

ss Great Britain iron hull: modelling corrosion to define storage relative humidity

David Watkinson^a and Mark Lewis^b

^a Senior Lecturer, Conservation Section, School of History and Archaeology, PO Box 909, Cardiff University, Cardiff, CF10 3XU, UK.

^b Research Assistant, Conservation Section, School of History and Archaeology, PO Box 909, Cardiff University, Cardiff, CF10 3XU, UK.

Abstract

Brunel's wrought iron ship *ss Great Britain* is corroding in its dry dock in Bristol. Corrosion control will involve sealing and desiccating the dock. The corroding iron hull forms chloride rich βFeOOH and during desiccation ferrous chloride is likely to form. βFeOOH /iron and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ /iron were subjected to controlled relative humidity ($\pm 1\%$) and corrosion thresholds were experimentally determined. Iron in contact with these compounds corroded above the thresholds but not below them. Iron did not corrode in the presence of $\text{FeCl}_2\cdot 2\text{H}_2\text{O}$. The stability of this compound to moisture was determined. Corrosion was extremely slow just above corrosion thresholds, but increased significantly as relative humidity values rose to 30%. These results are being used to set an operational relative humidity for the desiccated environment around the *ss Great Britain* and to offer new conservation options for other historic ships.

Keyword: iron, corrosion, ferrous chloride, β -ferric oxyhydroxide, relative humidity, storage.

1. Introduction

1.1 ss Great Britain: Historical context

The 1843 wrought iron steamship *ss Great Britain* was salvaged from the Falkland Islands in 1970 and placed in the Great Western Dockyard in Bristol, which had been constructed especially for building the ship, making it the first integrated iron shipbuilding yard in the world (figure 1). In its open air dry dock the iron hull of the *ss Great Britain* equilibrated with its environment, which rarely drops below 70% due to climate, seepage of water through the docksides, faulty drainage and a leaking caisson (Cox and Tanner 1999, Turner *et al* 1999).

Insert - Fig 1.

Initial evaporation of seawater from the hull left behind highly soluble and deliquescent chloride salts, which are unlikely to be present in their solid crystalline form, due to the high ambient relative humidity in the dock. They will be solvated within corrosion layers, micro cracks, pits and in the overlaps between iron hull plates at rivet points. In this state their contribution to the electrolytic corrosion of the iron will be significant; even though rain-wash

^a Corresponding Author: TEL: +44 (0) 29 20 874249; FAX: +44 (0) 29 20 874929; email: Watkinson@cf.ac.uk

over the years and an aqueous pressure wash, which was used as an early conservation method, will have reduced their concentration. The hull is rapidly corroding in the high relative humidity within the dock environment and engineering reports estimate that it will be structurally unsafe in about 25 years (Turner *et al* 1999).

1.2 Conservation programme

Early conservation and maintenance of the hull had involved 10,000 psi aqueous pressure blasting and traditional shipyard practices that applied ‘protective’ coatings (Turner *et al* 1999). Understandably these measures failed to either stop corrosion or to appreciably slow its progress (Figure 2).

Insert - Fig 2

A long-term development plan adopted a mission statement in 1998:

“To preserve the ship, ss Great Britain, and its building dock for all time for the public benefit of all, and to place the same upon public display as a museum for the enhancement of public understanding and appreciation of her social, commercial, scientific and technological context and significance.”

The decision from the ss Great Britain Trust *“to conserve fully to the highest standards the extant fabric of the ss Great Britain (1843-1970) and its building dock”* (Cox and Tanner 1999) defined future preservation by firmly recognising it was a conservation task, rather than a restoration programme. The corroded wrought iron plates of the hull are considered an essential part of the ship’s fabric and are to be conserved in situ, with their corrosion in place, rather than replaced with mild steel replicas.

The current conservation plan identified the condition of the ship and reviewed conservation options (Turner *et al* 1999). It was clear that the condition of the iron and the length (322 feet) of the hull rules out many conservation approaches. Methods employing stripping or traditional surface treatments for ships would damage the badly corroded hull (Table 1). Treatments designed to remove or inhibit the action of chlorides are unpredictable and offer technical limitations on a large scale project (Table 2). The amount of chloride that remains in iron after chloride extraction procedures have been applied cannot be known. It will remain as an unknown threat to the future stability of the iron.

Insert - Table 1

Insert - Table 2

In order to employ a conservation method whose effectiveness could be successfully modelled and tested prior to implementation, it was decided to conserve the iron hull by controlling the availability of water to support the corrosion processes (Turner *et al* 1999). Desiccation is the both the least interventive and least unpredictable method for preserving the ss Great Britain. As part of their ethical framework the ss Great Britain Trust was pleased to be able to choose a treatment option that retained the iron corrosion layers on the hull.

To implement this conservation option the corrosion processes occurring on the hull need to be identified and their response to relative humidity assessed by modelling corrosion in the laboratory. In this way the degree of desiccation required to prevent them occurring can be measured. This data can then be used to design a controlled storage environment that moderates or prevents corrosion.

Desiccating the environment around the hull is a technically challenging task that involves constructing an envelope around the ship and controlling the relative humidity within this space. Consulting with architects and climate control engineers produced an option that would roof the dry dock with glass, from the waterline of the ship to ground level at the dockside. The interior of the ship would be modified to produce an environment with minimum air leakage between the lower and upper decks. Within this space encompassing the exterior and interior of the hull below its original water line, moisture levels will be controlled to a value that will either dramatically reduce or prevent chloride and chloride bearing compounds contributing to corrosion of the iron hull. Visitors would have access to both the interior of the hull below the waterline and the dry dock facility (Figure 3). The hull will appear to float in its dry dock, as the roof will have water across it. Above the waterline the hull has lower chloride levels and is in good condition, making it suitable for a coating system.

Insert - Fig 3

1.2 Desiccation for corrosion prevention

Desiccation of iron has been employed for over 40 years, with varying degrees of success, to store and preserve archaeological iron (Watkinson and Neal 1998). Remarkably, very little investigation of this process has been carried out, yet it remains the storage mainstay for archaeological iron. Turgoose (1982a and b) and Selwyn *et al.* (1999). provided some information on the corrosion of chloride infested iron during burial and following excavation, there are no accurate figures on the level of desiccation necessary to prevent corrosion of chloride infested iron.

