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Effects of relative humidity on the corrosion of iron: an experimental view

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Summary The storage of archaeological iron is a problem for museum collections, but a relative humidity (RH) of 12% has been reported to be the critical level to keep iron stable. However, it requires significant effort and expense to achieve and maintain storage conditions with such low RH levels.

Experimental tests on the effects of RH on the corrosion of iron were carried out and the results are reported. Powdered iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and iron foils with powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ applied to the surface were exposed at different RH levels, including 75, 54, 44, 33 and 23%, at room temperature for over a year. Changes in these tested materials were identified using microscopy, Raman spectroscopy, X-ray diffraction and ion chromatography.

The iron(II) chloride powder liquefied and the formation of akaganéite ($\beta\text{-FeOOH}$, a symptom of the deterioration of iron) occurred within hours at 75% RH and within a month at 54% RH. Deliquescence did not occur in the powder exposed at 44% RH and below over the period of a year, although akaganéite was detected in these samples. Pitting was observed on the tested foils after one week at 75% RH. It was observed under the microscope within a month and was visible without magnification after six months at 54% RH. Pitting was hardly observed on the foils exposed at 33% RH or below after exposure for one year.

Akaganéite also formed on the control foils indicating that akaganéite found on archaeological iron could be formed with little chloride present in the objects. The morphology and composition of the corrosion depends mainly on the RH levels, although the surface condition of the objects also has an effect. The elongated crystalline akaganéite often found on archaeological iron was probably formed at RH levels of 50–60%, while at higher RH levels akaganéite was formed as 'bubbles'. These findings indicate that keeping iron at RH levels below 35% can slow deterioration significantly.

INTRODUCTION

In the British Museum, the collection of archaeological iron covers all periods from the Iron Age to the post-Mediaeval. A small proportion of unstable metalwork including archaeological iron is, at present, kept in two dedicated dehumidified stores, while the majority of iron objects are in storage areas with no environmental control; in these latter locations some deterioration of some objects has been evident.

The formation of akaganéite ($\beta\text{-FeOOH}$) has been recognized as a major symptom of post-excavation deterioration for archaeological iron, although other corrosion products such as goethite ($\alpha\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$) may also form after excavation.

Investigation of deterioration of archaeological iron in the Museum collection indicated that no single method of conservation treatment, including desalination using alkaline sulphite solutions, has prevented corrosion for every object [1]. Objects stored in sealed boxes with silica gel

desiccant are, in general, in better condition than those located in storage cupboards without silica gel, suggesting that humidity is a major contributor to corrosion. Some objects kept in uncontrolled environments have deteriorated badly and disintegrated, Figure 1.

Removing chloride from iron objects and keeping them in dry storage are currently the two predominant approaches in the conservation and preservation of archaeological iron [2–8]. Keeping iron in controlled environmental conditions is considered a better practice because complete desalination is difficult to achieve and the procedure can result in the uncontrolled removal of evidence preserved in corrosion products [9].

Experiments have been carried out to establish a critical RH level for long-term preservation of archaeological iron.

Experiments by Turgoose revealed that in three months at RH levels below 55% no reaction occurred to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ alone, and that the formation of akaganéite occurred in



FIGURE 1. Anglo-Saxon sword GR93/1066 excavated at Broadstairs, Kent in 1974 stored in an uncontrolled environment, showing disintegration

two months in the mixtures of powdered iron and iron(II) chloride at a RH as low as 20% [10]. A similar, but more detailed study by Thickett, using mixtures of powdered iron with iron(II) chloride and other corrosion products such as copper(I) chloride or goethite, determined that 18% was the critical RH level [11]. A recent study by Watkinson and Lewis, again using powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and iron, recommended 12% as the allowable RH for long-term storage of archaeological iron with chloride present [8]. However, in reality, keeping iron in storage at such a low level of RH can be an expensive option and presents considerable practical challenges.

