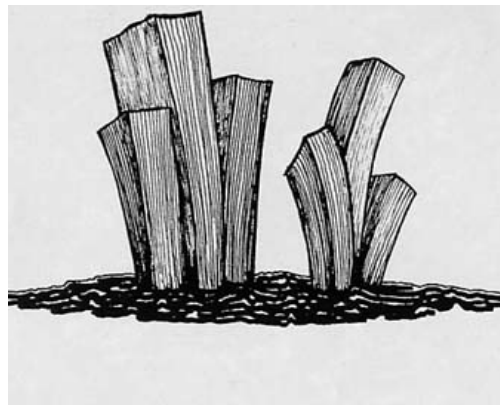


# Investigation into the Potential of Low-Oxygen and Dry/Cold Storage for Freshly Excavated Iron Artifacts



Thesis

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Illustrations title page:

Dry storage of archaeological metal at English Heritage, Centre of Archaeology, Fort Cumberland, Portsmouth, United Kingdom;

Diagram of vertically growing, voluminous akaganéite ( $\beta$ -FeOOH). (SELWYN L. S., SIROIS P.J., ARGYROPOULOS V., 1999, p226).

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## Abstract

Once archaeological iron artifacts are excavated their protective environment is lost. On exposure to the air the objects can dry out and the earthy as well as the corrosion layers become permeable due to the formation of cracks and fissures. Moisture from the air and oxygen get access to the objects. If chlorides are present in the corrosion layers and metallic iron remains in the artifact, active corrosion can be a consequence if the objects are left in an uncontrolled environment.

Akaganéite ( $\beta$ -FeOOH) is the visible sign of active corrosion. It is a voluminous orange-brown corrosion product that forms after excavation on iron artifacts in the presence of moisture and oxygen. Chlorides need to be present in the object, as they are the controlling factor of the reaction that leads to akaganéite ( $\beta$ -FeOOH).

Adequate methods of storing the iron finds can prevent these destructive corrosion reactions.

In this work, two different storage methods are examined with regard to their efficiency of preventing akaganéite ( $\beta$ -FeOOH). Synthetic and archaeological samples are packed into these storage environments. Synthetic samples submitted to the test conditions are made up of a powder mixture of iron and iron chloride hydrate in equal amounts. Archaeological samples (Roman nails from two Swiss excavation sites) are packed alongside the synthetic samples.

Dry or dry and cold storage are compared to results of oxygen-free storage. For dry and cold storage, samples are packed in resealable polyethylene (PE) bags that are placed into polypropylene (PP) boxes. Silica gel is used as a desiccant for dry microclimates. For the oxygen-free storage, two oxygen absorbers from the RP-System<sup>TM</sup> produced by Mitsubishi Gas Chemical Company are tested. These are the RP-A absorber that creates an oxygen-free dry climate and the RP-K absorber that lowers the oxygen level, but does not affect the relative humidity (RH). Samples in anoxic environments are packed into bags made of a high barrier film (ESCAL<sup>TM</sup>).

Changes over a period of five-and-a-half months in the samples are analysed using Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and optical microscopy.

Results of the present work show that dry packing of samples using resealable PE bags provided with holes placed into PP boxes as well as dry oxygen-free storage in fully heat-sealed barrier film bags show the most promising results. Temporary dry oxygen-free storage using barrier film bags closed with a clip could be an option for on-site packaging of objects until arrival in the laboratory, where dry storage could be an easy way of dealing with objects that have to be further examined or put on display. Dry oxygen-free storage is a realistic option for the large amount of iron objects that will never go on display, but be kept in storage.

Economic aspects of the tested storage methods are also examined. Anoxic storage proves to be expensive in the phase of setting up the packaging.

## Résumé

Après une fouille, le taux d'humidité et d'oxygène de l'air affecte tout objet archéologique en fer. Les couches de terre et de corrosion, par l'action de l'air, dessèchent et des craquelures peuvent alors s'y créer. Ainsi l'oxygène et l'humidité ont accès à ces couches de corrosion et à l'intérieur de l'objet. La

corrosion est activée par les conditions atmosphériques et est accentuée en présence de chlorures au sein de l'objet.

L'un des principaux produits de corrosion visible à l'oeil nu est l'akaganéite ( $\beta$ -FeOOH) de couleur brun-orangé. L'akaganéite ( $\beta$ -FeOOH) occupe beaucoup de volume et peut faire éclater des couches de corrosion qui lui sont superposées.

Cette étude montre l'importance d'un stockage adéquat afin de ralentir voir de stopper les réactions des agents corrosifs.

Deux méthodes de stockage sont analysées afin de déterminer leur efficacité à empêcher le processus de formation d'akaganéite ( $\beta$ -FeOOH). Les échantillons stockés sont de deux types:

- les échantillons synthétiques (fer et chlorure de fer hydraté en poudre)
- les échantillons archéologiques (clous romains provenant de deux sites suisses).

Ils sont soumis conjointement (en parallèle) à diverses conditions de stockage. Premièrement le stockage au sec et sec/froid où on a placé les échantillons dans des sachets en polyéthylène (PE) dans des container en polypropylène (PP). On utilise le gel de silice pour obtenir un climat sec. Deuxièmement l'anoxie sèche où on utilise le RP-System<sup>TM</sup> de Mitsubishi Gas Chemical Company avec ses deux absorbeurs d'oxygène RP-A et RP-K. Le premier crée un climat sec et sans oxygène, le deuxième baisse l'oxygène, mais n'influence pas l'humidité relative (HR). Dans ce cas on utilise des sachets en film plastique à indice de perméabilité très bas (ESCAL<sup>TM</sup>) pour l'emballage.

Les échantillons sont examinés et comparés sur une période de plus de 5 mois. Ils sont analysés par spectrométrie infrarouge transformée de Fourier (FT-IR), diffraction à rayons X (XRD) et microscopie optique.

Les résultats obtenus démontrent l'intérêt à considérer un aspect de stockage à long et court terme. Deux modes de stockage à long terme sont retenus. Le stockage sec, avec sachets PE troués dans des containers PP pour des objets d'exposition et ceux qui attendent des analyses et doivent être dessinés. L'anoxie sèche dans des sachets entièrement soudés pour les objets qui rentrent en réserve pour une durée indéterminée. Le stockage à anoxie temporaire utilisant des sachets de film peu perméable à fermeture clip est retenu pour le court terme pour les travaux in-situ, avant l'arrivée des objets au laboratoire.

Pour conclure, l'étude permet de mettre en évidence l'aspect économique des modes de stockage à long et court termes. En effet, la mise en œuvre de l'anoxie coûte cher dans la phase initiale.

## Zusammenfassung

Nach einer Ausgrabung können Feuchtigkeit und Sauerstoff uneingeschränkter Zugang zum ungeschützten Eisenobjekt haben. Sind Chloride und ein Metallkern im Objekt vorhanden, so kann aktive Korrosion eine Folge sein von unkontrollierter Lagerung der Funde.

Das sichtbare Anzeichen von aktiver Korrosion auf Eisenobjekten ist Akaganéit ( $\beta$ -FeOOH). Dies ist ein orange-braunes voluminöses Korrosionsprodukt, das nach der Ausgrabung unter Einfluss von Feuchtigkeit und Sauerstoff entsteht. Bedingung für diese Korrosion ist das Vorhandensein von Chloriden, da sie den massgebenden Faktor darstellen, der zur Akaganéit ( $\beta$ -FeOOH)-Bildung führt.

Angemessene Lagerungsmethoden können diese zerstörerischen Reaktionen verhindern.

Die vorliegende Arbeit untersucht zwei Lagerungsmethoden und deren Fähigkeit, Akaganeit ( $\beta$ -FeOOH)-Bildung zu verhindern. Dazu werden synthetische und archäologische Proben während fünfeinhalb Monaten den Lagerungsbedingungen unterworfen. Die synthetischen Proben bestehen aus einer Mischung gleicher Mengen Eisen und Eisenchlorid. Weiter werden archäologische Proben (römische Nägel von zwei Schweizer Ausgrabungen) ebenfalls mitverpackt.

Untersucht werden die Eignung von Trockenlagerung und kalter Trockenlagerung sowie sauerstofffreier Lagerung zur Verhinderung von Akaganeit ( $\beta$ -FeOOH)-Bildung. Bei den Formen der Trockenlagerung werden die Proben in wiederverschliessbare Beutel aus Polyethylen (PE) verpackt und diese werden in Polypropylen (PP) Boxen gelegt. Als Trockenmittel wird Silica Gel verwendet. Bei der sauerstofffreien Lagerung werden zwei Sauerstoffabsorber des RP-System<sup>TM</sup> der Firma Mitsubishi Gas Chemical Company verglichen. Der erste Absorber, RP-A, ergibt ein trockenes sauerstofffreies Klima. RP-K, der zweite Absorber, führt zur Anoxie ohne die relative Feuchte zu beeinflussen. In dieser Untersuchung werden Beutel aus der Sperrschichtfolie ESCAL<sup>TM</sup> verwendet.

Veränderungen im Probenmaterial werden mit Hilfe von Fourier-Transform-Infrarotspektroskopie (FT-IR), Röntgendiffraktion (XRD) und optischer Mikroskopie untersucht.

Die Untersuchung zeigt, dass Trockenlagerung in gelochten PE-Wiederverschlussbeuteln in PP-Boxen sowie trockene, sauerstofffreie Lagerung viel versprechende Resultate ergeben. Temporäre trockene Anoxie, in der ein Sperrschichtfolienbeutel mit Hilfe eines Clips verschlossen wird, könnte eine effiziente Verpackung auf der Ausgrabung darstellen. Kommen die Objekte dann im Labor an, kann ein Wechsel zu Trockenlagerung für die Objekte vorgesehen werden, welche untersucht, gezeichnet oder ausgestellt werden. Trockene Anoxie in ganz zugeschweissten Beuteln ist eine Langzeitoption für all jene Objekte, die nie ausgestellt werden und für lange Zeit ins Depot zurückkehren.

Zusätzlich werden die finanziellen Konsequenzen der erwähnten Lagerungsmethoden mit in Betracht gezogen, wobei sich die sauerstofffreie Lagerung in der Anfangsphase als sehr kostenintensiv herausstellt.

## Abbreviations

### General

|                                       |   |
|---------------------------------------|---|
| ac/d                                  | Air changes per day                                     |
| $\alpha$ -FeOOH                       | Iron oxyhydroxide goethite                              |
| $\beta$ -FeOOH                        | Iron oxyhydroxide akaganéite                            |
| °C                                    | Degree Celsius  |
| cc/m <sup>2</sup> /day                | Cubic centimetres / square metre / day                  |
| cm                                    | Centimetres   |
| CO <sub>2</sub>                       | Carbon dioxide  |
| EH                                    | English Heritage, United Kingdom                        |
| Fe                                    | Iron  |
| FeCl <sub>2</sub>                     | Iron(II) chloride                                       |
| FeCl <sub>3</sub>                     | Iron(III) chloride                                      |
| FeCl <sub>2</sub> ·4H <sub>2</sub> O  | Iron chloride tetrahydrate                              |
| FeCl <sub>2</sub> ·2H <sub>2</sub> O  | Iron chloride dihydrate                                 |
| FeCl <sub>3</sub> ·6H <sub>2</sub> O  | Iron chloride hexahydrate / iron(III) chloride 6-water  |
| 2FeCl <sub>3</sub> ·7H <sub>2</sub> O | Iron chloride heptahydrate / iron(III) chloride 7-water |
| Fe <sub>2</sub> O <sub>3</sub>        | Iron oxide hematite                                     |

|  |  |
|--|--|
| Fe <sub>3</sub> O <sub>4</sub>         | Iron oxide magnetite   |
| FeOCl                                  | Iron oxide chloride  |
| FeS <sub>2</sub>                       | Marcasite and pyrite (polymorphs of FeS <sub>2</sub> )   |
| g                                      | Grams  |
| g.H <sub>2</sub> O/m <sup>2</sup> /day | Grams water / square metre / day   |
| g/m <sup>2</sup> /day                  | Grams / square metre / day   |
| H <sup>+</sup>                         | Hydrogen ion   |
| ICDD                                   | International Centre for Diffraction Data  |
| l                                      | Litres   |
| LLDPE                                  | Linear low-density polyethylene  |
| mg                                     | Milligrams   |
| ml                                     | Millilitres  |
| mm                                     | Millimetres  |
| NaOH                                   | Sodium hydroxide   |
| NHM                                    | Natural History Museum, London, United Kingdom   |
| O <sub>2</sub>                         | Oxygen   |
| OPP                                    | Orientated polypropylene   |
| PE                                     | Polyethylene   |
| PET                                    | Polyethylene terephthalate   |
| PP                                     | Polypropylene  |
| ppm                                    | Parts per million  |
| PVAC                                   | Poly(vinyl acetate)  |
| PVAL                                   | Poly(vinyl alcohol)  |
| RH                                     | Relative Humidity  |
| RP-A                                   | Oxygen absorber RP-A (part of the RP-System™ from Mitsubishi Gas Chemical Company): for dry oxygen-free enclosures |
| RP-K                                   | Oxygen absorber RP-K (part of the RP-System™ from Mitsubishi Gas Chemical Company): for oxygen-free enclosures     |
| RP-System™                             | Oxygen absorbing Revolutionary Preservation System (from Mitsubishi Gas Chemical Company)                          |

## Techniques

|       |   |
|-------|---|
| FT-IR | Fourier-transform infrared spectroscopy |
| SEM   | Scanning electron microscopy            |
| XRD   | X-ray diffraction                       |

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# 1 INTRODUCTION

## 1.1 General introduction to the topic

The conservation of archaeological iron comprises many aspects as excavation, treatments, storage and long-term conservation.

This work's starting position is to examine one problem involved with freshly excavated iron artifacts: the danger of active corrosion after excavation. The aim is to find storage methods applicable for the time interval between the excavation of the objects and their arrival in a laboratory where a further treatment could be carried out or where long-term packaging would be prepared. How could active corrosion be prevented directly after excavation, where the corrosion process often starts?

Many iron objects suffer from active corrosion once they are unearthed. On drying at the air cracks and fissures can form in the corrosion layers and oxygen and moisture can get free access to the core of the artifacts. Active corrosion of archaeological iron is characterised by the appearance of the iron oxyhydroxide akaganéite ( $\beta$ -FeOOH), an orange-brown corrosion product, which is in the centre of our interest. Physical damage and disappearance of the remaining iron are indicators of this active corrosion that leads to cracking, exfoliating and 'sweating' of the artifact. Akaganéite ( $\beta$ -FeOOH) is a voluminous corrosion product that causes, even if only present in small amounts, large physical damage.<sup>1</sup>

The present work looks at Swiss storage methods of archaeological iron as well as new options. Archaeological samples from Switzerland<sup>2</sup> and synthetic powder samples<sup>3</sup> are used for testing. Dry storage is investigated, used in Switzerland as well as other countries. Oxygen-free storage using high barrier plastic bags and oxygen absorbers is examined, even if not applied in Switzerland in this form.<sup>4</sup> It could be a new option for Swiss laboratories and this question is investigated. The storage methods were chosen based on a questionnaire sent to ten Swiss conservation laboratories<sup>5</sup> and by personal interest<sup>6</sup>. The reason why Swiss approaches are looked at is because this work is submitted in Switzerland where improvement of storage methods for iron objects is a concern. Incitation of further discussion on the topic is therefore of interest.

## 1.2 Review

Two main approaches have been followed until present to deal with active corrosion on archaeological iron: direct intervention by stabilisation or adapted storage by action on the environment surrounding the object.

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<sup>1</sup> TURGOOSE S., 1982 a, p97; KNIGHT B. 1982, p50-55; personal communication with David Thickett, English Heritage, 25/06/2006.

<sup>2</sup> Roman nails from two Swiss excavations, Vindonissa and Fribourg (summer / autumn period 2005).

<sup>3</sup> A mixture of equal amounts of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ).

<sup>4</sup> The Service Archéologique de l'Etat de Fribourg applies anoxic storage by means of flushing bags with nitrogen.

<sup>5</sup> See annex IV for the questionnaire.

<sup>6</sup> Oxygen-free storage in the form it is tested in this work is not mentioned by Swiss conservators as an option but seemed to be a possible alternative worth testing.



Figure 1: An efficient storage method is needed to preserve iron artifacts for the future. This iron knife blade, early 18<sup>th</sup> century AD, shows spots of active corrosion (Glassworks, Court (BE), Switzerland, excavation 2000). (Archaeological Office of the Canton of Bern, Switzerland).



Figure 2: Active corrosion can only be stopped or slowed down by means of efficient treatments or storage solutions (iron knife blade from the photo to the left). (Archaeological Office of the Canton of Bern, Switzerland).

Firstly, intervention to encounter the problem of active corrosion can be taken by treating the objects and trying to get the chlorides – that are responsible for the formation of akaganéite ( $\beta$ -FeOOH) – out of them. This can be achieved by stabilisation treatments of various natures (treatment with alkaline sulphite is a commonly used method in Switzerland, other methods like electrolysis, immersion in solutions of sodium hydroxide or lithium hydroxide, the Soxhlet treatment or the use of a hydrogen plasma treatment amongst others are – and were in the past – often more local traditions for treating objects). However, none of these methods has proven to be 100% effective and re-corrosion can occur when exposing the treated objects to unsuitable environments (e.g. high RH). This is due to remaining chlorides.<sup>7</sup>

The second possibility of prevention of active corrosion – which is also the topic of this work – is the intervention on the environment that surrounds the iron artifact. As mentioned above, access of moisture and oxygen are the major factors that cause active corrosion. By acting on those parameters corrosion can be slowed down.

Many conservators apply dry storage to excavated iron and this can be achieved by placing the objects into microclimates where a desiccant is added (often silica gel is used). Some work has studied the efficiency of dry storage of archaeological iron to prevent formation of akaganéite ( $\beta$ -FeOOH) and guidelines have been proposed for the level of desiccation.<sup>8</sup> It has been stated, that levels of 15-20% RH are needed to successfully prevent the formation of akaganéite ( $\beta$ -FeOOH).<sup>9</sup>

On the other hand, the use of anoxic enclosures could be another option more and more taken into account because of the little maintenance it seems to need once objects packed. Corrosion can also be slowed down.<sup>10</sup> Oxygen-free storage of archaeological iron has been applied by some conservators

<sup>7</sup> REGUER S., 2005, p12.

<sup>8</sup> WATKINSON D., LEWIS M., 2004, p88-102; WATKINSON D., LEWIS M., 2005, p241-252; THICKETT D., ODLYHA M., *in press*, 2006 ; SCOTT D. A., *in press*, p264; Museum and Galleries Commission, 1992, p57.

<sup>9</sup> WATKINSON D., LEWIS M., 2004, p88-102; WATKINSON D., LEWIS M., 2005, p241-252.

<sup>10</sup> MATHIAS C., RAMSDALE K., NIXON D., 2004, p28.

using different oxygen absorbers.<sup>11</sup> A recent trend is to choose RP-System™ oxygen absorbers from Mitsubishi Gas Chemical Company<sup>12</sup>, and they will be used in this project.

### 1.3 Choice of materials submitted for testing

In the present work, synthetic powder samples and archaeological Roman nails from two Swiss excavations are submitted to two different storage methods, trying to find out which of those is most efficient preventing active corrosion after excavation.

On one hand, the storage in dry and cold and dry/cold microclimates is examined. Samples are packed in resealable PE bags<sup>13</sup> placed into PP boxes. Silica gel is added as a desiccant and temperature either ambient or at 4°C. The combination of dry and cold conditions doesn't seem to have been examined but is used by some conservators in Switzerland.<sup>14</sup>

The second method involves packing in anoxic enclosures. Here, the Revolutionary Preservation System™ from Mitsubishi Gas Chemical Company is examined. Two different oxygen absorbers (RP-A and RP-K) are tested and compared. No work has examined in detail what exactly happens to the iron material during oxygen-free storage on the side of corrosion (which corrosion products would really form).

Monitoring and analysis of the corrosion products formed in the submitted samples are carried out using FT-IR and XRD as well as optical microscopy.

The results are compared on the amount of akaganéite ( $\beta$ -FeOOH) formed. Other aspects taken into account are the cost of the methods (in terms of material and time for monitoring) and the easiness of application.

### 1.4 Research project aims and objectives

Preventing active corrosion of archaeological iron by means of efficient storage methods is the topic of this work. The main question of this work always is, if there is formation of akaganéite ( $\beta$ -FeOOH), the sign of active corrosion. A storage method would be judged good and efficient, if no akaganéite ( $\beta$ -FeOOH) formed over the test period of five-and-a-half months.<sup>15</sup> XRD and FT-IR are used to monitor the samples over five-and-a-half months and this is used to make clear which of those techniques is more reliable in the detection of akaganéite ( $\beta$ -FeOOH) in its early stage.

How exactly an iron object would react in the chosen storage environments? Would the combination of the cold and the dry bring any advantages over the use of simple dry storage? What changes would oxygen-free storage using the oxygen absorbers RP-A and RP-K from Mitsubishi Gas Chemical

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<sup>11</sup> MAEKAWA S., ELERT K., 2003.

<sup>12</sup> REBIERE J., MOUREY W., FRANCOISE J., SIDOT E., 1998, p248-252; BECKER H., 1999, p72-76; GREIFF S., BACH D., 2000, p327; MATHIAS C., RAMSDALE K., NIXON D., 2004, p28-41.

<sup>13</sup> Differences in closing or leaving the bags open are looked at.

<sup>14</sup> See annex IV for details.

<sup>15</sup> As the test period was of only five-and-a-half months, the evaluation 'good' can of course only be proven for this time period. However, tendencies can be presumed for the long term.

Company cause in the submitted samples? Would akaganéite ( $\beta$ -FeOOH) really not form under these conditions? And what was the difference between the two absorbers from the RP-System<sup>TM</sup>?

Many Swiss conservators have problems with the storage of big amounts of archaeological iron. A lot of those objects are not thought to be taken out of the stores on a regular basis but seem rather to be forgotten or not enough important to be put on display. But these objects need to be conserved to be available for study to the future generations. For this important number of objects, an efficient method of storage is needed: little monitoring (as staff is not always available), efficient prevention of corrosion over a long period, cost-efficiency and an easy way of applying the packaging technique are requested. Also it seems that the formation of akaganéite ( $\beta$ -FeOOH) occurs quickly after excavation. We therefore need a way to pack objects on site and keep them free of active corrosion until they arrive at the laboratory for treatment or long-term packaging.

The work leads to conclusions on the efficiency of the storage methods in preventing active corrosion on freshly excavated iron objects. Costs and possibilities of applications are considered and advice could be given on efficient storage after this research.