The design for successful desiccation depended on the ss Great Britain Project identifying how relative humidity affected corrosion reactions that could occur on the hull. The cost of dehumidifying an environment is closely linked to the target relative humidity. Very low relative humidity values will cost much more money to achieve and sustain, due to plant requirements for dehumidification and tolerances in the architectural design of the controlled space.

The ss Great Britain Trust sought to:

- Determine how corrosion reactions occurring on the iron hull were influenced by relative humidity.
- Identify the relative humidity at which corrosion of iron in chloride infested environments ceases.
- Explore how the rate of corrosion of chloride infested iron changes with relative humidity.
- Use this data to model a storage environment that will enhance the life of the iron hull by either preventing or reducing corrosion rate according to the resources available to them;
- Offer this model as part of an £8.4 million bid to the Heritage Lottery Fund for support to conserve the ss Great Britain and its historic dockyard.

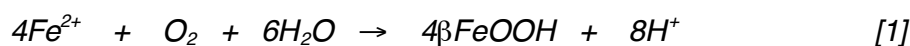
1.3 Corrosion of the ss Great Britain iron hull

Analysis of the hull revealed significant amounts of soluble chloride in the corrosion product and the presence of βFeOOH (Akageneite), Fe_3O_4 (Magnetite) and other FeOOH (ferric Oxy-hydroxide) polymorphs. βFeOOH was identified by XRD (Figure 4) and Soxhlet extraction of corrosion products from various parts of the hull revealed chloride levels within the 160 to 3200 ppm range (Turner *et al* 1999). Since chloride is concentrated at anode sites at the metal surface overall chloride levels in the hull are likely to be much higher than the

measurements suggest (Ishikawa *et al* 1988, Selwyn *et al* 1999, Turgoose 1982a, Watkinson 1983).

Insert - Fig 4

The presence of these corrosion products fits the corrosion model suggested by Turgoose (1982a and 1982b) in which Fe^{2+} is oxidised and resulting acid can attack iron directly to free more Fe^{2+} . There is also free chloride in solution acting as an electrolyte (Equation 1). Selwyn *et al* (1999) cited a cycle involving acid attack on iron by HCl, which is also described for pitting by Jones (1992).



In the environment within in the dock area the iron hull is currently corroding rapidly due to high ambient relative humidity that allows the soluble chloride to act as an electrolyte to support corrosion. This situation will change when the hull is dried within its new controlled storage environment. Chloride will concentrate as the moisture within the iron evaporates. Anode sites will become increasingly acid due to hydrolysed Fe^{2+} and this provides low pH conditions in which solid $FeCl_2 \cdot 4H_2O$ may form (Jones 1992, Turgoose 1982a).

1.4 Low humidity corrosion of chloride infested iron

Turgoose (1982a) identified iron corrosion processes involving $FeCl_2 \cdot 4H_2O$ and $\beta FeOOH$ that occur at low relative humidity. Iron corrodes when mixed with ferrous chloride at 20% relative humidity, but it does not corrode when the relative humidity is 15% (Turgoose 1982b). This is attributed to the stability of $FeCl_2 \cdot 4H_2O$ at the higher humidity and $FeCl_2 \cdot 2H_2O$ at the lower humidity. The water in $FeCl_2 \cdot 4H_2O$ is thought to support electrolytic corrosion, whereas $FeCl_2 \cdot 2H_2O$ does not contain enough water to do this.

Turgoose (1982b) postulated that $\beta FeOOH$ is hygroscopic and that this contributes to corrosion of iron in contact with it. $\beta FeOOH$ contains chloride in its crystal structure and adsorbs it onto its surface when it forms in chloride rich environments (Ishikawa *et al* 1988). This chloride can become mobile in moisture that is attracted to its surface and it may be this that facilitates either the electrolytic corrosion of iron or direct acid attack on iron (Lewis and Watkinson, forthcoming).

1.5 $\beta FeOOH$ on the hull of the ss Great Britain

The hull of the ss Great Britain will carry two forms of $\beta FeOOH$. The first will have formed in the atmosphere during the past 35 years. Much of this $\beta FeOOH$ is subject to rain wash, which is likely to have removed most of its surface adsorbed chloride. If mobile surface adsorbed chloride causes iron in contact with $\beta FeOOH$ to corrode, then washed $\beta FeOOH$ should not corrode iron.

$\beta FeOOH$ will also be present as a corrosion product in areas of the ship that are not rain-washed and it will form as iron corrodes during the proposed desiccation of the hull. This $\beta FeOOH$ will retain its surface adsorbed chloride and present a corrosion threat to iron that it is in contact with, provided the storage relative humidity supports the $\beta FeOOH$ /iron corrosion reaction.

It is reported that $\beta FeOOH$ is metastable with respect to $\alpha FeOOH$ over a 25 year time period (Gilberg and Seeley 1981). This offers dangers for the ship as its transformation to $\alpha FeOOH$ will release chloride that can potentially act as an electrolyte. An FTIR assay of a 23-year-old sample of $\beta FeOOH$ that was stored in a closed glass jar in the conservation laboratories at Cardiff University, revealed the same composition as when it was produced. It is also known that pH influences transformations of $\beta FeOOH$. These are areas that require further study.

Based on the corrosion model involving βFeOOH and ferrous chloride, experiments were carried out to link relative humidity to corrosion of chloride infested iron in low humidity environments. Results were used by the ss Great Britain Trust to design their storage environment.

2. Experimental Procedure

2.1 The experiments carried out in this study aimed to:

- Confirm that iron does not corrode in the presence of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$
- Identify the highest relative humidity at which $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ exists before it converts to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$
- Examine the corrosion of iron mixed with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at various relative humidities.
- Establish the relative humidity at which iron mixed with βFeOOH ceases to corrode.
- Examine the corrosion of iron mixed with unwashed βFeOOH at selected relative humidities.
- Remove surface adsorbed chloride from βFeOOH (this simulates rain-wash of this corrosion product) and determine whether washed βFeOOH corrodes iron.

