

KEEP COOL? DEEP-FREEZE STORAGE OF ARCHAEOLOGICAL IRON

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Abstract

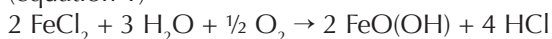
Post excavation corrosion of archaeological iron can cause severe damage to iron artifacts, particularly due to the formation of akaganéite. In this study, powder test samples of a 1:1 mixture of iron and iron(II) chloride tetrahydrate were stored at -23°C ($\pm 3^{\circ}\text{C}$) and at room temperature, 21°C ($\pm 3^{\circ}\text{C}$), to test whether storage at low temperature could inhibit corrosion. The oxidation of a synthetic iron and iron(II) chloride tetrahydrate mixture to form akaganéite, $\beta\text{-FeO(OH)}$, mimics the reactions that take place during post excavation corrosion of archaeological iron. The formation of akaganéite was observed by Fourier transform infrared (FTIR) spectroscopy on the test samples over a period of two and a half years. Compared to the test samples that were stored at room temperature, the conversion of the initial compounds appears to be delayed at -23°C ($\pm 3^{\circ}\text{C}$), but slow conversion is clearly visible. This study demonstrates that storage of archaeological iron artifacts at -23°C ($\pm 3^{\circ}\text{C}$) does not appear to completely inhibit post excavation corrosion.

Keywords: archaeological iron, storage, corrosion, akaganéite, FTIR spectroscopy, deep-freeze storage

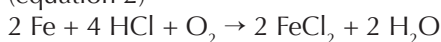
Introduction

The post excavation corrosion of archaeological iron artifacts can be described as an autocatalytic cycle by the following reaction equations:

(equation 1)



(equation 2)



Charge-balancing chloride ions from the surrounding soil are attracted by dissolved ferrous ions near the metallic iron core. This reaction results in the formation of an acidic solution of ferrous chloride in pores and cracks within the corrosion layer near anodic areas. Excavation leads to desiccation of the object and facilitates the access of oxygen to the metal enabling further oxidation to ferric ions and precipitation as the chloride containing phase akaganéite, $\beta\text{-FeO(OH)}$. The increase in volume and vertical crystal growth associated with the formation of akaganéite at the metal/corrosion interface can cause spalling of the corrosion crust, which may contain valuable information, such as the original surface of an object, decoration or tool marks. The hydrochloric acid formed in equation 1 promotes further dissolution of ferrous ions and sustains the corrosion cycle as long as oxygen, water and iron are available. (Turgoose 1982, Selwyn et al. 1999, Scott and Eggert 2009)

The corrosion process described can generate the formation of noticeable amounts of akaganéite within days after excavation in uncontrolled storage conditions.

In order to inhibit post excavation corrosion, both active and passive conservation strategies can be implemented. Various studies have shown that the extraction of chloride ions from the corrosion layers of iron artifacts significantly improves the stability of these objects; as demonstrated, for example, by Keene and Orton (1985). No desalination treatment for the extraction of chloride ions from corrosion layers is known to be 100% efficient. However, treatment in oxygen-free solutions of sodium hydroxide, often employed as the well-established alkaline-sulphite desalination method, show particularly good chloride extraction efficiency (North and Pearson 1975, Rinuy 1979, Selwyn and Logan 1993, Watkinson 1996, Al Zahrani 1999). As the formation of akaganéite proceeds, lower extraction efficiencies and longer treatment times have been reported (Gilberg and Seeley 1982). As a consequence, it is necessary to either start desalination immediately after excavation, or prevent post excavation corrosion using suitable storage systems.

Watkinson and Lewis (2004) have shown that storage below 12% relative humidity (RH) is effective in preventing post excavation corrosion. This level can be reached by packing objects with a desiccant or moisture and oxygen absorbers as tested by Guggenheimer and Thickett (2008). During storage, special packing materials with low permeability for water vapour and/or oxygen such as ESCAL must be used. The major problem with these storage systems is the need to regularly monitor the artifacts and storage conditions and replace packing materials.

