beta$ FeOOH chloride content [16], which has been reported as being from 1.3% to 17% by weight [13,15,17]. Natural  $\beta$ FeOOH can contain less chloride (0.3% to 5% by weight) than synthetic  $\beta$ FeOOH [18]. Water is located within the tunnels of  $\beta$ FeOOH and is chemisorbed and physisorbed onto its outer surface via oxygen and hydroxyl groups on the predominant crystal face [19,20]. The polar nature of  $\beta$ FeOOH is thought to make it hygroscopic enough to form a thin film of water below 44%RH, causing continued corrosion of iron that is in contact with it [4]. Consequently, it is important to know how both humidity and surface chloride influence water adsorption on  $\beta$ FeOOH and how this adsorption affects iron in contact with it. Aqueous washing of  $\beta$ FeOOH is thought to exchange OH from water for Cl on its surface [21], but not for Cl in the tunnel structure [22]. The influence of washing on chloride retention in  $\beta$ FeOOH merits examination. Of further importance is a reported 25 years metastability of  $\beta$ FeOOH with the potential to release tunnel-bound chloride for further, cyclic, corrosion of iron in contact with it [23].

### **EXPERIMENTAL**

$\beta$ FeOOH was synthesized by mixing  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  with an equal mass of iron powder at 92.5% relative humidity, maintained by saturated sodium carbonate solution at 25°C for 3 months. All iron powder used in the synthesis and reported tests was BDH GPR™ reduced by hydrogen. This method of  $\beta$ FeOOH synthesis approximated to how it might form on archaeological artifacts, unlike the more common laboratory synthesis path involving  $\text{FeCl}_2$  hydrolysis [13,15]. Assay by xrd confirmed  $\beta$ FeOOH as the only crystalline corrosion product. Experimental work examined the response of  $\beta$ FeOOH and iron/ $\beta$ FeOOH mixtures to relative

humidity by dynamic monitoring of sample weight, whilst maintaining relative humidity at fixed values ( $\pm 1\%$ ) using a Votsch™ climatic chamber combined with a Mettler™ AJ100 balance. Temperature was standardized to 20°C throughout all climatic chamber experiments to allow for conversion from relative to specific humidity if this was later required. Data were logged to file at 5-minute intervals. The focus of these investigations was to establish hygroscopic and corrosion trends, rather than absolute mass values for the chemical changes occurring. Initial and final masses were recorded in each instance but the precise contributions to mass change from corrosion and hygroscopicity are not considered here. IR Spectra, X-Ray Diffraction and macro and microscopic visual appearance were used to identify reaction products.

The response of  $\beta\text{FeOOH}$  to extremes of relative humidity was examined to determine the extent of its hygroscopicity.  $\beta\text{FeOOH}$  was conditioned to 41% relative humidity and then 2g of this was placed on the balance in the climatic chamber, which was set to 80% relative humidity. This relative humidity was similar to an aggressive storage environment for archaeological iron and was also towards the upper limit of safe exposure for the balance. Adsorption of water by  $\beta\text{FeOOH}$  was significant within an hour and was complete at 700 minutes (Figure 1). Desorption of  $\beta\text{FeOOH}$  from 80% to 18% relative humidity occurred within 250 minutes for the bulk of the water that it contained, but then slowed and was still incomplete when the experiment was terminated at 4000 minutes (Figure 1). These results show how any significant change in ambient relative humidity will fairly quickly be reflected in the moisture content of  $\beta\text{FeOOH}$ . However, once  $\beta\text{FeOOH}$  has dried significantly it is difficult for it to lose its remaining water and reach equilibrium with the prevailing low relative humidity.