Results of the experiments were used to recommend:

- A relative humidity below which iron does not corrode if mixed with ferrous chloride
- A relative humidity below which iron does not corrode if mixed with βFeOOH
- Offer comment on the rate of corrosion of ferrous chloride/iron and βFeOOH /iron mixtures at relative humidity values that were slightly above the “no-corrosion” relative humidity identified above.

This data was used by engineers and architects to design climate control plant and the tolerances of the dock and hull seals that would create the storage space around the ss Great Britain Hull.

2.2 Research method

Analar grade $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and pure iron powder were purchased and βFeOOH was synthesised by exposing pure iron powder and ferrous chloride to 92% relative humidity until the iron oxidised completely, which took several months. The resulting assay showed 99% βFeOOH and 1% αFeOOH (Figure 4).

Washed βFeOOH was produced by subjecting synthesised βFeOOH to aqueous Soxhlet wash until no more chloride was being released into the wash solution, as determined by specific ion meter. At this point it was deemed that mobile surface chloride is lost from the βFeOOH and only the chloride locked in the crystalline hollandite tunnel structure of the βFeOOH would remain (Childs *et al* 1980, Gilberg and Seeley 1981, Ishikawa and Inouye 1972, Ishikawa and Inouye 1975). Unless otherwise stated all βFeOOH used in experiments reported here is unwashed.

Testing involved the use of a climatic chamber that controlled relative humidity to $\pm 1\%$ (established by test calibrations) and $\pm 0.5^\circ\text{C}$. Test samples were placed on a balance (accuracy 0.0001g) in the chamber. The balance was calibrated for accuracy and drift using a standard weight, exposed to 20% relative humidity at 20°C for several days. Systematic error was reproducible and slight balance drift could be accounted for when analysing trends.

The chamber can be programmed to operate either at a particular relative humidity or on a particular relative humidity programme. Weight changes were dynamically monitored to file every 5 minutes. Visual inspection, XRD and FT-IR were used to determine change in the sample composition and attribute weight change to one or a combination of; iron corrosion; oxidation of corrosion product; desiccation or hydration. In this way the influence of relative

humidity on the corrosion process could be monitored and graphic results show weight variation of test samples against time for fixed humidity values. All tests were standardised at 20°C enabling conversion between relative and specific humidity. For consistency results are hereafter reported in terms of relative humidity.

3. Results

Samples of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed with iron powder and exposed to differing relative humidities. A sample comprising $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and iron powder did not gain weight after 20000 minutes (13.9 days) at 19% relative humidity (Figure 5). This showed that $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ is the stable form of ferrous chloride at 19% relative humidity and iron does not corrode in the presence of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$. Both hydration to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and oxidation of iron to FeOOH would have produced a weight increase. In contrast $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with iron powder gained weight at 22% and 27.5% and 35% relative humidity. This confirmed that $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is the stable form of ferrous chloride at 23% relative humidity and above and that it corrodes iron in contact with it. Corrosion is slow at 22% relative humidity but speeds up appreciably at 35% relative humidity.

Insert - Fig 5

The corrosive effect of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ on iron at different relative humidities is seen in figure 6. Samples comprising 2g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with 2g of iron powder were exposed to differing relative humidities. Percentage weight change at 4000 minutes is compared. Below 25% relative humidity corrosion is limited. As relative humidity rises corrosion increases and is ten times greater at 30% relative humidity as compared to the rate at 25% relative humidity.

Insert - Fig 6.

Using the 19% no-corrosion marker for iron chloride mixed with iron powder determined in figure 6, a mixture of βFeOOH and iron powder was exposed to 19% relative humidity for 4000 minutes (2.8 days). Initially weight was lost due to dehydration of the βFeOOH and this masked any corrosion taking place. At 2000 minutes the sample started to gain weight due to corrosion of the iron, whose contribution to weight gain exceeded any continued weight loss due to dehydration (Figure 7). Corrosion then continued at a slow steady rate. Iron in contact with unwashed βFeOOH corrodes at 19% relative humidity.

Insert - Fig 7

Mixtures of unwashed βFeOOH and iron powder were exposed to a range of relative humidities to determine the point at which the corrosion of iron ceased when in contact with unwashed βFeOOH (Figure 8). All samples showed a rapid initial desiccation of βFeOOH . Iron/ βFeOOH mixtures did not measurably corrode at 12% relative humidity over the duration (16000 minutes) of the test but clearly corroded at 15% relative humidity.

Insert - Fig 8.

A sample of washed βFeOOH /iron powder was exposed to 19% relative humidity. When compared to the unwashed sample at 19% relative humidity (figure 7), it is clear that removal of surface chloride has eliminated the immediate aggressive corrosive effects of the βFeOOH on iron (figure 9). The lack of weight loss by the sample may indicate that surface adsorbed

chloride is responsible for the majority of the hygroscopic behaviour of βFeOOH . Our initial comments are that this may be due to the association of chloride with water and subsequent production of HCl on the surface of the βFeOOH , which then attracts water. Once chloride has been removed surface sites are occupied by hydroxyl ions from the wash solution. More research is required to investigate this theory.

Insert - Fig 9.

A mixture of 2g quantities of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, unwashed βFeOOH and iron powder was exposed to 20% relative humidity. A significant loss in weight occurred from dehydration of the corrosion products during the first 12000 minutes (8.3 days) (figure 10). This was followed by steady weight gain due to corrosion of the iron. Corrosion of iron in contact with βFeOOH will occur at 20% relative humidity. Since $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ is stable at 19% relative humidity and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at 22% relative humidity, any hydration of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ will be slow at 20% relative humidity. Any contribution from ferrous chloride to corrosion will be negligible in the time frame of the experiment here.

Insert - Fig 10.

4. Discussion

The results reported here endorse the principle of desiccation as a means to preserve the iron hull of the ss Great Britain. The hull of the ss Great Britain contains a range of iron corrosion products that include βFeOOH . As it dries in its new storage environment, it is likely that $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and fresh (unwashed) βFeOOH will form. The experiments reported here show that βFeOOH and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are capable of corroding iron that is in contact with them. To prevent $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ corroding iron relative humidity will have to be lowered to 19% to form $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$. To prevent βFeOOH corroding iron requires a relative humidity of 12% or less. Where both compounds are present a relative humidity of 12% or less is necessary to stop the corrosion of iron in contact with them. If βFeOOH has been washed to remove surface adsorbed chloride, it does not measurably corrode iron in comparison to unwashed βFeOOH . Rain-wash of the ship's hull may have produced this effect on βFeOOH on its surface.