Deep-freeze storage at temperatures around -20°C has been applied for decades in several museums and conservation laboratories to store excavated iron artifacts. An example includes approximately 16 tons of excavated iron stored in a deep-freeze chamber of the Landesdenkmalamt Baden-Württemberg in Esslingen, Germany. Several authors have hypothesized that storage of archaeological iron at deep-freeze temperatures would achieve stability. However, systematic studies to confirm these statements have never been conducted (Born 1982, Scharff and Blumer 1994, Costain 2000, Greiff and Bach 2000).

The Arrhenius equation describes the dependence of the reaction rate constant on temperature and is the background for the simplified rule that the reaction rate is doubled by an increase in temperature of 10°C (Atkins 1993). Thus, slowing down of post excavation corrosion processes could be expected at deep-freeze temperatures. Nevertheless, the corrosion of iron meteorites (Buchwald and Clarke 1989)^[1] and iron building components of expedition huts in Antarctica (Hughes et al. 2002), follow the same mechanisms as post excavation corrosion, raising doubts about the long-term stability of archaeological iron in deep-freeze storage.

Objectives

In the present study, the reaction of post excavation corrosion was simulated at different temperatures to answer the following questions:

Can deep-freeze conditions (around -20°C) inhibit post excavation corrosion of archaeological iron finds? Is deep-freeze storage of iron artifacts acceptable as a short or long-term conservation storage option?

Experimental

Experimental procedure

Thirty test samples were prepared by mixing equal weights of synthetic iron powder and iron(II) chloride tetrahydrate. The samples were stored in a defrost-free Liebherr Elektronik freezer at -23°C ($\pm 3^{\circ}\text{C}$). One test sample was stored at room temperature of 21°C ($\pm 3^{\circ}\text{C}$)^[2]. Glass containers were used to house the test samples during the experiment. To exclude dust while allowing air circulation, the containers were sealed with pieces of cotton wool only^[3].

Instrumentation

To observe the transformation of the test samples, FTIR spectroscopic measurements were carried out using a Bruker Vertex 70 IR-spectrometer. Measurements included 16 scans in a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} with a 4 cm^{-1} resolution. All measured spectra were modified with a baseline correction using the standard setting of Brukers optics user software, before further evaluation.

Calibration

The IR-spectrum of akaganéite shows a specific

absorption band at 852 cm^{-1} , which is not overlaid by bands caused by the initial test sample compounds (see Figure 1) (Cornell and Schwertmann 1996, Thickett 2003)^[4]. The intensity of this peak can be used for a quantitative evaluation of the akaganéite content in a sample (Zeeh 2005).

Akaganéite was synthesised by the thermal hydrolysis of a 0.1 M ferric chloride solution at 70°C for 48 hours following Cornell and Schwertmann (1996). A calibration line was created by measuring pellets with known amounts of synthetic akaganéite and potassium bromide following Thickett's protocol (Thickett 2003). Spectra of these measurements showed a significant band between 939.5 cm^{-1} and 789.5 cm^{-1} with a peak at 856.6 cm^{-1} . A slight overlapping of this band with another akaganéite band at lower wavenumbers can be observed (see Figure 2). Two calibration test series were produced, each starting with a pellet with a known akaganéite and potassium bromide content. After the first FTIR measurement, the pellet was split into two parts; one part was weighed, powdered again, mixed with a known amount of potassium bromide and pressed again for the next FTIR measurement. Each test series was conducted until the measured spectra showed no significant peak at 856.6 cm^{-1} (see Figure 2).

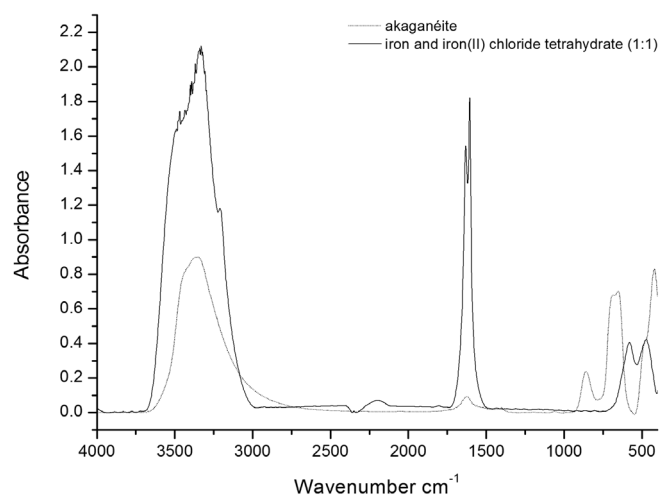


Figure 1. FTIR spectra of akaganéite and the initial powder mixture (ferrous chloride tetrahydrate and iron, 1:1)