## 2 CORROSION OF ARCHAEOLOGICAL IRON

### 2.1 Corrosion phenomenon

This chapter provides information about the corrosion reactions of iron during burial and after excavation. Stress will be put on the influence of chlorides in these processes, as they are a main factor for the development of akaganéite ( $\beta$ -FeOOH), a brown to bright yellow corrosion product that forms after excavation of the artifact.

No further referral will be carried out to burial environments, the emphasis of this chapter being on the main corrosion reactions taking place in any buried iron artifacts. A small part on marine cast iron has been added, as this material has to be differentiated from wrought iron.



Figure 3: The spalling of corrosion layers due to active corrosion is visible on this blowpipe (iron, early 18<sup>th</sup> century AD, Glassworks Court in the canton of Bern, Switzerland, excavation 2001). (Archaeological Office of the Canton of Bern, Switzerland).



Figure 4: Active corrosion on a knife blade (iron, early 18<sup>th</sup> century AD, Glassworks Court, excavation 2003). (Archaeological Office of the Canton of Bern, Switzerland).

#### 2.1.1 Corrosion during burial

Barkman said in 1975: „*The extent of corrosion is to a high degree dependent on the environment. In archaeological contexts a distinction must be made between corrosion in maritime environment, in air and in soil. A metal corrodes if it is exposed simultaneously to oxygen and water. Corrosion takes place electrochemically, as the corrosion medium is an electrolyte. The dissolution of the metal is an anodic process occurring simultaneously with a cathodic process in which oxygen, and sometimes hydrogen ions, are consumed.*”<sup>16</sup> The author underlined that in the deep soil where only little oxygen is available corrosion would be slower.<sup>17</sup> This statement brings us directly to our focal point. Corrosion of iron artifacts during burial and after excavation is a complex phenomenon. Many aspects have to be considered. The characteristics of the soil<sup>18</sup>, the climate and geographical region<sup>19</sup>, the state of the

<sup>16</sup> BARKMAN L., 1975, p169.

<sup>17</sup> Ibid.

<sup>18</sup> SCHARFF W. et al., 2000, p41.

<sup>19</sup> Ibid., p48.

artifact before and after burial, influences of deterioration agents such as water, oxygen or temperature. The type of object we are dealing with is also significant. Is it a marine cast iron artifact or a wrought iron object from a terrestrial site?

Gerwin mentioned that the three main aspects influencing the corrosion process during burial were the amount of water and oxygen available, the acidity (pH-levels) and the amount of dissolved salts in the soil.<sup>20</sup> Réguer confirmed this statement.<sup>21</sup>

An iron object is usually covered with an oxide film during its 'life-time'. Later, when the artifact is buried, this film is no longer protective. In the presence of an aqueous electrolyte in the soil, corrosion takes place.<sup>22</sup>

Electronic conductivity between the anode and the cathode in the solid part, and ionic conductivity in the solution are required for corrosion of the iron to take place. Anions and cations carry the current between the anodic and cathodic sites. The solution surrounding and embedding the iron always 'aspires' to be neutral, so if there are too many anions, ferrous ions have to be produced to counterbalance the reaction.<sup>23</sup>

The main chemical reactions found in this corrosion process are:<sup>24</sup>



Which can then be further oxidized to  $\text{Fe}^{3+}$  in the following way:



To this oxidation reaction there needs to be the reducing counterpart (oxygen reduction or hydrogen evolution):



It seems that hydrogen evolution takes places in low-pH environments (4 and below).<sup>25</sup>

Turgoose stated that the first reaction, oxygen reduction, was the most significant during burial.<sup>26</sup>

Gerwin said that the occurrence of either oxygen reduction or hydrogen evolution was dependent on the pH-value and the access of oxygen.<sup>27</sup>

<sup>20</sup> GERWIN W., 1999, p174-175.

<sup>21</sup> REGUER S., 2005, p15, p17, p19.

<sup>22</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p217-218.

<sup>23</sup> TURGOOSE S., 1993, p37.

<sup>24</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p217-218.

<sup>25</sup> Ibid., p218.

<sup>26</sup> TURGOOSE S., 1993, p37.

<sup>27</sup> GERWIN W. 1999, p173.



The oxidation of iron would then be as follows tells us Selwyn, if one takes into account Turgoose's statements.<sup>28</sup>



Or following Pötzsch:<sup>29</sup>



In these equations we can see that the initial corrosion product from which all following reactions will start is the ferrous ion.<sup>30</sup>

Gerwin provided further formulas to understand the ongoing corrosion reactions in the soil:<sup>31</sup>



Reaction between ferrous ions ( $\text{Fe}^{2+}$ ) and hydroxyl ions ( $\text{OH}^-$ ) can take place easily on the metal surface in the beginning, where anodic and cathodic sites are located. Iron hydroxide,  $\text{Fe}(\text{OH})_2$ , is formed and constitutes a passivating film. Later,  $\text{Fe}^{2+}$  ions can undergo secondary reactions as they diffuse away from the anodic surface. Concentrations of  $\text{Fe}^{2+}$ ,  $\text{O}_2$ ,  $\text{H}^+$  and other anions affect these reactions. Iron hydroxide,  $\text{Fe}(\text{OH})_2$ , and ferrous hydroxychloride,  $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ , can form at low-oxygen levels. Partial oxidation of these will lead to the so-called 'green rusts' (these are further oxidized to iron oxyhydroxides<sup>32</sup>). These species include other anions as chlorides or sulphates. Under high oxygen levels and low pH levels (less than 6),  $\text{Fe}^{2+}$  remains in solution. Acidic environments lower the oxidation rate of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . If the same environment has a pH greater than 6, then iron(II) hydroxide,  $\text{Fe}(\text{OH})_2$ , will form and be oxidized and hydrolysed to iron(III) hydroxide,  $\text{Fe}(\text{OH})_3$ .  $\text{Fe}(\text{OH})_3$  can further transform to goethite,  $\alpha\text{-FeOOH}$ , while losing water. An important aspect in the corrosion process is that the anodic and cathodic sites get separated more and more. In the end, the cathode is situated at the outermost electrically conducting material, the anode on the metal surface. Around the anodic region, the environment becomes acid and rich in chlorides: the pores of the corrosion products get filled with an acidic iron(II) chloride solution ( $\text{FeCl}_2$ -solution). Chloride ions will diffuse into the object as long as  $\text{Fe}^{2+}$  ions are liberated in the corrosion process.<sup>33</sup>

Turgoose advised to use a thermodynamic approach in regarding corrosion products that might be formed on buried iron. Taking a Potential-pH diagram for iron, Turgoose determined goethite,  $\alpha\text{-FeOOH}$ , and magnetite,  $\text{Fe}_3\text{O}_4$ , to be the stable solid corrosion products formed in natural environments. Other compounds may be present under specific conditions.<sup>34</sup>

<sup>28</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p218.

<sup>29</sup> PÖTZSCH A. in: SCHARFF W. et al., 2000, p26.

<sup>30</sup> TURGOOSE S., 1993, p38.

<sup>31</sup> GERWIN W., 1999, p173.

<sup>32</sup> SELWYN L. S., 2004, p295.

<sup>33</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p218-219.

<sup>34</sup> TURGOOSE S., 1993, p39.

In a few words the use of the Potential-pH diagrams will be explained, also called Pourbaix Diagrams (named after Marcel Pourbaix who developed the ideas), often taken into consideration to find out about the potential danger of an environment in which the metal object remains.

Scharff et al. give a short explanation: „Die Metallkorrosion wird unter anderem stark von der Oxidationskraft (Redoxpotential) und dem pH-Wert der Umgebung beeinflusst. Aus Potential-pH-Wert-Diagrammen (sog. Pourbaix-Diagrammen) kann abgelesen werden, ob bei den momentan herrschenden Potential-pH-Bedingungen Korrosion stattfindet, und, wenn das der Fall ist, welche Korrosionsprodukte gebildet werden können. Ferner kann abgeschätzt werden, ob eine leichte Veränderung eines Parameters (z.B. eine Absenkung des pH-Wertes) zu einer Gefährdung führen kann.“<sup>35</sup> The author explains that the corrosion of metals depends on the redox-potential and the pH level of the surrounding environment.

The Pourbaix Diagram shows us whether, at the given conditions of potential-pH, corrosion could take place and which corrosion products are formed. One can also read from the diagram whether a slight change in one of the parameters (as the pH) will bring danger to the metal.

Pourbaix Diagrams explain the behaviour of metals in aqueous solutions (Potential versus pH).<sup>36</sup> In the diagram, the pH is noted on the x-axis, the potential on the y-axis. This means that the left side of the diagram represents an acidic, the right side the alkaline environment. The upper part shows an oxidising and the lower part a reducing environment.<sup>37</sup>

Pourbaix himself said of his model in 1971 that it could give us a ‘thermodynamic framework’ for all chemical and electrochemical processes occurring during corrosion. Conditions of thermodynamic stability could be expressed. These graphs could be used to generate other graphs, specific to a metal and its general conditions of corrosion

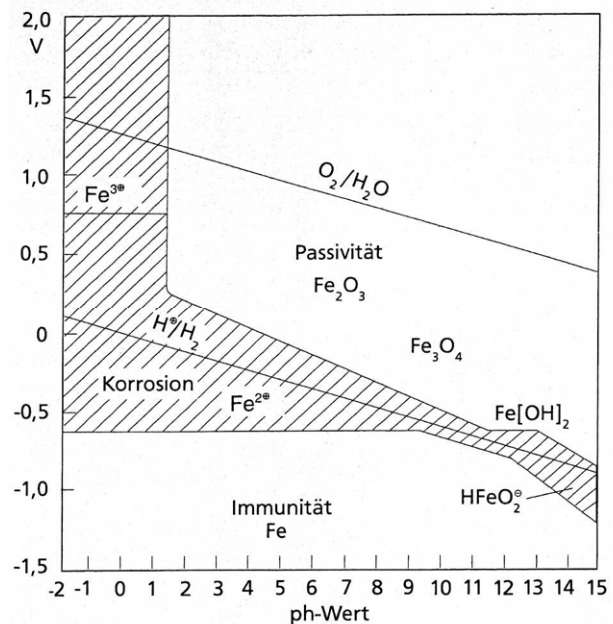


Figure 5: Pourbaix Diagram (of 1966) of the iron – water system at 25°C with zones of immunity, passivation and corrosion. (SCHARFF W. et al., 2000, p28).

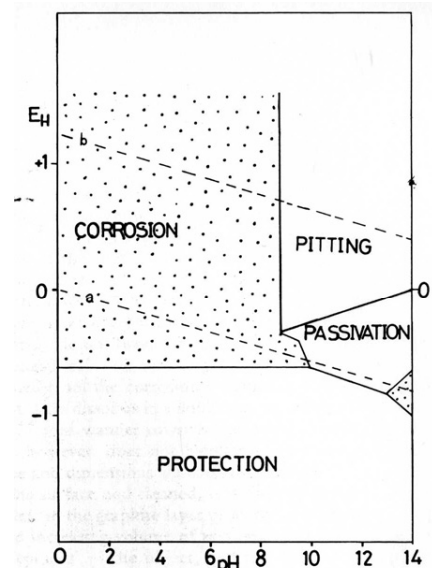


Figure 6: The iron – NaCl (1M) system at 25°C: zones of corrosion and passivation are different than for the water – iron system. (NORTH N. A., PEARSON C., 1975 b, p181).

<sup>35</sup> SCHARFF W. et al., 2000, p20-21.

<sup>36</sup> VERINK E. D., 1968, p371.

<sup>37</sup> REGUER S., 2005, p17.

(stability of a dissolved species), to express immunity (stability of the metal) or passivation (stability of solid oxides or salts).<sup>38</sup>

Regarding an archaeological iron artifact one can say that it is covered by a layered structure of corrosion products. The outer layer contains heterogeneous elements such as sand, soil minerals, clay and small rocks. A congregation of iron corrosion products (such as goethite,  $\alpha$ -FeOOH) is mixed to these elements. Under this layer, other corrosion products of a lower oxidation state (such as magnetite,  $\text{Fe}_3\text{O}_4$ ) lie on the remaining metal.<sup>39</sup>

Of course the nature of the corrosion products can vary, according to the environment in which the artifact has been buried.

For marine cast iron, we can find some other details regarding their corrosion reactions. Recovered marine cast iron usually consists of a metal core surrounded by graphitized corrosion products. The border between corroded and uncorroded zones cannot always be easily determined. Sometimes no metal will be left. On a partly corroded object, one can usually find water, iron oxyhydroxide ( $\text{FeO}(\text{OH})$ ), iron chlorides, silica ( $\text{SiO}_2$ ) cementite ( $\text{Fe}_3\text{C}$ ) and graphite in the graphitized corrosion products.<sup>40</sup>

Cast iron from the sea, compared to wrought iron, remains solid when corroded. This is even the case if the artifact is totally corroded. Ferrous concretion surrounds the object. Under this concretion, the surface of the corroded artifact is soft. In these objects, the graphite of the grey cast iron acts as a cathode and the iron as the anode. Remaining iron oxides and carbonates are held in place between the graphite flakes. Thanks to this, the shape of the object, in its mineralized form, is preserved. A so preserved object is called 'graphitized'.<sup>41</sup>

Gilberg and Seeley provided evidence of corrosion products present on marine cast and wrought iron. They could detect small amounts of iron(III) chloride ( $\text{FeCl}_3$ ), iron(II) chloride ( $\text{FeCl}_2$ ), green rust, magnetite ( $\text{Fe}_3\text{O}_4$ ), goethite ( $\alpha$ -FeOOH) and iron sulphides (for anaerobic conditions). The presence of iron oxychloride, ( $\text{FeOCl}$ ) was doubted by these authors.<sup>42</sup> North added that basic iron(II) chlorides ( $\alpha$ -,  $\beta$ 2- or  $\gamma$ 3- $\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$ ) might be present in marine iron corrosion products.<sup>43</sup>

Selwyn mentioned that corroded marine iron is usually covered by calcium carbonate ( $\text{CaCO}_3$ ). She stated that the  $\text{Fe}^{2+}$  ions in this case rather react in the concretion layer than on the surface of the object. Selwyn also added that wrought iron in marine environments would have the characteristic fibrous structure when recovered whereas cast iron would keep its original shape in the porous matrix of soft graphite.<sup>44</sup>

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<sup>38</sup> POURBAIX M. in: AILOR W. H., 1971, p661.

<sup>39</sup> SELWYN L. S., 2004, p295.

<sup>40</sup> NORTH N. A., 1987, p212.

<sup>41</sup> CRONYN J. M., 1990, p185.

<sup>42</sup> GILBERG M. R., SEELEY N. J., 1981, p50-56.

<sup>43</sup> NORTH N. A., 1982, p80.

<sup>44</sup> SELWYN L. S., 2004, p295.

However, Turgoose stated that whatever the burial environment, the cause of damage to excavated artifacts was the same. „Difference between, for example, marine sites and soil burial are only of magnitude and not of type.“<sup>45</sup>

### **2.1.2 Post-excavation corrosion**

The presence of an iron(II) chloride solution ( $\text{FeCl}_2$ -solution) in the pores of excavated iron artifacts seems to be a major problem in the post-excavational corrosion. If oxygen and moist air have suddenly access to the unearthed object, damaging corrosion reactions can take place, leading, in the worst case scenario, to the complete loss of the artifact. Conversion of the iron(II) chloride solution becomes possible due to this access of oxygen and humidity. This chapter will elucidate these phenomena and take a look back at some theories that led to the present understanding of corrosion phenomena.

In 1924 Evans said that for corrosion to take place on iron objects, water must be present in some form. He mentioned that heavy corrosion could be seen on iron where it was exposed to big changes in the temperature (day and night changes). The author also pointed out that acid gases could influence corrosion behaviour. He said that iron objects in the urban atmosphere where a lot of sulphur dioxide was present (use of coal as fuel) corroded more quickly than in a rural environment. Corrosion was accentuated when water was present. The presence of salt on iron surfaces accelerated the corrosion. Objects with this problem showed drops of liquid containing chlorine when exposed to moisture. The drops later became coated with a film of rust. Evans said that if the air was pure and moisture present, corrosion would be very slow. That iron did not rust if placed in the high mountains was explained by the author as being so because of low temperatures and high purity of the air. When Evans exposed iron to moist hydrogen chloride ( $\text{HCl}$ ), he found that iron(II) chloride ( $\text{FeCl}_2$ ) was formed. This further oxidized in air to ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) and iron(III) chloride ( $\text{FeCl}_3$ ) and gave the surface a damp appearance.<sup>46</sup>

However, the presence of salt needed to be connected to the presence of water and the amount of oxygen available in order to have more indications of the intensity of the corrosion. If the object was immersed in water, then oxygen was the controlling factor, if the object was kept at atmospheric conditions, then moisture would be the controlling factor.<sup>47</sup>

Evans also took up the work of W. H. J. Vernon, who dealt with similar questions in the same years. The latter said that if rust was present on iron and the object exposed to high humidity, the rust stimulated subsequent rusting.<sup>48</sup> In a later publication, Evans mentioned that rust could only be protective if it didn't contain ferrous salts (iron(II) chloride and ferrous sulphate).<sup>49</sup>

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<sup>45</sup> TURGOOSE S., 1993, p47.

<sup>46</sup> EVANS U. R., 1924, p128-134.

<sup>47</sup> EVANS U. R., 1948, p75.

<sup>48</sup> EVANS U. R., 1924, p143.

<sup>49</sup> EVANS U. R., 1960, p505.

Evans provided models to explain his theories. He placed a drop of potassium chloride solution (KCl) on the surface of an iron sheet. He observed the formation of a membrane shortly after this, in a circle running round the drop. This membrane was first white and then turned brown. Liquid at the interior of the membrane contained

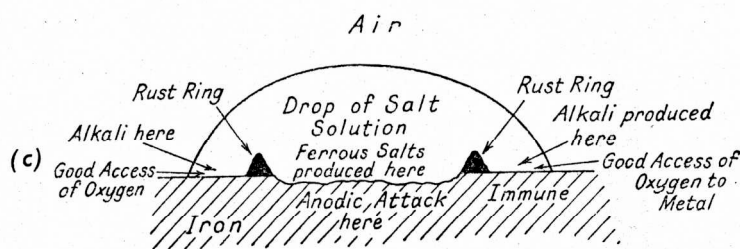


Figure 7: Evans' model of a drop of potassium chloride solution on iron with formation of ferrous salts at the interior of the drop. (EVANS U.R., 1948, p29).

ferrous salts. The liquid around the membrane was alkaline. Evans claimed that this was due to the formation of a cathodic zone at the outer parts of the drops once the oxygen had been used up in the centre of the drop. This was an immunizing zone. The inner zone was anodic. Where alkali and iron(II) chloride ( $\text{FeCl}_2$ ) met, a membrane of white ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) would form, later changing to brown ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ).<sup>50</sup>

Evans made a list of factors affecting the velocity of corrosion (such as nature of the dominant metal, internal stresses, characteristics of the grains, salts present in the liquid, temperature, etc.). They were called the controlling factors (factors that control the corrosion).<sup>51</sup>

He proposed a distinction of three types of atmospheric corrosion: 'Dry', 'Damp' and 'Wet', following the importance of reaction including water vapour on the metal surface. In the 'Dry' type (low humidity) moisture did not play a significant role. In the 'Damp' type (medium and high humidity) Evans said corrosion could become very harmful above 70% RH. However, he added that this critical value could be lower in certain cases. The presence of hygroscopic bodies on the iron surface could also bring down the critical value. For 'Wet' atmospheric corrosion, the objects needed to be exposed to rain or other sources of liquid water.<sup>52</sup>

Near the sea iron could corrode heavily, to increasing extents the closer it was to the beach. This was related to the deposition of salts.<sup>53</sup>

All these reflections were important to understand what happened to iron objects exposed to harmful conditions. And the presence of salt was considered an important parameter.

Arrhenius said in 1973: „The chlorides, mostly in the form of iron chloride, are the most dangerous enemy of iron. Iron chloride, which has entered into rust and iron on most artefacts is difficult to wash out and deliquesces. If water vapour is present, it is absorbed and the  $\text{FeCl}_3$  solution migrates to the iron, dissolves it and forms  $\text{FeCl}_2$ . Under the action of oxygen from the air iron hydroxide is precipitated and  $\text{FeCl}_3$  is formed again. Heavy destruction of the iron in the form of pitting occurs.“<sup>54</sup>

North and Pearson discussed the role of water in combination with chlorides: „Corrosion will not occur in the absence of water but, as iron chloride is deliquescent, any dried artifact containing chlorides will

<sup>50</sup> EVANS U. R., 1924, p77; EVANS U. R., 1948, p29.

<sup>51</sup> EVANS U. R., 1924, p146.

<sup>52</sup> EVANS U. R., 1960, p481-484.

<sup>53</sup> Ibid., p504.

<sup>54</sup> ARRHENIUS O., 1973, p2.

*extract moisture from the atmosphere and so form a very corrosive solution with a high chloride content.*"<sup>55</sup>

Today, it is the model proposed by Turgoose in 1982 that is widely accepted.<sup>56</sup> He said that at the moment of excavation, the solid corrosion products present on the iron artifact were mostly magnetite (Fe<sub>3</sub>O<sub>4</sub>) and goethite (α-FeOOH), thermodynamically stable under burial conditions. Within pores of these layers, one could find an acidic solution containing ferrous ions and chloride ions (iron(II) chloride solution).<sup>57</sup>

After excavation, if the object was exposed to humidity and oxygen, one could see it break up and a reddish-brown powdery deposit could appear. This deposit consisted of akaganéite (β-FeOOH).<sup>58</sup> A solution of ferrous, ferric and chloride ions, of yellow colour and a very acid nature could sometimes be present in combination with akaganéite (β-FeOOH).<sup>59</sup>

Turgoose stated that for the formation of akaganéite (β-FeOOH) at room temperature ferrous and usually chloride ions (halide ions) must be present. He described the following reaction.<sup>60</sup>



In zones of active corrosion on iron artifacts, Zucchi et al. could already establish the presence of akaganéite (β-FeOOH) in 1977. The corrosion was accelerated on remaining metallic iron if akaganéite (β-FeOOH) was present. The main actor in this corrosion was seen to be chloride ions.<sup>61</sup>

Refait, Génin and Ståhl et al. found that akaganéite (β-FeOOH) was a symptom of high chloride concentrations and an acidic environment.<sup>62</sup>

Coming back to the model of Turgoose, we can say that the solution of iron(II) chloride present at the moment of excavation will dry and crystallize to iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O). If at this moment moist air has access to the object, the FeCl<sub>2</sub>·4H<sub>2</sub>O will transform to solid akaganéite (β-FeOOH) and a solution containing ferrous, ferric and chloride ions. If metallic iron is present with the iron(II) chloride, this transformation under moist air will be rapid.<sup>63</sup>

To locate where akaganéite (β-FeOOH) was formed in this corrosion process, Turgoose gave us some indications. He said that ferrous ions diffused away from the metal surface and met oxygen coming in from outside. As this reaction was taking place under acidic conditions, other corrosion products could dissolve. If the pH was very low the solubility of the β-FeOOH would be important and ferric ions remain in solution. This was known as the 'weeping' of artifacts.<sup>64</sup>

<sup>55</sup> NORTH A., PEARSON C., 1975 a, p75/13/3.1.