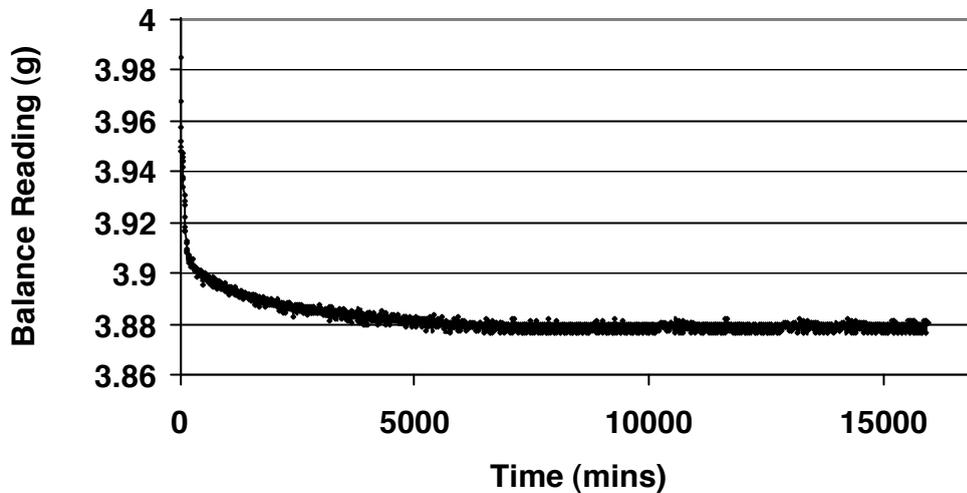


**Figure 1.** Adsorption curve for 2g  $\beta\text{FeOOH}$  conditioned to 41% relative humidity and placed in 80% relative humidity. Desorption curve for  $\beta\text{FeOOH}$  conditioned to 80% relative humidity, weighing 2.257g, and placed in 18% relative humidity. This is incomplete at the termination of the experiment.

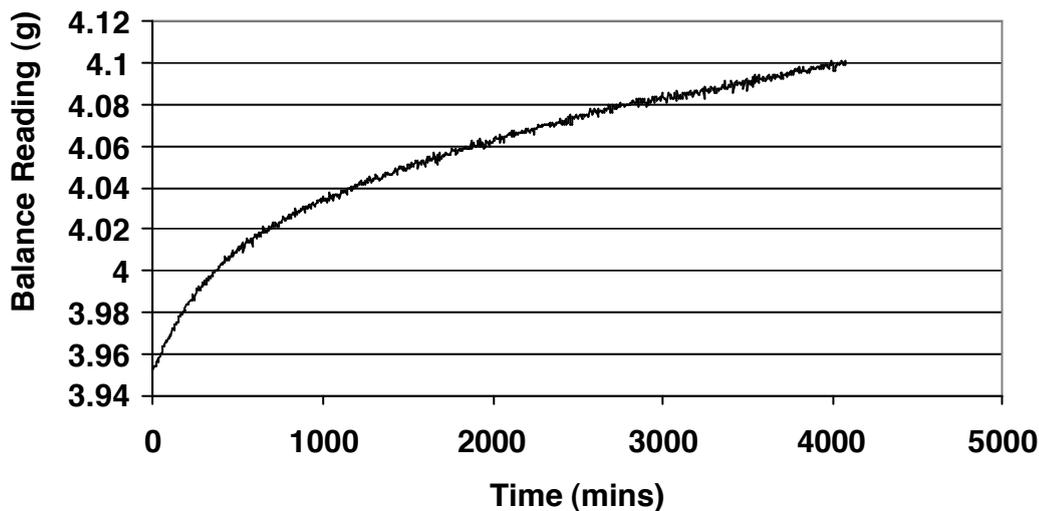
### **Hygroscopicity of beta-FeOOH and corrosion of iron**

Corrosion of iron powder in the presence of  $\beta\text{FeOOH}$  was examined at low humidity to investigate the potentially aggressive role of  $\beta\text{FeOOH}$  in the post excavation corrosion of wrought iron. Due to its polar make-up  $\beta\text{FeOOH}$  has been suspected of attracting water capable of acting as electrolyte with its reservoir of chloride ions [4]. Four test samples containing 2g of  $\beta\text{FeOOH}$  equilibrated to 41% relative humidity were each mixed with 2g of iron powder using a clean spatula, which caused some loss of both iron powder and  $\beta\text{FeOOH}$  to the spatula. The resulting mixtures were exposed to environments of 35%, 21%, 15% and 12% relative humidity for periods of one week. This range of relative humidities was chosen to examine reaction of  $\beta\text{FeOOH}$  in relative humidities typical for controlled desiccated storage environments for chloride infested archaeological iron. Storage environments within closed containers desiccated with freshly regenerated silica gel may be around 10% relative humidity or less. With time, air exchange and the moisture reservoir capacity of silica gel will mean systems often above 25% relative humidity.