The corrosion of an iron object comprises one or more reactions between its surface and the corrosive materials in the environment; as such it differs from the reaction between the powdered materials used in the experiments mentioned above. In the research reported here, experimental tests on the effects of RH on the corrosion of iron were carried out using two types of iron foils: modern industrial rolled iron and wrought iron produced by a modern smith. These were tested in contact with powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as a source of chloride to simulate corrosion of archaeological iron more closely. The reason for using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in these experiments, rather than an alternative source of chloride ions, was that $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is often found on excavated iron objects [12–14]. All the experiments reported here were carried out at room temperature in order to establish a realistic RH level for storage of archaeological iron.

EXPERIMENTAL

The five levels of RH used in the experiments were 23, 33, 44, 54 and 75%; these were achieved by using saturated aqueous salt solutions in sealed chambers [15]. The RH was monitored using Testo thermohygrometers, which showed a variation of RH at each level of about $\pm 5\%$, although this could be greater when the chamber was opened on a very humid or dry day. Two combinations of materials, powdered iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) alone, and iron foils with powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ applied to the surface, were tested in the experiments.

Powdered iron(II) chloride

The powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was spread in a weighing boat and placed in a humidity chamber. It was weighed after one, two and seven days, after one month and then at monthly intervals. The powder was examined using Raman spectroscopy when visible changes were observed. Three samples at each RH level were tested to improve the consistency of the results. The experiments were conducted over a year at 75 and 54% RH and over two years at the lower RH levels.

Iron foils covered with iron(II) chloride

Two types of iron foil – industrial iron and wrought iron – were used in the experiment. The industrial iron foil was ‘as-rolled’, with a smooth surface, a purity of 99.5% and traces of manganese, silicon, carbon, phosphorus and sulphur. The wrought iron was produced from modern recycled iron, which was forge welded and finally rolled; it had a rough surface and a heterogeneous composition. The samples of both foil types used in the experiments were 25×25 mm and 1 mm thick.

The experimental procedure for both types of iron foils, each covered with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, was as follows. The foils were degreased with propanone and then placed in a desiccator for one day before the experiments started. The foil was put on a piece of microscope slide for easy handling and weighed. Powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0625 g) was spread on the surface of the foil as evenly as possible, covering approximately half of the surface area, giving a ‘concentration’ of the chloride of approximately 0.02 g.cm^{-2} . The foils covered with powder were placed on a tray in each RH chamber and samples of both types of foil without chloride powder were included in each chamber as controls. Prior to use in the experiments, the wrought iron foils were cleaned in 20% sodium hydroxide containing 200 g.L^{-1} of zinc dust to remove the corrosion products [16].

After each exposure period was complete, all the foils were weighed and examined, and any change in appearance of the chloride powder or metal was analysed by Raman spectroscopy. The corrosion products were then removed with sodium hydroxide solution containing zinc dust and the

remaining metal was re-weighed and the iron substrate was investigated. The experiments with the foils lasted six months at 75 and 54% RH and one year at lower RH levels.

The corrosion products were examined by stereomicroscopy, Raman spectroscopy and X-ray diffraction (XRD). The chloride ion content in the corrosion products formed on the control samples was determined using ion chromatography; the experimental details for each technique are described elsewhere [1].

RESULTS AND DISCUSSIONS

Powdered iron(II) chloride

At 75% RH, the formation of akaganéite bubbles occurred within hours, and the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powder had completely liquefied within three days, Figure 2. The mass of the samples increased rapidly over the first seven days of exposure but decreased thereafter. After five months the samples

seemed to have reached equilibrium, and little further change in mass was recorded, Figure 3. This was due to the formation of a film on the surface which prevented the liquid underneath from absorbing more moisture and oxygen.

At 54% RH, some of the chloride powder turned yellow and a droplet of akaganéite formed after three weeks of exposure. Formation of akaganéite was quite apparent after a month and almost complete within three months. The mass of the samples increased sharply between one and two months and more slowly until the fifth month, after which the mass began to fall, Figure 3.

