DESICCATED STORAGE OF CHLORIDE-CONTAMINATED IRON: A STUDY OF THE EFFECTS OF LOSS OF ENVIRONMENTAL CONTROL.

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1 INTRODUCTION

1.1 Corrosion and electrolytes

In damp aerated environments, at mid range pH values, iron corrosion is an electrolytic process. [1] The anode reaction involves oxidation of the metal [1] and the cathode reaction is the reduction of water to produce hydroxyl ions [2].

Anode $\quad Fe \ ? \ Fe^{2+} + 2e$ [1]

Cathode $\quad H_2O + O_2 + 4e \ ? \ 4OH^-$ [2]

The extent and rate of corrosion will be governed by a wide range of thermodynamic and kinetic factors.

Corrosion control can be initiated in many ways and may involve either a reduction in corrosion rate or corrosion prevention.[2] Electrolytic corrosion can be prevented by removing a corrosion parameter such as oxygen, moisture or the soluble ions that form the electrolyte. Removing moisture will prevent the formation of an electrolyte solution and is normally cheaper and technically less challenging to implement than either eliminating oxygen or removing soluble ions.

Electrolyte composition, amount and distribution are important factors in the corrosion process. The contribution of electrolytes to corrosion is complex and does not continually increase with rising concentration of soluble ions. A 3% NaCl solution is much more aggressive to iron in aerated atmospheres than a 10% solution, as oxygen solubility is reduced in concentrated salt solution and this limits cathode reaction.[1] Chloride electrolytes also cause extensive pitting in iron.[1, 2, 3] Reducing ambient relative humidity can cause evaporation of water from electrolytes, which will lead to concentration of dissolved ions and, eventually, formation of various solid compounds in combination with the oxidised metal, according to solubility product relationships. Many of the compounds formed will be highly soluble, hydrated and hygroscopic, which may allow them to continue to support corrosion via the water they attract. Alternatively electrolyte ions may be adsorbed on insoluble compounds, where their mobility and the adsorption of water may allow them to provide electrolytes to corrode metal in contact with them.[4, 5] Successful corrosion control by desiccation requires both an understanding of what corrosion products can form as a particular corroding metal is dried and the corrosive effect of these compounds as a function of relative humidity.

1.2 *ss* Great Britain: A big corrosion problem

Unstable corroding metal objects do not come much bigger than the *ss* Great Britain. This world famous technological and engineering milestone was built by Isambard Kingdom Brunel and launched in 1843, as the largest all iron screw driven ship in the world.[6] The ship ended her marine life resting in the shallow water of Sparrow Cove in the Falkland Islands, but in 1970 was reunited with the original dry dock where she was constructed in Bristol to create a historic site of international importance. Various interventions did little to prevent ongoing corrosion of the iron hull until a new director commissioned consultants to assess the importance of the site, condition of the ship and formulate a conservation plan.[7, 8] The length (324 feet) of the hull and its condition, along with the unpredictable and limited success of treatments designed to remove soluble corrosion accelerators from highly corroded iron,[9, 10] led to the choice of a non-interventive environmental control system to preserve the hull.

1.3 Implementation of environmental control

Design for corrosion control of the highly unstable lower hull section of the ship was based on maintaining a low relative humidity in an enclosure created between dock side and hull (Figure 1). According to the level of desiccation, the corrosion process would be fed with either a reduced amount of electrolyte or be entirely deprived of it. This would either slow or prevent corrosion of the hull. Achieving this goal presented both technical and theoretical challenges. The design and construction of the desiccated area would tax engineers, architects and conservators, while determining the degree of desiccation would rely on laboratory modelling of the corrosion process to supply engineers with data to aid plant design. Cardiff University carried out tests to examine iron corrosion at low relative humidity.[11, 12, 13]

Figure 1 *Completed environmentally controlled space for ss Great Britain hull. (Picture courtesy of ss Great Britain Trust and Mandy Reynolds.)*

Full conservation of the ship is now complete and the controlled environment is operating.[13] The study reported here contributes to the long-term management of this environment by modelling short-term relative humidity rises from the operational target values for the system. The resulting data can be used to guide the prediction and understanding of the effect of failure to maintain low humidity on the chloride infested iron of the ship's hull.