Initially the 41% relative humidity conditioned  $\beta\text{FeOOH}$  rapidly loses weight as it seeks to equilibrate with the 12% relative humidity, then it slowly loses water until it achieves equilibrium at 9000 minutes (Figure 2). Thereafter there is no weight change. At this point the environment is too dry for  $\beta\text{FeOOH}$  to form an electrolyte to support corrosion of iron powder in contact with it, so there is no weight gain due to corrosion. In contrast, at 35% relative humidity no loss in weight of the sample is recorded (Figure 3). The iron corrodes almost immediately producing a weight gain, which obscures any moisture loss as the 41% relative humidity conditioned  $\beta\text{FeOOH}$  seeks equilibrium with the 35% relative humidity in the climatic chamber. Corrosion of iron occurs because adsorbed moisture on the polar  $\beta\text{FeOOH}$  and its mobile surface chloride produce an electrolyte at 35% relative humidity. The resulting  $\text{Fe}^{2+}$  ions oxidize either to  $\beta\text{FeOOH}$  in the high chloride environment or to  $\alpha\text{FeOOH}$  if chloride ion concentration is sufficiently low. This is visible as an orange 'skin' on the purple/grey  $\beta\text{FeOOH}$ /iron powder mixture.

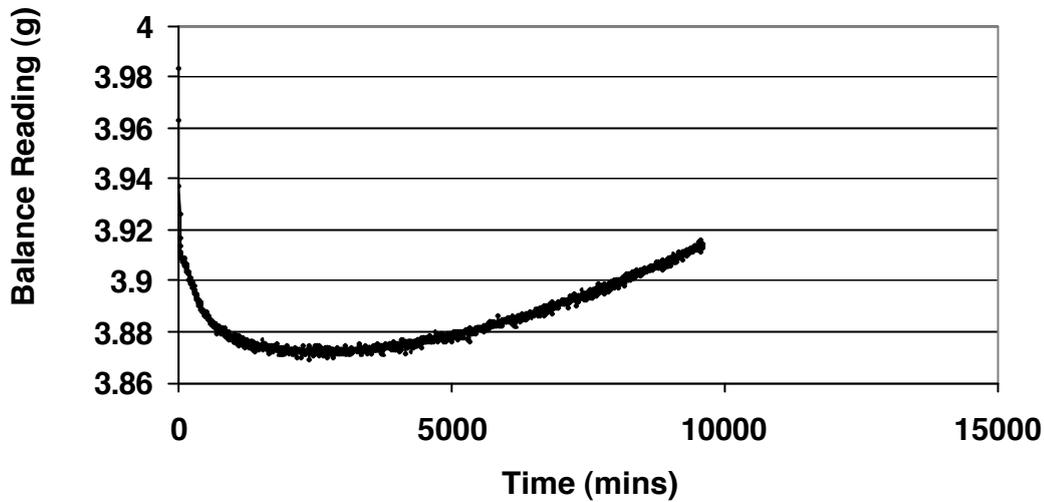


**Figure 2.** Balance reading for 2g  $\beta\text{FeOOH}$  (equilibrated pre-testing to 41% relative humidity) mixed with 2g of iron powder and exposed to 12% relative humidity.