At 44% RH, the chloride powder became yellow after six months of exposure. Raman analysis showed that some of the powder had changed to akaganéite. The formation of akaganéite, identified by Raman spectroscopy, occurred after ten months at 33 and 23% RH. At RH levels of 44% and below, the chloride stayed as a powder throughout the experiment and little change in mass occurred. Table 1 provides a summary of the experimental results for the samples containing iron(II) chloride powder.

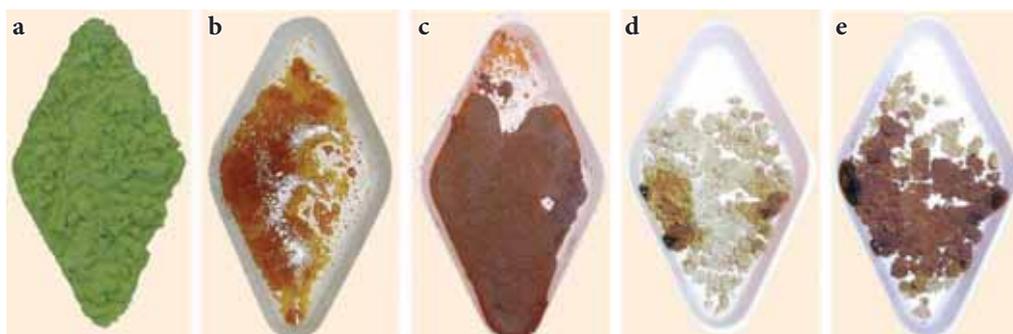


FIGURE 2. Powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ exposed at different RH levels for increasing lengths of time: (a) raw material; (b) exposed at 75% RH for three days; (c) exposed at 75% RH for one year; (d) exposed at 54% RH for one month; (e) exposed at 54% RH for three months

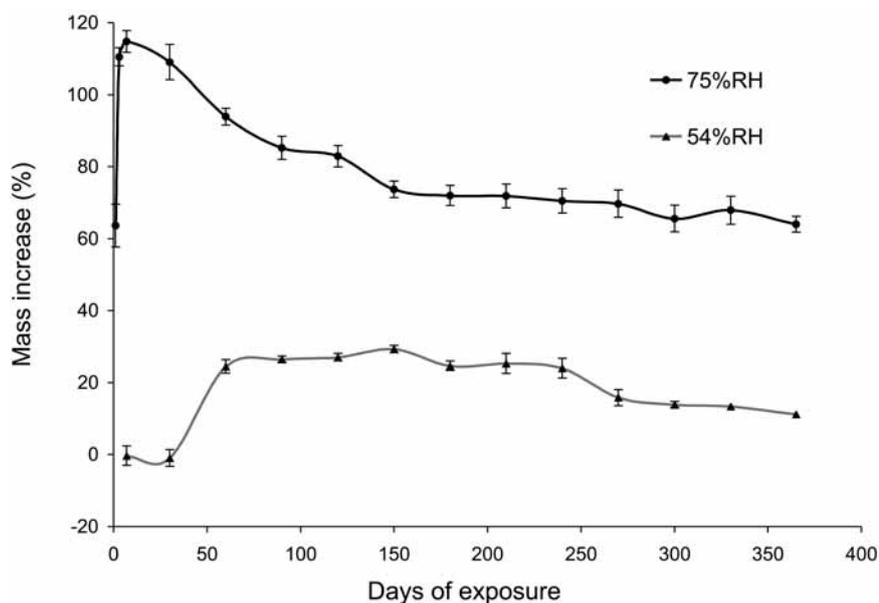


FIGURE 3. Mass increase in $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with time at 75 or 54% RH

TABLE 1. Time after which akaganéite formed in $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powder (formation indicated by an 'x')

RH (%)	1 week	3 weeks	6 months	10 months
75	x	x	x	x
54		x	x	x
44			x	x
33				x
23				x

Iron foils covered with iron(II) chloride

At 75% RH, corrosion was apparent on both types of foils within three days. After one week, the control samples were largely covered with brown rust. The chloride powder on the foil liquefied and brown corrosion, a black film and yellow bubbles formed on the foil surface, Figure 4. The brown corrosion and the yellow bubbles were identified as akaganéite by Raman spectroscopy and, although it was not identified by Raman spectroscopy, the black film was identified as a mixture of FeOCl and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ by XRD. The Raman spectrum of the dark brown rust on the control showed a broad peak at 710 cm^{-1} .

