Desiccated Storage of Chloride–Contaminated Archaeological Iron Objects

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Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects

David Watkinson and Mark T. Lewis

Desiccation has long been used to store chloride-contaminated archaeological iron but there are no precise guidelines on the degree of desiccation required to prevent corrosion occurring. Akaganéite (β-FeOOH, ferrous chloride tetra-hydrate ($FeCl_2 \cdot 4H_2O$) and ferrous chloride di-hydrate ($FeCl_2 \cdot 2H_2O$) have been recorded on archaeological iron. Iron corrodes in the presence of $FeCl_2 \cdot 4H_2O$ and β-FeOOH but not in the presence of $FeCl_2 \cdot 2H_2O$. The rate of desiccation of $FeCl_2 \cdot 4H_2O$ at various levels of relative humidity (RH) was determined by experiment and found to be an exponential relationship. The point at which $FeCl_2 \cdot 2H_2O$ first becomes a stable hydrate was established. Rates of corrosion for iron mixed with $FeCl_2 \cdot 4H_2O$ and with β-FeOOH were examined for a range of RH. The hygroscopicity of β-FeOOH and the RH at which it ceases to cause iron to corrode were established. Corrosion of iron in contact with $FeCl_2 \cdot 4H_2O$ and β-FeOOH speeds up as RH rises and is appreciable at 25% RH and above. On the basis of these results, recommendations are made that 12% should be the maximum allowable RH for long-term storage of archaeological iron from chloride-bearing soils. Low RH requirements raise problems for long-term monitoring of storage microclimates.

INTRODUCTION

Although archaeological conservators are familiar with the challenge of preventing the corrosion of archaeological iron during storage, museum stores across the world contain evidence of the failure of many storage and treatment systems [1, 2]. In order to design a successful, cheap and easy-to-maintain storage system, it is essential to understand the corrosion processes taking place on archaeological iron. A common approach to storage is to control parameters that support electrolytic corrosion of iron. In broad terms this offers options for removing soluble electrolytes, the water in which they dissolve or oxygen that supports oxidation.

Of these methods, oxygen removal is seldom practical as it is both difficult and expensive to implement, while removal of soluble ions is unpredictable, inefficient, time consuming and often destructive [3–7]. Moisture removal is the favoured approach of conservators, sometimes in conjunction with prior attempts to remove soluble corrosion accelerators [8–9]. Despite the

large quantities of archaeological iron within the museum world, details such as precise levels of desiccation required to prevent corrosion have received limited attention [9]. This is surprising, since the higher the permissible RH within a desiccated storage environment, the lower the cost to establish and maintain it.

This paper examines the corrosion processes occurring on chloride-contaminated iron and establishes the highest storage RH before corrosion of iron is observed to occur. The resulting corrosion threshold value is used to advise on storage conditions for archaeological iron.
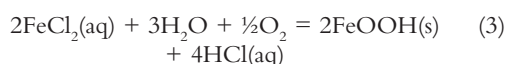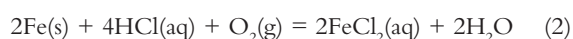
ELECTROLYTES IN ARCHAEOLOGICAL IRON

Most archaeological iron in moist aerated burial conditions contains intrusive chloride ions that congregate at anodic sites, where they exist as iron chloride solutions to satisfy the charge balance of anodically produced Fe^{2+} ions [10–12]. Dissolved chloride produces electrolyte solutions that promote electrolytic corrosion. Following excavation, total desiccation can prevent electrolytic corrosion of metals, but this is both expensive to achieve and technically challenging to maintain. Identifying a

corrosion model for chloride-contaminated iron and then testing its response to RH will determine if total desiccation is necessary to prevent corrosion. Turgoose [9] examined the corrosion of archaeological iron after excavation and identified these concepts for his post-excavation corrosion model based on oxidation of Fe^{2+} to produce ferric oxyhydroxide (FeOOH) and acid (Equation 1). This occurs in the presence of large quantities of chloride and the β-FeOOH polymorph (aka-geneite) is expected to form [13, 14] along with the more stable α-FeOOH (goethite) [15]. The acid can attack the iron directly producing Fe^{2+} ions to feed the reaction:

$$4Fe^{2+} + O_2 + 6H_2O = 4FeOOH + 8H^+ \qquad (1)$$
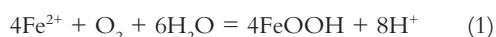
Later work by Selwyn et al [11] discussed and reviewed Turgoose's model and reported the acid corrosion cycle described by Askey et al [16] based on the direct attack of HCl on iron:

$$2Fe(s) + 4HCl(aq) + O_2(g) = 2FeCl_2(aq) + 2H_2O \qquad (2)$$

$$2FeCl_2(aq) + 3H_2O + \tfrac{1}{2}O_2 = 2FeOOH(s) \qquad (3)$$
$$+ 4HCl(aq)$$

IRON CHLORIDES AND THE CORROSION OF IRON

Thermodynamic data suggest that post-excavation changes in archaeological iron can produce solid ferrous chloride, but the formation of ferric chloride is highly unlikely unless local pH values drop to a very low level [12]. Solid ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) in contact with iron causes it to corrode, but the solid ferrous chloride dihydrate ($FeCl_2 \cdot 2H_2O$) does not [12]. These ferrous chloride hydrates have stability ranges that extend between fixed RH values. There is a 'threshold' RH, below which $FeCl_2 \cdot 2H_2O$ becomes the stable ferrous chloride hydrate and an iron/ferrous chloride mixture does not corrode. This is a safe storage range for iron in contact with ferrous chloride. While Turgoose [9] showed that iron in contact with ferrous chloride corroded at 20% RH (as controlled by a saturated solution of CH_3COOK) and not at 15% RH (as controlled by a saturated solution of $LiCl \cdot H_2O$); no specific corrosion threshold value was provided.

β-FEOOH AND POST-EXCAVATION CORROSION OF ARCHAEOLOGICAL IRON

In addition to the influence of ferrous chloride on the post-excavation corrosion of iron, the presence of β-FeOOH (Equation 1) also has to be considered. β-FeOOH is an oxidation product of ferrous chloride and it has long been suspected that it causes iron in contact with it to corrode [9]. Kaneko & Inouye [17] reported that water is chemisorbed to the surface of β-FeOOH, connected by hydrogen bonds and weak charge transfer bonds. If the number of monolayers of surface-adsorbed water were to rise above three [18], the layer would be likely to possess the chemical properties of bulk water. No RH corrosion range exists for the effect of β-FeOOH on iron. To predict a safe storage environment for iron subject to the reaction outlined in Equation 1, it is necessary to examine how both ferrous chloride and β-FeOOH react with iron at various levels of RH.

The mechanism of the corrosion of iron in the presence of ferric oxyhydroxides has not been investigated. Corrosion is likely to be affected by the nature of FeOOH polymorphs, which have surface hydroxyl and surface oxygen defects that provide large numbers of adsorption sites for water vapour, some gases and halide ions [19]. Adsorption of anions and cations from solution at the water/FeOOH interface is governed by anion type, solution pH and other solution variables [20, 21]. Both a-FeOOH and β-FeOOH strongly adsorb chloride ions on their surfaces [22].

β-FeOOH is formed in halide-rich environments. In a chloride-rich environment it will have chloride ions adsorbed onto its outer surface [23] and contained within its hollandite-type ($BaMnO_{16}$) crystal structure [24]. This rod-like crystal structure contains tunnels with diameters estimated at 3.5 angstroms (Å), but with necks of only 2.7 Å in diameter [25] and these contain chloride ions (diameter 3.6 Å) and water molecules [17, 24]. The chloride content of β-FeOOH varies widely, with values of 4.6–17% w/w being recorded for synthetic precipitates [26, 27] and values of 0.3–5.4% w/w in naturally produced β-FeOOH associated with meteoric iron [28]. Outer surface adsorbed chloride is mobile and can be fully or partially washed off. In contrast, the internal chloride is 'locked' inside the tunnels and can only be removed by decomposition of the β-FeOOH. Although α-FeOOH adsorbs chloride ions from very dilute solutions, these are tightly bound and are not removed by aqueous washing. Turgoose [12] cites absorption of <0.2% w/w on α-FeOOH.

As chloride-contaminated archaeological iron dries following excavation, there is a relative increase in oxygen and chloride ion concentration, which will allow β-FeOOH to form (Equation 1). This will remove chloride ions from the electrolyte solution. Later, the interaction of water vapour with oxygen and hydroxyl groups on the surface of β-FeOOH, will

produce chemisorbed and physisorbed water that may dissolve surface-adsorbed chloride to produce an electrolyte [23, 29]. It may be that this effect provides an electrolyte for the corrosion of iron in contact with it.

This brief and simple review of post-excavation corrosion of chloride-contaminated archaeological iron shows that in order to preserve this material it must be stored at a RH that does not allow:

- surface-adsorbed chloride on β-FeOOH to become mobile;
- ferrous chloride to exist as $FeCl_2 \cdot 4H_2O$;
- ferrous chloride to deliquesce (possibly around 55–56% RH at 25°C [9, 30]).

The work reported here:

- examines the RH at which $FeCl_2 \cdot 4H_2O$ changes to $FeCl_2 \cdot 2H_2O$;
- examines the reaction of $FeCl_2 \cdot 4H_2O$ with iron powder at differing levels of RH, in order to determine the rate of corrosion of iron in contact with $FeCl_2 \cdot 4H_2O$;
- confirms that iron does not corrode in the presence of $FeCl_2 \cdot 2H_2O$;
- examines how β-FeOOH responds to RH;
- determines the response of iron/β-FeOOH mixtures to changes in RH;
- uses these results to identify a RH below which chloride-contaminated archaeological iron should be stored in order to prevent corrosion of iron by the mechanisms examined.