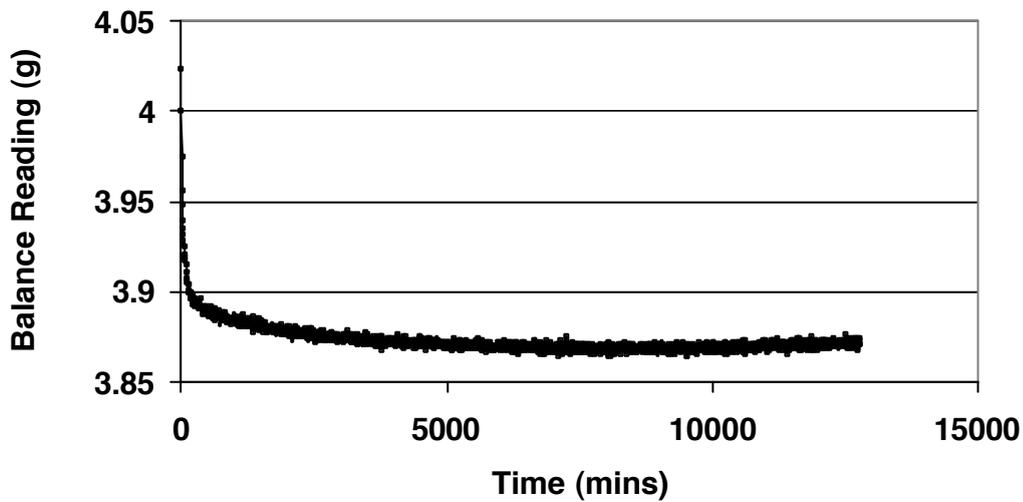


**Figure 3.** Balance reading for 2g  $\beta\text{FeOOH}$  (equilibrated pre-testing to 41% relative humidity) mixed with 2g of iron powder and then exposed to 35% relative humidity.

At 21% relative humidity the  $\beta\text{FeOOH}$  /iron mixture initially shows a net weight loss, as  $\beta\text{FeOOH}$  loses moisture to equilibrate from 41% relative humidity to 21% (Figure 4). This masks any weight increase from iron oxidation until 3000 minutes, when weight gain from iron oxidation exceeds any possible continued weight loss from  $\beta\text{FeOOH}$  desiccation. The  $\beta\text{FeOOH}$  /iron mixture at 15% shows a similar pattern (Figure 5). Since there is more desiccation of  $\beta\text{FeOOH}$  and less water is available than at 21% relative humidity, iron corrosion is not recorded as a weight gain until 9000 minutes. It also produces as an observable color change .



**Figure 4.** Balance reading for 2g  $\beta$ FeOOH (equilibrated pre-testing to 41% relative humidity) mixed with 2g of iron powder and exposed to 21% relative humidity.



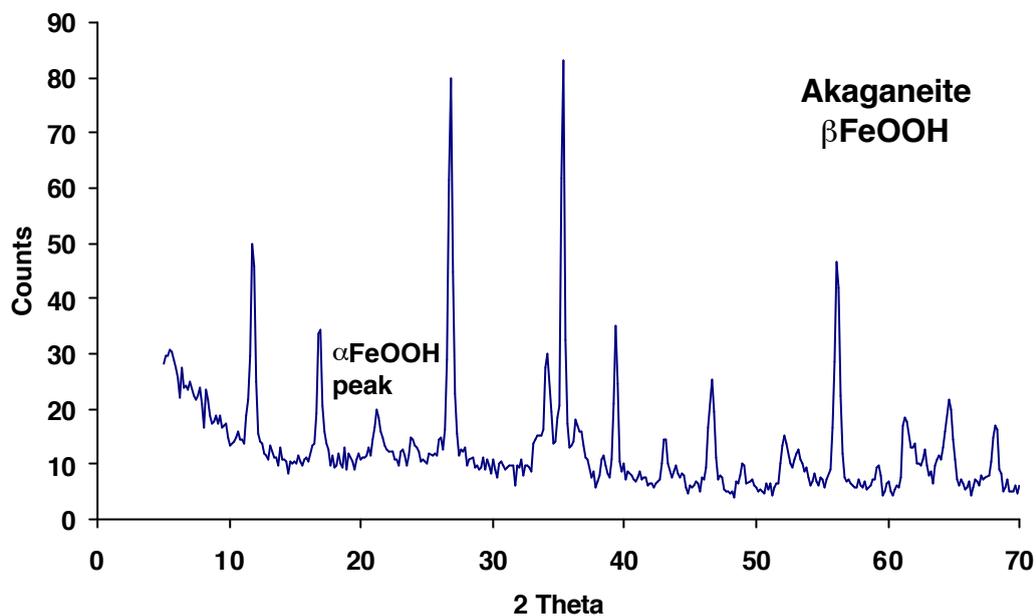
**Figure 5.** Balance reading for 2g  $\beta$ FeOOH (equilibrated pre-testing to 41% relative humidity) mixed with 2g of iron powder and exposed to 15% relative humidity.