After three months at 75% RH, the foil covered with iron(II) chloride was fully covered with corrosion (Figure 4)

and the corrosion even spread onto the back of the foil. The black material on the industrial iron was identified as magnetite by XRD and the black film on the wrought iron was identified by Raman spectroscopy as a mixture of akaganéite and magnetite. The rust on the industrial foil control sample contained a mixture of goethite, akaganéite and lepidocrocite, while the rust on the wrought iron control sample was denser and the main component was identified as lepidocrocite by Raman spectroscopy.

After six months, the morphology of the corrosion at 75% RH, as well as at other RH levels, was similar to that seen after three months of exposure. The black film on the industrial iron was identified as akaganéite by Raman spectroscopy and XRD, as was the brown patch. The corrosion on the wrought iron control was more homogeneous and denser than that on the industrial iron control.

Once the corrosion had been cleaned off, pitting was visible on the area of foil covered by the chloride powder in the sample exposed for one week. Pitting increased with time of exposure and was so severe after three months that both the industrial and the wrought iron were corroded through their entire depth, Figure 5. The appearance of the surfaces of the metal foils exposed at each RH is summarised in Table 2.

At 54% RH, brown rust was noted on both control foils after three days and covered the entire foil within one

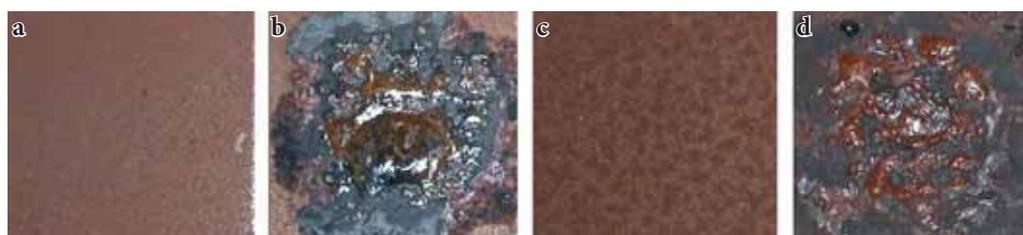


FIGURE 4. Samples exposed at 75% RH for one week: (a) control (industrial foil); (b) industrial iron foil covered with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. Samples exposed at 75% RH for three months: (c) control; (d) foil covered with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

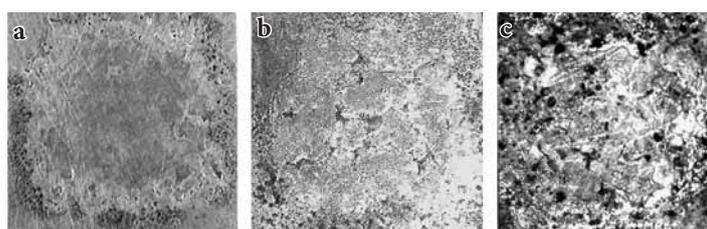


FIGURE 5. Industrial iron foils covered with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ showing pitting after exposure at 75% RH for (a) one week; (b) four weeks; (c) three months

TABLE 2. Summary of pitting corrosion on the iron foils covered with iron(II) chloride powder, exposed to variable RH levels; after cleaning

RH (%)	1 week		4 weeks		3 months		6 months	
	Industrial iron	Wrought iron	Industrial iron	Wrought iron	Industrial iron	Wrought iron	Industrial iron	Wrought iron
75	visible	visible	visible fracture	visible loss of metal	penetration	penetration	deep pitting	penetration
54	macroscopic	macroscopic	macroscopic	macroscopic	macroscopic extensive pitting	worse than industrial iron	severe pitting	severe pitting
44	–	–	–	–	macroscopic	macroscopic	macroscopic	macroscopic
33	–	–	–	–	–	–	pitting was hardly seen	pitting was hardly seen
23	–	–	–	–	–	–	–	–