<sup>56</sup> TURGOOSE S., 1982 a, p97-101; WATKINSON D., 1982, p28; MATHIAS C., 1999, p1845-1846; WATKINSON D., LEWIS M., 2004, p88-102; THICKETT D., ODLYHA M., *in press*, 2006.

<sup>57</sup> TURGOOSE S., 1982 b, p6.

<sup>58</sup> ZUCCHI F., MORIGI G., BERTOLASI V., 1977, p103-105; TURGOOSE S., 1982 b, p6.

<sup>59</sup> TURGOOSE S., 1982 b, p6.

<sup>60</sup> TURGOOSE S., 1982 a, p98.

<sup>61</sup> ZUCCHI F., MORIGI G., BERTOLASI V., 1977, p103-105.

<sup>62</sup> REFAIT P., GENIN J.-M., 1993, p797-819; STÅHL K., NIELSEN K., JIANG J., LEBECH B., HANSON J. C., NORBY P., VAN LANSCHOT J., 2003, p2563-2564.

<sup>63</sup> TURGOOSE S., 1982 a, p98.

<sup>64</sup> *Ibid.*; TURGOOSE S., 1993, p45.

Another important insight was that if no iron core left in a corroded iron artifact then these reactions would not take place, as ferrous ions were a main partner for the formation of akaganéite ( $\beta$ -FeOOH).<sup>65</sup>

A new point added by Turgoose to the current knowledge at the time of his publication was his claim that excavated iron artifacts should be stored at RH levels as low as 20% or less to prevent ongoing reactions of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and iron (which would not take place below 15% RH).<sup>66</sup>

The model proposed by Turgoose can to some extent be found in articles already published in 1969 and 1970 by Keller. He said that akaganéite ( $\beta$ -FeOOH) could for example be obtained by oxidation of a mixture of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and ferrum reductum. The mixture was sprayed with water to transform it to akaganéite ( $\beta$ -FeOOH). He also observed akaganéite ( $\beta$ -FeOOH) being formed during pitting corrosion of iron when  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was in contact with metallic iron.<sup>67</sup>

To the same questions, Watkinson stated: *„It has long been accepted that chlorides are one of the chief causes of continued corrosion in archaeological ironwork. As a consequence of this thinking most treatments aim to remove or inhibit chlorides contained within the artifacts. The form of this chloride has been variously suggested as iron(III) chloride (Plenderleith and Werner, 1971), or as  $\beta$ -FeOOH in areas of active corrosion (Zucci, Morigi and Bertolasi, 1977), and as FeOCl in marine ironwork (North and Pearson, 1977). It has been suggested recently that the chlorides present at the time of excavation are probably in solution within the pores of the corrosion products (Turgoose, this volume).“*<sup>68</sup>

Mathias could see the described reactions by Turgoose: *„Observations presented here correlate with the model proposed by Turgoose since an iron oxide and iron oxyhydroxide phases have been identified in the corrosion layers. Cracking and spalling of artifacts in the post-storage environment, as well as chloride concentrations identified by elemental mapping, provide evidence for an akaganéite phase resulting after excavation and further oxidation.“*<sup>69</sup>

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<sup>65</sup> TURGOOSE S., 1982 a, p98.

<sup>66</sup> Ibid., p100.

<sup>67</sup> KELLER P., 1969, p103, 108; KELLER P., 1970, p31.

<sup>68</sup> WATKINSON D., 1982, p28.

<sup>69</sup> MATHIAS C., 1999, p1845-1846.



Figure 8: Active corrosion with akaganéite ( $\beta$ -FeOOH) formation leads to spalling of corrosion layers (blowpipe, iron, early 18<sup>th</sup> century AD, Court (BE), Switzerland).

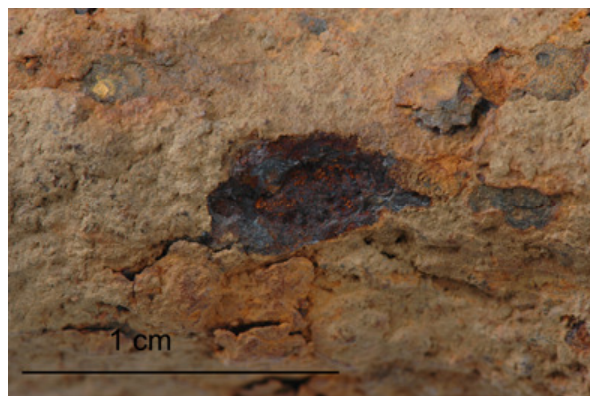


Figure 9: Cracking and spalling are visible signs for active corrosion (detail from the object to the left).

Selwyn et al. again took up the corrosion reactions described by Turgoose in 1982. They gave a very clear description of the model in action: „[...] the pores of corrosion products on freshly excavated iron are filled with an acidic  $\text{FeCl}_2$  solution, i. e., a solution containing  $\text{Fe}^{2+}$ ,  $\text{FeOH}^+$  and  $\text{H}^+$  ions charge-balanced by  $\text{Cl}^-$  ions. If iron is excavated and allowed to dry, the acidic  $\text{FeCl}_2$  solution concentrates, the corrosion layers crack, and oxygen becomes readily available. The sudden supply of oxygen rapidly oxidizes the  $\text{Fe}^{2+}$  ions in solution. [...] Solid iron oxide hydroxides ( $\text{FeOOH}$ ), more usually called iron oxyhydroxides, precipitate, and the solution becomes more acidic.”<sup>70</sup>

It also became clear that as long as oxygen was available, the corrosion cycle involving an acidic solution with chloride ions could go on. This all could now explain why iron objects exposed to the air after excavation would be destroyed so rapidly. As iron oxyhydroxides increase in volume during formation, corrosion layers on an object may crack and further oxygen and moisture could access the depth of the object.<sup>71</sup>

Selwyn et al. gave more details on the phenomenon of ‘weeping’. It seemed true that a low pH of 1-3 and the presence of ferrous ions ( $\text{Fe}^{2+}$ ) and iron(II) chloride ( $\text{FeCl}_2$ ) mentioned by North<sup>72</sup> and Turgoose<sup>73</sup> were conditions occurring during ‘weeping’. Selwyn et al. thought the phenomenon was due to the hygroscopic properties of the iron(II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  crystals would act as deliquescent materials being able to absorb moisture from the air and dissolve to form a solution). Ferric ions ( $\text{Fe}^{3+}$ ) were also observed in the solution formed during weeping. They might contribute to the deliquescence of the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . ‘Weeping’ could leave behind solid spherical shells.<sup>74</sup> The authors identified goethite ( $\alpha$ -FeOOH) and lepidocrocite ( $\gamma$ -FeOOH) as constituents of the shells, but no akaganéite ( $\beta$ -FeOOH). They said this might have been due to the experimental conditions used or that akaganéite ( $\beta$ -FeOOH) had initially formed and then transformed to goethite ( $\alpha$ -FeOOH). The

<sup>70</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p219.

<sup>71</sup> Ibid., p220.

<sup>72</sup> NORTH N. A., 1982, p75-83.

<sup>73</sup> TURGOOSE S., 1982 a, p97-101.

<sup>74</sup> SELWYN L. S., 2004, p296.



authors said that compared to Turgoose's observations of 'weeping' occurring away from metal surface, they could find 'weeping' occurring only from a metal surface on outwards.<sup>75</sup>

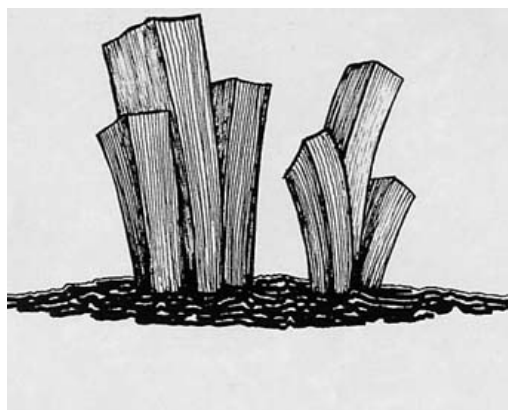


Figure 10: Diagram of vertically growing, voluminous akaganéite ( $\beta$ -FeOOH). (SELWYN L. S., SIROIS P.J., ARGYROPOULOS V., 1999, p226).

The authors said that akaganéite ( $\beta$ -FeOOH) could form on the iron/corrosion interface, at the place where iron(II) chloride ( $\text{FeCl}_2$ ) was concentrated. As akaganéite ( $\beta$ -FeOOH) was growing, elongated particles were formed and pressure put onto the overlying corrosion layers. These could then crack. To prevent these reactions, the authors advised removing the acidic iron(II) chloride solution because then chemical and physical damage could be stopped.<sup>76</sup>

Once all metallic iron lost in the artifact, chloride ions would move out of it.<sup>77</sup>

Another important aspect mentioned was the fact that the corrosion of iron was dependent on temperature

(corrosion was much more important at 20°C than at 4°C).<sup>78</sup>

Extensive research on the influence of the RH was carried out in 2004 by Watkinson and Lewis. They

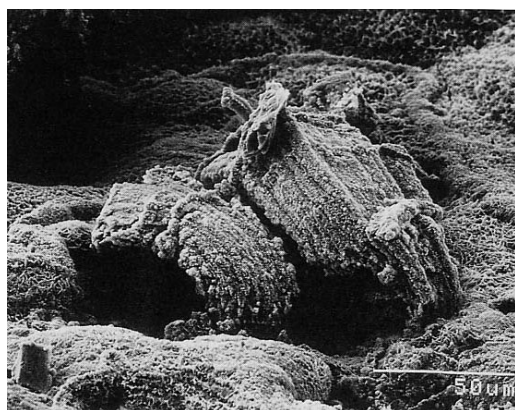


Figure 11: Scanning electron micrograph of akaganéite ( $\beta$ -FeOOH). (SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p226).

did some further tests on the model proposed by Turgoose, basing their results on gains in weight of their samples (see chapter 3.2.3). They found that iron in combination with iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ) did not corrode at a RH of 19%. But if  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was mixed with the iron powder, the mixture gained weight at 22%, 27.5% and 35% RH. The corrosion of the iron in this case would be slow at 22% RH and speed up at 30% and 35% RH. If akaganéite ( $\beta$ -FeOOH) was present on the iron powder, corrosion could take place at 15% RH (at 12% RH no significant corrosion was visible).<sup>79</sup>

Thickett showed that the critical RH for pure iron(II) chloride to oxidise to akaganéite ( $\beta$ -FeOOH) was situated at about 18%. The increase of akaganéite ( $\beta$ -FeOOH) formation was dramatic from 30% RH upwards. The author was able to show that the presence of copper or humic acids increased the amount of akaganéite ( $\beta$ -FeOOH) formed while goethite ( $\alpha$ -FeOOH) could reduce it.<sup>80</sup>

Lately another corrosion product forming in high chlorine-containing environments (chloride content of about 15-20 %mass) was detected in archaeological material: ferrous hydroxy-chloride ( $\beta$ -

<sup>75</sup> SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p220-221.

<sup>76</sup> Ibid., p225-227.

<sup>77</sup> SCHARFF W. et al., 2000, p26, p28.

<sup>78</sup> Ibid.

<sup>79</sup> WATKINSON D., LEWIS M., 2004, p88-102.

<sup>80</sup> THICKETT D., 2004, p90.

$\text{Fe}_2(\text{OH})_3\text{Cl}$ ). As akaganéite ( $\beta\text{-FeOOH}$ ), this corrosion product formed at the interface metal/oxide in the presence of chlorides. In zones with a high chloride concentration (15-20 %mass) preferably ferrous hydroxy-chloride formed whereas akaganéite ( $\beta\text{-FeOOH}$ ) formed where 5-8 %mass of chloride in the corrosion zone was present.<sup>81</sup>

Regarding recovered marine cast iron we can cite North and Pearson: „*Firstly, at room temperature,  $\text{FeOCl}$  will slowly convert to  $\text{FeCl}_3$  and  $\text{FeO}(\text{OH})$  in the presence of water.*”<sup>82</sup> For wrought and cast iron from the sea their analysis showed: „*Our X-ray diffraction analysis of untreated wrought and cast iron corrosion products show that the iron is present predominantly as a mixture of magnetite ( $\text{Fe}_3\text{O}_4$ ), iron oxy-hydroxide ( $\text{FeO}(\text{OH})$ ), iron oxy-chloride ( $\text{FeOCl}$ ) and, in the case of cast iron, iron carbide or cementite ( $\text{Fe}_3\text{C}$ ).*”<sup>83</sup> The authors advice was to aim for levels of less than 100 ppm (parts per million) in chloride in the object's corrosion layers after treatment and not go over a maximum of 200 ppm. This seemed to them a satisfactory level.<sup>84</sup>

North gave some indications on corrosion behaviour after recovery of marine cast iron objects. He said that if the object was allowed to dry out, then the chloride components would decompose to form hematite ( $\text{Fe}_2\text{O}_3$ ), iron(III) chloride ( $\text{FeCl}_3$ ), hydrogen chloride ( $\text{HCl}$ ) and iron oxyhydroxide ( $\text{FeO}(\text{OH})$ ). All these chemical products provided a good corrosion environment and if oxygen was available, corrosion could take place. Ferrous and ferric ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) in solution in the graphitized zones precipitated to form iron oxyhydroxide ( $\text{FeO}(\text{OH})$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The volume increase could cause the graphitized zone to crack. One should keep these objects wet to minimize access of oxygen to the graphitized layers and so oxygen reduction (the cathodic reaction) could be minimized.<sup>85</sup>

### **2.1.3 Observed corrosion products on iron from soil burial site**

Neff introduced a terminology to describe the layers found on a corroded archaeological iron object. The model shows the metallic substrate (M), then a layer of dense corrosion products (CPD for 'couche de produits denses') composed of oxides and oxyhydroxides. Follows a zone of transition, which separates the CPD from the burial environment. This layer is the transformed environment (MT for 'milieu transformé'), containing soil elements and corrosion products. The soil layer (S) surrounds the whole system of layers.<sup>86</sup>

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<sup>81</sup> REGUER S., DILLMANN P., MIRAMBET F., BELLOT-GURLET L., *in press*, 2005, p3-5.

<sup>82</sup> NORTH N. A., PEARSON C., 1975 b, p174.

<sup>83</sup> Ibid.

<sup>84</sup> NORTH N. A., PEARSON C., 1978, p179.

<sup>85</sup> NORTH N. A., 1987, p212-213.

<sup>86</sup> NEFF D. et al., 2005, p515-535.

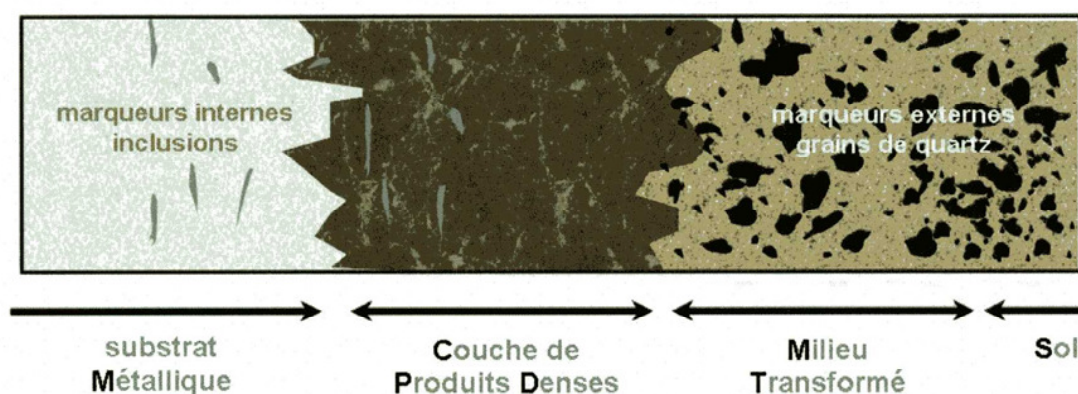


Figure 12: The different layers that can be found in an archaeological iron object: the metallic substrate with intern markers, a layer of dense corrosion products as oxides or oxyhydroxides followed by a transformed environment with elements of corrosion as well as soil components and a soil layer surrounding the whole. (REGUER S., 2005, p20).

Réguer told us about the corrosion products that had formed on iron objects in long-term burial conditions. Mainly goethite ( $\alpha\text{-FeOOH}$ ) was detected. Sometimes magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) were mixed in the layer alongside goethite. Siderite ( $\text{FeCO}_3$ ) could form in de-aerated environments.<sup>87</sup>

#### ***2.1.4 Some general reflections on evidence preserved in corrosion products and attitudes of conservators influencing further treatment success***

We shall finish this chapter with some more general reflections on corrosion layers, what information they might contain (affecting the choice of treatment) and on some aspects related to the way of dealing with excavated iron, which influences the forms of treatments after excavation.

Turgoose published an article on evidence preserved in corrosion products (organic material, information on the original shape and surface, metallurgical structure, prediction of original composition, information about burial environment). Sometimes, he stated, no adequate analysis techniques had been developed yet to fully understand all the aspects. So it seemed tempting to the author to leave corrosion layers on the artifact for future researchers and the application of future techniques. As this was not always possible, Turgoose emphasized the fact that with the removal of corrosion layers, information about the artifact itself, its burial context and environment could be lost.<sup>88</sup> Keene and Orton found out that the time-lapse between excavation and treatment might affect the results of a desalination treatment.<sup>89</sup> This seemed to be a key factor for post-excavation corrosion of iron artifacts. Regarding this aspect Greiff and Bach said that the removal of the chlorides out of the akaganéite ( $\beta\text{-FeOOH}$ ) network was a slow process. The desalination could be much faster if there was no akaganéite ( $\beta\text{-FeOOH}$ ) present. The iron chlorides in form of the iron chloride hydrates

<sup>87</sup> REGUER S., 2005, p20-21.

<sup>88</sup> TURGOOSE S., 1989, p30-31.

<sup>89</sup> KEENE S., ORTON C., 1985, p140.

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  were easier to remove (than akaganéite) even in a solution without addition of alkalis and this removal could be achieved within a short period of time.<sup>90</sup>

The protection of archaeological iron should start directly after excavation. Adequate storage is needed until treatment can be started. In the best-case scenario, the conservation and restoration begin immediately on the freshly excavated artifacts.<sup>91</sup>

## 2.2 Akaganéite ( $\beta\text{-FeOOH}$ )

This chapter contains some basic information on the occurrence, the formation, the chloride content and the structure of  $\beta\text{-FeOOH}$  (mineral name: akaganéite). This iron oxyhydroxide, a corrosion product, is – as we have already seen – believed to cause major problems in the conservation of archaeological iron artifacts.

For more detailed information on the formation, structure and characteristics of akaganéite ( $\beta\text{-FeOOH}$ ) one can refer to the following publications:

MACKAY A. L., 1962; KELLER P., 1969 and 1970; FEITKNECHT W. et al., 1973; CHILDS C. W. et al., 1980; GONZALES-CALBET J. M. et al., 1981; SELWYN L. S. et al., 1999; STÅHL K. et al., 2003; POST J. E. et al., 2003; WATKINSON D., LEWIS M. T., 2005; REGUER S., 2005 (this author gives an exhaustive list of further publications).

### 2.2.1 Occurrence

$\beta\text{-FeOOH}$  (akaganéite) was produced synthetically first in 1925 by J. Böhm<sup>92</sup>, who thought it was a new form of iron(III) oxide hydrate.<sup>93</sup> Synthetic  $\beta\text{-FeOOH}$  (akaganéite) was first identified by XRD in 1935 by Weiser and Milligan.<sup>94</sup> The compound was named  $\beta\text{-FeOOH}$  (as against  $\alpha\text{-}$  and  $\gamma\text{-FeOOH}$ ) and presented as an iron oxyhydroxide rather than an iron(III) oxide hydrate.<sup>95</sup>  $\beta\text{-FeOOH}$  can contain fluorine ions ( $\text{F}^-$ ) or chlorine ions ( $\text{Cl}^-$ ).<sup>96</sup> It has also been possible to produce chloride-free  $\beta\text{-FeOOH}$  (akaganéite).<sup>97</sup>

Later than its synthetically obtained form  $\beta\text{-FeOOH}$ , the mineral akaganéite was discovered in 1961 by Dr. M. Nambu in the Japanese limonite mine Akagane. The mineral was named akaganéite after the location of the mine (we can also find this name applied to the synthetic form  $\beta\text{-FeOOH}$ ).<sup>98</sup> The mineral akaganéite ( $\beta\text{-FeOOH}$ ) is free of chloride.<sup>99</sup> Akaganéite ( $\beta\text{-FeOOH}$ ) is a weathering product

<sup>90</sup> GREIFF S., BACH D., 2000, p324.

<sup>91</sup> SCHARFF W. et al., 2000, p362.

<sup>92</sup> BÖHM J., 1928, cited in: GALLAGHER K. J. et al., 1969, p465-470.

<sup>93</sup> KELLER P., 1969, p103; GALLAGHER K. J., 1970, p1225.

<sup>94</sup> WEISER H. B., MILLIGAN J., 1935, cited in STÅHL K. et al., 2003, p2565; SELWYN L. S., SIROIS P. J., AGYROPOULOS V., 1999, p223.

<sup>95</sup> KELLER P., 1969, p103.

<sup>96</sup> MACKAY A. L., 1960, p551.

<sup>97</sup> FEITKNECHT W. et al., 1973, p2847; DEGRIGNY C. et al., 1999, p34.

<sup>98</sup> MACKAY A. L., 1962, p270.