2 CHLORIDE INFESTED IRON: CORROSION AND CORROSION PRODUCTS

2.1 Chloride on the iron hull of the ss Great Britain

A survey of chloride within the iron hull of the ss Great Britain revealed it was infused with chloride from its time as an ocean going ship and later as a hulk partially submerged in seawater.[8] While chloride could occur as NaCl and $MgCl_2$ from seawater,[15] these salts are hygroscopic and highly soluble. Over 35 years of rain wash in the open air dry dock and several aqueous pressure washes of the hull, will have mostly removed them. Chloride can occur in iron corrosion products such as ß-FeOOH, where it is both adsorbed on the surface and trapped in the hollandite crystalline structure of the ß-FeOOH.[16, 17, 18, 19] ß-FeOOH is an insoluble compound, but its surface adsorbed chloride is mobile, which gives it the capacity to initiate corrosion of iron.[4,5] ß-FeOOH was visually identified on the hull and detected by XRD.[11] The high solubility of ferrous and ferric chlorides means that their formation is unexpected outside of particularly dry environments and low pH values.[19, 20] Most chloride will be held as a counter ion at anode sites on the corroding iron, where its negative charge counter balances the positive charge of anodically produced ferrous ions.[3, 20, 21] Additionally metastable compounds like ß-FeOOH are reported to eventually break down to release soluble ions bound in their structure.[22] These could form electrolytes provided sufficient water was available, but no evidence of instability was found for 25 year old ß-FeOOH stored dry.[13]

2.2 Modelling iron corrosion during drying of chloride infested iron

As the ship dries in its new controlled environment, loss of moisture from the hull will concentrate electrolyte and enrich chloride concentration. Hydrolysis of ferrous ions from corrosion of the iron can generate a low pH in the limited amount of electrolyte present.[4, 5, 19, 20, 22] Thermodynamic and solubility product considerations in low pH solutions containing high concentrations of chloride and ferrous ions favour the formation of solid ferrous chloride.[20] Turgoose [20] reported ferrous chloride corroded iron in contact with it above 20% relative humidity, while at 15% relative humidity corrosion did not occur. This was attributed to the differing hydration states of ferrous chloride at the two humidities; $FeCl_2.4H_2O$ at 20% and $FeCl_2.2H_2O$ at 15%. He also noted that iron mixed with ß-FeOOH corroded at low humidity. Not only was ß-FeOOH already present on the *ss* Great Britain, but more of it would form as the hull corroded during drying.

The present authors extensively examined the influence of ferrous chloride and ß-FeOOH on the corrosion of iron powder at various relative humidities (20°C) using dynamic weight change.[11, 12, 13] The transition point for $FeCl_2.4H_2O$ to $FeCl_2.2H_2O$ was determined as being 21% relative humidity at 20°C.[7] Iron corrosion was confirmed as occurring in the presence of $FeCl_2.4H_2O$ and was absent in the presence of $FeCl_2.2H_2O$ (Figure 2).[11] Corrosion accelerated as relative humidity rose above 22% relative humidity (Figure 2).