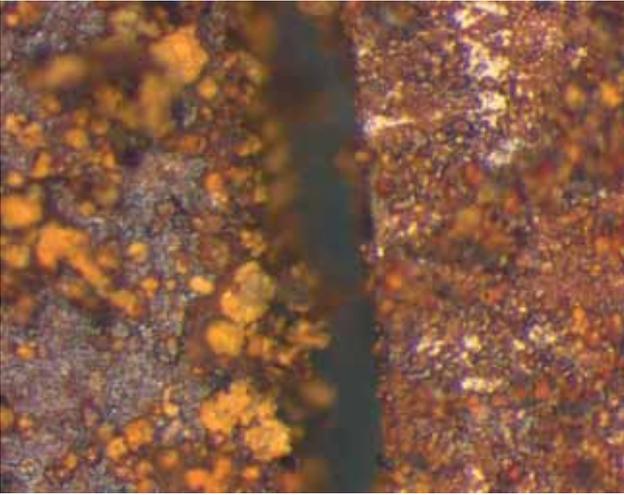


FIGURE 6. Stereo microphotograph of the control industrial foils at 75% RH (right) and 54% RH (left) after four weeks of exposure, showing different corrosion morphology at these two RH levels. Image width: 1.75 mm

week. The Raman spectrum of the brown rust formed on the control showed a broad peak at 710 cm^{-1} , consistent with the spectra for the material on the foils exposed at 75% RH. After four weeks, the control sample was completely tarnished and the number of yellow particles increased. The yellow particles were identified as akaganéite by both Raman spectroscopy and XRD. It is interesting that after a given period the control samples exposed at 54% RH were more highly corroded than those exposed at 75% RH. This was confirmed by stereomicroscopy, Figure 6; the yellow particles were identified as akaganéite. The source of chloride was probably from both the ambient environment and the chloride powder used in the experiment. Pitting of the foils was observed under the microscope within a week but was not apparent to the naked eye until after six months.

At 44, 33, and 23% RH, the iron(II) chloride powder had changed colour after four weeks. It partially converted to akaganéite (identified by Raman spectroscopy) even at 23% RH and the yellow film underneath the powder was also identified as akaganéite. However, the metal itself did not show pitting, which suggests that the akaganéite formed as the result of reaction of the iron(II) chloride with oxygen and moisture rather than a reaction of the iron substrate,

although the iron could have acted as a catalyst. After three months, slight pitting was observed under the microscope on the foils exposed at 44% RH (Table 2), although it was not visible to the naked eye.

ATMOSPHERIC CORROSION OF IRON

The rust formed on the control foils contained yellow particles and dark corrosion matrix. The yellow corrosion particles were identified as akaganéite by Raman spectroscopy. The compact dark corrosion again has a broad peak at 710 cm^{-1} in its Raman spectrum. This species is probably one of the ferrihydrates, which are not particularly crystalline and for which the general formula is not yet known [17].

To investigate the significance of atmospheric corrosion of iron, iron foils alone were tested in two humidity chambers held at 54% RH; one was well sealed to limit access to oxygen and the other had two small 5 mm diameter holes at the top. The results showed that the foil in the well-sealed chamber was less corroded than that in the chamber with two holes, Figure 7. This suggests that atmospheric corrosion can play an important part in the deterioration of iron. The formation of akaganéite on the control foils was difficult to understand because no source of chloride ions was deliberately placed in the chamber. This suggests that the ambient environment can be the source of chloride ions.

The corrosion products formed on the control foils of industrial and wrought iron were collected for chloride analysis using ion chromatography. The foils were cleaned and examined, and the results are shown in Table 3. The chloride ion contents in the corrosion formed on the foils exposed at 54% RH were higher than those from the material that formed on the foils exposed at 75% RH. This agrees with the microscopic observations and the identification of the corrosion products by Raman spectroscopy and XRD, i.e. the corrosion on the foils exposed at 54% RH was mainly akaganéite, and the corrosion on the foils exposed at 75% RH comprised a mixture of goethite, akaganéite and lepidocrocite.