Desiccating the 322 feet long hull of the ss Great Britain to 12% relative humidity would be costly and technically challenging, with potentially high maintenance costs. Examining the influence of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and βFeOOH on the rate of iron corrosion, as measured by the weight increases shown in figures 6 - 8 indicates that corrosion is many times slower at 20% relative humidity, as compared to 25% or 30% relative humidity. It is worth taking a pragmatic view of the $\beta\text{FeOOH} / \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ iron corrosion model and considering the overall effect of relative humidity on the rate of corrosion (figure 11). The stability of the iron hull of the ss Great Britain could be significantly enhanced and its life-span prolonged by storage environments that control relative humidity to 20%.

Insert - Fig 11.

Cost effectiveness often promotes compromises. The results of these experiments allow informed decisions as to the effectiveness of a particular humidity for the preservation of chloride infested iron. Capital expenditure and future income can be related to best value decisions for the long-term preservation of the iron hull (Table 3). At the ss Great Britain it is planned that costs will be minimised by controlling relative humidity in the immediate vicinity of the hull. The ss Great Britain Trust plans to force dried air over the hull to create and sustain a localised relative humidity that prevents or significantly reduces corrosion of the type examined in this research. Currently experiments are underway to determine the effects of small short-lived fluctuations in relative humidity above the chosen control relative

humidity. Simulations of the effect of catastrophic plant failure on corrosion rates are also underway. The results of this work successfully supported a £8.4 million grant from The Heritage Lottery Fund in the UK.

Insert – Table 3

The results of these laboratory experiments are discussed in the context of the ss Great Britain and the juxtaposition of these corrosive products and iron on the hull must be considered in any corrosion model. The large surface area contact provided by powders used in the experiments and the large quantities of reactants are not duplicated on the hull. The physical nature of the corrosion layers on the ship will be likely to have a very significant effect on reaction rates. However, experience with chloride infested archaeological iron suggests that corrosion can be rapid and invariably occurs at the interface between metal and corrosion layers, creating spalling of the corrosion layers.

The results of this research and their successful implementation offer a new model for the conservation of large iron ships. Both the level of relative humidity and its effects have now been linked to specific chloride based corrosion reactions. When compared to chloride removal treatments for corroded iron, desiccation can now offer greater predictability, with the option of monitoring effectiveness to maintain standards. It also provides its user with measurable choices. Since its efficacy can be graded according to the prevailing relative humidity, it is possible to model the level of corrosion control that a particular sum of money can buy, in terms of plant and operational costs. The application of this conservation technique can be extended to other chloride contaminated iron objects, both large and small.

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References

Argyropoulos, V., Selwyn, L. S. and Logan, J. A. (1997). Developing a conservation treatment using ethylenediamine as a corrosion inhibitor for wrought iron objects found at terrestrial archaeological sites. In Macleod, I.D., Pennec, S. and Robbiola, L.(eds.) *Metal 95 Proceedings of Metals in Conservation Conference 25-28 September 1995*, 153-8 James and James, London

Barker, B.D., Kendell, K. and O'Shea, C. (1982). The Hydrogen Reduction Process for the Conservation of Ferrous Objects. In Clarke, R. and Blackshaw, S. (eds.) *Conservation of Iron* National Maritime Museum Monograph, **53**, 23-27 National Maritime Museum, London.

Barker D., Johnston A. and O'Shea C. (1997). Conservation of the submarine Holland: a practical overview. In Macleod, I.D., Pennec, S. and Robbiola, L.(eds.) *Metal 95 Proceedings of Metals in Conservation Conference 25-28 September 1995*, 286-90 James and James, London

Birchenall, E.C. and Meussner, R.A. (1977). Principles of Gaseous Reduction of Corrosion Products. In Brown, F. B.(ed.) *Corrosion and Metal Artifacts: A dialogue between Conservators, and archaeologists and Corrosion Scientists*. National Bureau of Standards Special publication **479**, 39-58.

- Childs, C. W., Goodman, B. A., Paterson, E. and Woodhams, F. W. D. (1980). The Nature of Iron in Akaganeite (β -FeOOH). In *Australian Journal of Chemistry* **33**, 15-26.
- Cox, J. with Tanner, M. (1999). *Conservation plan for the Great Western Steamship Company Dockyard and the ss Great Britain*. Volume 1. ss Great Britain Trust.
- Gilberg, M.R. and Seeley, N.J. (1982). The Alkaline Sulphite reduction process for archaeological iron: a closer look. *Studies in Conservation* **27**, 180-4.
- Gilberg, M.R. and Seeley, N.J. (1981). The identity of compounds containing chloride ions in marine iron corrosion products: a critical review. *Studies in Conservation* **26**, 50-6.
- Ishikawa, T. and Inouye, K. (1972). The Structural Transformation of Ferric Oxyhydroxides and Their Activity to Sulfur Dioxide. *Bulletin of the chemical Society of Japan*, **45**, 2350-2354.
- Ishikawa, T. Sakaiya, H. and Kondo, S. (1988). Adsorption of water on colloidal iron(III) oxide hydroxides by infrared spectroscopy. *Journal Chemical Society Faraday Transactions I*, **84**, 1941-8
- Ishikawa, T. and Inouye, K. (1975). Role of Chlorine in β -FeOOH on Its Thermal Change and Reactivity to Sulfur Dioxide. *Bulletin of The Chemical Society of Japan*, **48** (5), 1580-1584.
- Jones, D. (1992). *Principles and Prevention of Corrosion*.. Macmillan. New York.
- Knight, B. (1997) The stabilisation of archaeological iron : past present and future. In Macleod, I.D., Pennec, S. and Robbiola, L.(eds.) *Metal 95 Proceedings of Metals in Conservation Conference 25-28 September 1995*, 36-42, James and James London
- North, N.A. and Pearson, C. (1975). Alkaline sulphite reduction treatment of marine iron. *ICOM Triennial Venice*, 1-13 (75/13/3)
- North, N.A. and Pearson, C. (1978) Washing methods for chloride removal from marine iron artifacts *Studies in Conservation* **23**, 174-86.
- Rinuy, A. and Schweizer, F. (1982). Application of the Alkaline Sulphite Treatment to Archaeological Iron: A Comparative Study of Different Desalination Methods of Conservation of Iron. In Clarke, R. and Bradshaw, S. (eds.) *Conservation of Iron*. National Maritime Museum Monographs and Reports, no. **53**, 44-49. National Maritime Museum London
- Scott, D.A. and Seeley, N.I. (1987). The washing of fragile iron artifacts. *Studies in conservation* **32**, 73-76.
- Selwyn, L.S. and Logan, J.A. (1993). Stability of treated iron: A comparison of treatment methods. In Bridgland, J. (ed). *International Council for Museums Committee for Conservation 10th Triennial Meeting Washington DC*. 803-07. James and James
- Selwyn, L.S., McKinnon, M.R. and Argyropoulos, V. (2001). Models for chloride ion diffusion in archaeological iron. *Studies in Conservation* **46**, 109-121
- Selwyn, L. S., Sirois, P.J. and Argyropoulos, V. (1999). The corrosion of archaeological iron with details on weeping and akaganeite. *Studies in Conservation* **44**, 217-232