These tests show that  $\beta$ FeOOH can cause corrosion of iron in contact with it and corrosion is influenced by ambient relative humidity. At 12% relative humidity no corrosion of iron in contact with  $\beta$ FeOOH was detected during a 16000 minute contact time. Storage at this relative humidity will prevent  $\beta$ FeOOH contributing to corrosion of iron.

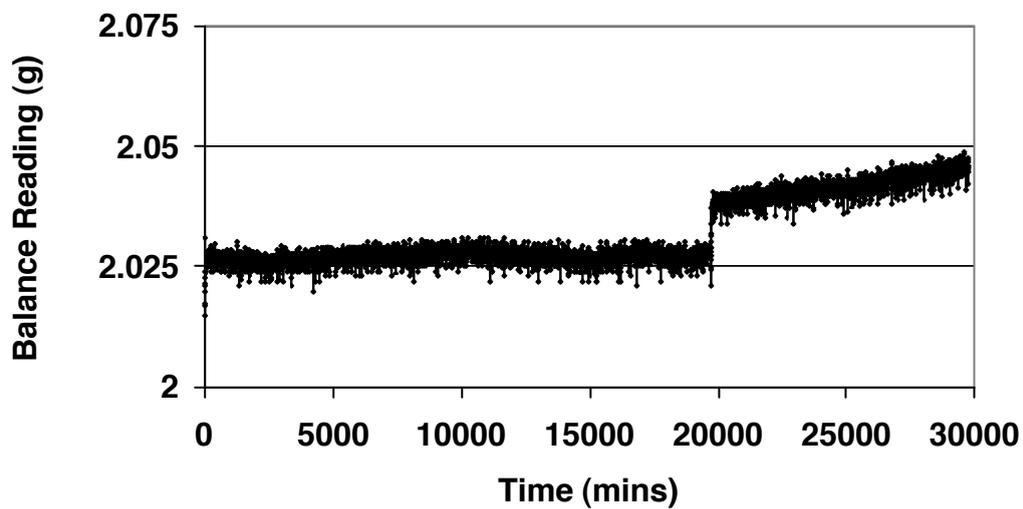
### **Washed $\beta$ FeOOH and corrosion of iron**

Since the surface chloride and hygroscopic properties of  $\beta$ FeOOH cause corrosion of iron, it is necessary to determine if washing treatments used to desalinate archaeological iron [9,10] can remove this surface chloride from  $\beta$ FeOOH, influence its hygroscopicity and ability to corrode iron. The particular wash method examined is Soxhlet washing. This has been employed in conservation to wash chloride out of archaeological iron [10,24]. In this technique the sample is placed in a syphon-emptied Soxhlet washing chamber and is repeatedly covered with aqueous condensate at 60°C, from a reflux condenser over boiling de-ionised water. Washing lasted for 7 days, until Cl<sup>-</sup> ion extraction from  $\beta$ FeOOH ceased, as measured using a Radiometer PHM250 ion analyzer. Assay by xrd re-identified the washed sample as  $\beta$ FeOOH with a very small amount of  $\alpha$ FeOOH (Figure 6). Transformation of  $\beta$ FeOOH to Fe<sub>2</sub>O<sub>3</sub> in warm alkali and at elevated temperatures in aqueous systems to  $\alpha$ FeOOH is reported [14,25]. This wash technique replicates what would occur to  $\beta$ FeOOH in iron objects washed using the Soxhlet system.

The influence of Soxhlet- washed  $\beta$ FeOOH on iron was determined by conditioning  $\beta$ FeOOH to 41% relative humidity and mixing it with iron powder. This was exposed to 25% relative humidity for 20,000 minutes then to 75% relative humidity for 10,000 minutes (Figure 7). Corrosion of iron did not occur at 25% relative humidity and there was no initial dehydration of the sample. This contrasts with unwashed  $\beta$ FeOOH at 21% relative humidity, which exhibited both hygroscopicity and corrosion capacity (Figure 4). Loss of surface adsorbed chloride by Soxhlet washing removed the measurable hygroscopicity of  $\beta$ FeOOH and prevented it corroding iron in contact with it at 25% relative humidity. A small amount of residual chloride is thought to be trapped in the  $\beta$ FeOOH tunnel structure, where it cannot form an electrolyte. Subsequent exposure to 75% relative humidity for a significantly long time period (10,000 minutes) produced a very small weight gain, which must be due to some water absorption, but may also include some iron corrosion, although this could not be established visually or with microscopy on this occasion (Figure 7). These results suggest that surface adsorbed chloride influences moisture response of  $\beta$ FeOOH and its corrosive ability towards iron in contact with it.