The formation of akaganéite on the control foils suggested that some akaganéite found on archaeological iron in the



FIGURE 7. Stereo microphotograph of three control foils after four weeks exposure at 54% RH: (a) industrial iron in a sealed chamber; (b) wrought iron in a sealed chamber; (c) industrial iron in a chamber with two holes. Width of each image: 3.5 mm

TABLE 3. Appearance of the control foils and the Cl⁻ ion contents in the corrosion products formed on the foils after six months of exposure at 75 and 54% RH

Foils	RH (%)	Appearance after cleaning	Cl ⁻ (Wt%)	RSD%
Wrought iron	75	no obvious pitting	0.231	2.722
Industrial iron	75	patterned pitting due to microstructure	0.177	0.696
Wrought iron	54	macroscopic extensive pitting	3.839	0.371
Industrial iron	54	pitting without a pattern	2.580	0.071

RSD: relative standard deviation

Museum collection might not be due to chloride present in the objects; it could be a result of atmospheric oxidation. Furthermore, the elongated crystals of akaganéite formed on the control foils at 54% RH are very similar to those normally found on archaeological iron in the collection, suggesting that the latter were likely to have formed at RH levels between 50 and 60%. The akaganéite bubbles found on archaeological iron were more likely to be formed at higher RH levels. It has been reported that the critical RH for FeCl₂·4H₂O is 55.9% at 25°C, the RH at which the water in contact with FeCl₂·4H₂O is saturated with iron(II) chloride [18]. Tests using untreated archaeological nails also confirmed that at 54% RH elongated akaganéite crystals dominated, while at 75% RH akaganéite bubbles dominated in the freshly formed corrosion products, but this influence of RH level on the corrosion morphology needs further study.

Influence of surface condition on iron corrosion

A difference in the appearance of the rust was observed on the wrought iron and industrial iron control samples exposed at 54% RH, Figures 7 and 8; the wrought iron was more corroded than the industrial iron. Akaganéite was detected in the iron(II) chloride powder on the wrought



FIGURE 8. Stereo microphotograph of control foils exposed at 54% RH for six months, showing akaganéite formed on the industrial iron (left) was less developed than that formed on wrought iron (right). Image width: 3.5 mm

iron exposed for a week, while it was not detected on the industrial iron exposed under the same conditions and for the same period. After three months of exposure, it became more apparent that the corrosion morphology was different on the industrial iron control from that on the wrought iron control when both were exposed at 54% RH. The same difference was also observed for the control foils exposed at 75% RH. This is probably due to the uneven surface of the wrought iron on a microscopic scale. Corrosion of iron is an electrochemical process, and corrosion rate is determined by diffusion of the reactant ions, which can be affected by the surface condition of the metal [19]. The rust that developed on the control samples of both types of iron at 54% RH was identified by Raman spectroscopy as akaganéite. However, the crystals of akaganéite were more developed on the wrought iron than on the industrial iron foil. After six months of exposure, the akaganéite on the wrought iron control sample was further developed and in the typical elongated crystalline form that is often seen on archaeological iron, Figure 8. The influence of surface condition was also proven by the mass loss of the foils, discussed below.

Rates of corrosion

The corrosion rate can be evaluated by the mass gain of the iron foils covered with iron(II) chloride, or the mass loss of the foils alone after they were cleaned. The mass gain at different RH levels is shown in Figure 9 and the mass loss of the foils alone shown in Figure 10. The mass gain and the mass loss show a similar trend, although there are small differences in the figures at each RH level. The mass gain is very useful in evaluating the deterioration rate of archaeological iron objects because mass loss cannot be measured for archaeological objects without causing damage.