- Skerry, B. (1985). How corrosion inhibitors work. In Keene, S.V. (ed.) *Corrosion Inhibitors in Conservation*. UKIC occasional Paper 4., 5-12, UKIC London
- Turgoose, S. (1982a). The Nature of Surviving Iron Objects. In Clarke, R. and Blackshaw, S. (eds.), *Conservation of Iron* National Maritime Museum, Monograph No. **53**, 1-8, National Maritime Museum, London
- Turgoose, S. (1982b). Post excavation changes in iron antiquities. *Studies in Conservation* **27**, 97-101.
- Turgoose, S. (1985) The corrosion of Archaeological Iron During Burial and Treatment. *Studies in Conservation* **30**, 13-18.
- Turner, R., Tanner, M. and Casey, S. (1999). *Conservation plan for the Great Western Steamship Company Dockyard and the ss Great Britain. Volume 2 – Condition report and recommendations for the ss Great Britain*. ss Great Britain Trust.
- Tylecote, R.F. and Black, J.W.B. (1980). The effect of hydrogen reduction on the properties of ferrous materials *Studies in Conservation* **25**, 87-96.
- Watkinson, D. and Neal, V. (1998). *First Aid for Finds*. UKIC.
- Watkinson, D.E. (1996) Chloride extraction from archaeological iron : comparative treatment efficiencies. In Roy, A. and Smith, P (eds.), *Archaeological Conservation and Its Consequences*. International Institute for Conservation Copenhagen Congress 208-212. IIC London
- Watkinson, D.E. (1982) An Assessment of Lithium Hydroxide and Sodium Hydroxide treatments for archaeological ironwork. In Clarke, R. and Blackshaw, S. (eds.), *Conservation of Iron* National Maritime Museum, Monograph No. **53**, 28-40. National Maritime Museum London
- Watkinson, D.E. (1983) Degree of mineralisation: its significance for the stability and treatment of excavated ironwork. *Studies in Conservation* **28**, 95-90.

| Condition | Percentage of hull |
|--|--------------------|
| Good condition | 3% |
| Areas covered with GRP, concrete or timber | 8% |
| Areas severely corroded – likely to disappear upon abrasive cleaning | 17% |
| Areas in fair condition – much iron likely to survive abrasive cleaning | 29% |
| Areas of severe corrosion – likely to be perforated by abrasive cleaning | 43% |

Table 1.

| Treatment | Comment on treatment within context of ss Great Britain conservation plan |
|----------------------------|--|
| Aqueous wash | Inefficient and unpredictable level of chloride extraction; aerated environments provide lower chloride extraction than deaerated (Selwyn and Logan 1993, Scott and Seeley 1987, Watkinson 1982 and 1996). |
| Alkaline sulphite | Better aqueous chloride extraction due to alkali and deaerated environment, but normally less than 90% chloride removed; caustic solution; impractical on scale required (Gilberg and Seeley 1982, Knight 1997, North and Pearson 1975, Rinuy and Schweizer 1982, Selwyn and Logan 1993, Turgoose 1985, Watkinson 1996). |
| Sodium hydroxide | Between 55% and 80% chloride removed in aerated environments; caustic solution; impractical scale (North and Pearson 1978, Watkinson 1982, 1983 and 1996). |
| Alkali wash | Sodium Carbonate wash; used with Holland 1 submarine; efficiency as chloride remover unknown; practical application problems with very corroded structures; disposal of treatment solution (Barker <i>et al</i> 1997, Knight 1997). |
| Electrolysis | Varying reports on efficiency and stability; disposal of electrolyte is a problem; challenging on a large scale; better with substantial metal cores; hull is extensively mineralised in places (Knight 1997, Selwyn and Logan 1993, Selwyn <i>et al</i> 2001). |
| Hydrogen reduction | Effective chloride removal; reactive pyrophoric iron produced; ethically questionable; impractical on scale required (Barker <i>et al</i> 1982, Birchenall and Meussner 1977, Tylecote and Black 1980). |
| Inhibitors | Inhibitor action is unpredictable on heavily corroded iron surfaces that are contaminated with chloride; toxicity limits choice (Argyropoulos <i>et al</i> 1997, Skerry 1985, Turgoose 1985) . |
| Cathodic protection | Hull lacks metallic continuity due to areas of total mineralisation that are being retained as part of the conservation rationale. |

Table 2

| Storage category | Relevance for the ss Great Britain |
|-------------------------|--|
| very poor | Current storage conditions for the ss Great Britain. Humidity lies above the deliquescence point of ferrous chloride (~55% relative humidity). Corrosion will be accelerated very greatly due to the presence of the very strongly conducting electrolyte. |
| enhanced | Humidity is below the deliquescence point for iron chloride and above the corrosion threshold established for ferrous chloride/iron mixtures in this research. Within this region the rate of corrosion increased significantly with increasing relative humidity. |
| optimal | Any relative humidity beneath the 'threshold humidity' for the corrosion of ferrous chloride and iron powder mixtures. Ferrous chloride no longer contributes directly to the corrosion of the iron. βFeOOH still contributes to corrosion. |

Table 3

Captions

Table 1. Assessment of condition of the ss Great Britain hull (data from ²)

Table 3. Storage categories for chloride contaminated wrought iron.