CURRENT PRACTICE FOR DESICCATING ARCHAEOLOGICAL IRON

For the iron/ferrous chloride corrosion model, although it is unknown whether corrosion is still occurring between the recorded no-corrosion point of 15% RH and the corrosion point of 20% RH [9], both 20% and 18% RH have been cited as the maximum allowable for the storage of chloride-contaminated wrought iron [10].

Attaining and maintaining desiccated storage environments remain an area of debate. Although some basic advice on desiccation has been offered [31], the lack of a specified technical standard for storage is a problem. Iron archaeological objects are often placed in polyethylene sandwich-seal boxes with self-indicating desiccated silica gel, with no accurate means of measuring internal RH or any long-term monitoring programme. Leakage will mean that these environments will soon exceed 20% RH and support corrosion of chloride-contaminated metallic iron. The colour change produced by indicating silica gel is of little use as it occurs at around 35% RH. By the time this occurs the environment will have been aggressive to chloride-contaminated iron for some time.

Also of concern is that some conservators voice the opinion that desiccation of corrosion products causes 'shrinkage' and lamination of corrosion layers at the iron/corrosion product interface. The authors have not been able to establish whether such lamination during desiccated storage was due to a failure to maintain a low RH, leading to fresh corrosion at the metal surface, which promotes lamination of mineralized layers. It remains a topic that merits further investigation.

INTERPRETING EXISTING DATA ON RH CORROSION THRESHOLDS

Although Turgoose [9] cited values of 20% and 15% RH for the environments in which he conducted his experiments with ferrous chloride and iron powder mixtures, conflicting reports for equilibrium values for saturated salt solutions mean that these could be reinterpreted (Table 1). The no-corrosion threshold could be as low as 11.1% and the corrosion threshold as high as 23.11% RH. Although temperature influences the value of equilibrium vapour pressure above a saturated salt solution, Turgoose [9] did not report the temperature of his experiments.

Using Turgoose's [9] results to construct a graph examining how corrosion varies with RH for an iron/ferrous chloride mixture suggests that extrapolation might feasibly support an intercept near 18% RH as the corrosion cut-off point for this reaction (Figure 1). It was acknowledged that the linearity or otherwise of the relationship between just three points could not be safely predicted without further work. This was used as a starting point for the design of experiments to explore the effect of RH on the iron/ferrous chloride reaction.

EXPERIMENTAL METHOD

All experiments were carried out in a Votsch VC4018 climatic chamber. Calibration tests over the ranges used in the experiments showed that RH could be maintained to an accuracy of $\pm$1% (often 0.5%) and temperature to $\pm$0.5°C. Within the chamber RH values were measured using wet and dry bulb temperatures (the primary standard). All tests were standardized at 20°C

Table 1 *Relative humidities cited for saturated salt solutions of lithium chloride and potassium acetate.*

Reference	Lithium Chloride @ 20ºC	Lithium Chloride @ 25ºC	Potassium Acetate @ 20ºC	Potassium Acetate @ 25ºC
Greenspan, L. (1977) [32]	11.31+0.31	11.30+0.27	23.11+0.25	22.51+0.32
CRC Handbook, (1996) [33]	11.31+0.31	11.30+0.27		
Lafontaine, R.H. (1984) [34]	12.4	12		
Hickman, M.J. (1970) [35]	12		23	
Anon (1973) [36], Anon (1964) [37]	12		22	
Richardson & Malthus, (1955) [30]				22.7
Wink & Sears, (1950) [38]	11.1 @ 22.8 ºC		22.9 @ 22.8 ºC	
Stokes & Robinson, (1949) [39]		11.1		22.5
Spencer, H.M. (1926) [40]	15		20	
Turgoose,S (1982) [9]	15		20	
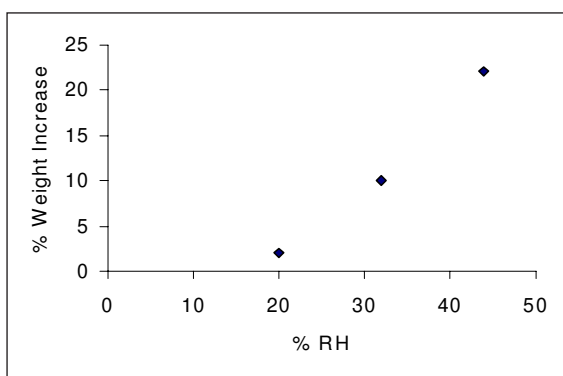
Figure 1 *Weight increases for iron/FeCl$_2$·4H$_2$O mixtures at varying RH (after Turgoose [9]).*

allowing conversion of results to specific humidity from RH values.