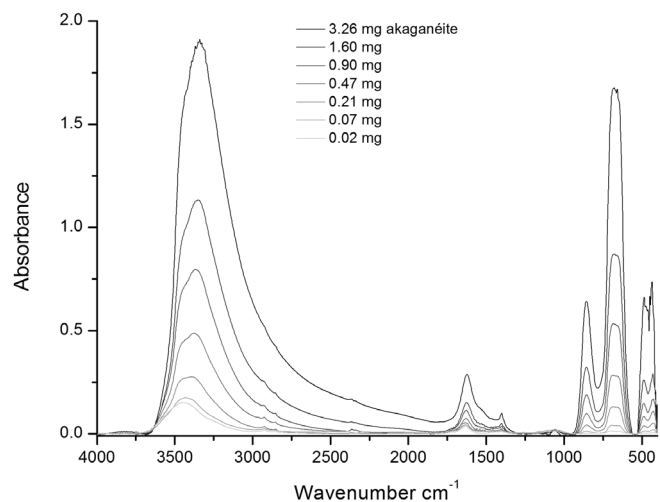


Figure 2. Spectra from one series of FTIR spectroscopic measurements used for the creation of a calibration line.

Calibration measurements with 0.07 mg and 0.12 mg of akaganéite in the pellet still showed a weak, but identifiable band in the significant area. The peak height at 856.6 cm⁻¹ was calculated by creating a straight line, at the intersection between the curve of the spectrum at 939.5 cm⁻¹ and 789.5 cm⁻¹. The height of this line at 856.6 cm⁻¹ was subtracted from the total absorption value at 856.6 cm⁻¹, thereby eliminating the background under the akaganéite peak (see figure 3). The calculated peak height at 856.6 cm⁻¹ was plotted against the weight of akaganéite in each pellet and a linear least-squares fit was used to create a calibration line (see figure 4)^[5].

Evaluation of test samples

Test samples stored in deep-freeze conditions were assessed with FTIR spectroscopy after 7, 25, 46, 131, 210, 417, 754 and 901 days. Test samples stored at room temperature were assessed in the same manner after 7, 25, 46, 131, 210 and 901 days. For analysis, one test sample from the freezer was removed at each date, weighed, ground with potassium bromide, pressed as three or four pellets, the pellets were weighed and analyzed. An amount of about 20 mg from the test sample stored at room temperature was removed at each date with a spatula and processed in the same manner

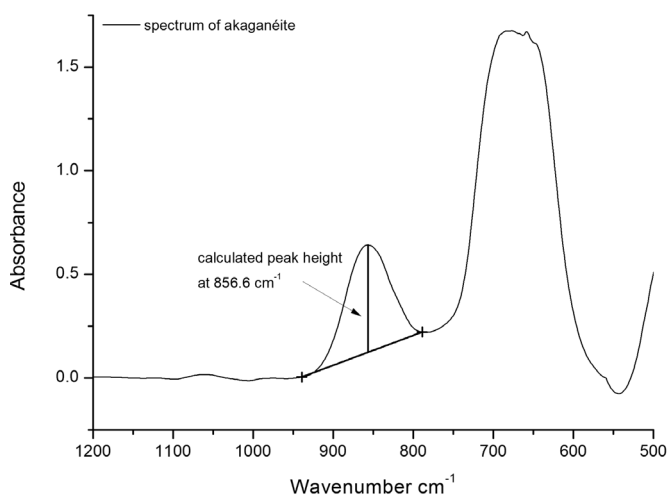


Figure 3. Method of calculating the peak height at 856.6 cm⁻¹ for the evaluation of calibration and test sample measurements.