The mass loss of the foils versus time is shown in Figures 11 and 12. At 75% RH, the industrial iron foils were more corroded than the wrought iron for each exposure period, except after one week, Figure 11. At 54% RH, the wrought iron was more corroded than the industrial iron, a pattern repeated at lower RH levels, Figure 12. The rough surface of the wrought iron (compared to the smooth industrial foil) is probably the major factor contributing to a greater degree of corrosion. However, at 75% RH, the rapid corrosion that caused pitting of the industrial iron foil could have accelerated its deterioration. The mass loss of the foils was nearly

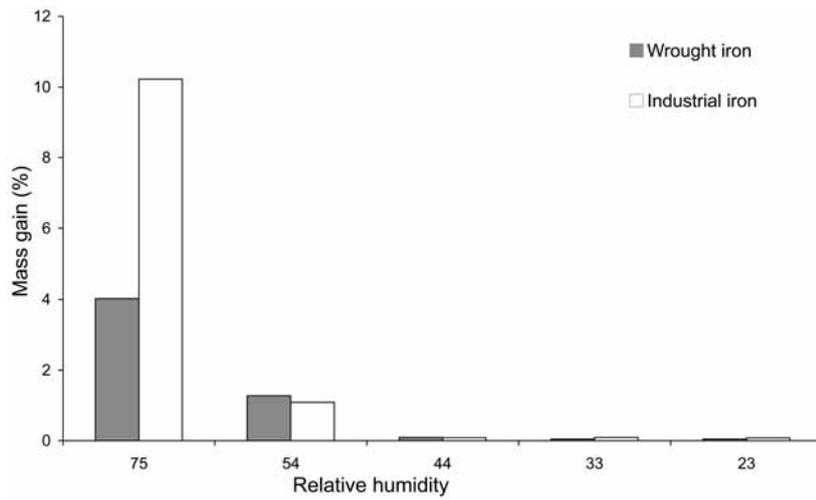


FIGURE 9. Mass gain of the two types of iron foil covered with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ exposed to different RH for six months

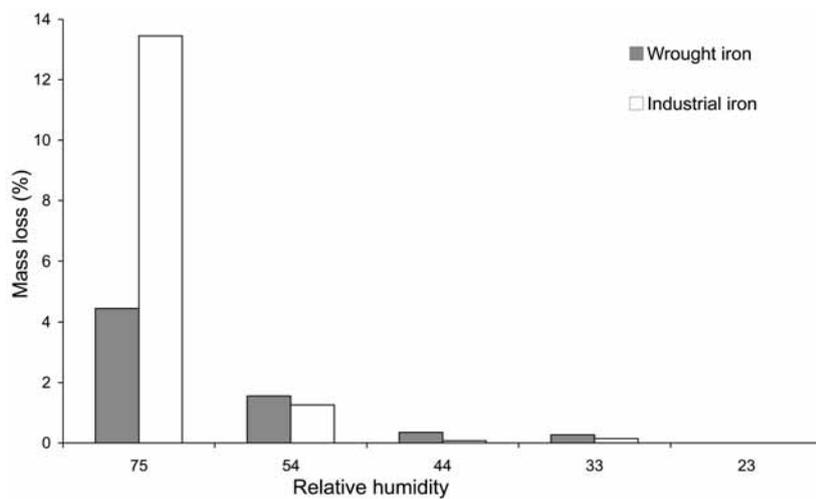


FIGURE 10. Mass loss of the two types of foils exposed at different RH for six months