<sup>99</sup> KELLER P., 1969, p103; FEITKNECHT W. et al., 1973, p2847.

and has also been observed in meteorites, on rock art, on iron exposed to a marine atmosphere and on archaeological iron.<sup>100</sup>

## 2.2.2 Structure

Réguer detailed that in the structure of akaganéite ( $\beta$ -FeOOH), each  $\text{Fe}^{3+}$  ion was surrounded by six atoms of oxygen and/or hydroxyl groups, forming an octahedron (see figure 13). These octahedra are linked to each other sharing edges and corners to form double chains that are parallel to the b-axis. The double chains in turn are linked with other double chains via the tops of the octahedra. This creates a cavity (also called channel or tunnel<sup>101</sup>) in which  $\text{Cl}^-$  ions or  $\text{F}^-$  ions, hydroxyl groups or water molecules can be trapped to stabilize the structure (see figure 14).<sup>102</sup>

Chlorides can be adsorbed on the surface area of akaganéite ( $\beta$ -FeOOH) and eventually be released in washing off.<sup>103</sup> When the chloride content is smaller, less chloride can be found adsorbed in the akaganéite ( $\beta$ -FeOOH). The structure of the compound is not influenced by this surface adsorption of chloride ions. These chlorides can be adsorbed via substitution of OH-groups in the octahedra on the surface of the compound. If there are fewer chloride ions in the structure the unit cell in the crystal structure becomes smaller and the octahedra deformed (Réguer could see this in the changes of the *a*- and *b*-values with the help of XRD). The adsorption-chlorine can leave the compound more easily than the structural chlorine. It is not known if all the chlorine can be removed from the compound without a break-down of its structure.<sup>104</sup> Watkinson et al. claimed the internal (or structural) chloride could only be removed by decomposition of the akaganéite ( $\beta$ -FeOOH).<sup>105</sup> Akaganéite ( $\beta$ -FeOOH) remains stable up to 200°C. The chlorides released during washing are the chloride ions adsorbed at the surface of the akaganéite ( $\beta$ -FeOOH) particles.<sup>106</sup>

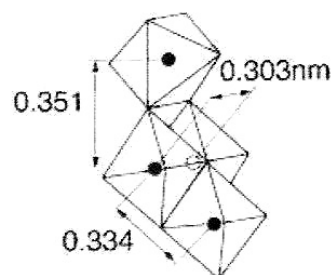


Figure 13: The octahedron-structure described by Réguer, the distances between the iron ions are given. (MANCEAU A. et al., 1988, cited in: REGUER S., 2005, p32).

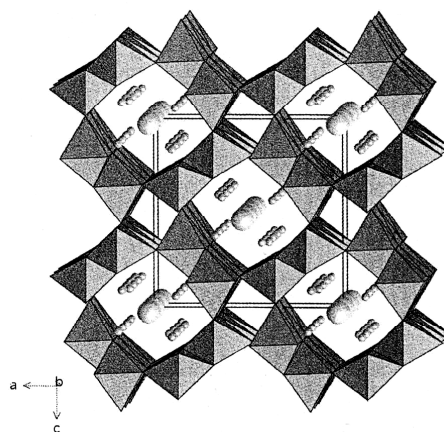


Figure 14: Structure of akaganéite ( $\beta$ -FeOOH) with chlorides (large circles) and hydrogens (small circles) in the tunnel region. (POST J. E., et al., 2003, p783).

<sup>100</sup> SELWYN L. S., SIROIS P. J., AGYROPOULOS V., 1999, p223.

<sup>101</sup> The tunnel measures  $5 \times 5 \text{ \AA}^2$  (two octahedra each side). (REGUER S., 2005, p31).

<sup>102</sup> REGUER S., 2005, p31. Ståhl et al. gave the most recent description of akaganéite ( $\beta$ -FeOOH), claiming it could be proved to be monoclinic with space group  $I2/m$ ,  $a = 10.6000\text{\AA}$ ,  $b = 3.0339\text{\AA}$ ,  $c = 10.513\text{\AA}$  and  $\beta = 90.24^\circ$ . (STÅHL K. et al., 2003, p2565).

<sup>103</sup> STÅHL K. et al., 2003, p2574. These chlorides are mobile and can corrode iron in contact with the akaganéite,  $\beta$ -FeOOH. (WATKINSON D., et al., 2005, p81).

<sup>104</sup> REGUER S., 2005, p93, p 119, p120, p178.

<sup>105</sup> WATKINSON D., LEWIS M. T., 2005, p242.

<sup>106</sup> STÅHL K. et al., 2003, p2574.

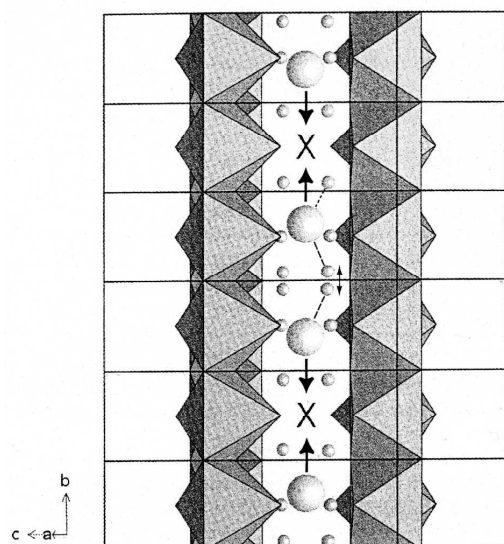


Figure 15: Possible ordering of chloride ions in the tunnels of akaganéite ( $\beta$ -FeOOH). The large circles indicate Cl anions, the small circles represent H atoms. Where the tunnel site is vacant, this is indicated by 'X'. (POST J. E., et al., 2003, p786).



Figure 16: This electron micrograph of akaganéite ( $\beta$ -FeOOH) crystals shows an aspect of bundles of 'rods' or 'needles' ( $\times 120,000$ ). (GALLAGHER K. J., 1970, p1226).

Akaganéite ( $\beta$ -FeOOH) can show two morphologies: somatoids or cigar shaped crystals on the one hand and smaller rod-like crystals.<sup>114</sup>

Earlier it was thought that if chlorides were present in the structure of akaganéite ( $\beta$ -FeOOH), they could be washed out with water from the tunnels in which they were located (which would lead to the washed form  $\text{FeO.OH} \cdot 1/4\text{H}_2\text{O}$  in places where water molecules occupy the tunnels instead of chlorides).<sup>107</sup>

The chloride in the tunnels is arranged in a random manner. The distance between two chlorides has to be at least twice the ionic radius of the chloride (which means 3.6 Å). Every two out of three of the sites can be occupied to a maximum and the others left vacant (see figure 15). This means that there is 1.3 to 1.6 atoms of chlorine in the unit cell of the crystal structure (6-7 %mass of chlorine).<sup>108</sup> Water cannot be placed in the channels, as the vacant space left by the chlorine is too small. Hydrogen appears in hydroxide groups and the hydrogen points into the tunnel to form hydrogen bonds with the chlorides.<sup>109</sup> When less structural chlorine is present, this can possibly be made visible, as demonstrated by Réguer, with Raman spectroscopy, as the number of hydrogen bonding diminishes when less chloride is present (effect visible on the Raman vibrations).<sup>110</sup>

Based on XRD patterns, Bernal et al. noted that the structure of akaganéite ( $\beta$ -FeOOH) was similar to that of hollandite ( $\text{BaMn}_x\text{O}_{16}$ ).<sup>111</sup> Later, Keller confirmed, using XRD and infrared (IR) spectroscopy that akaganéite ( $\beta$ -FeOOH) was isostructural with hollandite.<sup>112</sup> In 1991 Post and Buchwald found the unit cell of akaganéite ( $\beta$ -FeOOH) to be monoclinic (and not tetragonal as assumed previously).<sup>113</sup>

<sup>107</sup> GALLAGHER K. J., 1970, p1225.

<sup>108</sup> REGUER S., 2005, p177.

<sup>109</sup> STÄHL K. et al., 2003, p2572.

<sup>110</sup> REGUER S., 2005, p99.

<sup>111</sup> BERNAL J. D. et al., 1959, p15-30.

<sup>112</sup> KELLER P., 1970, p29-49.

<sup>113</sup> POST J. E., BUCHWALD V. F., 1991, p272-277.

<sup>114</sup> SCHWERTMANN U., CORNELL R. M., 2000, p113.

## 2.2.3 Formation

### 2.2.3.1 Conditions of formation

Akaganéite ( $\beta$ -FeOOH) is formed in halide-rich environments containing chlorides  $\text{Cl}^-$  or fluorides  $\text{F}^-$ .<sup>115</sup> The number of  $\text{Cl}^-$  in its structure is related to the amount present in the solution from which akaganéite ( $\beta$ -FeOOH) is formed. The more chloride ions present in the solution, the more chloride will be trapped in the final structure.<sup>116</sup> The environment in which akaganéite ( $\beta$ -FeOOH) is formed shows a low pH.<sup>117</sup>

Akaganéite ( $\beta$ -FeOOH) can be produced in the laboratory. Different approaches have been suggested. Iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) crystals can be oxidized in the air to become akaganéite ( $\beta$ -FeOOH). Diluted iron(III) chloride ( $\text{FeCl}_3$ ) solutions can be hydrolysed to obtain akaganéite ( $\beta$ -FeOOH). Mackay used several methods, amongst them a solution of  $\text{FeCl}_3$ , which he left at room temperature for six months to hydrolyse. He found differences in crystallization behaviour of akaganéite ( $\beta$ -FeOOH) when changing temperatures during hydrolysis.<sup>118</sup> Keller applied hydrolysis of iron oxide chloride ( $\text{FeOCl}$ ) as well as mixing  $\text{FeCl}_3$  with potassium carbonate ( $\text{K}_2\text{CO}_3$ ) at  $75^\circ\text{C}$ . He himself advised mixing 20g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  with 16.5g of iron (ferrum reductum) and spraying water ( $\text{H}_2\text{O}$ ) on the mixture daily. The mixture should transform to akaganéite ( $\beta$ -FeOOH) within three to five days.<sup>119</sup> According to Réguer the most often used procedure today is the hydrolysis of a solution of  $\text{FeCl}_3$  at  $60$ - $100^\circ\text{C}$  and a pH of  $1.7$ - $1.2$ .<sup>120</sup>

Akaganéite ( $\beta$ -FeOOH) can be transformed into goethite ( $\alpha$ -FeOOH) or hematite ( $\text{Fe}_2\text{O}_3$ ) depending on the pH values used.<sup>121</sup> Iron oxide chloride ( $\text{FeOCl}$ ) has also been reported as a possible transformation product from akaganéite ( $\beta$ -FeOOH).<sup>122</sup>

In this work, the reference akaganéite ( $\beta$ -FeOOH) to elaborate detection limits on analysis equipment has been produced in the following way. 100ml of  $0.3\text{M}$   $\text{FeCl}_3$  was kept heated at  $70^\circ\text{C}$  in a sealed glass flask for 48 hours. The precipitate was collected by centrifuging, washed four times in the centrifuge with freshly deionised water and then left to dry in the air.<sup>123</sup>

### 2.2.3.2 Process of formation (imitation of the corrosion reactions in freshly excavated iron)

As part of the quest for possible storage solutions for freshly excavated iron objects, the possible formation of akaganéite ( $\beta$ -FeOOH) from a powder mixture of iron chloride hydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and pure iron (Fe) will be examined. The mixture was made of equal amounts of iron (Fe) and iron chloride

<sup>115</sup> WATKINSON D., LEWIS M. T., 2005, p242; REGUER S., 2005, p26.

<sup>116</sup> SELWYN L. S., SIROIS P. J., AGYROPOULOS V., 1999, p224-225.

<sup>117</sup> STÅHL K. et al., 2003, p2564.

<sup>118</sup> MACKAY A. L., 1960, p546; MACKAY A. L., 1962, p273-277.

<sup>119</sup> KELLER P., 1969, p103.

<sup>120</sup> REGUER S., 2005, p27.

<sup>121</sup> CRONYN J. M., 1990, p195; SELWYN L. S., SIROIS P. J., AGYROPOULOS V., 1999, p223.

<sup>122</sup> STÅHL K. et al., 2003, p2565.

<sup>123</sup> THICKETT D., *unpublished*, 2003, p6.

tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ). The approach was used by Keller in 1969<sup>124</sup> and was also referred to in the work of Turgoose in 1982, in which he described post-excavation corrosion<sup>125</sup>. Turgoose presented the following overall formula:



To begin with, the two compounds (Fe and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) are thoroughly mixed together. First the iron(II) chloride transforms into iron(III) chloride, then akaganéite ( $\beta\text{-FeOOH}$ ). The higher the RH, the quicker the transformation to akaganéite ( $\beta\text{-FeOOH}$ ) occurs. Also, the higher the RH, the more iron will convert to akaganéite ( $\beta\text{-FeOOH}$ ). After two months at 20% RH, approximately 1% of the iron in the Fe/  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  mixture will turn to akaganéite ( $\beta\text{-FeOOH}$ ). At 25% RH, a conversion of 4% of the iron occurs. The higher the RH levels get, the more conversion takes place.<sup>126</sup>

## 2.2.4 Composition

Akaganéite ( $\beta\text{-FeOOH}$ ) contains iron (Fe), hydrogen (H) in hydroxide groups (OH), chlorine (Cl) and oxygen (O). In 2003, Ståhl gave the tentative chemical formula  $\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$  to akaganéite ( $\beta\text{-FeOOH}$ ).<sup>127</sup> Akaganéite ( $\beta\text{-FeOOH}$ ) can also contain fluorine (F) instead of chlorine (Cl).

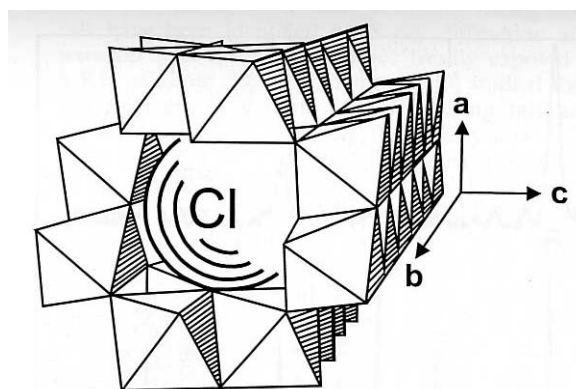


Figure 17: Idealized model of akaganéite ( $\beta\text{-FeOOH}$ ). (SELWYN L. S., SIROIS P. J., ARGYROPOULOS V., 1999, p224).

### 2.2.4.1 Chlorine content

The real chlorine content and the position of the chlorides in the structure of akaganéite ( $\beta\text{-FeOOH}$ ) remains a subject of discussion. The role of chlorine is important for the understanding of post-excavation corrosion processes, where chlorine is the main actor causing objects to get damaged.

Synthetic akaganéite ( $\beta\text{-FeOOH}$ ), produced with various techniques, was tested by Keller in 1970<sup>128</sup> and he found the following:

Cl: 2.28-6.40 %mass.

Chemical formula:  $(\text{Cl},\text{OH})_{<2}\text{Fe}_8(\text{O},\text{OH})_{16}$ .

According to Childs, this gives the formula  $\text{Cl}(\text{H}_2\text{O})\text{Fe}_8\text{O}_7(\text{OH})_9$  for a maximum of 4.6 %mass chloride content (one  $\text{Cl}^-$  per unit cell).<sup>129</sup>

<sup>124</sup> KELLER P., 1969, p103.

<sup>125</sup> TURGOOSE S., 1982 a, p97-101.

<sup>126</sup> Personal communication with David Thickett, English Heritage, London, 17/02/2006.

<sup>127</sup> STÅHL K. et al., 2003, p2573.

<sup>128</sup> KELLER P., 1970, p46-47.

<sup>129</sup> CHILDS C. W. et al., 1980, p17.



An iron-nickel meteorite studied by Post and Buchwald in 1991<sup>130</sup> gave this:

Cl: 3.6 – 6.3 %mass (NiO: 0.4 – 5.6 %mass; Fe<sub>2</sub>O<sub>3</sub>: 69 – 76 %mass; H<sub>2</sub>O: 12 – 14 %mass).

Chemical formula: Fe<sup>3+</sup><sub>7.6</sub>Ni<sup>2+</sup><sub>0.04</sub>O<sub>6.35</sub>(OH)<sub>9.65</sub>Cl<sub>1.25</sub>

Akaganéite (β-FeOOH) obtained through hydrolysis of a solution of iron(III) chloride (FeCl<sub>3</sub>) by Ståhl et al. in 2003<sup>131</sup>:

Cl: 6.2 %mass (Fe: 58.9 %mass; O: 33.7 %mass; H: 1.2 %mass).<sup>132</sup>

Chemical formula<sup>133</sup>: FeO<sub>0.833</sub>(OH)<sub>1.167</sub>Cl<sub>0.167</sub>.

Schwertmann and Cornell claimed that akaganéite (β-FeOOH) contained between 1 and 7% chloride.<sup>134</sup>

As Réguer stated, variation in chlorine content could be due to the origin of the material (natural or synthetic) or the preparation parameters of the compound. But chlorine always seems to be present in akaganéite (β-FeOOH). Even washing the compound in solutions of a pH>7 did not lower the chlorine-concentration below 2-3 %mass. The chlorine seems to stabilise the structure of akaganéite (β-FeOOH).<sup>135</sup> Watkinson et al. said removing the structural chloride would result in the decomposition of akaganéite (β-FeOOH).<sup>136</sup>

Degrigny et al. were able, however, to produce akaganéite (β-FeOOH) that did not contain chlorides. They immersed small iron plates in demineralised water. Besides magnetite (Fe<sub>3</sub>O<sub>4</sub>), akaganéite (β-FeOOH) was formed on the plates and detected by means of Mössbauer spectroscopy. However, it was difficult to see on XRD spectra.<sup>137</sup>

## 2.3 Akaganéite (β-FeOOH) in the daily life of conservators

This chapter shall list some experiences made by conservators, researchers or archaeologists confronted with iron artifacts suffering from active corrosion as early as in 1880. These authors did not always know what kind of a phenomenon was responsible for the ongoing reactions they saw. Nor did they usually know – especially in the first half of the 20<sup>th</sup> century – that they were confronted with akaganéite (β-FeOOH). So it is especially interesting to see that even without being aware of the exact reactions, the authors gave detailed descriptions, which show us today that the same problems we are facing caused a lot of headache to our predecessors!

Let's make an excursion into history and to our colleagues at the time. In 1887, Salzer mentioned in the *Chemiker-Zeitung* that re-corrosion of ancient iron artifacts was a well-known problem. He had

<sup>130</sup> POST J. E., BUCHWALD V. F., 1991, p272-273.

<sup>131</sup> STÅHL K. et al., 2003, p2573.

<sup>132</sup> REGUER S., 2005, p29.

<sup>133</sup> STÅHL K. et al., 2003, p2573.

<sup>134</sup> SCHWERTMANN U., CORNELL R. M., 2000, p113.

<sup>135</sup> REGUER S., 2005, p29-30. The author doesn't state which solutions are used for washing.

<sup>136</sup> WATKINSON D., LEWIS M. T., 2005, p242.

<sup>137</sup> DEGRIGNY C. et al., 1999, p34, p40.

seen brown droplets on the surface of objects (the so-called 'Dunstperlen'). Earlier Krause had found that those droplets contained ferrous and ferric iron chloride.<sup>138</sup>

Rosenberg described active corrosion on iron artifacts after having put the objects into a humidity chamber. He saw beads of exudation, black and brown droplets. The droplets were the size of a needle head. The author had also come across the phenomenon of cracking objects due to the increase in volume of the corrosion products. Rosenberg claimed that even with the washing treatments one could never get rid of all the chlorides. It was clear to him that the action of the chloride destroyed the artifacts.<sup>139</sup>

In 1933 Scott stated regretfully that iron artifacts often seemed to be „[...] a meagre skeleton of the metal covered with a coating of very varying thickness of black iron oxide [...]”<sup>140</sup> and that „[...] comparatively little can be done [...]”<sup>141</sup>. He saw little brownish liquid drops on the surface of those artifacts. In the drops chlorine was present.<sup>142</sup> In an earlier publication in 1921 he mentioned the formation of clear drops that later became coated over with a film of reddish rust. It seemed clear to him at that moment that this was due to water vapour contained within the air. Even if one kept the objects in a dry atmosphere in the museum, reactions would not stop, as the British climate contained a high level of water vapour.<sup>143</sup>

When iron objects were excavated from a site under a stockyard in 1938, Kenttämää described them as follows: The objects were covered with rust bubbles. These were filled with salt crystals. The crystals were either small black discs or needle-like prisms. If the objects were left at the air brown droplets would form and the author described this as sweating. The droplets were of acidic nature and contained chlorides, oxygen and iron.<sup>144</sup>

Salin and France-Lanord detected crevices in objects in uncontrolled environments. Major factors in the deterioration seemed to be the presence of chlorides, oxygen and atmospheric humidity.<sup>145</sup> In another publication from 1946, the authors described the appearance of brown droplets, which seemed to them characteristic of corrosion due to chlorides. Flakes of oxides were often visible and powdery objects were quite frequent.<sup>146</sup>

In 1966 Eriksen and Thegel tried to explain reactions they could see on corroding iron artifacts. They had seen iron guns 'sweating' after recovery from the sea. They supposed this reaction was caused by iron(II) chloride seeping outwards from the object. The authors examined drops of exuded water found on the surface of the artifacts. They expected sodium chloride (NaCl) to be present but found that there was no sodium. Sodium seemed to react to form sodium hydroxide (NaOH) and leave the iron object. The Cl-ions appeared to react with the Fe-ions to form iron(II) chloride, which under the influence of oxygen would transform to iron(III) chloride.<sup>147</sup>

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<sup>138</sup> SALZER T., 1887, p574.

<sup>139</sup> ROSENBERG G. A., 1917, p8-9, p32.

<sup>140</sup> SCOTT A., 1933, p7.

<sup>141</sup> Ibid.

<sup>142</sup> Ibid.

<sup>143</sup> SCOTT A., 1921, p11.

<sup>144</sup> KENTTÄMAA M., 1938, p3-4.

<sup>145</sup> SALIN E., FRANCE-LANORD A., 1943, p11-12.

<sup>146</sup> SALIN E., FRANCE-LANORD A., 1946, p262-263.

<sup>147</sup> ERIKSEN E., THEGEL S., 1966, p63, p91.

Typical formation of droplets and small structures growing out of the iron were described by Wihr in 1972. These structures were surrounded by a more or less hard skin. The content of these drops was most often a dry powder and sometimes a caliginous whitely or clear yellow solution, always very rich in chlorides. Wihr also witnessed cracking, dilapidating artifacts.<sup>148</sup>

Arrhenius reported having seen iron objects from salty environments (near the sea or in salt mines) stored untreated in museums. He reported having seen iron(III) chloride ( $\text{FeCl}_3$ ) in a large amount emanating from those artifacts.<sup>149</sup>

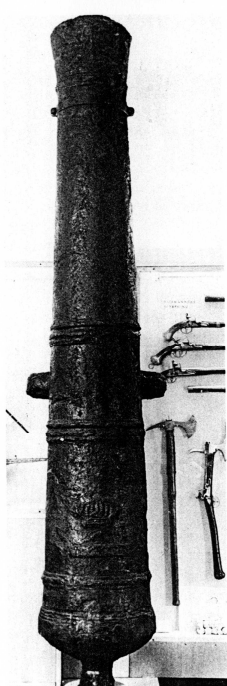


Figure 18: The cannon from the 'Riksäpplet' salvaged in 1953 after recovery. (BARKMAN L., 1973, p22).