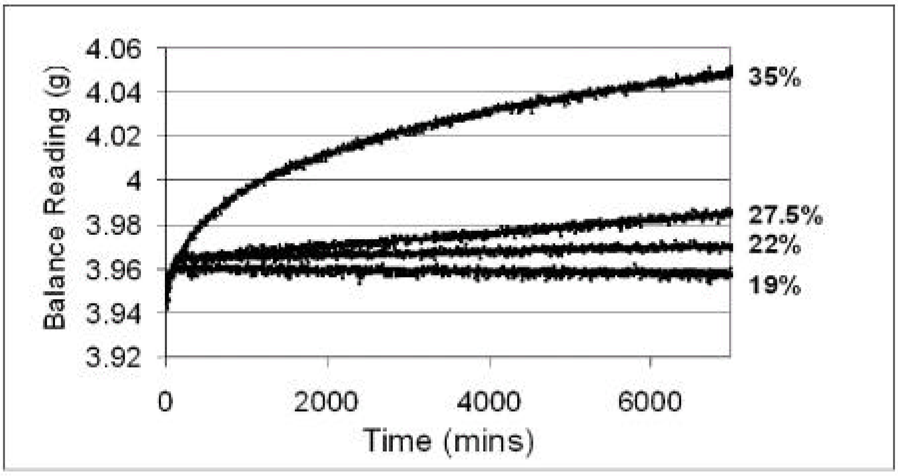

Figure 2 *The response of samples comprising equal masses of iron powder and* $FeCl_2$. $4H_2O$ *to different fixed relative humidity values at 20°C.*[11]

ß-FeOOH conditioned to 40% relative humidity was shown to be hygroscopic, as evidenced by initial weight loss from iron powder/ß-FeOOH mixtures at the low humidity range 15%-21% (Figure 3). After desiccation all samples exposed above 15% relative humidity gained weight due corrosion of iron. Increasing relative humidity significantly speeded up corrosion (Figure 3).

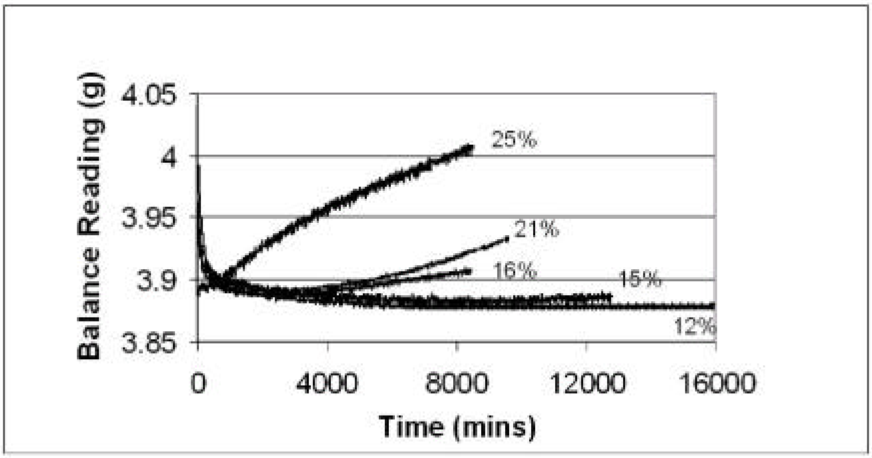

Figure 3 *Response of samples comprising equal masses of iron powder and ß-FeOOH to different fixed relative humidity values at 20°C.*[11]

No-corrosion point for iron and ß-FeOOH is below 15% relative humidity and below 20% for ferrous chloride.

2.3 Environmentally controlled storage in practice

Identifying the effect of relative humidity on iron corrosion is only the first part of a corrosion control process. The financial impact of maintaining relative humidity at low values will be part of the equation that determines how low the target relative humidity will be. Simply stated, "Lower relative humidity offers better corrosion control, but costs more to establish and maintain." Control of relative humidity involves outlay on hardware. This can range from plastic boxes and silica gel for the storage of archaeological iron in closed containers, to the erection of highly specified structures and engineering plant for projects like the *ss* Great Britain. There is also a long-term financial commitment in maintaining environments as man hours and material cost for servicing plant, maintaining buildings and buying energy to operate plant. These costs will influence initial environmental specification.