The experimental method involved mixing known weights of analar ferrous chloride and iron powder or β-FeOOH and iron powder, then exposing them to a fixed RH and temperature. The weight of each mixture was then dynamically monitored to computer file every five minutes, using a Mettler AJ100 balance (accuracy ±0.0001 g for normal use) for the duration of the experiment.

The balance had been calibrated by dampening it with closed-cell polyethylene foam, followed by loading it with a standard mass control whose weight was dynamically recorded at 20% RH and 20ºC for a number of days. This determined actual balance accuracy and any drift in weight reading with time. The resulting weight drift and vibration 'noise' were found to be reproducible systematic errors that did not influence the readings relative to the mass being recorded. Due to machine vibration some noise is visible on the graphs produced here, but this does not influence the trends sought from the results. Further confirmation of the validity of the balance data was obtained through the measurement of the loss in mass attributable to the loss of two water molecules of hydration during the desiccation of known masses of FeCl$_2$·4H$_2$O (Figure 2).

During the experiments, corrosion, desiccation and water adsorption of the test samples could produce weight change. Corrosion of the iron produces weight gain and colour change as the iron combines with oxygen and water to produce FeOOH. Desiccation reduces sample weight and water adsorption increases weight. If some of these processes take place simultaneously weight may be lost or gained or may remain static. The nature of change in the samples was determined by visual examination and the use of X-ray diffraction (XRD) or Fourier transform infrared (FTIR) spectroscopy. Since one method of synthesizing β–FeOOH is to expose a ferrous chloride and iron powder mixture to a high RH, this is the expected corrosion product formed from the analar iron/chloride mixture.

THE IRON/FERROUS CHLORIDE CORROSION MODEL

Dehydration of FeCl$_2$·4H$_2$O

The influence of RH on the dehydration rate of FeCl$_2$·4H$_2$O to FeCl$_2$·2H$_2$O was examined. A 1.0000 g sample of FeCl$_2$·4H$_2$O was placed on the balance and subjected to a fixed RH ±1%. This was carried out for a range of RH, but for clarity only data for 20%, 18%, 16%, 14% and 12% RH are shown in figure 2.

All the FeCl$_2$·4H$_2$O samples desiccated at the humidities used in the tests. Since the calculated loss in weight when 1.0000 g of FeCl$_2$·4H$_2$O fully desiccates to
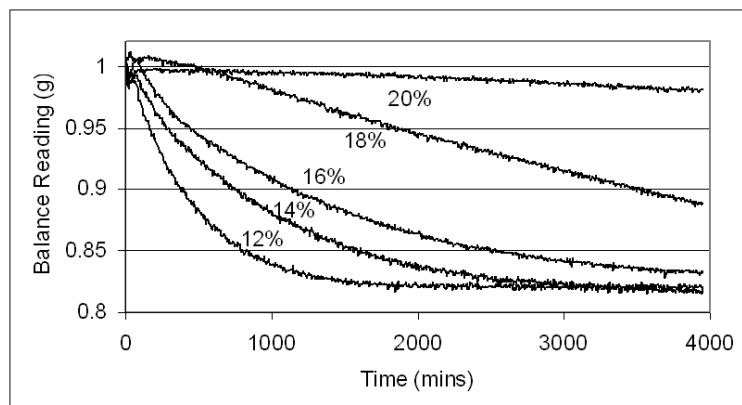
Figure 2 *Desiccation – recorded as weight loss – from a range of FeCl$_2$·4H$_2$O (1.0000 g) samples run at different levels of RH.*

FeCl$_2$·2H$_2$O is 0.1812 g, the 18%, 16%, 14% and 12% RH test samples fully converted to FeCl$_2$·2H$_2$O. Tests run at 18% and 20% RH are closer to the point where FeCl$_2$·4H$_2$O is the stable iron chloride and consequently show slow dehydration gradients.

There exists a RH value where the rate of change from FeCl$_2$·4H$_2$O to FeCl$_2$·2H$_2$O is so small that it tends towards zero. This RH marks the beginning of the stability range for FeCl$_2$·4H$_2$O. Plotting rate constants for each of the FeCl$_2$·4H$_2$O dehydrations against RH provides a graphic representation of the predicted asymptote. Extrapolation of the trend would either determine the intercept on the RH axis, where the rate constant is zero, or the asymptote which the trend tends towards as it approaches zero. At this point dehydration of FeCl$_2$·4H$_2$O is not occurring and it is the stable form of iron chloride. The rate constants required to do this are calculated below and plotted against RH in Figure 3.