Figure 19: The same cannon in 1972: severe corrosion is visible. The ornamentation has disappeared. (BARKMAN L., 1973, p22).

Barkman described the corrosion of a cannon from the 'Riksäpplet', salvaged in 1953. The cannon was brushed clean and anti-rust oil was applied. After 18 years of exhibition of the cannon in the museum in Stockholm, the corrosion was so strong that all ornamentation had disappeared (see figures 18 and 19).<sup>150</sup>

Concerns were voiced by Ersfeld and Bleck about the position of chlorides in the iron artifact. They said in 1981: „Bei der Beschäftigung mit den verschiedenen Entsalzungsmethoden geht man üblicherweise von der Vorstellung aus, dass sich die Chloride und andere Salze in Hohlräumen, Poren und Kapillaren der Rostschicht befinden, in denen sie benetzt und aus denen sie herausgewaschen werden müssen.“<sup>151</sup> Apparently the chlorides should be located in cavities and pores in the rust layers from where they could be washed out. The authors could not find the presence of the predicted pores in which the

chlorides were said to be located and from where they had to be washed out. The microscope at a 100-fold magnification could not bring any evidence of the mentioned cavities. They found that corroded iron without a metal core would not show any reactions involving chlorides in the humidity chamber whereas the same type of artifact with a metal core left would show chloride-blisters after one to five days in a humidity chamber. Where metallic iron and rust lay next to one another, the authors could see active blisters.<sup>152</sup>

<sup>148</sup> WIHR R., 1972, p31.

<sup>149</sup> ARRHENIUS O., 1973, p3.

<sup>150</sup> BARKMAN L., 1975, p170.

<sup>151</sup> ERSFELD J., BLECK R.-D., 1981, p25.

<sup>152</sup> Ibid., p25-26.



Figure 20: The voluminous active corrosion makes flakes fall off this metal fitting (iron, early 18<sup>th</sup> century AD, Glassworks Court, Switzerland, excavation 2003). (Archaeological Office of the Canton of Bern, Switzerland).



Figure 21: Another blade suffering from the formation of akaganéite ( $\beta$ -FeOOH) after excavation (iron, early 18<sup>th</sup> century AD, Glassworks Court, Switzerland, excavation 2000). (Archaeological Office of the Canton of Bern, Switzerland).

Argo stated correctly in 1982 that: „Akaganéite is a prime cause of corrosion in excavated objects which have been allowed to dry out prior to treatment.”<sup>153</sup>

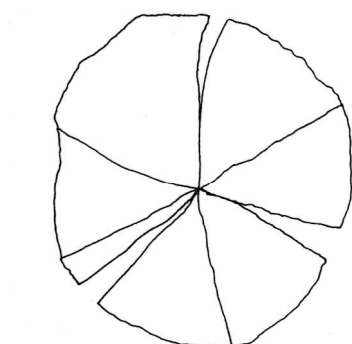


Figure 22: Illustration of a mineralized object disintegrating into wedges. (KNIGHT B., 1982, p50).

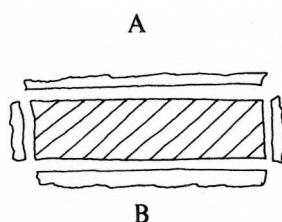


Figure 23: If metal remains in the iron artifact flaking can be a sign of active corrosion. (KNIGHT B., 1982, p50).

Two different ways of iron objects' break-down were described by Knight. He mentioned the break-down into wedges or flakes. In the first category there are mineralized objects or those containing only a small amount of metallic iron. The second category, where flaking appears, is more that of solid objects, according to the author.

Flaking is said to be due to the

drying out of the object (shrinkage of the magnetite layer) and akaganéite ( $\beta$ -FeOOH) formation. The akaganéite ( $\beta$ -FeOOH) crystals could push superior layers off as flakes.<sup>154</sup>

In 1993 Selwyn and Logan described the active corrosion due to chlorides on iron objects as follows: „Unstable iron was recognized by the presence of either surface sweating or akaganéite ( $\beta$ -FeOOH). Surface sweating (weeping) is defined as the formation of yellow, brown or orange droplets when the relative humidity is above about 70%, or the formation of similarly coloured blisters from the desiccation of sweating iron. Akaganéite appears as long, thin, orange crystals that form at the metal/corrosion interface. The crystals have a fuzzy appearance. Cracks in the outer layer of corrosion

<sup>153</sup> ARGO J., 1982, p7.

<sup>154</sup> KNIGHT B., 1982, p50-51.

*are often the first indication that akaganéite is present.*"<sup>155</sup> The authors are fully aware of the ongoing reactions. Akaganéite ( $\beta$ -FeOOH) is seen to be a major factor in post-excavation corrosion.

Some authors observed the time interval at which corrosion on freshly excavated iron started very closely. One description gave us details of a horseshoe fragment placed into a resealable plastic bag after the excavation. No control was taken on the climate. Six weeks after the excavation, corrosion was in full flow. After five months, heavy efflorescence of chloride was visible. Big flakes fell off the object. After three years, this object was so far deteriorated that any restoration would have been very time-consuming and costly. All zones of the old surface were detached from the metal core.<sup>156</sup>

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<sup>155</sup> SELWYN L. S., LOGAN J. A., 1993, p804.

<sup>156</sup> MEIER M., TEGGE C., 1996, p150.

## 3 DEALING WITH THE EXCAVATED IRON OBJECTS: TREATMENT AND STORAGE METHODS

This chapter shall give a survey on approaches made by conservators to preserve iron objects from deterioration due to influences of the environment after excavation. The emphasis shall be on the storage of chloride infested archaeological iron artifacts with the help of a desiccant (silica gel) and low oxygen environments (storage in nitrogen atmosphere, addition of oxygen absorbers to the storage system).

The chapter starts with an overview on stabilisation treatments (alkaline sulphite, electrolysis, heat treatments, etc.). We can say that none of the proposed treatments aiming to remove all chlorides and stabilise the iron artifacts have proved 100% effective. Re-corrosion of treated objects is due to the presence of remaining chlorides.<sup>157</sup> There have been various approaches to the preservation of iron objects. As the topic of this research is storage in low-oxygen environments and in dry and cold conditions, the chapter gives most details on storage under these mentioned conditions (anoxia with oxygen absorbers as well as inert gases, low RH storage and storage in the cold). But the storage methods examined in this work have their disadvantages, too: regular monitoring is needed and as soon as conditions change, corrosion can occur due to the presence of chlorides.

### 3.1 Stabilisation treatment

A hundred years back, washing treatments for iron finds were very popular amongst conservators. It seemed logic that the chlorides had to be washed out of the iron artifacts.<sup>158</sup> Water washing methods were actual in the 1880s up to the 1920s, as well as impregnation with oils and waxes to prevent influences due to the environment. Heat treatments were well known (and used from about 1920 to the end of the 1970s in some countries), with the idea to volatilize any chlorine. Reduction treatments in the field of stabilisation of iron objects with electrolysis or gas plasma reduction were applied as early as in the end of the 19<sup>th</sup> century and some still remain in use. The alkaline sulphite method to extract chlorides of the object in an aqueous solution was developed in 1975 and is further examined and in use today. This chapter will give a very brief view on some major approaches without being exhaustive. For further information, see the following reference: SCOTT D. A., *Iron and Steel in Art: Corrosion, Colourants, Conservation. In Press*, Archetype Publications Ltd., 2006.

#### 3.1.1 Washing with water and early protective layers

One of the first treatments, applied from the 1880s, consisted of washing the iron finds in water to extract harmful substances. This approach was introduced in 1882 by the German Krause.<sup>159</sup> Treatment with spirits of wine followed by soaking in boiling paraffin was suggested little later by

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<sup>157</sup> REGUER S., 2005, p12.

<sup>158</sup> KNIGHT B., 1997, p37.

<sup>159</sup> KRAUSE E., 1882, p533-537.

another German, Salzer.<sup>160</sup> Washing of objects in water followed by application of paraffin wax was also carried out by Englishman W. M. F. Petrie, an excavator in the Middle East. Petrie remarked that these so-treated objects did not stay stable, because some salt remained in them. He observed the re-crystallization of salts in 'damp' countries (probably objects he brought back to England).<sup>161</sup> In Norway immersion in a boiling bath of linseed oil and yellow beeswax (later also copal varnish) was commonly used in the 1870s.<sup>162</sup>

In these early times of conservation, lead-based paints were applied on the surface of objects until the early decades of the 20<sup>th</sup> century. Pliny (23 – 79 AD) had already claimed that iron objects could be protected from rust by cerussa, gypsum or vegetable pitch.<sup>163</sup>

The washing with water was soon claimed not to be efficient in the prevention of further corrosion: many objects re-corroded when replaced in the uncontrolled environment.

### **3.1.2 Early approaches in electrolysis**

In Norway stripping with electrochemical or electrolytic reduction began to be applied in 1892. Evidence of hidden Roman letters and signs was discovered on Viking swords under the thick wax and oil layers applied at that time to the objects. Krefting advised to remove the corrosion layers by stripping to unveil the signs. Objects were wrapped in a zinc filament and placed into caustic soda. Molten paraffin wax was applied as a protective layer.<sup>164</sup> Delamination by heating to red heat followed by treatment with dilute sulphuric acid was applied by Blell in Prussia in 1883.<sup>165</sup>

In Denmark Rosenberg wrapped iron objects in moistened asbestos paper, heated them to 800°C and then they were soaked in cold potassium carbonate. Washing in distilled water followed before immersion in boiling paraffin wax.<sup>166</sup> Apparently this method was used until the 1980s by the National Museum of Denmark in Copenhagen but is considered obsolete today.<sup>167</sup> The heating up to these high temperatures surely destroys the original metallurgical structure.

These sometimes very radical and extreme methods seem out of interest today, as loss of corrosion layers – and therefore evidence – is not an option anymore.

### **3.1.3 Impregnation**

Paraffin was the most often used material for impregnation in the 1880s. Salzer and Petrie widely worked with it in 1887 and 1888.<sup>168</sup> But also rubber was applied to impregnate objects.<sup>169</sup> Rathgen used solutions of natural rubber as a consolidant and dammar resin in solvents or linseed oil.<sup>170</sup>

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<sup>160</sup> SALZER T., 1887, p574.

<sup>161</sup> SEASE C., 2001, p183-188.

<sup>162</sup> JAKOBSEN T., 1988, p53.

<sup>163</sup> SCOTT D. A., *in press*, 2006, p246.

<sup>164</sup> KREFTING A., 1892, p3-13; HANSEN J., 2001, p101.

<sup>165</sup> RATGHEN F., 1924, p45-67.

<sup>166</sup> ROSENBERG G. A., 1917, p1-11; CHRISTENSEN B. B., 1968, p299-301.

<sup>167</sup> SCOTT D. A., *in press*, 2006, p249.

<sup>168</sup> SALZER T., 1887, p574; SEASE C., 2001, p183-188.

<sup>169</sup> KRAUSE E., 1882, p533-537.

<sup>170</sup> SCOTT D. A., *in press*, 2006, p250.

Scott introduced the treatment of iron and bronze with sodium sesquicarbonate in the 1920s. He also advised to use chlorinated rubber instead of natural rubber to impregnate objects.<sup>171</sup> Sodium sesquicarbonate was used later in the 1970s at the British Museum.<sup>172</sup>

### **3.1.4 Cleaning with chemicals**

Traditionally, vinegar, lemon juice, oxalic acid and fruit acids were used for cleaning of iron objects.<sup>173</sup> In the 1880s Maynard, curator at the Saffron Walden Museum in London worked with immersion solutions of potassium cyanide. The cyanides would react with the iron oxides to form soluble ferrocyanides that could be washed out.<sup>174</sup> Immersion in boiling potassium cyanide was another method used by Rathgen in 1905. Cyanide is highly poisonous but was widely used in the turn of the 19<sup>th</sup> century.<sup>175</sup> Treatment with disodium salt of ethylene diamino-tetraacetic acid (EDTA) for plated objects was introduced in 1969 by Emmerling not to mechanically damage artifacts on cleaning.<sup>176</sup>

### **3.1.5 Methods based on reduction and heat**

Electrolytic reduction treatments aimed to remove the corrosion layers on the object whereas heat treatments were said to 'volatilise' the chlorides in the artefacts.

In the late 19<sup>th</sup> century, Rathgen applied electrolytic reduction in a potassium cyanide solution in water with platinum anodes.<sup>177</sup> He also described heat treatments where objects were heated to redness, sometimes soaked in diluted sulphuric acid or simply impregnated after heating with paraffin wax or linseed oil.<sup>178</sup> Aqueous sodium hydroxide as electrolyte with stainless steel anodes was the next important reduction method. It was most often used in the period between 1950 and 1970. Today it is still in use but only for large marine finds (as the surface loss is important).<sup>179</sup> In 1972 Wihr proposed a method with two steps including ionophoresis coupled with cathodic desalination.<sup>180</sup>

Hydrogen reduction was a widely applied method, especially in Scandinavia from the early 1970s to the 1980s. Many objects from the Swedish warship Vasa (recovered in 1961) were treated in this way. Arrhenius, Barkman and Sjöstrand describe the technique applied to iron objects. In a furnace the objects to treat were heated to 600 – 700 °C in a hydrogen atmosphere. Afterwards they were coated under vacuum with paraffin.<sup>181</sup> This method was obviously followed by the loss of the metallographic structure of the ferrous material. It was mostly applied to big marine finds.<sup>182</sup>

<sup>171</sup> SCOTT A., 1921, p11; SCOTT A., 1926, p36.

<sup>172</sup> ODDY W. A., HUGHES M. J., 1970, p183-189.

<sup>173</sup> SCOTT D. A., *in press*, 2006, p252.

<sup>174</sup> ENTWISTLE R. M., 2001, p71.

<sup>175</sup> *Ibid.*, p67-73.

<sup>176</sup> EMMERLING J., 1969, p3-6.

<sup>177</sup> SCOTT D. A., *in press*, 2006, p257.

<sup>178</sup> RATGHEN F., 1924, p45-67.

<sup>179</sup> PLENDERLEITH H. J., 1956, p275-277; SCOTT D. A., *in press*, 2006, p257.

<sup>180</sup> WIHR R., 1972, p31-40.

<sup>181</sup> ARRHENIUS O., 1973, p2-6; SJÖSTRAND E., 1973, p8-13; BARKMAN L., 1973, p30-31.

<sup>182</sup> SCOTT D. A., *in press*, 2006, p259.



Gas plasma reduction was first introduced by Daniels in 1979 and further developed by Veprek in the 1980s.<sup>183</sup> This method was later – at the end of the 1990s – thoroughly examined in Swiss National Museum in Zurich and is still in use in a modified form that uses lower temperatures than the initial method (120°C instead of 400°C).<sup>184</sup> This method aims to weaken the corrosion layers and rendering them more porous to facilitate chloride extraction in the following immersion in alkaline sulphite.<sup>185</sup>

### **3.1.6 Chloride extraction by means of aqueous solutions**

The techniques that today are most discussed come from the idea of chloride extraction in aqueous media. The Soxhlet treatment, applied mostly in the United Kingdom, was modified and described by Scott and Seeley in 1987. They used the Soxhlet treatment in a nitrogen atmosphere (and not in air as the initial method) where the object was submitted to cycles of hot distilled water. The idea was to use oxygen-free environments during treatment and not to use high temperature levels.<sup>186</sup> A very important step was done by North and Pearson in 1975 when they proposed to treat cast marine objects in alkaline sulphite.<sup>187</sup> Rinuy and Schweizer applied the treatment to objects from land burial context.<sup>188</sup>

Lithium hydroxide was another compound used in solution for reduction treatments in the 1980s.<sup>189</sup> Today it is not used any more as it does not seem very efficient.<sup>190</sup>

Today, other chemicals are discussed as hydroxylamine (NH<sub>2</sub>OH) which is an alkaline reducing agent and oxygen scavenger and leaves only volatile compounds behind after treatment.<sup>191</sup> Hydrazine (NH<sub>2</sub>NH<sub>2</sub>) (carcinogen) is also considered as a strong reducing agent.<sup>192</sup>

The methods described in this section are still in use today, especially the treatment with alkaline sulphite. Concerns remain about dealing with iron objects carrying organic remains, as they should not be treated with this approach<sup>193</sup> as well as the real efficiency of the treatment in the long-term prevention of active corrosion.

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<sup>183</sup> DANIELS V. D., PASCOE M. W., HOLLAND L., 1979, p61; VEPREK S., ECKMANN CH., ELMER J. T., 1989, p171-180; VEPREK S., 1993, p71-88.

<sup>184</sup> SCHMIDT-OTT K., 1997, p45-47; SCHMIDT-OTT K., BOISSONNAS V., 2002, p81.

<sup>185</sup> SCHMIDT-OTT K., BOISSONNAS V., 2002, p81.

<sup>186</sup> SCOTT D. A., SEELEY N. J., 1987, p73-76.

<sup>187</sup> NORTH N. A., PEARSON C., 1975 a, p75/13/3.1-14.

<sup>188</sup> RINUY A., SCHWEIZER F., 1982 a, p160-174; RINUY A., SCHWEIZER F., 1982 b, p44-49.

<sup>189</sup> WATKINSON D., 1982, p28-40.

<sup>190</sup> SCOTT D. A., in press, 2006, p267.

<sup>191</sup> SCHARFF W. et al., 2000, p369; GREIFF S., BACH D., 2000, p319-339.

<sup>192</sup> GILBERG M., 1985, p3; SCOTT D. A., in press, 2006, p268.

<sup>193</sup> GREIFF S., BACH D., 2000, p328-336.

## 3.2 Four different ways of storing archaeological iron artifacts

### 3.2.1 Oxygen-free storage with oxygen absorbers

Oxygen-free storage applied to the field of conservation is not a new approach. It is known that oxygen can act as an agent of deterioration. Several materials can be affected such as metals, pigments, mineralogical specimens (as pyrite), etc. This chapter introduces the topic of oxygen-free storage obtained with oxygen absorbers. These have been developed in the late 1960s. Not for conservation of artifacts but for the preservation of food.

The development of oxygen absorbers originated from the need for better storage conditions in the food industry. The beginning of the use of such products can be located in Japan.

In 1989, Abe and Kondoh wrote: *„Oxygen absorbers are composed of substances chemically reactive to oxygen, packaged in gas permeable materials, in the form of small pouches. Placed in a closed container, the packet contents completely remove oxygen from within the package. Oxygen absorbers play important roles in food preservation and distribution in Japan today, and recently have been drawing worldwide attention as a unique method of keeping food fresh.“*<sup>194</sup>

Oxygen absorbers for the food industry were developed because gas substitution (flushing) or vacuum packaging did not always show satisfactory results: some oxygen generally remained in the package (2-3% and even more if food was porous). And if oxygen penetrated the packaging it could not be removed.<sup>195</sup>

Oxygen absorbers were first brought to the Japanese market in 1969 with sodium hydrosulphite as a main component. These products lacked in stability and showed further disadvantages due to side reactions. So

in 1977, Mitsubishi Gas Chemical Company developed an iron-powder-based oxygen absorber called Ageless<sup>TM</sup>.<sup>196</sup>

When conservators became interested to use these oxygen absorbers for the preservation of artifacts it was a good thing for them that the developed absorbers already had to meet safety criteria from the



Figure 24: Round craters where active corrosion caused layers to fall off the object (blowpipe, iron, early 18<sup>th</sup> century AD, Court (BE) Switzerland, excavation 2000). (Archaeological Office of the Canton of Bern, Switzerland).



Figure 25: If moisture and oxygen get access to the excavated iron, active corrosion is likely to occur (knife blade, iron, early 18<sup>th</sup> century, Court (BE), Switzerland, excavation 2003). (Archaeological Office of the Canton of Bern, Switzerland).

<sup>194</sup> ABE Y., KONDOH Y., 1989, p149.

<sup>195</sup> Ibid.

<sup>196</sup> Ibid., p150.

food industry. For example, they had to be harmless for the human body, absorb oxygen even if exposed to air for a short while before packaging, not generate harmful gases, be economical and have a high oxygen absorption capacity.<sup>197</sup>

This survey will concentrate on the use of oxygen absorbers as a means of creating oxygen-free environments to store iron objects.

The different products (Ageless™, Atco™, RP-System™) are described in details in chapter 3.3.2. A section on barrier films and oxygen-indicating tablets can also be found in chapter 3.3.3 and 3.3.5.

It has been said that anoxic storage using bags of high barrier film and oxygen absorbers might be a more interesting storage method for artifacts than using PE boxes with conditioned silica gel to create a dry atmosphere. PE appeared not to be the most efficient material to build enclosures.<sup>198</sup> The use of PE boxes is said not to be a low-cost solution and not applicable for large numbers of objects or very large artifacts. And compared with many barrier films one cannot see the object through the walls of some of the thicker PE.<sup>199</sup>

First the oxygen absorbers have found application in the combat of museum pests (see figure 26). Where the volume of the artifacts to be treated is quite small, small plastic bags where one puts in the artifact and adds oxygen absorbers are used. Where the number of objects to treat becomes very important, nitrogen flushing is more often used, as it is lower in costs for big volumes (with tents to place objects in).<sup>200</sup>



Figure 26: Objects placed in a tent for treatment against museum pests using nitrogen. (MAEKAWA S., ELERT K., 2003, p62c).

The first oxygen absorber from Mitsubishi Gas Chemical Company used by conservators, Ageless™, has found application in the combat of museum pests as an alternative to the more complicated equipment of nitrogen purging and has been widely examined.<sup>201</sup> Elert and Maekawa mentioned that the iron-powder-based oxygen absorbers (such as Ageless™ and Atco™) could pose problems. Water contained within the sachets used for the oxidation process of the iron powder (to reduce the oxygen) was often not entirely used up and could be released into the atmosphere. This would increase the RH in the enclosure. The temperature could also increase, as the oxidation reaction of the iron powder is exothermic. The authors were able to show that a RH of 72% was to be expected in an enclosure after the oxygen level lowered to less than 0.1% by the absorber.<sup>202</sup> Sensitive objects must be packed

<sup>197</sup> ABE Y., KONDOH Y., 1989, p151.

<sup>198</sup> The water vapour transmission rate of the material is quite high with 1-5 g.H<sub>2</sub>O/m<sup>2</sup>/day. Silica gel needs regular changing. (COLLINS C., unpublished, 1999, p1.).

<sup>199</sup> COLLINS C., unpublished, 1999, p1.

<sup>200</sup> MAEKAWA S., ELERT K., 2003, p15.

<sup>201</sup> GILBERG M., 1990, p812-816, GILBERG M., GRATTAN D., 1994, p177-180; MAEKAWA S., ELERT K., 2003, p15.