A high environmental specification with minimal fluctuation is more challenging to set up and is likely to be prone to short and long periods of operation outside designated parameters. Common sense suggests that maintaining either very low relative humidity or fairly static (±3%) mid range relative humidity is likely to miss its target point more often than operating within a ±10% relative humidity range for a 50% target value. By understanding how relative humidity influences iron corrosion the level and effectiveness of corrosion control can be balanced against initial outlay and operating costs. Given that no system is fail safe, how does failure to meet target relative humidities for fixed periods of time influence corrosion control? Many questions need to be addressed here. Do short-term fluctuations at values slightly above the operating relative humidity result in significant corrosion? Is high humidity resulting from short-term shutdown of the environmental control system capable of producing rapid corrosion? Following an environmental transgression how quickly can the corrosion process be slowed again using RH control? These questions are investigated by modelling environmental scenarios.

3 EXPERIMENTAL

3.1 Method

Dynamic weight monitoring was used to examine the effect of humidity change on corrosion of iron. Iron powder (Analar) was mixed either with $FeCl_2$. $4H_2O$ (Analar) or ß-FeOOH in equal (w/w) quantities. These were then subjected to sequential programmed relative humidity fluctuations within a climatic chamber. The ß-FeOOH had been made by slow oxidation of ferrous chloride mixed with iron powder at 92% relative humidity, assayed by XRD as being 99% ß-FeOOH [11] with trace goethite and then equilibrated to 40% relative humidity prior to use. All experiments were carried out in a Votch VC4018 climatic chamber whose relative humidity could be varied to an accuracy of ±1% and temperature to ±0.5^{o}C. Weight changes were recorded to computer every 5 minutes using a Mettler AJ100 analytical balance (±0.0001g accuracy).

Target storage was modelled at 15% relative humidity, where $FeCl_2$. $2H_2O$ is the stable ferrous chloride hydrate and iron will not corrode in contact it. [11] In contrast ß-FeOOH can be expected to corrode iron very slowly at 15% relative humidity (Figure 3).[11] Relative humidity was raised to a selected value for 6 hours every 48 hours, in order to offer opportunity for hydration of corrosion products and corrosion of iron. This was then followed by an extended period of readjustment to the target relative humidity of 15% over 48 hours.

4 RESULTS

4.1 $FeCl_2.4H_2O$/ iron powder mix: 15%-22% relative humidity (Figure 4)

Since $FeCl_2.2H_2O$ is the stable ferrous chloride hydrate at 15% relative humidity there is slow dehydration of the $FeCl_2.4H_2O$ during the first 48 hours. This ceases during the first 6 hour period at 22% relative humidity. Dehydration then recommences until only $FeCl_2.2H_2O$ exists. Although some iron corrosion may occur during the dehydration it is not registered as a weight gain, since weight loss from dehydration masks any weight gain from corrosion. All further 6 hour periods at 22% relative humidity fail to register an increase in weight. This indicates that hydration of $FeCl_2.2H_2O$ at this humidity is not rapid enough to register and that any oxidation of iron is not at a detectable level. It can be concluded that short-lived fluctuations away from a constant operating relative humidity of 15% to 22% will not cause iron to corrode in the presence of ferrous chloride.