Rate of dehydration equation

Regression analysis gave good correlation with an exponential relationship in each case. By treating the rate of change in weight (mass) as exponential for all the dehydrating humidities tested, an equation to describe each dehydration curve on Figure 3 can be derived:

$$\text{Mass} = (\text{Initial Mass} - \text{Final Mass})\ e^{-\Lambda t} \qquad (4)$$

Since the initial mass of FeCl$_2$·4H$_2$O in these experiments is always 1.0000 g the theoretical final mass will always be the same, as all the sample will have lost
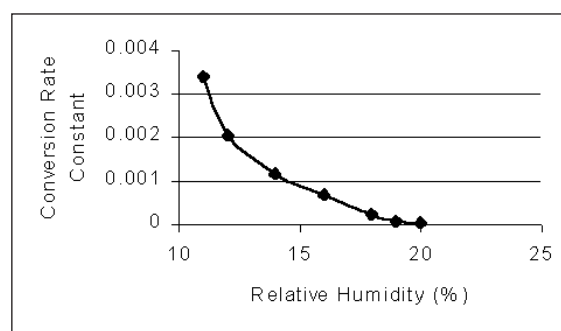

Figure 3 *Exponential hydrate rate conversion constants plotted against RH.*

the same amount of water in converting entirely to FeCl$_2$·2H$_2$O. This is two water molecules per mole of FeCl$_2$·4H$_2$O or 0.1812 g from the starting weight of 1.0000 g. Thus the final mass should always be 0.8188 g. Inserting these values into Equation 4 produces:

$$\text{Mass} = (1 - 0.8188)\ e^{-\Lambda t} \qquad (5)$$

which simplifies to:

$$\text{Mass} = 0.1812\ e^{-\Lambda t} \qquad (6)$$

where t is a given time elapsed since the start of the drying cycle and Λ is a constant hereafter referred to as the 'exponential hydrate conversion rate constant'. This constant will be different for each RH used. It is the element of the equation that ultimately determines

the time necessary for conversion of a set mass of $FeCl_2 \cdot 4H_2O$ to $FeCl_2 \cdot 2H_2O$ at a given RH.

Weight loss resulting from loss of water of hydration from the $FeCl_2.4H_2O$ can be expressed in terms of a 'half life', which is defined as the time required for half the expected total change in mass to occur. This is a loss of 0.0906 g of water from the calculated total loss of 0.1812 g. It is the time required for the weight of the sample to change from 1.0000 g to 0.9094 g. The half-life may either be calculated using a standard equation for half-life (Equation 7) or read from the RH curves on the graph showing the rate of weight loss (Figure 2). Half-life ($t_{0.5}$) is where the balance reading is:

$$\text{initial mass} - \frac{(\text{initial mass} - \text{theoretical final mass})}{2} \quad (7a)$$

and at time:

$$\frac{\ln 2}{\Lambda} \quad (7b)$$

Inserting values into these equations, half-life ($t_{0.5}$) is defined at mass:

$$1 - \frac{(1.0000 - 0.8188)}{2} = 1 - 0.0906 \text{ g} \quad (8a)$$
$$= 0.9094 \text{ g}$$

and at time:

$$t_{0.5} = \frac{0.693}{\Lambda} \quad (8b)$$

Values for the exponential hydrate conversion rate constant Λ (Table 2) were obtained by inserting half-life readings from Table 2 into the equation:

$$\Lambda = \frac{0.693}{t_{0.5}} \quad (9)$$

Table 2 *Derived exponential hydrate conversion rate constants (Λ for each of the curves in figure 3).*

RH (%)	Measured half-life (minutes)	Λ
11	205	3.4×10^{-3}
12	340	2.0×10^{-3}
14	660	1.1×10^{-3}
16	800	8.7×10^{-4}
18	2800	2.5×10^{-4}
19	7500	9.2×10^{-5}
20	13800	5.0×10^{-5}

These exponential hydrate conversion rate constants can now be plotted against RH (Figure 3). A non-linear relationship results. The continued dehydration measured at 19% RH and 20% RH suggests that the corrosion cited at 20% RH (Figure 1) either took place before full conversion (dehydration) had taken place or that the RH maintained by the saturated salt solution was slightly above 20% RH.

The relationship between half-lives for each curve and the RH at which they were obtained shows that there is no linear relationship between dehydration and half-life (Figure 4). This figure includes the data for all of the humidities tested. The half-life will tend towards infinity above 20% RH.
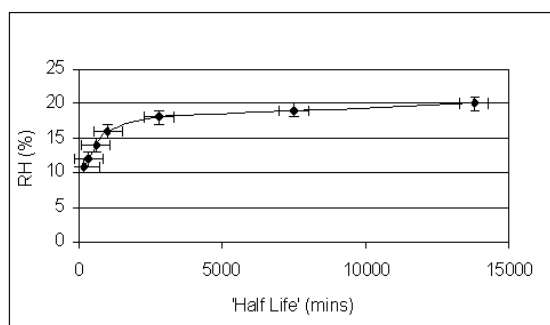

Figure 4 *The relationship between half-life of partially desiccated $FeCl_2 \cdot 4H_2O$ and RH.*

The logarithmic correlation for the above relationship is good, but there must be a point (which is termed 'threshold' RH by the authors), where the gradient on Figure 4 tends towards zero as time tends towards infinity. This will be followed by a point (the asymptote) where the gradient is zero, when $FeCl_2.4H_2O$ stops converting to $FeCl_2.2H_2O$. The logarithmic relationship is expected to be asymptotic to this limiting RH, above which no loss of water of hydration takes place. A value for this limiting RH cannot be obtained by extrapolating a logarithmic relationship as, while these tend towards a value (our asymptote), they never reach it. The limiting RH was therefore determined experimentally.