Table 2. Limitations of more traditional interventive methods used on chloride infested iron.

Figures



Figure 1.



Figure 2.



Figure 3.

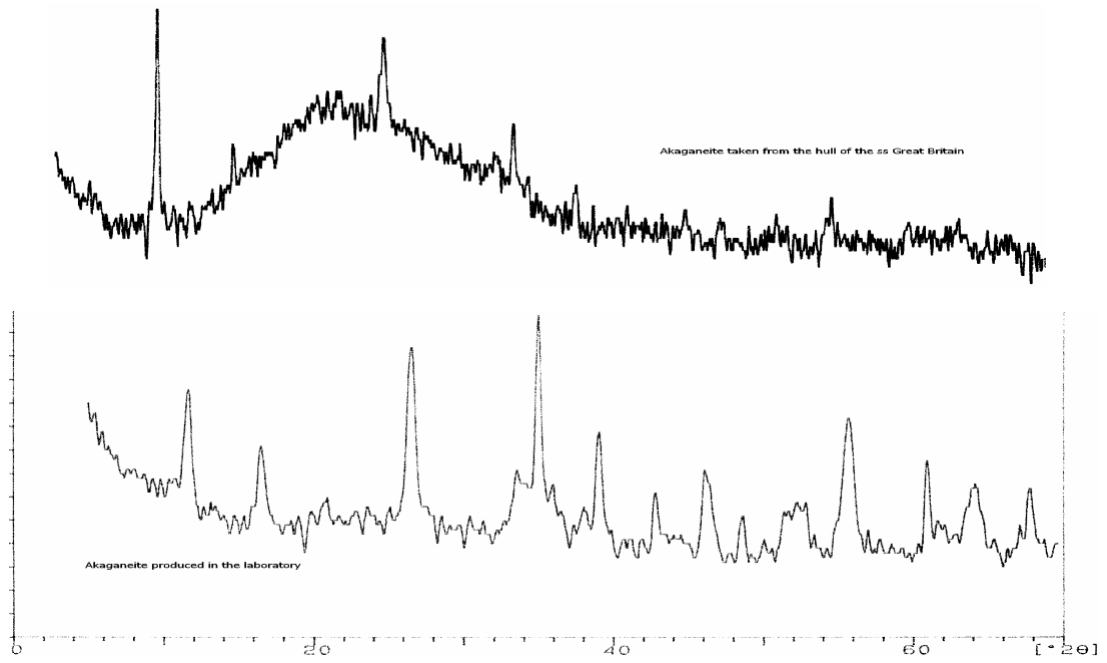


Figure 4.

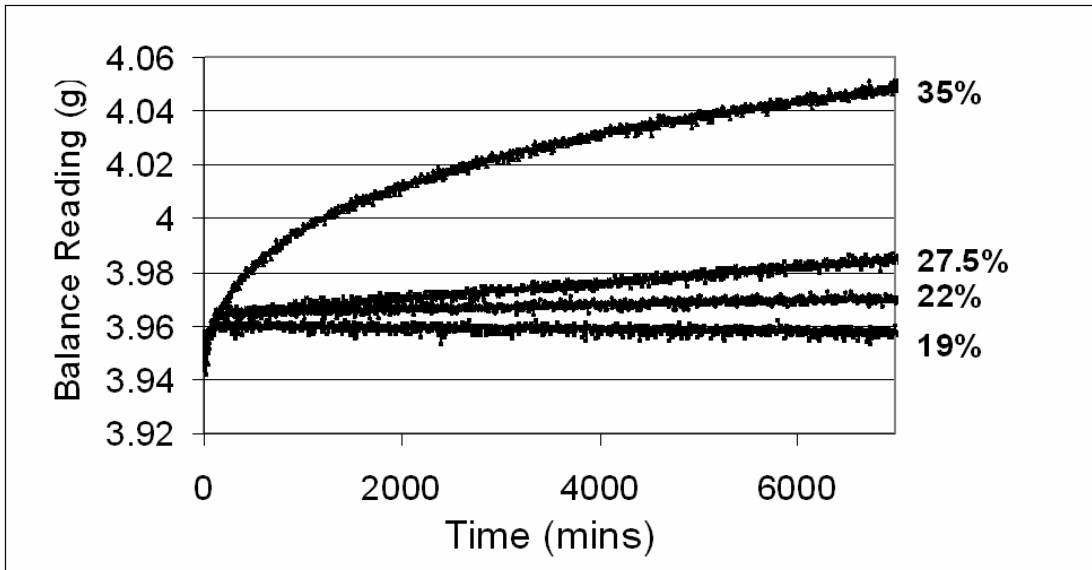


Figure 5.