<sup>202</sup> ELERT K., MAEKAWA S., 2000, p348-352.

carefully and one ought to be sure the materials can withstand this oxygen-free environment. For the use and efficiency of oxygen-free atmospheres in the preservation of metals (bronze, steel, silver, lead, iron, zinc and copper) tests are currently being conducted with different absorbers.<sup>203</sup>

In the late 1990s, more and more authors began to publish works on the use of a then new oxygen absorber: the Revolutionary Preservation System (RP-System<sup>TM</sup>). This system employs an oxygen absorber called RP (RP-A for metals and RP-K for organic materials) produced by Mitsubishi Gas Chemical Company. The absorber is delivered in the form of sachets for specific volumes of air of storage (for example 300ml). The oxygen absorber and the object to be conserved are placed in an airtight bag (made for example by heat-sealing the barrier film called ESCAL<sup>TM</sup> from Mitsubishi Gas Chemical Company) and the oxygen level is lowered to almost zero (by the absorbing capacity of the absorber) in the bag to preserve the artifact. For more details on the absorbers RP-A and RP-K, see chapter 3.3.2.

Many researches have been conducted to find out more about the possible use of the RP-System<sup>TM</sup>. Rebière et al. were planning to test the oxygen absorbers from the RP-System<sup>TM</sup> in museum storage environments. The RP-System<sup>TM</sup> was chosen after major disadvantages in the use of the oxygen absorber Ageless<sup>TM</sup> were identified. The fact that Ageless<sup>TM</sup> sachets might liberate humidity into the enclosure and that the reagent used was iron powder which could oxidise an iron object placed within the bag convinced the authors to test the oxygen absorber RP-A.<sup>204</sup>

Becker pointed out in 1999 that the oxygen absorbers from the RP-System<sup>TM</sup> could offer new possibilities in the storage of corrosion-sensitive objects. He mentioned the absorber RP-A for metals (of the RP-System<sup>TM</sup>) in combination with bags made of ESCAL<sup>TM</sup> barrier film for metal objects as an easy way of packaging sensitive artifacts.<sup>205</sup>

Elert and Maekawa mentioned the possible use of the RP-System<sup>TM</sup> oxygen absorbers for archaeological metals (type RP-A) and for organic materials (type RP-K). They advised users to add some dry silica gel within the enclosure with the absorber RP-A, as the capacity of this absorber to pick up humidity was limited and the silica gel would guarantee dry storage. The authors considered storage of dry archaeological metal finds with the oxygen absorber RP-A a good option, but suggested that another method should be used with wet metal finds (as the oxygen absorber RP-A creates an oxygen-free dry environment).<sup>206</sup> The authors claimed that it could be of interest to keep valuable metal objects in a low-oxygen and low-moisture atmosphere with the help of the RP-System<sup>TM</sup> (RP-A). However, they found one disadvantage: objects could not be removed from the enclosures for study because this would break up the protective environment.<sup>207</sup>

The RP-System<sup>TM</sup> oxygen absorbers were also mentioned by Greiff and Bach in 2000 as a way of storing ground-damp archaeological iron finds before further treatment.<sup>208</sup>

Another situation occurred in Canada, where Mathias et al. were confronted in 2004 by a situation where large amounts of an iron collection already treated (with sodium hydroxide solutions for

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<sup>203</sup> ARGEMI M., GONZALO D., PUGES M., MASPOCH L., MOUREY W., ALONSO M., 1998, p245-247.

<sup>204</sup> REBIERE J., MOUREY W., FRANCOISE J., SIDOT E., 1998, p248-252.

<sup>205</sup> BECKER H., 1999, p72-76.

<sup>206</sup> ELERT K., MAEKAWA S., 2000, p353-354.

<sup>207</sup> MAEKAWA S., ELERT K., 2003, p48.

<sup>208</sup> GREIFF S., BACH D., 2000, p327.

stabilisation) were re-corroding. Obviously not all chlorides had been washed out. This enhanced the risk of further corrosion due to high RH during the summer. Akaganéite ( $\beta$ -FeOOH) was appearing on the objects once they had been treated, dried and in storage for a period of at least one year. The decision was made to use a low-oxygen storage approach with the RP-System<sup>TM</sup> to prevent ongoing corrosion until further treatment. The authors stated that it was too early to know how effective their approach was, but results observed to date seem to be promising.<sup>209</sup>

In the field of geological specimens Day presented the practical application of the RP-System<sup>TM</sup> for a collection of marcasite ( $\text{FeS}_2$ ). Oxygen-free and dry storage using the oxygen absorber RP-A was used to prevent degradation of the marcasite due to oxidation processes involving high humidity levels and the presence of oxygen.<sup>210</sup> Oxygen-free storage could be an option for both geological specimens pyrite and marcasite (dimorphs of ferrous disulphide).<sup>211</sup>

At present, some institutions, as the Tate Gallery, London, or the Natural History Museum, London, investigate in low-oxygen storage. The development of rigid enclosures

is considered (to put items on exhibition). But it seems especially difficult to obtain a good and reversible seal for the enclosure. Tate Gallery also works on projects concerning transport of objects in oxygen-free enclosures when an item goes on loan. For others it becomes more and more interesting to pack objects on site in a low-oxygen environment while they are transported to a laboratory to undergo further treatment (National History Museum London and English Heritage are working on the idea). It is felt that packing an archive in an oxygen-free system (with a flexible package and oxygen absorbers) gives some interesting protection: the sealed objects are protected from being touched directly but can still be examined as the enclosure is transparent, they are well preserved in a microclimate that does not need any heavy instrumentation as air conditioning, and it has even been mentioned that in case of natural catastrophes like floods, the archive is fully protected by the sealed enclosure. Some questions remain though: it is not clear yet what exact oxygen levels our collections need to be preserved in. How low do the levels have to be? The Tate Gallery London for example would like to investigate the ideal oxygen level for certain pigments. And if we know what level is needed, how can we achieve it? Another open question is how long we would like our system



Figure 27: Specimen stored in an anoxic enclosure at the Natural History Museum, London, Palaeontology Department (mollusc, *thermoconus shadlunae*, Russia).

<sup>209</sup> MATHIAS C., RAMSDALE K., NIXON D., 2004, p28-41.

<sup>210</sup> DAY J., 2005, p435.

<sup>211</sup> Personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

to last for. 20 years? 50 years? This seems to be a question depending on the packaging material (barrier films and rigid materials as glass) as well as on the quality of the seals.<sup>212</sup>

### **3.2.2 Inert gases**

In the relevant literature we can find numerous articles related to storage and treatment of museum objects in transformed atmospheres using inert gases. These publications discuss different groups of artifacts such as paintings, metals, wood, paper work, etc.<sup>213</sup> This chapter gives some principal ideas without exhaustive treatment of the topic.

There are various paths that can be taken, ranging from nitrogen flushing to the addition of oxygen absorbers to control leakage in a nitrogen-atmosphere container.<sup>214</sup> Nor are the aims of the different approaches the same. An oxygen-free environment could be chosen to fight insect pests, but also to lower degradation in plastic objects. This method also seems especially appropriate to prevent further loss of metal in the case of corroding metals like iron.

An excursion into history shows that first investigations on low-oxygen environments were carried out by Russell and Abney in 1888. They had observed the fading of water-colour paintings in the South Kensington Museum and the National Gallery in London due to the influence of light, moisture and oxygen. The proposed solution was the construction of an airtight vacuum container to prevent degradation due to the mentioned influences. The patent for this container was obtained in 1893.<sup>215</sup>

Often nitrogen or argon are used to create an inert atmosphere. The Constitution of Puerto Rico is preserved in a nitrogen atmosphere, as is the linen Shroud of Turin.<sup>216</sup> The Constitution of India was put into a nitrogen atmosphere too in 1995.<sup>217</sup> The Declaration of Independence, the United States Constitution and Bill of Rights, all of them parchment documents, are stored in a humidified argon atmosphere.<sup>218</sup> Argon is also used when paper is put on display.<sup>219</sup>

Concerning iron objects, they have been put into dry nitrogen environments from 1943 onwards.<sup>220</sup> In the 1940s France-Lanord described the exhibition of a fragile Merovingian helmet with ongoing corrosion of the iron parts. The object had been placed in a case made of Plexiglas and air was replaced by nitrogen. The author had already used this system for other iron objects and they seemed to have remained stable even after a seven years period.<sup>221</sup> Born advised, in 1982, that excavated iron be stored in sealed plastic bags with the addition of nitrogen to replace air.<sup>222</sup>

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<sup>212</sup> Discussions at „The Use of Oxygen-Free Environments in the Care of Historic & Artistic Materials“, Conservation Seminar, National Museum Wales, Cardiff, 16 March 2006.

<sup>213</sup> FRANCE-LANORD A., 1949, p277-280; BULST W. A., 1986, p125-126; LOCKETT K., MCKENZIE B., 2005, p67-74; HANSEN E. F., 1998, p17.

<sup>214</sup> LOCKETT K., MCKENZIE B., 2005, p67-74.

<sup>215</sup> BROMELLE S., 1964, p140-151; HANSEN E. F., 1998, p16.

<sup>216</sup> HANSEN E. F., 1998, p17.

<sup>217</sup> KISHAN H., MAEKAWA S., 1998, p66.

<sup>218</sup> NICHOLSON C., RITZENTHALER M. L., 2005, p75-80.

<sup>219</sup> PURINTON N., IRVING J., 2005, p81-85.

<sup>220</sup> HANSEN E. F., 1998, p17.

<sup>221</sup> SALIN E., FRANCE-LANORD A., 1943, p26; SALIN E., FRANCE-LANORD A., 1946, p261-267; FRANCE-LANORD A., 1949, p277-280.

<sup>222</sup> BORN H., 1982, p60.

In 1996, two German conservators proposed storage in nitrogen for iron finds. Objects were put into sealed high-barrier film bags, where air had been replaced by nitrogen. Results were promising, as the thus packed, freshly excavated objects showed only minor corrosion (compared to material packed in a resealable bag which was found to be less airtight).<sup>223</sup>

Höpfner advised packing excavated objects, within their surrounding damp-earth burial context, into a heat-sealed aluminium laminated barrier film bag. This enclosure was filled with nitrogen. The idea was to imitate the burial environment, to limit the access of oxygen and to avoid negative experiences made when drying iron artifacts containing chlorides. This method also provided protection for organic remains and the finds were protected against mechanical harm.<sup>224</sup>

Greiff and Bach mentioned the storage of freshly excavated iron in a nitrogen environment as an effective way of preventing corrosion before further treatment. Obviously it could be a disadvantage not to be able to remove the objects from their enclosure for the means of studying them, as removal would interrupt the protection offered by the inert atmosphere.<sup>225</sup>

In 1967, Kuhn proposed the replacement of air by nitrogen in the environment of dyes and pigments. The nitrogen was constantly flushed into the storage-case, creating positive pressure. The advantage of this system was the possibility of humidifying the nitrogen and taking influence on the RH in the case.<sup>226</sup>

In 1986, Bulst reported about his visit to an exhibition in Florence. He had seen restored bronze reliefs from the bronze doors of the Florence baptistry. They were stored in Plexiglas containers flushed with nitrogen to prevent degradation due to air pollution.<sup>227</sup>

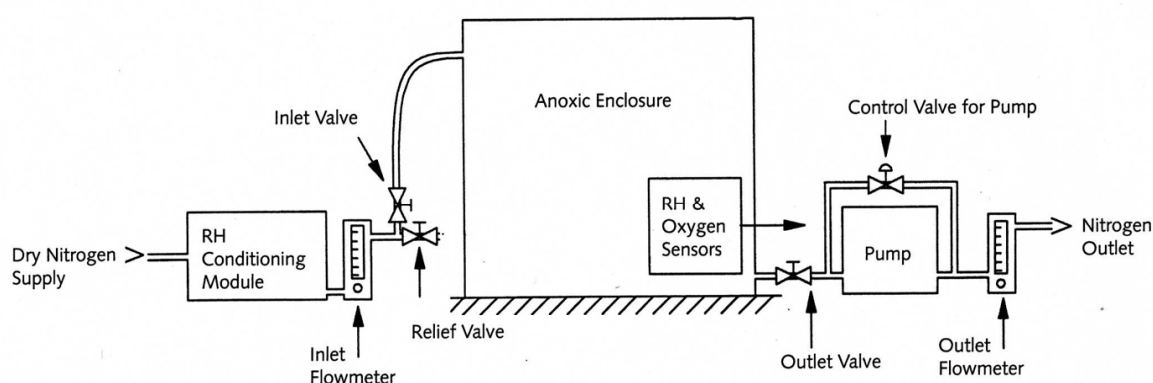


Figure 28: The rather heavy setup for nitrogen treatment with nitrogen source, humidification system, enclosure for anoxia, vacuum pump, flowmeters and monitors for humidity and oxygen concentration. (MAEKAWA S., ELERT K., 2003, p59).

A very important field of application of oxygen-free environments is the control of insect pests in museums.<sup>228</sup> Many approaches have been tested. Argon and nitrogen (at various levels of RH) have

<sup>223</sup> MEIER M., TEGGE C., 1996, p150.

<sup>224</sup> HÖPFNER M., 1999, p79-80.

<sup>225</sup> GREIFF S., BACH D., 2000, p327.

<sup>226</sup> KÜHN H., 1967, p79-85; HANSEN E. F., 1998, p16.

<sup>227</sup> BULST W. A., 1986, p125-126.

<sup>228</sup> RUST M. K., KENNEDY J. M., 1993; MAEKAWA S., ELERT K., 2003.



been found more effective in killing museum pests than carbon dioxide<sup>229</sup>. For the application of carbon dioxide, the temperature levels and the concentration of the gas have to be adjusted.<sup>230</sup> Tests on pests exposed to various oxygen, carbon dioxide and nitrogen levels have also proved very important in the field of grain storage.<sup>231</sup> Studies have been undertaken to determine the exact oxygen level at which mortality of museum pests occurs in nitrogen atmospheres.<sup>232</sup>

The use of carbon dioxide is more frequent in Canada, where the regulations are favourable for its use and where its application is supported by the industrial suppliers. On the other hand, carbon dioxide is classified as a pesticide in the United Kingdom, which explains its low level of use in this country.<sup>233</sup>

Transformed environments in argon or nitrogen can either be static (a tightly sealed case is needed and an oxygen absorber can be added for minor leakage) or dynamic (constant flushing with the inert gas).<sup>234</sup> For the static approach the oxygen level can be lowered following different methods: either the case can be purged with many exchanges of high-purity nitrogen, oxygen absorbers can be used to lower the oxygen level, or purging and absorbing are used in combination. For the dynamic approach, the case needs to be flushed with oxygen-free argon or nitrogen. When the oxygen level is lowered to the desired amount, the flush of the inert gas can be reduced to a minimum to maintain the system. A static-dynamic method is a third approach: the gas then passes through the system very slowly.<sup>235</sup> Static-dynamic can also mean that the bag is first purged with the inert gas and then oxygen absorbers are swiftly added to maintain the low oxygen level in the sealed bag.<sup>236</sup> Literature, however, does not provide a very clear picture of this third approach.

The use of (humidified) nitrogen in various enclosures is the most widely used method. Every system is adapted to specific needs. However, there are some aspects that have to be considered for all of the methods. There is the need of high quality barrier films with low oxygen permeability, high capacity oxygen absorbers are important and if one chooses the nitrogen method, then one should find inexpensive suppliers of the requisite gas with a low oxygen content. The enclosures themselves need to be airtight to a greater extent.<sup>237</sup>

### ***3.2.3 Storage at low relative humidity***

For the last twenty years, more and more interest has been directed towards the preservation of the iron artifacts in their integrity. Corrosion layers are no longer stripped off and conservators are looking for passive conservation methods, which can ensure long-term preservation. One approach is the storage at very low RH levels.<sup>238</sup>

This chapter will follow the idea of low RH storage for chloride-containing iron artifacts.

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<sup>229</sup> VALENTIN N., LINDSTROM M., PREUSSER F., 1990, p222-230; GILBERG M., 1991, p93-98; MAEKAWA S., ELERT K., 1996, p48-53; VALENTIN N., 1998, p26-38.

<sup>230</sup> SELWITZ CH., MAEKAWA S., 1998, p50.

<sup>231</sup> BAILEY S. W., BANKS H. J., 1980, p101-118.

<sup>232</sup> MAEKAWA S., ELERT K., 2003, p6-7.

<sup>233</sup> SELWITZ CH., MAEKAWA S., 1998, p50.

<sup>234</sup> MAEKAWA S., 1998 c, p40; SELWITZ CH., MAEKAWA S., 1998 a, p31; BROKERHOF A. W., 1999, p15.

<sup>235</sup> SELWITZ CH., MAEKAWA S., 1998, p31.

<sup>236</sup> DANIEL V., MAEKAWA S., PREUSSER F. D., 1993, p864.

<sup>237</sup> SELWITZ CH., MAEKAWA S., 1998, p31.

<sup>238</sup> KNIGHT B., 1997, p38.



Some of the earlier approaches we look at might seem outdated today. The curator at the Saffron Walden Museum from 1880 to 1904, G. N. Maynard, left a 'recipe book' in which he also mentioned some treatments for metals. He said that metals should be stored dry and all moisture removed from the object before storage too. Storage in powdered quick lime could prevent steel objects from rust.<sup>239</sup>

A little later Ratghen said that if an excavated iron object could not be treated, it had to be stored in a closed space with a desiccant. He proposed a glass cylinder with an airtight lid (to be achieved by covering the lid with Vaseline). Into the enclosure one put some caustic soda, which absorbed all the moisture. This prevented any reaction between the iron and chlorides.<sup>240</sup>

As museums have realised that control of the RH is essential in the preservation of their collections, various methods to obtain a regulated climate have been applied. The use of air-conditioning systems has been proven to be cost-intensive and not always efficient. More research has been undertaken in the development of microclimates. The idea here is to put small groups of sensitive objects into cases where humidity levels could be controlled with buffers (either the museum object itself acts as a buffer or a buffer can be added). The air in the case can also be replaced by an inert gas.<sup>241</sup>

If creating a microclimate in a case, one should remember that the case must be as air-tight as possible.<sup>242</sup> Monitoring the RH in the microclimate can be achieved via different ways.

Initially, salt hydrates and saturated solutions of certain salts were used to monitor the RH levels in microclimates. Magnesium nitrate was used for the Brooklyn Museum case and the Victoria and Albert Museum tested sodium bromide. Sodium chloride was employed by the Dresden Museum, potassium chromate and calcium nitrate was tested in Baroda, India. The Scottish National Gallery used salt hydrates (zinc sulphate) for the preservation of early Flemish panels.<sup>243</sup>

Curister described the characteristics of such salt hydrates by showing their ability to absorb and release moisture. He underlined the importance of limiting the rate of air change in the environment.<sup>244</sup>

Other desiccants can be added to an enclosure: silica gel or dry cotton textile.<sup>245</sup> Silica gel has been used in the field of conservation since the 1950s and 1960s.<sup>246</sup>

Using silica gel in showcases prevents the short-term variations in humidity levels and keeps the long-term variations at an acceptable level.<sup>247</sup>

Looking at some research in the field of prevention of corrosion keeping humidity levels low, Evans and Taylor can be cited. They took up results developed by K. A. Chandler in 1966, who said that the more salts (sulphate and chloride) were present in the objects the greater the corrosion. Lowering the RH level should slow the corrosion. If the RH was below 40%, corrosion became unlikely. The authors wanted to find out at what RH level steel articles carrying sea salt particles or salt water could be stored. They found that corrosion was much slower at 40% RH than at 70% RH. If stored at 35% RH,

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<sup>239</sup> ENTWISTLE R. M., 2001, p71.

<sup>240</sup> RATGHEN F., 1924, p67-68.

<sup>241</sup> STOLOW N., 1977, p52-54.

<sup>242</sup> Ibid., p54.

<sup>243</sup> CURISTER S., 1936, p109-116; STOLOW N., 1977, p54.

<sup>244</sup> CURISTER S., 1936, p109.

<sup>245</sup> STOLOW N., 1977, p55.

<sup>246</sup> ORGAN R. M., 1957, p265-272; STOLOW N., 1966, p24.

<sup>247</sup> ASHLEY-SMITH J., MONCRIEFF A. J., 1984, p84.17.1-5.; SCHWEIZER F., 1984, p84.17.50-53.

the steel article suffered less attack than at 70% RH. However, 35% RH did not always suffice to prevent corrosion.<sup>248</sup>

North and Pearson said in their article of 1975 that, after chloride-removal treatment, the metal objects should be dried and kept dry. The latter could be achieved by the application of a protective coating



Figure 29: Dry storage of archaeological artifacts in microclimates using dry silica gel is a frequently applied method (here at English Heritage, Fort Cum-berland, Portsmouth).

(for wrought iron) or of microcrystalline wax to fill the pores (in cast iron).<sup>249</sup> Scott and Seeley stated in 1987 that iron objects could be stored in very dry conditions to prevent any change in their state.<sup>250</sup>

Negative aspects were considered by Höpfner, who

pointed out that long-term storage of iron objects with the help of silica gel was very time-consuming and laborious. He also mentioned that the drying of the corrosion layers did harden them and was not favourable during desalination.<sup>251</sup>

Sometimes standards can be advised through a widely accepted authority. In the publication by the Museums and Galleries Commission of 1992, standards for the storage of ferrous metals include the recommendation of less than 15% RH in a microclimate.<sup>252</sup>

Concerning freshly excavated iron objects Watkinson and Neal advised to pack iron without moisture on site. Storage should be carried out below 15% RH. But if organic remains were found on the artifacts, these ought not to be desiccated but stored damp in PE boxes. One could also vacuum pack finds in heat-sealed metallised packing films to prevent corrosion by exclusion of oxygen.<sup>253</sup>

In 2000, Greiff and Bach in their article about alkaline sulphite treatment said, that a storage of the iron finds after excavation in a very dry environment was one of the possibilities to prevent the formation of akaganéite ( $\beta$ -FeOOH). They advised to dry the finds in an oven at about 110°C before putting them into bags (PE or PP) with silica gel. They found it rather difficult to dry

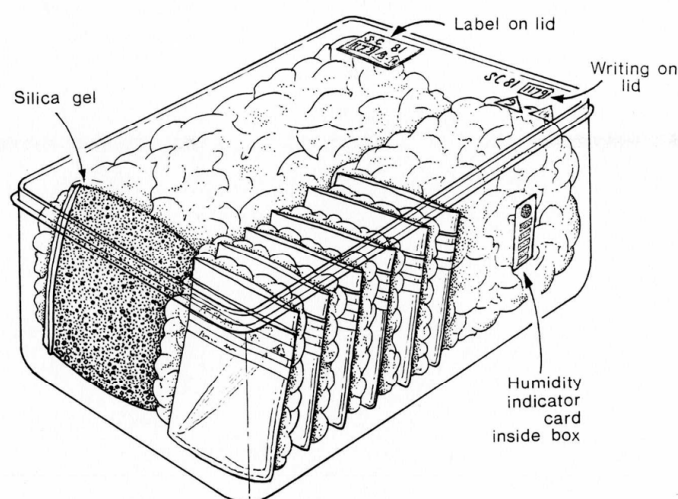


Figure 30: Container with silica gel to create a microclimate for storage of small finds. (WATKINSON D., NEAL V., 1998, p22).