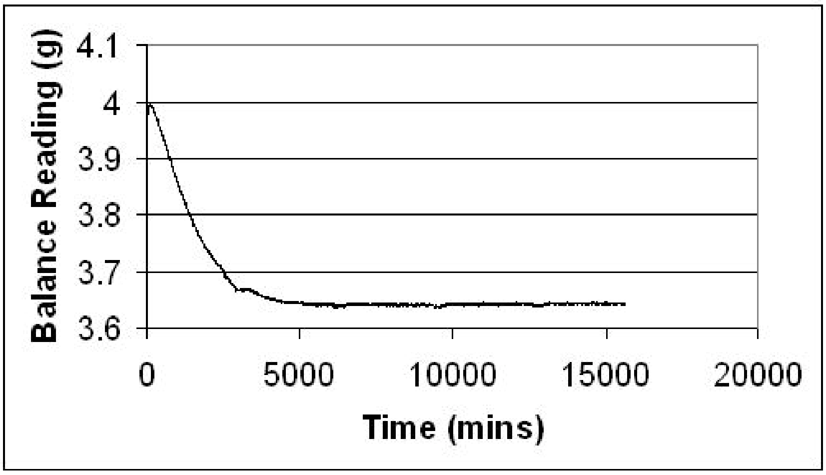

Figure 4 *$FeCl_2.4H_2O$ mixed with an equal mass of iron powder and sequentially subjected to 48 hrs at 15% relative humidity followed by 6 hrs 22% relative humidity at 20^oC.*

4.2 $FeCl_2.4H_2O$/ iron powder mix: 15%-30% relative humidity (Figure 5)

More severe changes to the storage environment were modelled by raising the 6 hour relative humidity fluctuation to 30% (Figure 5). As before $FeCl_2.4H_2O$ slowly dehydrates to $FeCl_2.2H_2O$. The first 30% relative humidity rise occurs during this dehydration and produces temporary re-hydration and, probably, iron corrosion. These are recorded as a slight weight gain. By the beginning of the second 6 hour period at 30% relative humidity $FeCl_2.4H_2O$ dehydration is complete and the sample is at constant weight. During the rise to 30% relative humidity the sample gains weight as it attempts to re-hydrate. Not all of the weight gained is lost by dehydration during the following 48 hour period at 15% relative humidity. This pattern is repeated with every period at 30% relative humidity producing a small permanent incremental gain in weight. This is attributed to oxidation of the iron during the high humidity period. Short-lived fluctuations at 30% relative humidity are sufficient to cause detectable corrosion of iron by hydration of $FeCl_2.2H_2O$ to $FeCl_2.4H_2O$.

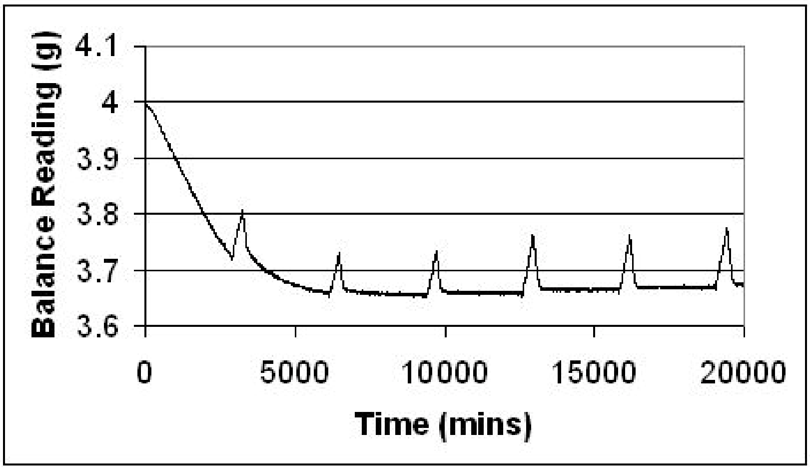

Figure 5 *$FeCl_2.4H_2O$ mixed with an equal mass of iron powder and subjected to 48 hrs at 15% relative humidity followed by 6 hrs 30% relative humidity at 20^oC.*

4.3 ß-FeOOH/iron powder mix: 15%-22% relative humidity (Figure 6)

Iron powder mixed with βFeOOH and exposed to 15% relative humidity, with fluctuations to 22% relative humidity for 6 hour periods every 48 hours, produced a clear corrosion pattern after only 7500 minutes. The βFeOOH rapidly loses the adsorbed water that is present from its initial conditioning at 40% relative humidity during storage prior to use and reaches constant weight during the first 48 hour period at 15% relative humidity. The first 6 hour period at 22% relative humidity produces a weight gain which is not lost. An explanation of this is provided by the majority of the weight increase being due to corrosion of iron, which continues at 15% relative humidity and masks any loss of water picked up by βFeOOH during the 6 hours at 22% relative humidity. This is in keeping with earlier work where corrosion of iron in contact with βFeOOH at 21% relative humidity was fairly rapid (Figure 3).