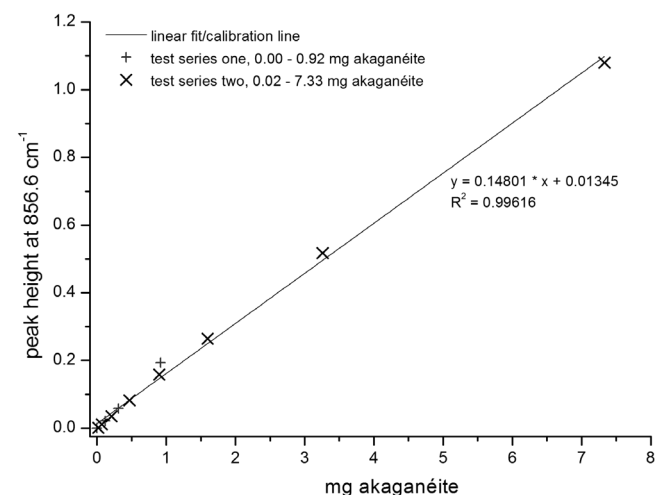


Figure 4. Calibration line.

^[6]. The weight of akaganéite in each pellet was determined using the calculated peak height at 856.6 cm⁻¹ and the equation of the calibration line. The percentage of akaganéite in the test sample was then calculated using its weight in the KBr pellet. Each pellet produced for this test contained between 1.54 and 8.00 mg test sample. Results of the FTIR analysis for all of the test samples is presented in Table I.

Results

The average content of akaganéite calculated in the test samples after a given period of time in storage is shown in Figure 5. The test sample stored at room temperature showed a significant akaganéite content of 6.18 % after seven days, which further increased during storage. The variation in the result after 131 days was not clear. After seven days, the powder had developed a rusty, orange brown colour, which seemed to intensify further after 25 days. No additional changes were observed during subsequent analysis.

In the test samples stored at deep-freeze temperatures, akaganéite was not detected before 754 days. However, when compared to the initial spectrum, slight changes could be observed in the spectrum of one measurement after seven days, and in all following spectra obtained

sample #	date of measurement	storage temperature (°C)	weight of test sample in pellet in mg	calculated peak height at 856.6 cm ⁻¹	calculated weight of akaganéite in pellet in mg	calculated wt% of akaganéite in test sample	mean value
1		-	5.08	0.00531	-0.05497	-1.08%	
2	22.06.2007 (0 days)	-	4.55	0.00265	-0.07299	-1.60%	-1.34%
3			3.33	0.03259	0.12935	3.88%	
4	29.06.2007 (7 days)	21	2.65	0.03861	0.16998	6.42%	6.18%
5			3.06	0.05079	0.25228	8.24%	
6			3.53	0.00311	-0.06985	-1.98%	
7	29.06.2007 (7 days)	-23	4.19	-0.04947	-0.42507	-10.15%	-4.55%
8			4.78	0.00260	-0.07330	-1.53%	
9	17.07.2007 (25 days)	21	3.78	0.09170	0.52870	13.99%	13.99%
10	17.07.2007 (25 days)	-23	3.53	-0.00200	-0.10438	-2.99%	-2.99%
11			3.50	0.17421	1.08616	31.03%	
12	07.08.2007 (46 days)	21	3.30	0.15783	0.97546	29.56%	30.46%
13			4.43	0.21530	1.36375	30.78%	
14			4.19	-0.02587	-0.26564	-5.35%	
15	07.08.2007 (46 days)	-23	4.78	-0.02121	-0.23416	-4.02%	-4.61%
16			5.73	-0.02438	-0.25556	-4.46%	
17			1.54	0.17692	1.10448	71.72%	
18	31.10.2007 (131 days)	21	2.00	0.20399	1.28737	64.37%	66.84%
19			1.97	0.20937	1.32371	67.19%	
20			1.98	0.20125	1.26884	64.08%	
21			4.06	0.00331	-0.06850	-1.69%	
22	31.10.2007 (131 days)	-23	2.89	0.00264	-0.07305	-2.53%	-2.04%
23			3.05	0.00310	-0.06994	-2.29%	
24			3.76	0.00419	-0.06254	-1.66%	
25			2.37	0.16954	1.05461	44.50%	
26	18.01.2008 (210 days)	21	2.36	0.16864	1.04853	44.43%	44.64%
27			2.61	0.18581	1.16452	44.62%	
28			2.98	0.21208	1.34200	45.03%	
29			4.25	0.00258	-0.07345	-1.73%	
30	18.01.2008 (210 days)	-23	3.91	0.00419	-0.06254	-1.60%	-1.53%
31			4.03	0.00401	-0.06379	-1.58%	
32			4.76	0.00483	-0.05824	-1.22%	
33			5.35	-0.00949	-0.15500	-2.90%	
34	12.08.2008 (417 days)	-23	3.98	0.00243	-0.07448	-1.87%	-2.20%
35			4.50	-0.00333	-0.11340	-2.52%	
36			5.05	0.00217	-0.07619	-1.51%	
37			4.61	0.02274	0.06279	1.36%	
38	14.07.2009 (754 days)	-23	6.54	0.03542	0.14843	2.27%	2.33%
39			5.23	0.03577	0.15081	2.88%	
40			8.00	0.04672	0.22480	2.81%	
41			4.42	0.32006	2.07158	46.87%	
42	08.12.2009 (901 days)	21	3.73	0.28557	1.83850	49.29%	47.68%
43			3.88	0.29951	1.93267	49.81%	
44			3.12	0.22010	1.39617	44.75%	
45			4.12	0.03407	0.13932	3.38%	
46	08.12.2009 (901 days)	-23	5.57	0.03933	0.17485	3.14%	3.28%
47			5.79	0.03916	0.17370	3.00%	
48			5.89	0.04469	0.21108	3.58%	