<sup>248</sup> EVANS U. R., TAYLOR C. A. J., 1974, p26-28.

<sup>249</sup> NORTH N. A., PEARSON C., 1975 b, p174.

<sup>250</sup> SCOTT D. A., SEELEY N. J., 1987, p73.

<sup>251</sup> HÖPFNER M., 1999, p79.

<sup>252</sup> Museum and Galleries Commission, 1992, p57.

<sup>253</sup> WATKINSON D., NEAL V., 1998, 37.

excavated objects with silica gel only, as a lot of the desiccant was needed. This was probably only possible for isolated finds but not for a whole excavation campaign.<sup>254</sup>

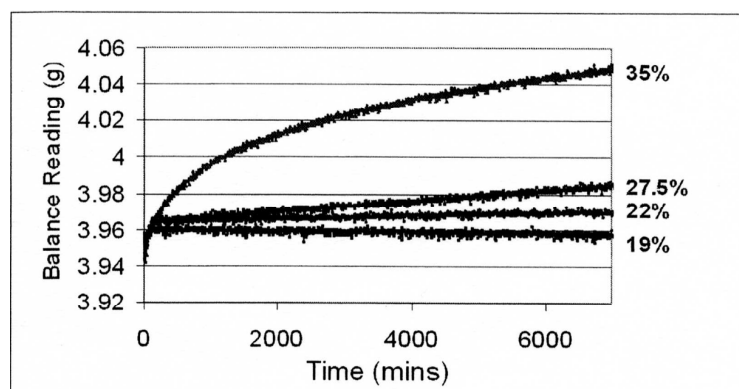


Figure 31: Watkinsons' tests regarding weight gains in different powder mixtures exposed to different RH. At 19% RH a mixture of iron chloride dihydrate and at 22% RH, 27.5% RH, 35% RH a mixture of iron chloride tetrahydrate and iron. The powders were exposed for 14 days. Differences in the weight gain are well visible. (WATKINSON D., LEWIS M., 2004, p95).

Some authors performed extensive research on the exact level of desiccation needed to prevent corrosion on chloride-containing iron. Watkinson and Lewis based their measurements on the weight-gain in their powder samples (see figure 31) and claimed that, at 25% and at 30% RH, corrosion increased rapidly. Iron in contact with unwashed (fresh) akaganéite ( $\beta$ -FeOOH) corroded at 15% and 19% RH but not at 12% RH. If only

iron(II) chloride was present on the artifact storage at 19% RH was possible. As most often akaganéite ( $\beta$ -FeOOH) also seemed to be present, RH in the storage should be below 12%. Storage at 12% RH seemed costly and technically difficult, so the authors advised storage at 20% RH at least to slower corrosion processes.<sup>255</sup>

Thickett based his analysis of the corrosion of iron with akaganéite ( $\beta$ -FeOOH) formation on quantitative and qualitative tests. The amount of akaganéite ( $\beta$ -FeOOH) formed from the mixture of iron(II) chloride and iron powder was evaluated at different RH levels. The influence of copper ions and humic acid on the reactions was tested. Thickett confirmed the corrosion model established by Turgoose in 1982<sup>256</sup> and stated that at 30% RH the corrosion dramatically increased. At 16% RH corrosion did not occur.<sup>257</sup>

Scott recently asked how viable the level of less than 20% RH for a long-term storage of iron artifacts was and how it could be achieved best over longer periods.<sup>258</sup>

### 3.2.4 Storage in the cold

Low temperature storage has been examined for excavated artifacts.

There is Eichhorn from the State Museum of Württemberg (Württembergisches Landesmuseum) in Germany, who described in his 1975 article, that some iron finds were stored in very cold atmospheres after excavation until further treatment could start. A deep-freeze device with a temperature level of -30°C was used.<sup>259</sup>

<sup>254</sup> GREIFF S., BACH D., 2000, p327.

<sup>255</sup> WATKINSON D., LEWIS M., 2004, p88-102; WATKINSON D., LEWIS M., 2005, p241-252.

<sup>256</sup> TURGOOSE S. 1982 a, p97-101; TURGOOSE S. 1982 b, p1-7.

<sup>257</sup> THICKETT D., ODLYHA M., *in press*, 2006.

<sup>258</sup> SCOTT D. A., *in press*, 2006, p264.

<sup>259</sup> EICHHORN P., 1975, p74.

Born for his part talked about shock-freezing the excavated objects at -40°C and then storing them in the cold at -20°C to -25°C. In this way the objects would be safely stored up to the beginning of their treatment.<sup>260</sup>

Knight as well evocated the possibility of storing excavated iron artifacts in a deep-freezer to reduce any chemical reaction.<sup>261</sup>

In Niedersachsen (Germany) in the department of conservation at the Denkmalpflege (preservation of ancient monuments and buildings), excavated iron artifacts were stored in the cold at -24°C to slow down corrosion processes in the 1990s. But this did not seem to be a method suitable for large-scale application in big storage spaces.<sup>262</sup>

Greiff and Bach mentioned the freezing of freshly excavated iron finds. This was meant to be an effective way of slowing down corrosion reactions until further treatment could be carried out. But the authors pointed out that one had to be very careful about frost wedging and therefore use a freezing process that worked by shock. Ice crystals should be kept small, but they still tended to grow over time. So this storage procedure should not be used for very long periods of time. Besides, the thawing process was also a problematic aspect.<sup>263</sup>

The archaeological unit of Baden-Württemberg in Germany used cold storage for freshly excavated iron (refrigerator or deep-freezer) until further treatment started. By this method, corrosion layers seemed to get a bit harder than they were just after excavation (due to the phase transformations and the drying processes). The deep-freezer made the corrosion layers slightly harder than the refrigerator. However, the authors believed this increase in hardness was possibly due to a loss of water after excavation, as freshly excavated objects showed less hard corrosion layers.<sup>264</sup>

One must be careful not to deep-freeze damp iron artifacts (because of frost wedging). A freeze-drying procedure could be considered for air-dry metal finds.<sup>265</sup>

### 3.3 Oxygen absorbers

#### 3.3.1 General introduction

The idea of an oxygen absorber is to decrease the oxygen level in completely sealed enclosures to below zero (often the producer stated values of about 0.001%). Oxygen absorbers consist of a powder, packed in small gas-permeable sachets. The ingredients, for many of the oxygen absorbers, are composed of moist iron powder, which oxidises during the absorbing process.<sup>266</sup> Iron powder absorbers undergo an exothermic reaction during oxidation. It should be remembered that the larger the sachet's surface the more efficient the reaction is. It is important to note that the sachets based on iron powder need water for their reaction with the oxygen. This means that water is included in the

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<sup>260</sup> BORN H., 1982, p59-60.

<sup>261</sup> KNIGHT B., 1990, p41.

<sup>262</sup> MEIER M., TEGGE C., 1996, p149.

<sup>263</sup> GREIFF S., BACH D., 2000, p327.

<sup>264</sup> SCHARFF W. et al., 2000, p235-237.

<sup>265</sup> Ibid., p350.

<sup>266</sup> MAEKAWA S., ELERT K., 2003, p43.

product. The water is held either by amorphous silica, diatomaceous earth or a zeolite. It is used for the reaction with the iron powder and partly released into the enclosure's atmosphere. This can cause an increase of the RH in the container (which could be buffered by added dry silica gel).<sup>267</sup> Products of this group are Ageless<sup>TM</sup> (see figure 32), ATCO<sup>TM</sup> and FreshPax<sup>TM</sup>.

Nowadays we can also find oxygen absorbers that contain unsaturated organic compounds. These can absorb oxygen and corrosive gases. Not much is known about the active compounds of these sachets (as the producer keeps the details secret).<sup>268</sup> The Revolutionary Preservation System (RP-System<sup>TM</sup>) is based on the details mentioned above.



Figure 32: The oxygen absorber Ageless<sup>TM</sup>, which is composed of an iron oxide powder. (MAEKAWA S., ELERT K., 2003, p62b).

Often more of the reactive substance is added to the sachet to ensure the efficiency of the product. So even if the sachet is exposed to oxygen for some minutes before the enclosure into which it is placed is closed, it stays active enough (this is certainly the case for Mitsubishi Gas Chemical Company and Standa Industries products).<sup>269</sup> As oxygen is removed during oxygen absorbing, the volume will decrease in the anoxic enclosure by about 20% (this is the amount of oxygen present in the air). Flexible packaging is therefore recommended.<sup>270</sup> The attained level of oxygen in the enclosure by means of oxygen absorbers depends on the volume of the enclosure, the oxygen-absorbing capacity of the sachet and the leak rate (oxygen entering from outside the enclosure).<sup>271</sup>

Oxygen absorbers have been widely used in the food industry. There are two main suppliers. Atco SA is a French-based company (Standa Industrie) distributing its products throughout Europe. Mitsubishi Gas Chemical Company is based in Japan and operates in the world market. Ageless<sup>TM</sup> and the RP-System<sup>TM</sup> are produced by latter.<sup>272</sup> These companies have introduced oxygen absorbers in the food industry as an alternative to nitrogen purging or vacuum packaging.<sup>273</sup> This paper will discuss the RP-System<sup>TM</sup> and to a lesser extent Ageless<sup>TM</sup> and Atco<sup>TM</sup>, its precursors.

### 3.3.2 Product descriptions

Atco<sup>TM</sup> oxygen absorbers can reduce the oxygen concentration in a sealed container to about 0.01%. They can also be used after the flushing of a container with nitrogen to counterbalance leakage in the system. The sachets contain a fine iron powder covered with sea salt. A natural zeolite is added,

<sup>267</sup> [www.cwall.de/oxygen.htm](http://www.cwall.de/oxygen.htm), 14/10/05; MAEKAWA S., ELERT K., 2003, p45.

<sup>268</sup> MAEKAWA S., ELERT K., 2003, p43.

<sup>269</sup> Ibid., p44.

<sup>270</sup> DANIEL V., LAMBERT F. L., 1993, p13; GILBERG M., GRATTAN D., 1994, p177.

<sup>271</sup> MAEKAWA S., ELERT K., 2003, p47.

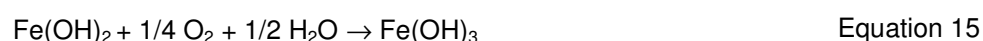
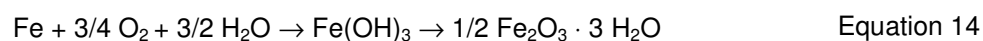
<sup>272</sup> SELWITZ CH., MAEKAWA S., 1998, p36.

<sup>273</sup> GILBERG M., 1990, p812.

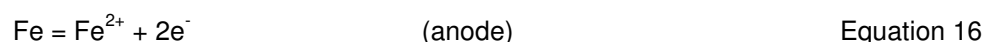
impregnated with NaCl-solution. It holds water for the oxidation reaction of the iron powder. The system can be used in atmospheres above 55% RH, as humidity is needed for the scavenging.<sup>274</sup>

There are two commercialised products: Atco™LH and Atco™HV. Standa Industries state that both of them can be used at low and high RH. The product takes up to forty hours to lower the oxygen level below 0.1%.<sup>275</sup>

Ageless™ from Mitsubishi Gas Chemical Company is an oxygen absorber introduced for the preservation of product freshness and the extension of product shelf life.<sup>276</sup> Ageless™ has also found application in the prevention of deterioration of air-sensitive chemicals in agricultural and pharmaceutical industries.<sup>277</sup> Mitsubishi Gas Chemical Company stocks various sachets for different purposes. The product used in the field of conservation is Ageless-Z. It contains moist iron (ferrous) oxide in a finely divided state and potassium chloride.<sup>278</sup> This powder is sealed in a gas-permeable film.<sup>279</sup> The supplier indicates the following reactions taking place inside the bag:<sup>280</sup>



based on the electrochemical reaction of:<sup>281</sup>



while the oxygen is absorbed.

At the anode, iron oxidises to iron(II) ions, which then form, due to their instability, other iron oxides. Molecular oxygen is reduced at the cathode. For these reactions to take place, moisture is needed, which is the reason why Ageless™ bags require a certain water activity of the object in their environment.<sup>282</sup> Ageless™ sachets should be used with a minimum RH of 50-55%, as below this level the product loses in efficiency.<sup>283</sup> Lower RH levels may be used for treatments of a very short time.<sup>284</sup> When handling the sachets, more than a ten minutes' exposure to air should be avoided, because of the start of the exothermic warming and loss of oxygen-absorbing capacity (0.02% per minute).<sup>285</sup> It must be remembered that Ageless™ sachets warm up during the reaction with oxygen and that the RH can increase during the absorption process.<sup>286</sup> A buffer can be added to the package to equilibrate

<sup>274</sup> <http://www.cwall.de/oxygen.htm>, 14/10/05.

<sup>275</sup> MAEKAWA S., ELERT K., 2003, p47.

<sup>276</sup> Mitsubishi Gas Chemical Company MGC, 1994, p2.

<sup>277</sup> GILBERG M., GRATTAN D., 1994, p177.

<sup>278</sup> DANIEL V., LAMBERT F. L., 1993, p12.

<sup>279</sup> GILBERG M., GRATTAN D., 1994, p177.

<sup>280</sup> Mitsubishi Gas Chemical Company MGC, 1994, p5.

<sup>281</sup> GILBERG M., GRATTAN D., 1994, p177.

<sup>282</sup> Ibid.

<sup>283</sup> LAMBERT F. L., DANIEL V., PREUSSER F. D., 1992, p271; DANIEL V., LAMBERT F. L., 1993, p13; MAEKAWA S., ELERT K., 2003, p46.

<sup>284</sup> MAEKAWA S., ELERT K., 2003, p47.

<sup>285</sup> LAMBERT F. L., DANIEL V., PREUSSER F. D., 1992, p272; DANIEL V., LAMBERT F. L., 1993, p13.

<sup>286</sup> DANIEL V., LAMBERT F. L., 1993, p13; GILBERG M., GRATTAN D., 1994, p177.



the increase in humidity caused by Ageless™ in an airtight system.<sup>287</sup> All those stated requirements define the field of application: an oxygen-free but not very dry atmosphere.

Ageless™ is quite easy to use, non-toxic and residue-free. It is economical if a low-oxygen level has to be maintained over long periods.<sup>288</sup> Ageless™ will absorb the oxygen entering the enclosure (as most often the packaging material is not completely impermeable to oxygen) before a stored object absorbs the incoming oxygen.<sup>289</sup>

FreshPax™ from Multisorb Technologies in the USA works in the same way as Atco™ and Ageless™. FreshPax™ D can be used for an RH range of 50-70%.<sup>290</sup>

The last absorbers described here are part of the Revolutionary Preservation System™ (RP-System™) developed by Mitsubishi Gas Chemical Company in the mid-1990s. Two products exist: RP-A and RP-K



Figure 33: Different oxygen absorbers: ATCO™ (top left), Ageless™ (top right), FreshPax™ (bottom left) and RP-A (bottom right). (MAEKAWA S., ELERT K., 2003, p62b).

oxygen absorber. What is contained in RP-sachets is the producers' secret. For RP-A sachets the producers states that it contains 10-50% mordenite, 10-45% calcium oxide, 5-15% unsaturated organic compounds (which take part in the oxygen absorbing process); 10-30% polyethylene, 5-15% activated carbon.<sup>291</sup>

The advantage of the PR-System™ is that no heat is generated during the absorbing process. RP-A can absorb moisture and does not release it into the enclosure, due to desiccant included (calcium oxide).<sup>292</sup> RP-A reduces oxygen to a level near zero, the RH to below 10%, and absorbs corrosive gases and pollutants by means of mordenite and activated carbon.<sup>293</sup> Absorbed compounds are H<sub>2</sub>S (hydrogen sulfide), SO<sub>2</sub> (sulfur dioxide), HCl (hydrogen chloride) and NH<sub>3</sub> (ammonia).<sup>294</sup> RP-A creates an oxygen-free, low RH environment (less than 10% RH) in an airtight package. RP-K absorbs corrosive gases and reduces the levels of SO<sub>2</sub> (sulfur dioxide), HCl (hydrogen chloride) and NH<sub>3</sub> (ammonia) to less than 1 ppm due to added activated carbon, and does not influence the RH in the bag while reducing the oxygen level to about zero.<sup>295</sup> It seems to be important to use only fresh absorbers. This means, that if receiving the absorbers they are usually packed in sealed bags containing 10 – 25 of the absorbing sachets. Once this sealed bag is opened, all the absorbers should

<sup>287</sup> GILBERG M., GRATTAN D., 1994, p179.

<sup>288</sup> GILBERG M., GRATTAN D., 1994, p177.

<sup>289</sup> Ibid.

<sup>290</sup> MAEKAWA S., ELERT K., 2003, p44, p48.

<sup>291</sup> DAY J., 2005, p436; personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>292</sup> MAEKAWA S., ELERT K., 2003, p48.

<sup>293</sup> www.cwall.de, 08/12/2005.

<sup>294</sup> BECKER H., 1999, p72.

<sup>295</sup> Measurements during this work have shown the RH to be situated most often between 27 – 45%.

be used and packed within the next half hour. If resealing the original bag because of left absorbers, one should be aware that the absorbing capacity of the remaining absorbers will be less for further use.<sup>296</sup>

### **3.3.3 Barrier films used with oxygen absorbers**

An easy way of oxygen-free packaging of artifacts is to work with bags of sealed plastic barrier films. When choosing the barrier film, some criteria are important to be aware of. Desired properties of a barrier film used for anoxic storage include resistance to gas or vapor permeability, flexibility, ease of sealing, resistance to distortion while sealed, strength, oxygen impermeability, transparency and inexpensiveness.<sup>297</sup> Gilberg and Grattan underlined the fact that a barrier film was needed that showed virtually no oxygen permeability.<sup>298</sup> As the maintenance of the low-oxygen concentration in the enclosure depends on the oxygen permeability of the enclosure material, it is important to choose the right barrier film.<sup>299</sup>

An oxygen-barrier film usually consists of three to five layers. The inner layer is the sealing layer. If one presses it against a similar layer under the influence of heat, the two will unite by dissolving. The next layer is the oxygen-barrier film. Then comes another protective layer for the oxygen-barrier to prevent the latter from damage. The top layer must be tough, puncture- and tear-resistant. Top layers can be made of Mylar (a type of PET) or nylon. If the aim is to exclude moistness, a moisture barrier layer can be added. There can also be a layer made of aluminium coating, almost completely impervious to oxygen. This layer has to be protected by another film to avoid damage.<sup>300</sup>

As ESCAL<sup>TM</sup> barrier film has been chosen for this work, we will give some more details concerning this product.

Maekawa, Elert and Collins gave an exhaustive list of barrier films used to produce anoxic environments.<sup>301</sup> Barrier films can be characterised by different properties. ESCAL<sup>TM</sup> barrier film has an oxygen transmission rate (OTR) of 0.05 cc/m<sup>2</sup>/day (at 25°C and 60% RH). The values for ESCAL<sup>TM</sup> film are measured on a film of 0.11mm thickness. The moisture barrier is very effective as well with 0.01 g/m<sup>2</sup>/day (at 25°C and 60% RH).<sup>302</sup> One can also measure the air exchange rate (AER) of an enclosure.<sup>303</sup> It gives an indication on the quality of enclosure in terms of leakage. A common way to measure the AER of an enclosure is to monitor the decrease in carbon dioxide (CO<sub>2</sub>). One can fill an important quantity of CO<sub>2</sub> into the enclosure and measure its decrease with a carbon dioxide meter. From this decrease the AER can be calculated.<sup>304</sup> Leakage can occur in the following ways: diffusion

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<sup>296</sup> Personal communication with Chris Collins, Natural History Museum, London, 26/06/2006; POLLARD T., unpublished, 2006, p33.

<sup>297</sup> MAEKAWA S., ELERT K., 2003, p19.

<sup>298</sup> Gilberg and Grattan said that copolymers of propenenitrile (acrylonitrile), vinylidene chloride, ethenevinyl alcohol and chlorotrifluoroethene were considered for use as high-barrier films, as they have a low permeability to oxygen. (GILBERG M., GRATAN D., 1994, p178).

<sup>299</sup> SHASHOUA Y., 1999, p883.

<sup>300</sup> MAEKAWA S., ELERT K., 2003, p20.

<sup>301</sup> Ibid., p20-27; COLLINS C., unpublished, 1999, p6.

<sup>302</sup> Ibid.

<sup>303</sup> See annex II for calculations of air exchange rates.

<sup>304</sup> CALVER A., HOLBROOK A., THICKETT D., WEINTRAUB S., 2005, p599.



along gaps (here CO<sub>2</sub> will be 32/44 slower than oxygen), infiltration through gaps (here CO<sub>2</sub> and oxygen comport equally and this point might probably be of less importance for ESCAL<sup>TM</sup> bags) and permeation through the ESCAL<sup>TM</sup> film (where CO<sub>2</sub> and oxygen are likely to comport differently). It has been found that the AER for a fully sealed ESCAL<sup>TM</sup> bag was lower than for a bag closed with three heat seals and a clip. Although it seems questionable if CO<sub>2</sub> is the suitable tracer gas for AER measurements on ESCAL<sup>TM</sup> barrier film. It seemed that leakage of the tracer gas through the film itself occurred and influenced the results.<sup>305</sup>

ESCAL<sup>TM</sup> layers were detailed as follows, pointing out the most important information to know about the product: an outer layer of co-extruded oriented polypropylene (OPP) followed by the barrier layer of ceramic-coated polyvinyl alcohol (PVAL) and low-density polyethylene (LDPE) on the inside (this inner layer is the sealing layer).<sup>306</sup>

The supplier of ESCAL<sup>TM</sup> film, Mitsubishi Gas Chemical Company, states that the product consists of seven layers<sup>307</sup> (information is only provided on three of them which will be detailed below).