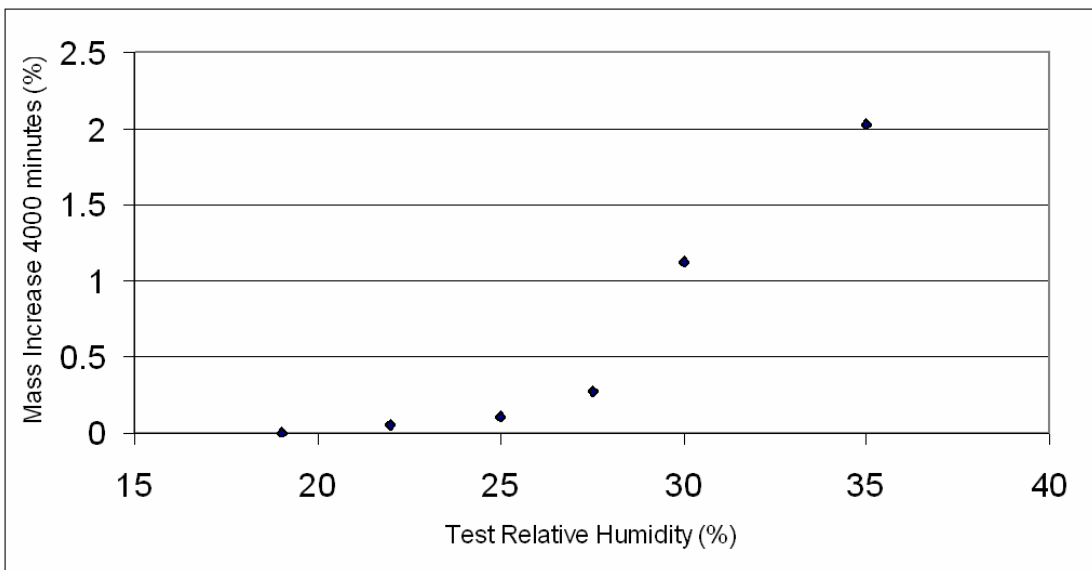


Figure 6.

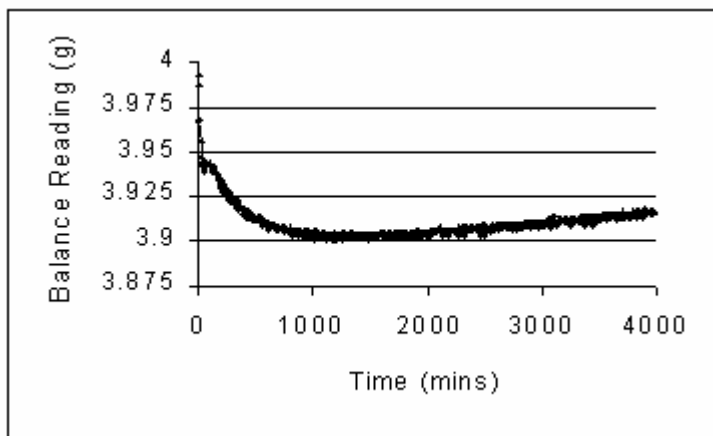


Figure 7.

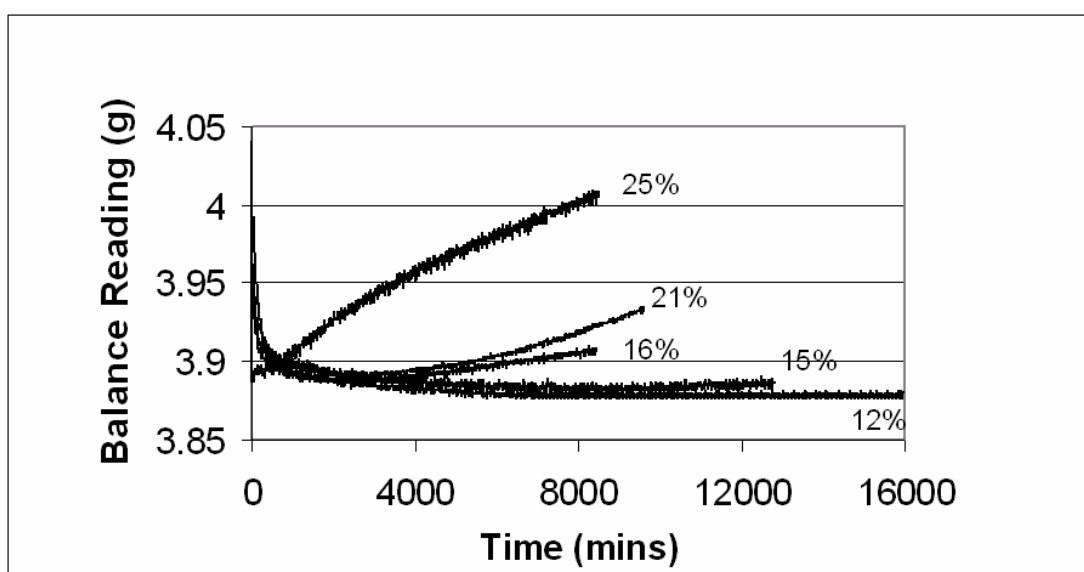


Figure 8.

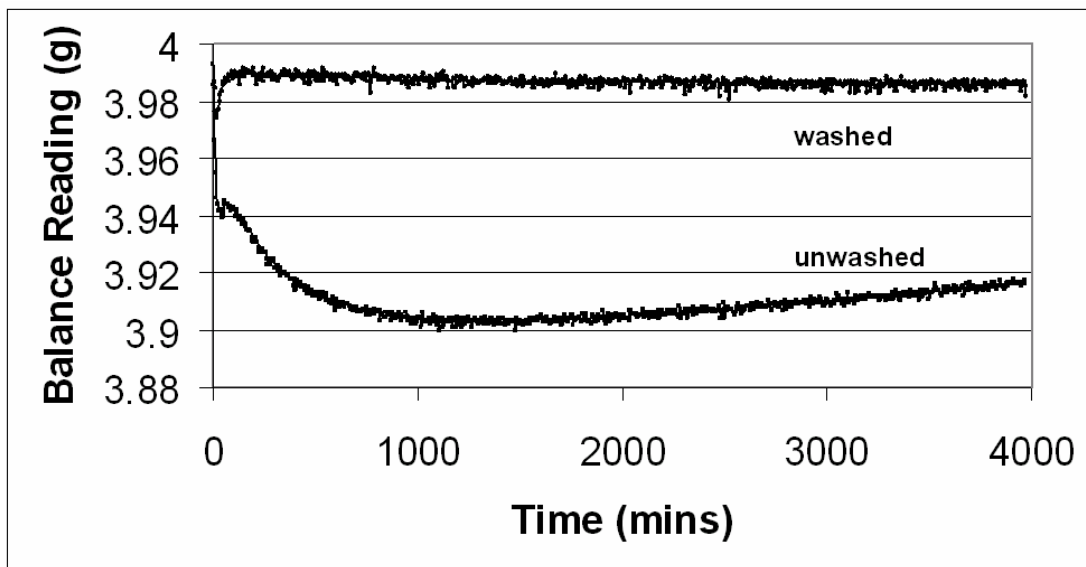


Figure 9.