**Figure 6.** X-Ray Diffraction data for Soxhlet-washed  $\beta$ FeOOH. A small  $\alpha$ FeOOH peak is visible.

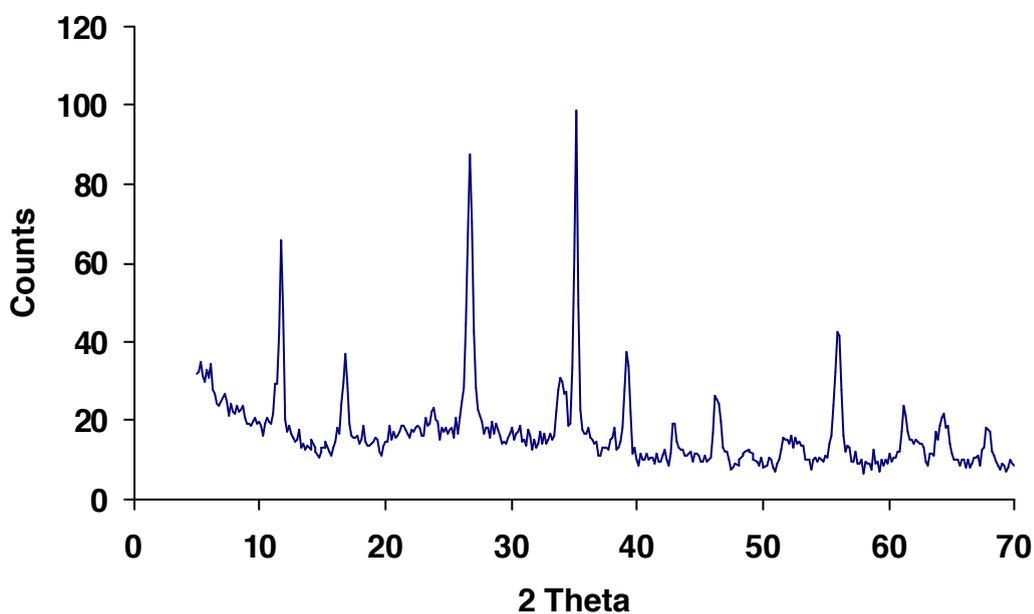


**Figure 7.** (a) Soxhlet-washed  $\beta$ FeOOH (1g) and iron powder (1g) exposed to 25% then 75% relative humidity. (The sudden jump at 20,000 minutes is a balance phenomenon.)