Iron powder mixed with $FeCl_2.2H_2O$

An $FeCl_2 \cdot 2H_2O$/iron powder mixture exposed to 19% RH showed no weight gain and no visible change over a period of two weeks (Figure 5). This indicates that
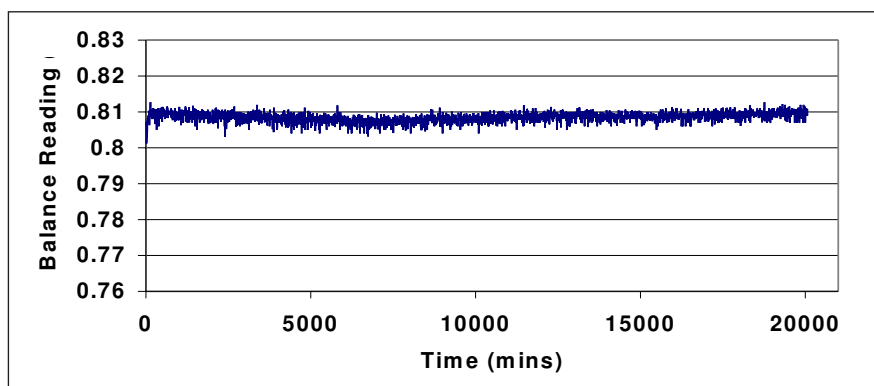
Figure 5 *The behaviour of 0.31 g ferrous chloride dihydrate mixed with 0.50 g iron powder at 19% RH for two weeks. No change in micro/ macroscopic appearance (corrosion) of the mixture was observed between the start and the end of this test.*

$FeCl_2 \cdot 2H_2O$ is the stable form of iron chloride at this RH and that iron does not corrode in contact with $FeCl_2 \cdot 2H_2O$. Turgoose [12] had shown this for 15% RH. These results raise the corrosion threshold for this reaction to 19% RH.

It should be noted that the fluctuations apparent in Figure 5 can be attributed to balance drift caused by internal balance vibration correction. Fluctuations of this magnitude were reproduced with polished silver controls. The magnitude is negligible compared with the real weight changes observed during desiccation and corrosion.

The climatic chamber used for this work struggles to maintain RH below 20% much beyond two weeks at a time, due to icing of the refrigeration coil which results

in up to 3% RH variation from the set point. So two weeks was the limit of the duration of the studies at these low humidities. For this reason the examination of the rates of change in mass was important in establishing their trend, so that instances of no reaction could be inferred from such short test periods.

Corrosion of iron in the presence of $FeCl_2 \cdot 4H_2O$

The influence of RH on the rate of corrosion of iron powder in the presence of $FeCl_2 \cdot 4H_2O$ was determined by exposing samples comprising 2.0 g $FeCl_2 \cdot 4H_2O$ mixed with 2.0 g of iron powder to fixed RH values. Over a period of three days, each sample increased in weight and the iron powder visibly corroded (Figure 6).
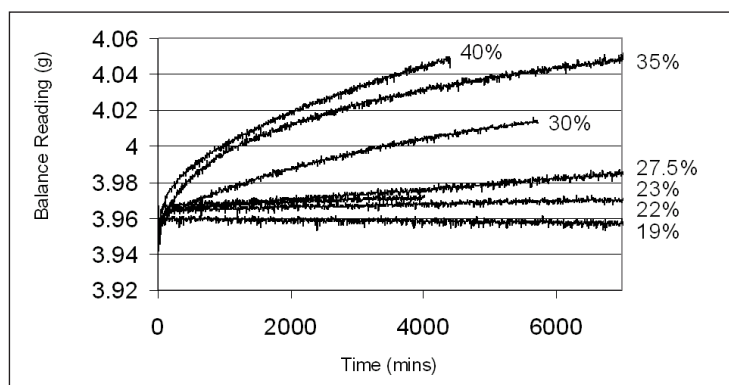

Figure 6 *Corrosion of iron in the presence of ferrous chloride tetra-hydrate at fixed RH values. All tests were conducted with 2.0 g of $FeCl_2 \cdot 4H_2O$ mixed with 2.0 g of iron powder.*

While corrosion in the region 23% to 25% RH is very slow, raising RH by 5% from 25% to 30% produces a significant increase in corrosion rate (Figure 6). The higher the RH, the faster the corrosion rate for FeCl$_2$·4H$_2$O/iron powder mixtures.