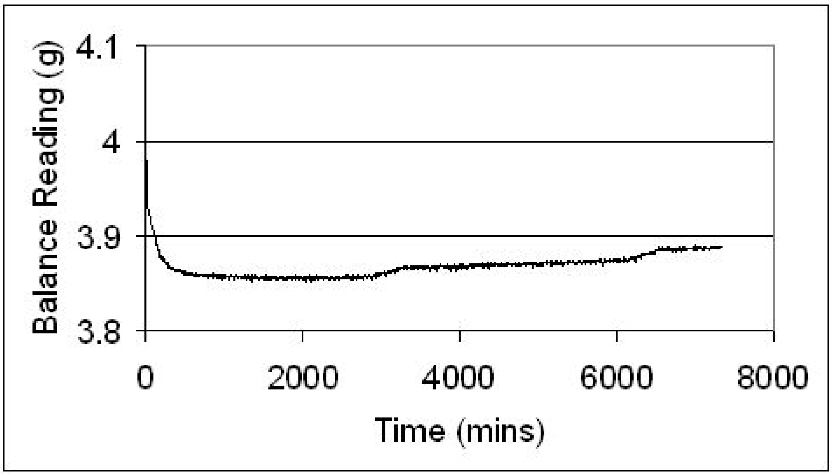

Figure 6 β*FeOOH mixed with an equal mass of iron powder and subjected to 48 hrs at 15% relative humidity followed by 6 hrs 22% relative humidity at 20^oC.*

4.4 βFeOOH/iron powder mix: 15%-30% relative humidity (Figure 7)

Raising relative humidity to 30% for 6 hours after every 48 hours at 15% relative humidity causes significant weight gain. At 30% relative humidity much more water is adsorbed by the βFeOOH than at 22% relative humidity and this is shown as a slight loss at the beginning of the 48 hour period at 15% relative humidity. However, much of the weight gain that occurring at 30% relative humidity is retained, as it is due to oxidation of the iron. The weight gain of the sample during each consecutive 6 hour cycle at 30% relative humidity becomes less. This is most likely due to the iron oxide produced limiting corrosion geometry as the metal powder becomes intimately coated with corrosion product. Corrosion of the iron may be aided by the formation of βFeOOH as a corrosion product.

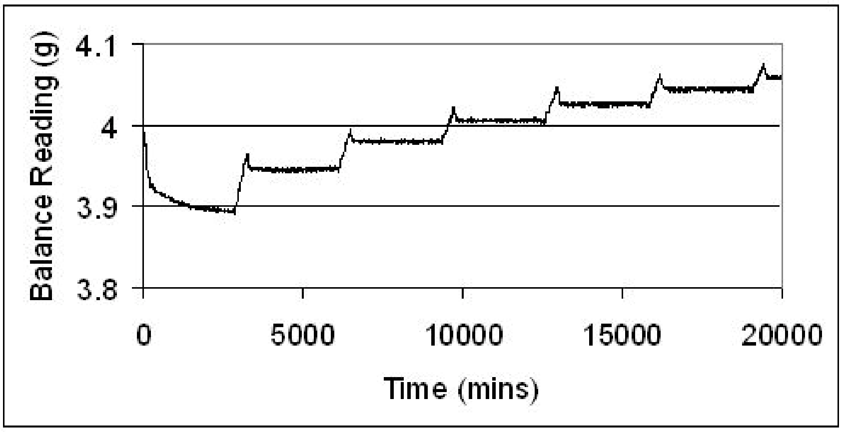

Figure 7 β*FeOOH mixed with an equal mass of iron powder and subjected to 48 hrs at 15% relative humidity followed by 6 hrs 30% relative humidity at 20^{o}C.*