Table 1: Results for test sample measurements and their evaluation

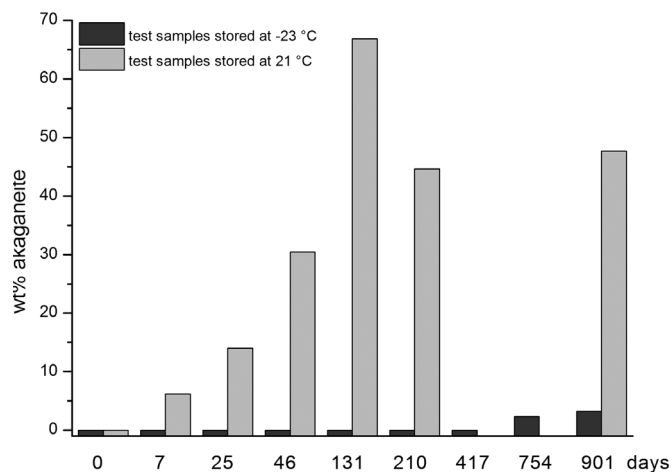


Figure 5. Graph of average akaganéite content (wt%) versus time (days) for powdered test samples exposed at -23°C (dark grey) and 21°C (light grey).

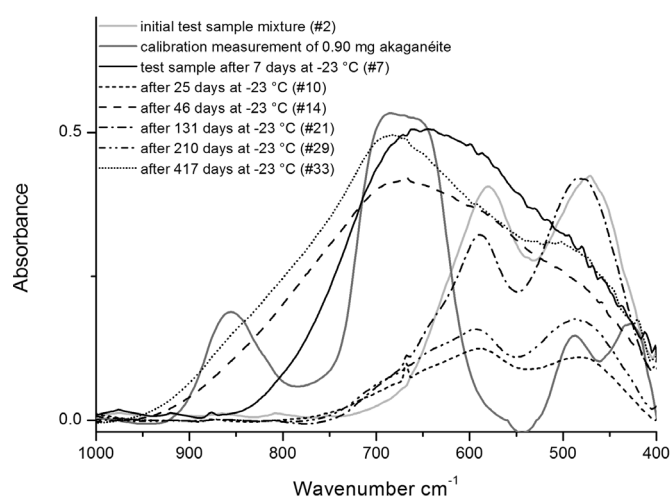


Figure 6. Details of the FTIR spectra of test samples after different periods of storage at -23°C (refer to Table 1).