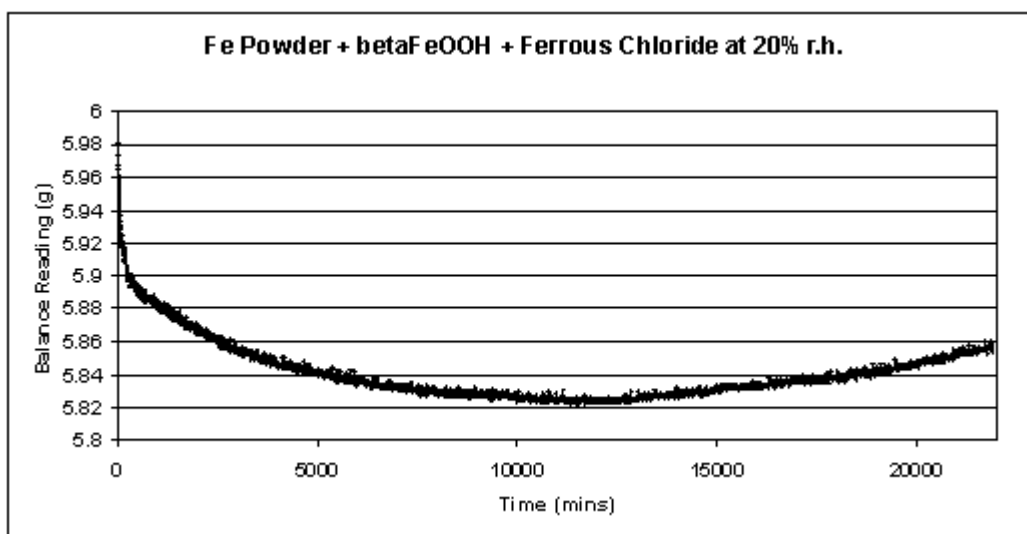


Figure 10.

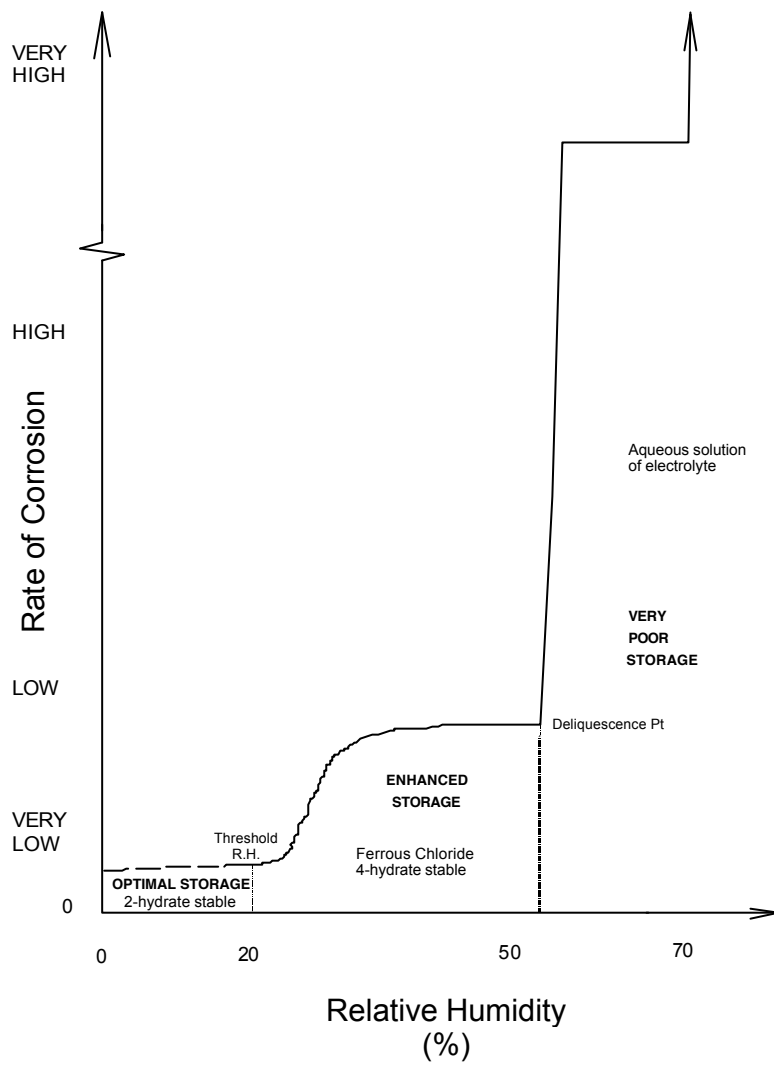


Figure 11.

Figure Captions

Figure 1. ss Great Britain in the historical Great Western Dockyard Bristol.

Figure 2. Ongoing corrosion of the ss Great Britain hull in dry dock.

Figure 3. Artist's impression of the controlled dock space enclosing the ss Great Britain's hull.

Figure 4. Comparison of XRD spectra for laboratory produced βFeOOH (Akaganeite) (bottom) and a sample taken from the hull of the ss Great Britain (top). The broad hump in the upper spectra was due to mounting the sample on a glass plate. (International powder diffraction files JCPDS 42-1315 and 34-1266.)

Figure 5. The line at 19% relative humidity is $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ mixed with iron powder. The lines at 22%, 27.5% and 35% relative humidity are $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with iron powder. All samples exposed for 14 days

Figure 6. The response of 2g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ /2g iron powder mixtures to relative humidity. Increase in mass as a percentage, after 4000 minutes at a particular humidity.

Figure 7. βFeOOH mixed with iron powder exposed to 19% relative humidity for 4000 minutes.

Figure 8. Samples comprising 2g of βFeOOH mixed with 2g of iron powder exposed to 12%, 15%, 16% 21% and 25% relative humidity.

Figure 9. Washed βFeOOH /iron powder mixture exposed to 19% relative humidity, as compared to an unwashed sample of βFeOOH /iron powder.

Figure 10. Unwashed $\beta\text{FeOOH}/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ /iron powder mixture exposed to 20% relative humidity.

Figure 11. Schematic diagram of proposed corrosion rate/ relative humidity model.