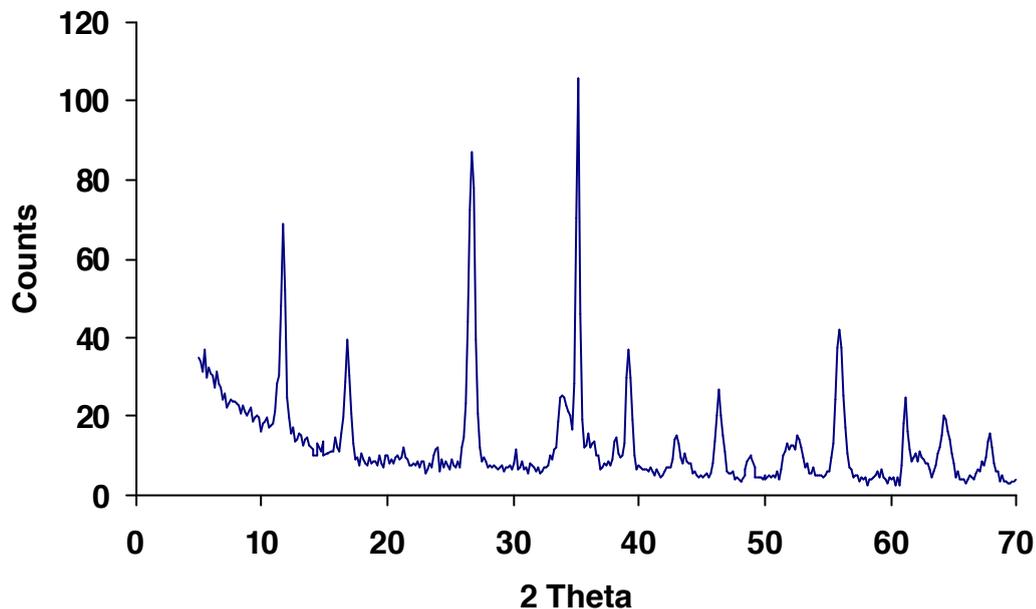
### Metastability of beta-FeOOH

Although the Soxhlet washed  $\beta$ FeOOH did not corrode iron at 25% relative humidity, if  $\beta$ FeOOH was metastable and transformed to  $\alpha$ FeOOH, it could release chloride retained in the tunnels of its hollandite structure. These would then be free to form an electrolyte with moisture and corrode iron. In this way  $\beta$ FeOOH on washed archaeological iron objects may be initially non corrosive but will be damaging to iron in the long-term. A range of synthesised  $\beta$ FeOOH samples of varying age and origin were examined using FT-IR and xrd to identify any compound transformations.

$\beta$ FeOOH synthesised by the iron powder/ferrous chloride method used in this paper remained unchanged at 41%RH and 22°C over a three year period. Cold washed (pH 1.9 during washing)  $\beta$ FeOOH was dried at 70°C and subsequent assay showed there to be no change in its composition. Examination of  $\beta$ FeOOH produced by Turgoose [4] using the iron powder/ferrous chloride method 23 years ago and stored in a glass jar, which had been repeatedly opened, was confirmed as still being 100%  $\beta$ FeOOH (Figure 8). Its diffraction properties were identical to the product produced and used in the research reported here (Figure 4a). No evidence of the reported  $\beta$ FeOOH long-term metastability of  $\beta$ FeOOH was detected. In addition, xrd data for Soxhlet-washed (60°C)  $\beta$ FeOOH exhibited a small peak attributable to  $\alpha$ FeOOH (Figure 6).



**Figure 8.** X-Ray Diffraction data for 25 year old  $\beta$ FeOOH.



**Figure 9.** X-Ray Diffraction data for recently synthesized, unwashed  $\beta\text{FeOOH}$

### **Surface adsorbed chlorides – initial results and comment**

The possibility that direct contact of iron with  $\beta\text{FeOOH}$  is not required for corrosion to occur was noted when a spatula was left in proximity with  $\beta\text{FeOOH}$  in a closed environment. An stainless steel spatula (BDH, 175mm Trulla spatua) in a desiccator, which was maintained at 41% relative humidity and contained 20g of  $\beta\text{FeOOH}$  on an open Petri dish, corroded without contact with  $\beta\text{FeOOH}$ . It grew thread like crystals, which were identified by xrd as  $\beta\text{FeOOH}$  with an unidentified product thought to be a nickel-substituted  $\beta\text{FeOOH}$ , where the nickel must derive from the steel alloy. Up to 19% nickel substitution has been recorded in  $\beta\text{FeOOH}$ , but 3% to 5% is the norm [18]. It is thought that excess surface chloride on  $\beta\text{FeOOH}$  provided mobility for chloride as highly corrosive vapor phase HCl. Similarly, aluminium foil was oxidised to a mixture of aluminium oxide and aluminium chloride through exposure to the vapour (probably HCl) above a ferrous ion and chloride ion-rich solution resulting from reflux-washing  $\beta\text{FeOOH}$ .

### **CONCLUSIONS**

Unwashed  $\beta$ FeOOH adsorbs moisture in response to changing relative humidity. Its surface adsorbed chloride and water together can corrode iron in contact with it. This is regulated by prevailing relative humidity. At 12% relative humidity no corrosion of iron was detected over a 166 hour period, while at 35% relative humidity it is detected in a few hours. Removal of the majority of the chloride from  $\beta$ FeOOH by aqueous Soxhlet washing removes its measurable hygroscopic properties at low relative humidity (25%RH) and prevents it aggressively corroding iron. At 75% relative humidity washed  $\beta$ FeOOH exhibits limited hygroscopicity and may corrode iron in contact with it.  $\beta$ FeOOH produced by the ferrous chloride and iron powder synthesis method may release acidic vapors that can cause remote corrosion of iron.