4.4 $FeCl_2$. $4H_2O$/iron powder mix: 22%- 65% relative humidity (Figure 8)

Finally a particularly aggressive scenario was enacted. A system operating at a target relative humidity of 22% was subjected to 6 hour fluctuations at 65% relative humidity. This might be expected if a control system broke down or was being serviced. There is no initial dehydration of the $FeCl_2.4H_2O$, as it is the stable ferrous chloride hydrate at 22% relative humidity. Weight gains are very large during the 6 hours at 65% relative humidity, with only small weight loss from the desiccation effect of the 48 hour periods at 22% relative humidity. This indicates that most weight gain is from conversion of iron to iron oxide.

With each 6 hour fluctuation the weight gain is less and there is relatively more loss in weight during the 48 hour period at 22% relative humidity. This may be due to both a reduced amount of iron being available for oxidation and the production of corrosion product making it difficult for moisture and oxygen to access the iron. The likely formation of hygroscopic βFeOOH as a major corrosion product could explain how more of the weight gain at 65% relative humidity is lost during the subsequent drop to 22% relative humidity. βFeOOH absorbs water faster than $FeCl_2.4H_2O$ (Figures 2 and 3). As corrosion increases with time the proportion of βFeOOH to $FeCl_2.4H_2O$ increases and this is reflected in the larger pick-up of water during the 6 hours at 65% relative humidity. This water is quickly desorbed at the beginning of following period at 22% relative humidity.

The remaining weight gain is due to oxidation of iron. Corrosion is very rapid and significant at 65% relative humidity in the presence of $FeCl_2.4H_2O$.

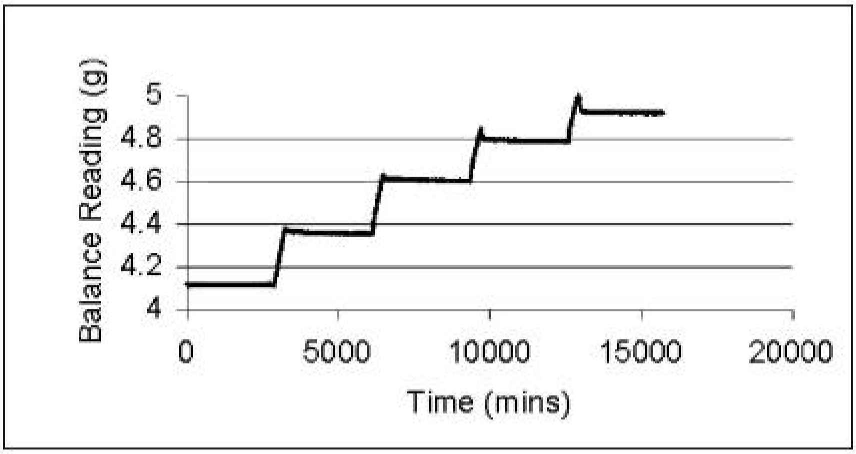

Figure 8 $FeCl_2.4H_2O$ *mixed with an equal mass of iron powder and subjected to 48 hrs at 22% relative humidity followed by 6 hours 65% relative humidity at* 20^oC.

5 DISCUSSION

Guidance on corrosion rate resulting from relative humidity fluctuations can be gained by a semi-quantitative review of cumulative weight data (Table 1). For comparisons between differing tests it is assumed that the only product of corrosion is FeOOH. XRD data from corrosion modelling in previous studies suggests that this is a reasonable assumption.[11] All samples initially used 2.000g each of iron and either βFeOOH or $FeCl_2.4H_2O$. Theoretical weight gain due to total oxidation of 2.000g of iron to FeOOH is 1.180g. Further weight gain from the hygroscopic βFeOOH formed when the iron corrodes will not influence any calculation, as the end weight for each test lies within a 48 hour period of low relative humidity, which dehydrates βFeOOH to constant weight.