Two controls were run:

- pure iron powder;
- analar FeCl$_2$·4H$_2$O.

Neither of these increased in weight at any of the RH values used. This suggests that iron alone does not measurably corrode at the RH values used over the timescales of the experiments and that FeCl$_2$·4H$_2$O is the stable phase of ferrous chloride at these RH levels.

Summary of results for the iron/ferrous chloride corrosion model

The outcomes of the tests with iron and ferrous chloride mixtures show that:

- Iron and ferrous chloride mixtures do not measurably or observably corrode within the stability region of FeCl$_2$·2H$_2$O.
- Iron and ferrous chloride mixtures corrode significantly within the stability region of the FeCl$_2$·4H$_2$O.
- The corrosion threshold for iron in association with ferrous chloride lies in the region 20–21% RH.
- Iron failed to corrode in the presence of ferrous chloride at 19% RH.

THE IRON/β-FEOOH CORROSION MODEL

Synthesis of β-FeOOH for experimental use

β-FeOOH was synthesized by mixing equal masses of ferrous chloride and iron filings together and exposing them to a high RH (92.5% controlled by saturated sodium carbonate solution at 25°C) with access of atmospheric oxygen for about four months [9]. The resulting product was assayed using FTIR spectroscopy, polarized light microscopy and XRD. It was found to consist of about 99% β-FeOOH and 1% α-FeOOH. This method of production best equates to the corrosion of iron contaminated with chloride in air and a high RH, as opposed to other wet precipitation methods of production.

The β-FeOOH formed was not washed after production. Washing finely divided powders of excess surface-adsorbed chloride (estimated at 9.2% w/w through

Soxhlet wash tests and a theoretical 15.6% w/w from initial admixture molar calculations, assuming consumption of all iron) would not replicate closely the composition of corrosion on post-excavation archaeological iron.

The effect of RH on β-FeOOH

A 1.00 g β-FeOOH sample conditioned to 41% RH was placed in a 19% RH for 2500 minutes (41.7 hours). It rapidly lost weight as it released adsorbed water during equilibration with its new ambient RH (Figure 7).
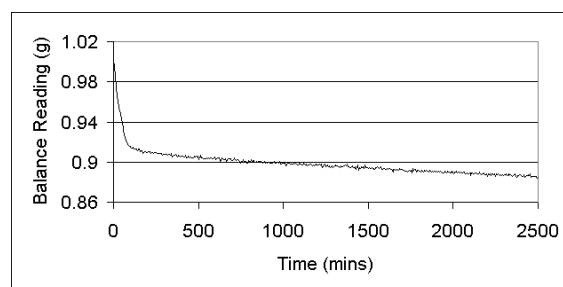

Figure 7 *β-FeOOH equilibrated to 41% RH and exposed to 19% RH for 2500 minutes.*

Compare this with the results of exposure of a 1.00 g β-FeOOH sample to 80% RH for 4000 minutes (Figure 8). Both sets of results are qualitative because the balance behaviour at the beginning of a test masks the true change in mass during this all-important period. The two tests demonstrate the ability of β-FeOOH to attract and lose adsorbed water.

The effect of RH on βFeOOH/iron powder mixtures

Samples of β-FeOOH (2.00 g) conditioned to 41% RH were mixed with iron powder (2.00 g) and exposed to RH values varying between 12% and 25% for a maximum of 16000 minutes (266 hours) (Figure 9). Samples exposed to low RH initially lost weight due to dehydration, then showed consistent weight gain as corrosion of the iron powder resulted in oxygen uptake. A sample exposed at 25% RH produced instant corrosion of iron, with a weight increase that masked any possible weight loss due to dehydration of the β-FeOOH. Corrosion of iron in the presence of β-FeOOH occurs at 15% RH and is rapid at 25% RH.
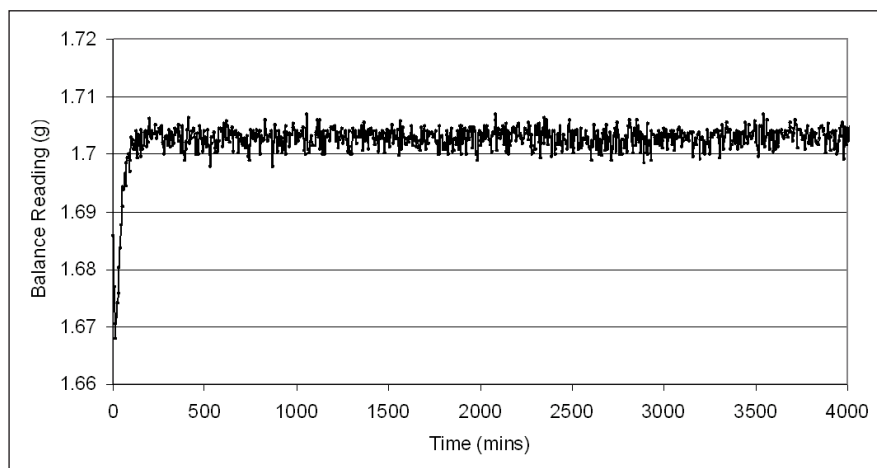
Figure 8 *β-FeOOH equilibrated to 41% RH and exposed to 80% RH for 4000 minutes.*
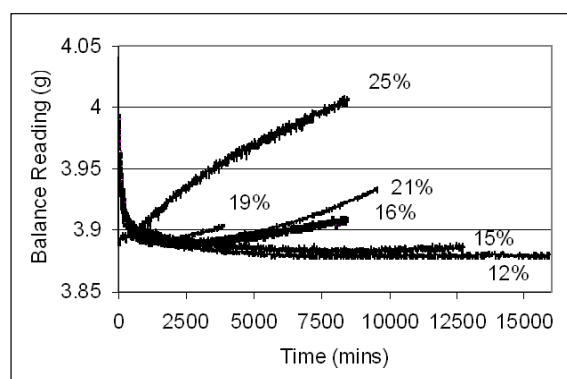