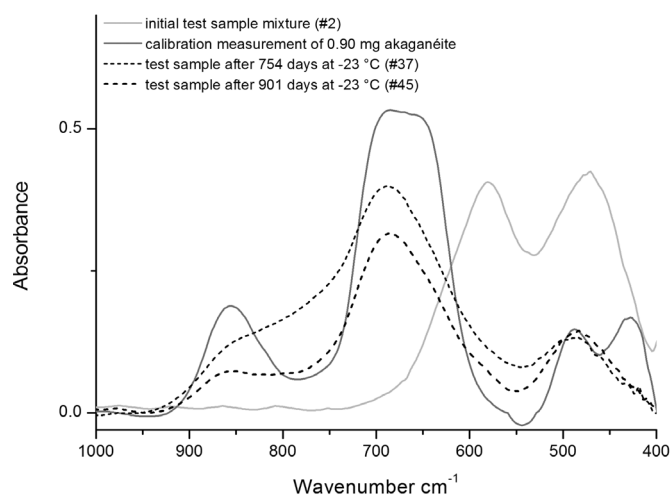


Figure 7. Details of the FTIR spectra of test samples after 754 and 901 days of storage at -23°C (refer to Table 1).

from test samples stored at -23°C , as shown in Figure 6. These spectra show a partial or complete fusion of the two initial bands at lower wavenumbers and a broadening of the absorption area between 950 cm^{-1} and

400 cm^{-1} . After 754 and 901 days, the typical akaganéite bands with peaks at 856.6 cm^{-1} and 680 cm^{-1} became clearly distinguishable in the spectra and akaganéite was clearly identified (see Figure 7). Earlier changes noted in the FTIR spectra are possibly due to an intermediate compound that could not be characterized.

No visible changes in the test samples stored in deep-freeze conditions were observed after seven days, but a slight color change to a more brownish shade was observable after 16 days. This change in colour seemed to gradually increase at each measurement after 25, 46, 131 and 210 days, but was still marginal, and seemed to be less reddish in colour compared to samples stored at room temperature. After 417 days the brown colour had clearly intensified. Until then, test samples stored in the deep-freeze appeared to be more moist than the reference sample, stored at room temperature. After 754 days, orange brown droplets — presumably an acidic solution containing iron chloride — had formed at the inner sides of the test sample containers stored in the deep-freeze. After 901 days the solution had dried and left an orange precipitate. Aside from this, the test sample powder showed a darker brown colour with a slight orange tint, and metallic iron particles could still clearly be observed in these particular test samples.

Conclusion

In reference to corrosion mechanisms occurring on archaeological iron, the experimental results of this study show that significant amounts of akaganéite can form within days in laboratory conditions of 21°C ($\pm 3^{\circ}\text{C}$). These reactions would cause visible changes to a real artifact. On test samples stored in deep-freeze temperatures of -23°C ($\pm 3^{\circ}\text{C}$), slight changes in colour and the IR spectra also indicate ongoing chemical reactions after only a few days. However, corrosion reactions are significantly delayed in deep-freeze storage conditions, as the formation of akaganéite was only detected after 754 days. Deep-freeze storage for archaeological iron may represent a short-term alternative to minimize post excavation corrosion between excavation and active treatment. However, this technique cannot be recommended as a long-term storage solution due to the increasing formation of akaganéite, as demonstrated in this study. Systematic observation of possible post excavation corrosion phenomena on real iron artifacts stored in deep-freeze conditions would be valuable to confirm the results of this study.

The method applied for the quantitative evaluation of FTIR spectroscopic measurements showed only limited applicability. Therefore, an exact comparison of reaction rates at different storage temperatures was not possible. The human eye proved to be a more sensitive detector of slight corrosion changes than FTIR spectroscopy, therefore systematic colour comparison of test samples using a colorimeter could also prove useful for further studies.

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Endnotes

[1] The average temperature in Antarctica is estimated at -30°C , but it has been observed that the temperature of meteorite surfaces may rise above the melting point of water for short periods. It is not possible to tell if the described corrosion phenomena are only due to this period of time above the melting point.

[2] The same amounts of test sample were stored in the freezer and at room temperature. For the storage in the freezer, several containers were used to avoid the removal of all test samples during sampling, which would have disrupted the storage schedule. A limited number of other chemicals (in closed containers) were stored in the freezer during the experiment. The freezer door was never opened for longer than 30 seconds.