For tests involving ferrous chloride predicted corrosion is more complex. Weight gain can occur from hydrolysis of ferrous chloride to βFeOOH at high humidity. However, this hydrolysis requires a high humidity for long time periods.[11] At the relative humidities used in these tests over their short lived time periods, any contribution to weight gain from hydrolysis will be negligible. The following discussion assumes conversion of iron solely to FeOOH and ignores any contribution to weight gain from hydrolysis of ferrous chloride.

Corrosion product plus iron powder	**Relative humidity cycle**	**Region of graph examined (minutes)**	**Duration (minutes)**	**Cumulative weight gain (grams)**
$FeCl_2$	15% - 22%	6120 – 15960	9840	0.00
$FeCl_2$	15% - 30%	6120 – 19080	12960	0.015
$FeCl_2$	22% - 65%	2880 – 15800	12960	0.80
βFeOOH	15% - 22%	2880 –7300	4420	0.03
βFeOOH	15% - 30%	2880 – 14400	12960	0.15

Table 1 *Cumulative weight gain of samples over selected time periods - figures 4 to 8.*

For $FeCl_2.4H_2O$ and iron powder, four cycles at 65% relative humidity produced a weight gain of 0.80g (Figure 8 and Table 1), which is 68% of the theoretical maximum for conversion of iron to FeOOH. This represents extensive corrosion. In contrast, the corrosive effect of $FeCl_2.4H_2O$ after four 6 hour cycles at 30% relative humidity produces a weight gain of only 0.015g. This is 1.2% of the maximum conversion of iron to FeOOH (Figure 5 and table 1) or 53 times less corrosion than at 65% relative humidity. Although this is a low corrosion rate it represents an unacceptable level of corrosion. No weight gain was detected during four 6 hour fluctuations at 22% relative humidity (Figure 4). The differential corrosion rate between short excursions to 65% and 30% relative humidity illustrates how corrosion escalates with rising relative humidity and shows that relative humidity should be as close as possible to the value at which ferrous chloride does not corrode iron.

For βFeOOH and iron four cycles at 30% relative humidity produced a weight gain of 0.25g, which is approximately 19% of the theoretical maximum conversion of iron to FeOOH (Figure 7). In comparison two fluctuations to 65% relative humidity were required to produce a similar level of corrosion for iron in the presence of $FeCl_2.4H_2O$ (Figure 8 and Table 1). Even with fluctuations set at 22% relative humidity corrosion was evident for iron mixed with βFeOOH (Figure 6). Following initial dehydration of the βFeOOH sample, two cycles at 22% relative humidity produced a weight gain of 0.03g or 2.5% of the theoretical maximum conversion to FeOOH (Figure 6), which is three times less than the weight gain for the same two cycles in a 15% to 30% relative humidity programme and twenty times greater than four cycles for an iron/$FeCl_2.4H_2O$ mixture in a 15% to 30% relative humidity programme (Figure 5 and Table 1). These semi-quantitative comparisons suggest that βFeOOH is much more aggressive to iron than $FeCl_2.4H_2O$ at similar humidity and short lived relative humidity fluctuations are enough for βFeOOH to significantly corrode iron. Relative humidity should not rise above 20% for effective corrosion control of iron where βFeOOH is present.

Extrapolating the results of these experiments to real life objects, like the *ss* Great Britain, should be carried out with caution. The scenarios represented here are extremely aggressive. The iron is a finely divided powder and is intimately mixed with the corrosion products being tested to offer a large surface area for corrosion reactions. The ratio of corrosion product to iron in the initial sample is purposefully high at 50/50 w/w. The kinetics of this corrosion system are designed to obtain significant reaction in limited time periods and are different to wrought iron with established corrosion layers. Nevertheless, the study offers an insight into corrosion possibilities and provides guidance on thresholds for corrosion control, as well as an indication that even short lived fluctuations above proscribed safe operating relative humidity could lead to significant corrosion.

Acknowledgements

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