### **Future work**

The influence of a wider range of relative humidities on the corrosiveness of washed and unwashed  $\beta$ FeOOH is being examined, as are the effects of cycling relative humidity. Chloride extraction from  $\beta$ FeOOH is being monitored on a real-time basis. Transformations of  $\beta$ FeOOH in alkali are being investigated in relation to conservation wash methods. The effect of synthesized  $\beta$ FeOOH on iron in closed environments, without contact, is being tested.

### **Acknowledgements**

We gratefully acknowledge the ss Great Britain Trust and the curator of the ship, Matthew Tanner, for sponsoring this research; Robert Turner of Eura Conservation Ltd. for access to his reports; Dr Anthony Oldroyd Cardiff University for XRD analysis.

### **REFERENCES**

1. D. Neff, S. Reuger, L. Bellot-Gurlet, P. Dillmann and R. Bertholon, *J. of Raman Spec.* **35** 739-745, 2004.
2. D. Watkinson, *Stud. in Conservation* **28**, 85-90, 1983.
3. S. Turgoose, *Conservation of Iron*, ed. R. Clark and S. Blackshaw, National Maritime Museum, Greenwich, London, 1-7, 1982.
4. S. Turgoose, *Stud. in Conservation* **27**, 97-101 1982 .
5. F. Zucci, G. Morigi and V. Bertolasi, *Corrosion and Metal Artifacts*, ed. B.F. Brown NBS Special publication 479, Washington D.C., 103-9, 1977.
6. M. Kiyama and T. Takada, *Bull. Chem. Soc. Japan*, **45**, 1923-1924, 1972.
7. R. M. Taylor, *Clays and Clay Minerals* **32**, 175-180, 1984.
8. L. S. Selwyn, P.J. Sirois and V. Argyropoulos, *Stud. in Conservation* **44**, 217-232. 1999.
9. B. Knight, *Conservator*, **14**, 37-43, 1990.
10. D. Watkinson, *Archaeological Conservation and its Consequences*, eds. A. Roy and P. Smith, IIC London, 208-212, 1996.
11. N. A. North and C. Pearson, *Stud. in Conservation*, **23**, 174-86, 1978.
12. A. L. Mackay, *Mineralogical Magazine*, **33**, 270-280, 1962.
13. C. W. Childs, B. A. Goodman, E. Paterson and F.W.D. Woodhams, *Aust. J. Chem.* **33**, 15-26, 1980
14. R. J. Atkinson, A. M. Posner and J. P. Quirk, *Clays and Clay Minerals*, **25**, 49-56, 1977

15. T. Ishikawa and K Inouye, *Bull. Chem. Soc. Japan*, **48**, 1580-1584, 1975.
16. J. V. Dousma, T. J. Den Hoven and P. L De Bruyn, *J. Inorg. Nucl. Chem.* **40**, 1089-1093, 1978.
17. P. Keller 1970, *Neues Jahrbuch fur Mineralogie Abhandlungen*, **113**, 29-49
18. V. F. Buckwald and R. Clark, *American Mineralogist* **74**, 656-676, 1989.
19. K. Kaneko, M. Serizawa, T. Ishikawa and K. Inouye, *Bull Chem. Soc. Japan* **48**, 1764-1769, 1975.
20. K. Kaneko and K. Inouye, *Bull. Chem. Soc. Japan*. **52**, 315-320, 1979.
21. J. H. Johnston and N. E. Logan, *J. Chem. Soc. Dalton Trans.*, 13-16, 1979.
22. K. Stahl, K. Nielsen, J.C. Norby, P. Jiang and J van Lanschot, *Jubilee Symposium*, Det Kongelige Danske Kunstakademi (Copenhagen) 157–160, 1998.
23. M.R. Gilberg and N.J. Seeley, *Stud. in Conservation* **26**, 50-56, 1981.
24. D.A. Scott and N.J. Seeley, *Stud. in Conservation* **32** 73-76.
25. K. Stahl, K. Nielsen, J. Jiang B. Lebech, J.C. Hansen, P. Norby and J van Lanschot, *Corrosion Science* **45**, 2563-2575, 2003.