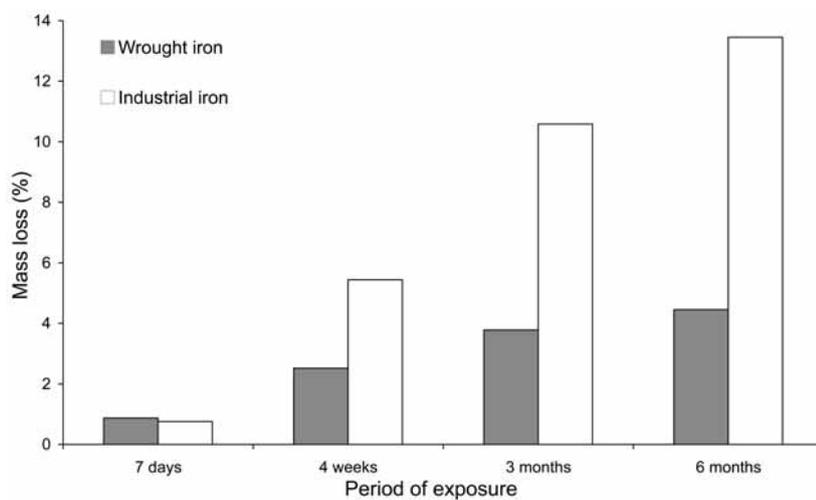


FIGURE 11. Mass loss of the foils exposed at 75% RH versus time

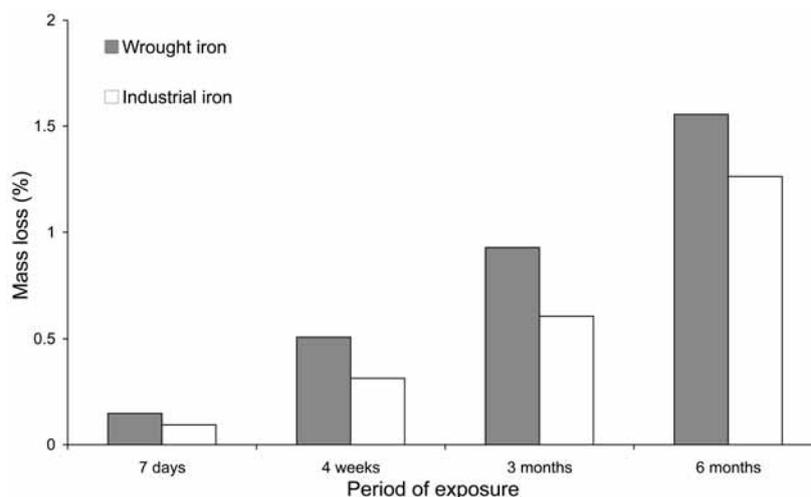


FIGURE 12. Mass loss of the foils exposed at 54% RH versus time

14% at 75% RH and 1.6% at 54% RH after six months of exposure, but even after one year of exposure, was less than 0.4% at RH levels of 44% and below.

CONCLUSIONS

Experiments on iron(II) chloride powder were carried out for a year at 75 and 54% RH and two years at the lower RH levels. It was found that the formation of akaganéite bubbles occurred within hours at 75% RH and within a month at 54% RH. Akaganéite was also detected in the powder after six months at 44% RH and after ten months at 33% RH, although the powder had not liquefied and its mass was still decreasing.

Experiments on iron foils covered with iron(II) chloride were carried out for six months at 75 and 54% RH and one year at lower RH levels. At 75% RH, pitting was visible on the foil after one week and the metal sample, which was 1 mm thick, was corroded throughout its depth after a three-month exposure. Severe pitting was observed on the foils exposed at 54% RH for six months. Corrosion was not obvious on the foils exposed at 44% RH and below, although the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powder was partially altered to akaganéite.

The wrought iron, with its rough surface, was more corroded than the industrial iron foil with a smooth surface at all RH levels except 75%, which suggests that surface conditions have an impact on the corrosion rates.

The experiments indicated that elongated crystalline akaganéite probably forms at RH levels of 50–60%, and the akaganéite bubbles found on archaeological iron form at higher RH levels. The elongated crystalline akaganéite formed on the control foils exposed at 54% RH indicates that similar crystals formed on archaeological iron could be the result of atmospheric oxidation, even if there is little chloride in the objects. The experimental results suggest that keeping archaeological iron objects in sealed containers

with RH levels below 35% can slow down their deterioration significantly.

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MATERIALS AND SUPPLIERS

- Industrial iron foils: Goodfellow Cambridge Limited, Huntingdon PE29 6WR, UK. Email: info@goodfellow.com
- Wrought iron: the wrought iron used in these experiments was provided by Peter Crew of the Snowdonia National Park Study Centre, Maentwrog, Blaenau Ffestiniog, Gwynedd LL41 3YU, UK

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