[3] Access of air was allowed at both storage conditions, as only the influence of different temperatures on the corrosion reaction was assessed in this study. RH was not monitored during the experiment.

[4] All observable absorption bands in the spectra of the initial compounds can be ascribed to iron(II) chloride tetrahydrate, as metallic iron is not IR-active. Bands in the spectrum of iron(II) chloride tetrahydrate are observable in the area around 1600 cm^{-1} and above 3000 cm^{-1} and can be due to O-H-vibrations. Iron(III)-chloride, which can occur as an intermediate compound, also produces absorption bands in the range above 1400 cm^{-1} . Both compounds show specific bands only in the area of very low wavenumbers below 700 cm^{-1} . The akaganéite-specific band at 852 cm^{-1} can be ascribed to interactions of water molecules with the hollandite structure. Further bands in the IR spectrum of akaganéite are observable in the area of lower wavenumbers at 670 cm^{-1} and between 300 cm^{-1} and 500 cm^{-1} , which are caused by Fe-O-vibrations. Absorptions at wavenumbers around 3450 cm^{-1} are caused by OH⁻ and H₂O-stretching vibrations. Less intense bands at around 1615 cm^{-1} and 1400 cm^{-1} are caused by OH⁻ und H₂O-bending vibrations (Raman et al 1991).

[5] Akaganéite as well as iron(II) chloride tetrahydrate are hygroscopic. Minor influences of differing hydration at variable RH on weighing, and hence calibration, cannot be excluded. However, the intensity of bands, which

are caused by water in the calibration and test sample spectra, seem to depend on the intensity of other bands, which are caused by the hygroscopic compounds. Hence there seem to be no significant differences in hydration levels during the experiment.

[6] Measurements after 25 days were kindly undertaken by a colleague in Tübingen. Only one measurement of a test sample from each storage environment was conducted at this time.

Materials

Iron(II) chloride tetrahydrate, reagent plus 99 %
Sigma-Aldrich Chemie GmbH
Munich, Germany
Phone: +49 89 6513 0
Fax: +49 89 6513 1169

Iron(III) chloride hexahydrate, puriss. p. a. and potassium bromide, IR-grade
Fluka Chemie AG
Industriestrasse 25
9470 Buchs, Switzerland
Tel: +41 (0)81 755 25 11
Fax: +41 (0)81 756 54 49

Iron powder
Merck KgaA
Frankfurter Strasse 250
64293 Darmstadt, Germany
Tel: +49 6151 72-0
Fax: +49 6151 72 2000

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Q & A SESSION

David Thickett: A comment on the Infra-Red: I'm not 100% sure but that intermediate phase you were seeing looks like an amorphous iron corrosion product that was identified but not fully characterized by Raman in 1992 and I could pass that reference on to you if you thought that would be worth comparing.

Paul Mardikian: Did you measure the relative humidity at cold temperatures?

Charlotte Kuhn: We didn't measure it over the whole storage period but we did it one time and it was about 40% RH then in the freezer. The relative humidity will also depend on the freezing system you use, and if you store your objects in sealed containers or...

Jannecke Nienhuis: While doing your visual examination did you take your samples out of the freezer? And how does that influence your results?

Charlotte Kuhn: Yes, each time we conducted a measurement we took out only one sample from the freezer. There were several samples stored in the freezer so we always took one out, took the measurement and looked at them.

Jannecke Nienhuis: Ok, and you compared the ones that were still in the freezer and the ones that you took out with

each other? Did you see any difference in the results?

Charlotte Kuhn: Yes, we compared the ones we took out from the freezer to the picture we had from the initial test sample.

Jannecke Nienhuis: Ok thank you.

Gerhard Eggert: I was very surprised when we saw that even after a few days we could see something. And it turned out that your eye is much more sensitive than the Infra-Red spectrometer, so really could see a color difference. And so there is a possibility of using visual optical light control to see if your objects change, so there might be some value in that. So this is a very interesting point that you can see the changes with your own eyes, they are so sensitive to the color changes – more sensitive than your analytical instrument.