Figure 9 *Weight changes of β-FeOOH /iron mixtures at 12%, 15%, 16%, 19%, 21%, 25% RH. All tests were conducted with 2.00 g of bFeOOH mixed with 2 g of iron powder.*

Summary of results for the iron/βFeOOH corrosion model

The following were determined:

• β-FeOOH contains surface-adsorbed chloride and water, possibly as HCl.
• β-FeOOH corrodes iron that is in contact with it.
• Corrosion of iron in contact with bFeOOH is detectable at 15% RH and is not detectable at 12% RH.

• The corrosion rate of iron in the presence of β-FeOOH increases appreciably as humidity rises above 20% RH.

DISCUSSION AND CONCLUSIONS

The results show that $FeCl_2·2H_2O$ does not corrode iron in contact with it. In contrast, iron in contact with $FeCl_2·4H_2O$ corrodes over the stability range of this corrosion product. The rate of corrosion increases with increasing RH. β-FeOOH corrodes iron in contact with it from 15% RH upwards, with increasing RH producing a faster corrosion rate.

Although iron in contact with ferrous chloride could be safely stored at 19% RH without any corrosion occurring, most archaeological iron objects have some β–FeOOH present on their surface, due to post-excavation corrosion. Since the iron/β-FeOOH corrosion model appears to have ceased to operate at 12% RH, all chloride contaminated archaeological iron should be stored at or below this RH to prevent corrosion. If RH exceeds this value, then over the range 15% to 20% RH β-FeOOH will determine the corrosion rate of chloride contaminated iron. Above 20% RH $FeCl_2·4H_2O$ will form and will also contribute to corrosion of iron. At 25% RH and above both the $FeCl_2·4H_2O$/iron and β-FeOOH/iron corrosion reactions progress at an appreciable rate and speed up, at least initially, as RH rises. Even if RH cannot be kept at a level where corrosion ceases, it is advantageous to keep

it as low as possible to reduce the rate of corrosion. While it is essential to store iron objects with a metal core in this way, totally mineralized objects can be stored in high humidity environments, as there is no more iron left to oxidize and they should be stable [41]. The problem facing the conservator is to successfully identify such objects. Radiography remains the best guide.

Comparing the rate of corrosion for $FeCl_2 \cdot 4H_2O$/iron powder at 25% RH, with that of β-FeOOH /iron powder at the same RH (Figures 6 and 9), indicates that β-FeOOH corrodes iron significantly faster than $FeCl_2 \cdot 4H_2O$ at this low humidity. Corrosion of iron at low humidity has implications for chloride-contaminated iron stored in sealed plastic boxes whose internal microclimate is controlled by a desiccant. Small rises in their internal RH are difficult to detect, but may be sufficient to support the iron corrosion model studied here. Synergistic effects of $FeCl_2 \cdot 4H_2O$/β-FeOOH/iron mixtures have not been considered in this paper. It may be that the corrosion rate is greater than the sum of the individual corrosion rates when both compounds are present. Work on this is currently being prepared for publication along with investigations into the effect of fluctuating RH on corrosion rate and deliquescence of $FeCl_2 \cdot 4H_2O$.

To gain quick results, the experiments reported here represent worst case scenarios. Experimental design produces large surface areas of metal in contact with quantities of $FeCl_2 \cdot 4H_2O$ and β-FeOOH that far exceed what might be expected on the surface of archaeological objects. This emphasizes the aggressive tendencies of the reactions examined. In reality, damage may be more localized and corrosion rates slower, although ultimately cleavage at the metal/corrosion layer interface will occur.

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