The heat-sealable layer of ESCAL<sup>TM</sup> barrier film is made of linear low-density polyethylene (LLDPE), which has very good hot tack properties important for the heat sealing. LLDPE has other properties such as good chemical resistance, high tensile and tear strength or puncture resistance.<sup>308</sup>

The vapour barrier, made of silica-coated PVAL does not contain plasticisers. What might be of a certain concern is that we do not know yet how the silica is deposited onto the PVAL and that the use of PVAL might be problematic. This is because of the fact that during the production of PVAL the acetate groups from poly(vinyl acetate) (PVAC) are removed and replaced by the OH-groups which will provide the PVAL. If this reaction is not fully completed, some acetate groups may stay in the copolymer. But if the reaction is complete, the PVAL is very stable to oxygen and ultraviolet (UV) ageing.<sup>309</sup> PVAL is stable at low RH levels, but sensitive to high humidity levels. However, it seems that for short-term use PVAL does not pose any problem.<sup>310</sup>

OPP is used as a protective layer. This material has a higher softening point than the heat-sealable layer and is also harder than the latter. The film is clear and glossy. The material is resistant to tear initiation (but once initiation has been effected, tear resistance is low).<sup>311</sup>

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<sup>305</sup> The decrease in CO<sub>2</sub> in a clipped ESCAL<sup>TM</sup> bag was measured as well as the decrease in an ESCAL<sup>TM</sup> bag covered with aluminium tape (where only the leakage through the clip was looked at). If AER measurements are reliable, the two values are the same (as we do not want leakage of the CO<sub>2</sub> through the film itself). The two values were visibly different and therefore CO<sub>2</sub> seems to be questionable as tracer gas for this experience.

<sup>306</sup> <http://www.keepsafe.ca/escal.shtml>, 15/12/2005; MACDONALD WELCH S., 2005, p43.

<sup>307</sup> POLLARD T., unpublished, 2006, p44.

<sup>308</sup> MC PHAIL D., LAM E., DOYLE A., 2003, p99.

<sup>309</sup> Ibid.

<sup>310</sup> Personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>311</sup> MC PHAIL D., LAM E., DOYLE A., 2003, p99.

| Escal®   |                             |
|--|-----------------------------|
| Orientated polypropylene (OPP) -----           | Structural/protective layer |
| Silica-coated poly(vinyl) alcohol (PAVL) ----- | Vapour barrier              |
| Polyethene (LLDPE) -----                       | Heat-sealable layer         |

Figure 34: The principal layers of ESCAL™ high barrier film. (MC PHAIL D. et al., 2003, p98).

### 3.3.4 The production of an enclosure made of ESCAL™ barrier film

The life-time of an anoxic enclosure made of ESCAL™ barrier film with the use of oxygen absorbers will depend on certain parameters. We have already considered impermeability of the film to oxygen and moisture. But it also depends on the quality of the heat seals to close the bag and on the quality of the barrier film itself as well as on the absorbing capacity of the oxygen absorber. To produce a bag made of ESCAL™ barrier film, a heat sealer can be used most easily. The principle of the procedure is to hold the two thermoplastic layers against each other with heated metal jaws while applying heat and pressure: this melts the material partially and provides a heat seal. The polymer chains can in this way form bridges between each other. Important factors for heat sealing are temperature (between the two barrier films) and heat seal time. Time is measured for the period during which the two films are held together at the weld temperature. A heat sealer has a cooling time, during which the two films are still held in place under pressure, and this allows the weld to set. On the available heat sealers, the temperature can often not be set (they have a graduation from 0-10 for both welding and cooling intervals). The longer the heat seal time, the higher the temperature. It has been found that for a CRISS CROSS Universal Heat Sealing Machine as used in this work, the following settings can be applied to obtain good seals: Weld setting should be at 3 (117°C, which is very close to 118°C, the melting temperature of LLDPE) and cool setting at 6.<sup>312</sup>

One can also use a clip, provided by Mitsubishi Gas Chemical Company, to close the barrier film bag. It has not been clarified yet whether these clips remain tight in long-term use or if they should only be

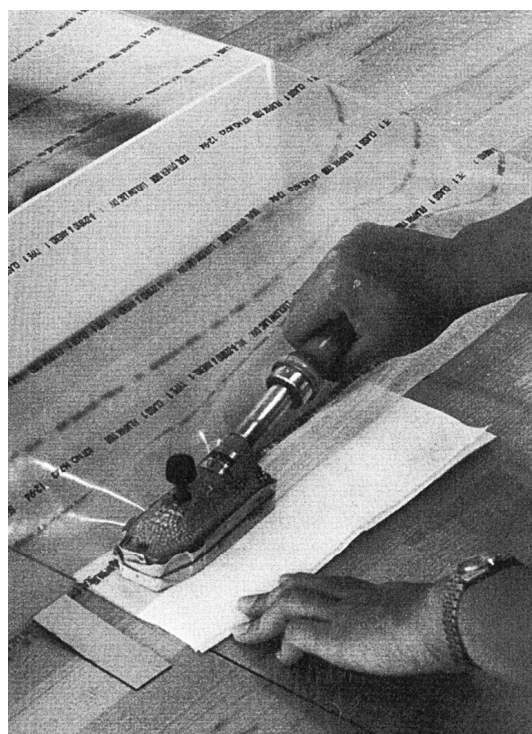


Figure 35: A plastic enclosure is produced with the help of a heat-sealing iron. (MAEKAWA S., ELERT K., 2003, p29).

<sup>312</sup> MC PHAIL D., LAM E., DOYLE A., 2003, p100-104; personal communication with Chris Collins, Natural History Museum, London, 21/03/2006.

used for short-term applications. Some people stated the clips were efficient in sealing anoxic bags.<sup>313</sup> Others voice some doubts.<sup>314</sup>

When packing objects into ESCAL™ barrier film bags one should be aware that the barrier film is sensitive to scratching. In order to avoid harm to the barrier film, objects can be placed on/in a non-abrasive material such as Ethafoam (PE foam), or else special supports can be produced (pillows).<sup>315</sup> It has been said that the life-time of the oxygen-free system depends on the quality of the barrier film and the quality of the heat seals. Another aspect is the absorption capacity of the oxygen absorber. Some conservators used initial oxygen removal with prior nitrogen flushing of the bags before introducing the oxygen absorber to obtain a longer life-time of the absorber (as it uses less of its capacity in the beginning).<sup>316</sup> Jerry Shiner from Microclimate Technologies International / Keepsafe Systems stated that the oxygen absorbers from the RP-System™ probably remained active once inserted into the anoxic enclosure for up to twenty years.<sup>317</sup>

### 3.3.5 Monitoring the anoxic climate

To get an idea of what climate prevails in the anoxic enclosure we can measure the oxygen level or the RH in the bag (as for an efficient RP-A absorber the RH has to be below 10%, this indication can be used as a measure of the efficiency of the enclosure).

To have a quick indication of whether the oxygen level in the enclosure has dropped after introducing an oxygen absorber one might use Ageless-Eye™, an oxygen-indicating tablet. This indicating tablet is produced by Mitsubishi Gas Chemical Com-pany in different forms. For the RP-A System, Type S is recommended (especially for dry environment with a range of 5-35°C and 0-92% RH). The tablet is first violet when oxygen is present (see figure 36) and turns pink (see figure 37) as the oxygen levels drops near zero (colour change when oxygen level drops below 0.1%). If the oxygen level rises to 0.5% or more, the tablet turns violet again. Mitsubishi Gas Chemical Com-pany states using methylene blue, an organic dye, as the oxidation-reduction



Figure 36: Oxygen-indicating tablets are violet when oxygen is present.



Figure 37: As soon as the oxygen level drops below 0.1%, the indicating tablets turn pink.

<sup>313</sup> CARRIÓ V., STEVENSON S., 2003, p38.

<sup>314</sup> Personal communication with Chris Collins, Natural History Museum, London, 21/03/2006.

<sup>315</sup> DAY J., 2005, p437; personal communication with Chris Collins, Natural History Museum, London, 21/03/2006.

<sup>316</sup> SHASHOUA Y., 1999, p886; NUTTGENS F., TINKER Z., 2000, p31.

<sup>317</sup> Personal communication with Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, 26/06/2006.

indicator. The product should be stored in the cold and dark (refrigerator) without access of oxygen. It has a guaranteed shelf life of six months. If the indicator is put into a cold environment the colour change may not occur rapidly when oxygen level is lowered. In theory, the colour changing behaviour of the oxygen indicator is said to be reversible for many cycles. It seems that the colour change from pink to violet is more rapid than from violet to pink (two to three hours).<sup>318</sup>

People who have tested the oxygen-indicating tablets have stated that the colour change might take longer than two hours and sometimes take weeks or even a month to occur. And repeated use seems to be impossible, as the indicator does not change colour any more after one cycle of use.<sup>319</sup> If working with oxygen-indicating tablets one should at least insert more than one tablet into the enclosure to have more indications if one tablet fails.<sup>320</sup> However, the indicating tablets obviously are



Figure 38: Reading the oxygen contents through the transparent ESCAL™ barrier film. The ruthenium sensor is placed in the blue light of the optical head.

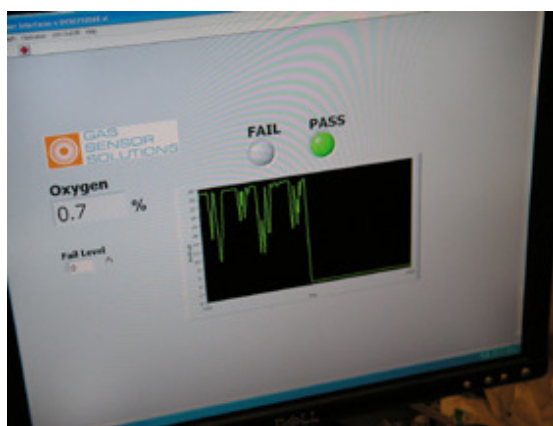


Figure 39: On the screen of the connected computer, direct readings of the oxygen contents in the enclosure are made possible.

not the most reliable of methods and have been found not to show always what happens in the bags in terms of oxygen levels.

We can also use oxygen meters to take measurements in the enclosures. Oxygen meters that take instant measurements through a needle (as a Mapcheck from Systech Instruments Ltd.) have been used.<sup>321</sup> Before piercing the bag a plastic re-closing patch can be applied, through which the measurement can be taken. However, doubts have been voiced upon the quality of the re-closure of the patch after piercing. This method cannot be used to monitor a system on a regular basis.<sup>322</sup>

Today new oxygen monitoring systems are available. The Natural History Museum in London uses the GSS450 Oxygen Analyser (see figures 38 and 39). This system works with the so-called SensiSpot, a printed sensor containing ruthenium.<sup>323</sup> The sensor is placed into the enclosure before sealing. With the GSS450 Oxygen Analyser one scans the sensor and the oxygen concentration inside the bag is recorded. If oxygen is present the ruthenium will alter and the sensor will reemit less light. The amount of

<sup>318</sup> MAEKAWA S., ELERT K., 2003, p30.

<sup>319</sup> MAEKAWA S., ELERT K., 2003, p30; personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>320</sup> CARRIÓ V., STEVENSON S., 2003, p37.

<sup>321</sup> This instrument has been used at the British Museum, London.

<sup>322</sup> Personal communication with James Parker, The British Museum, London, 30/11/2005.

<sup>323</sup> Research upon the quality and life-time of this ruthenium sensor is currently carried out at the National History Museum, London.

reemitted light is measured (the more the sensor reemits, the lower the oxygen content). The Oxygen Analyser is composed of an optical head using a light emitting diode (LED) to illuminate the sensor (blue light). The light that the sensor (SensiSpot) reemits is detected using photodiodes. This information has to be fed into an electronic circuitry where the signals are converted into oxygen concentration values. Specific software as well as calibrations of instruments for the reading and recording of the data is provided by Gas Sensor Solutions.<sup>324</sup> It seems that the sensor (SensiSpot) is sensible to RH above 75% (delamination of the sensor) and to very low temperatures (below -10°C). If the sensor is placed in such environments, its readings are affected (either by an increase in the reading, for high RH, or by decrease, for low temperatures). High temperatures might as well affect the readings. The producer advises to hold the sensor at a distance from 0 – 28mm to the detector (under the blue light). Readings can give results within a 2% error range if doing so and varying this distance. It seems to be important to hold the sensor at approximately the same distance to the detector every time. A minimum error value of 0.5% should be taken into account for readings.<sup>325</sup>

One can also use radio telemetry systems to monitor the RH, as produced by Meaco (see figure 40). The data are transmitted from the recording site to a remotely located computer. Data is then immediately accessible to be read and manipulated. The system can read over a long period, although batteries might have to be changed from time to time.<sup>326</sup> The disadvantage of this approach seems to be the fairly voluminous data-loggers and the dependence on battery life.<sup>327</sup>

Relative humidity-indicating strips (see figure 41) can be used to give a rough indication of humidity in the enclosure.

Dataloggers that read RH and temperature are provided by Hanwell Instruments amongst others (see figure 42).<sup>328</sup> We used the rh-t bug from Hanwell Instruments Limited for our tests and this

logger is said to have a battery life upon five years (depending on the use). Working with the RP-System™ the use of such a datalogger can give readings upon the RH that should drop to near zero with RP-A oxygen absorbers. The disadvantage is, that direct reading is not possible and reading can



Figure 40: Meaco radio telemetry system dataloggers. (www.meaco.com, 05/07/2006).

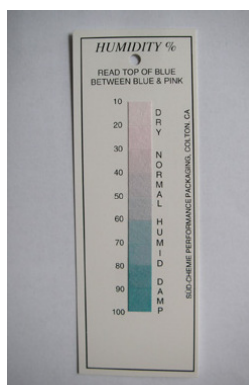


Figure 41: Humidity-indicating strip.



Figure 42: A Hanwell rh-t bug datalogger, measuring temperature and RH. (www.hanwell.com, 05/07/2006).

<sup>324</sup> Gas Sensor Solutions, www.gss.ie, 10/03/2006; personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>325</sup> POLLARD T., *unpublished*, 2006, p13, p30, p32.

<sup>326</sup> Light and Humidity, Safeguarding Historic Collections, Short Course Programme, *unpublished*, 2004, p22.

<sup>327</sup> Personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>328</sup> Hanwell Instruments Limited, Hertford SG13 7BJ, United Kingdom.

only be done after opening the anoxic enclosure and taking out the datalogger for downloading of data.

## 4 RESEARCH PROJECT

### 4.1 Aims

The aim of this study was to examine two different systems for storage of freshly excavated iron objects and the systems' efficiency in the prevention of active corrosion. On one hand the storage of material in dry or cold and dry/cold conditions was investigated and compared. On the other hand oxygen-free storage was tested with two different oxygen absorbers. Could the formation of akaganéite ( $\beta$ -FeOOH), much feared after excavation and the exposure of iron objects to air and humidity, be prevented by the application of these storage methods?

The work was essentially based on the examination of synthetic powder samples.<sup>329</sup> Some archaeological samples were packed alongside the synthetic samples to see whether they reacted similarly.<sup>330</sup> The testing period was five-and-a-half months.

Various parameters had to be taken into account. The chosen packaging systems should correspond to actual storage methods applied by Swiss conservators.<sup>331</sup> The synthetic samples should reproduce the corrosion reaction in question: the formation of akaganéite ( $\beta$ -FeOOH)<sup>332</sup>. The choice of testing two different storage approaches (cold/dry storage and oxygen-free storage) should reveal the advantages and disadvantages of each.

Examining the influence of RH/temperature and oxygen/RH respectively would show which of those climatic parameters exerts a major influence on the corrosion process of the samples and therefore can be considered dangerous for freshly excavated iron artifacts. It was to be clarified which of the tested methods was the most easily applicable, the best performing in terms of prevention of active corrosion and the most economic one.

Two test groups were set up. In the first test group the samples were packed in resealable PE bags and put into a PP box. The resealable bags were either completely closed or provided with holes, which had an influence on the climate in the bags. The box was either stored at room temperature or in the refrigerator at 4°C. To obtain dry climates, silica gel was added to some boxes. In the second test group examining oxygen-free storage, the samples were packed in bags made of a high-barrier film (ESCAL<sup>TM</sup>), either heat-sealed on all sides or with three seals and closed with a clip on the last side. An oxygen absorber was added to the bag. These oxygen absorbers (RP-System<sup>TM</sup>) either influenced only the amount of oxygen present (RP-K) or the level of RH (RP-A) as well.<sup>333</sup>

FT-IR, XRD and optical microscopy using reflected light were applied to monitor the corrosion compounds formed in the samples (monitoring and analysis were carried out on a monthly basis). FT-

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<sup>329</sup> Synthetic powder samples were produced from a mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ).

<sup>330</sup> Archaeological samples were Roman nails from two Swiss excavations of the summer/autumn period 2005. They were provided by the laboratories of Vindonissa, canton of Aargau and Fribourg (from the site of Bösingen, Fendringenstrasse, in the canton of Fribourg).

<sup>331</sup> See annex IV for the questionnaire on storage methods sent to ten Swiss conservation laboratories and one in Liechtenstein.

<sup>332</sup> See chapter 2 for corrosion reactions of archaeological iron.

<sup>333</sup> For details on the materials used in oxygen-free storage see chapter 3.3.



IR was used to quantify the amount of akaganéite ( $\beta$ -FeOOH) formed in the synthetic samples after a period of five-and-a-half months.

## 4.2 Criteria taken into account for the tested storage systems

Following a survey carried out with ten Swiss conservation laboratories<sup>334</sup> who deal with freshly excavated iron artifacts, two main packaging systems were chosen for examination. Many conservators mentioned packing objects into resealable PE bags (they either explicitly stated that the bags were left open, or were closed, or did not provide details on this point) and then putting these bags into plastic boxes (various trademarks and often made of PE, and/or PP). The resealable PE bags provide a separation for the objects as well as an additional protection from climatic changes. The plastic boxes provide a microclimate where silica gel can be added to keep the contents dry. Some conservators also mentioned the use of a cold atmosphere to store those boxes in (putting them into a refrigerator). The answers showed that the approach of oxygen-free storage was not widely developed and applied in Switzerland but that some institutions were trying to apply forms of it (for example nitrogen purging of bags). It thus became necessary to clarify if oxygen-free storage in general would be a good method of preventing akaganéite ( $\beta$ -FeOOH) to form. A specific system for anoxic enclosures (RP-System<sup>TM</sup> from Mitsubishi Gas Chemical Company) was chosen to carry out tests with, as this system is used in the world of conservation and museums and has shown interesting results. The system was also thought to be quite easily and economical to apply.



Figure 43: Often seen: dry storage of archaeological finds in resealable PE bags placed into PP boxes with dry silica gel (here at Fort Cumberland, Portsmouth, English Heritage).



Figure 44: Small storage space of freshly excavated finds at the treatment laboratory Fort Cumberland, Portsmouth, English Heritage Centre for Archaeology.

The storage systems used was to take into consideration first the combination of RH and temperature, and secondly access of oxygen and RH.

The first test group of packed samples was used to examine the corrosion behaviour of the samples in a very dry and cold climate compared to dry storage at room temperature. It was also necessary to

<sup>334</sup> See annex IV for details.



see whether the fact of closing or leaving open the resealable PE bag in which the sample was first placed would influence the reactions. The test group of packed samples in anoxic environments was meant to show whether storage without oxygen would perform efficiently. The two oxygen absorbers tested were to be compared.<sup>335</sup>

### 4.3 Criteria for the synthetic and archaeological samples

The key factors considered in the preparation of the synthetic samples imitating the corrosion reactions of freshly excavated archaeological iron were:

- whether to take samples produced in the laboratory and essentially synthetic or to take 'real' material (archaeological or historical samples)
- the choice of a material that would show the main reaction of interest, the formation of akaganéite ( $\beta$ -FeOOH) in a time period set over five-and-a-half months
- the search for a sample material that could be analysed with the set techniques (FT-IR and XRD)
- the appropriate sample size and number to use for each set

Details of the decisions and reasons involved are given below.

The choice of samples produced in the laboratory was justified as follows: these samples would show more comprehensive reactions than 'real' material often already heterogeneous in the beginning and less predictable in its reactions. It seemed to be difficult to choose a 'real' material that is representative of most excavated iron, and it was not possible to find material excavated on the day the tests started. Taking synthetic samples allows starting from a known product and working scientifically. It was decided to include archaeological material<sup>336</sup> and to see whether this material reacted similarly to the synthetic powders.



Figure 45: Preparation of the powder mixture for the synthetic samples.



Figure 46: Powder sample ready for experimentation.



Figure 47: Archaeological sample (FR 254-01) before beginning of experiments.

<sup>335</sup> One of the absorbers (RP-A) lowered the RH to near zero whereas the other one (RP-K) is said not to affect the RH in the enclosure.

<sup>336</sup> Roman nails from two Swiss excavation sites of summer/autumn 2005 have been used.

The samples were made from a powder mixture of an equal amount of iron (Fe)<sup>337</sup> and iron chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O)<sup>338</sup> and the total sample size was set at 0.1g (0.05g iron and 0.05g iron chloride tetrahydrate). In the relevant literature we can find examples of production of akaganéite (β-FeOOH). The chosen powder mixture had already proven reliable in forming akaganeite (β-FeOOH) and showing results within weeks (see chapter 2.2.3).<sup>339</sup>

Each synthetic sample group consisted of three powder samples per month. So every month, three samples were taken out of each enclosure and not replaced into the testing environment after analysis. Having more than one sample allows comparing for abnormalities. Archaeological samples were analysed after three and after five-and-a-half months.

## 4.4 Test setup

### 4.4.1 Cold/dry storage of samples in polyethylene (PE) bags placed in polypropylene (PP) boxes

The synthetic powder samples and archaeological samples used were all packed in resealable PE bags<sup>340</sup> and then placed into PP boxes<sup>341</sup>. The boxes were either provided with a desiccant (silica gel) or the RH was not influenced. The boxes were kept at room temperature or in the cold at 4°C in a refrigerator. Dataloggers<sup>342</sup> measuring temperature and RH were used to monitor the systems (one datalogger per PP box over five-and-a-half months; see table 2).

The intention of this part of the research project was to examine three different parameters.

The first step was to look into the difference of closing or leaving open the PE bag. For this reason, half the samples were packed in closed PE bags and the other half in PE bags provided with a dozen holes (see table 1). The latter system allows the air in the PP box to circulate more freely into the PE bag.

The second aspect was the influence of RH. The level of RH in the air influences the velocity of corrosion (see chapter 2.1.2). For archaeological iron it is known that the lower the RH the slower the corrosion processes. Storage of archaeological iron at a RH as low as 15 – 20% has been proposed.<sup>343</sup> To examine this aspect, half of the samples packed in PE bags were placed in a dry climate using dry silica gel (0-5% RH) that was filled into the PP boxes (see table 1 and table 2).<sup>344</sup> No desiccant was used for the rest of the samples.

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<sup>337</sup> Iron (Fe): Puriss. p. a.; Carbonyl-Iron powder; ≥ 99.5% (RT).

<sup>338</sup> Iron(II) chloride 4-hydrate (ferrous chloride): FeCl<sub>2</sub>·4H<sub>2</sub>O = 198.83 g/mol, assay (manganometric) ≥ 99.0%.

<sup>339</sup> Personal communication with David Thickett, English Heritage, autumn 2005; KELLER P., 1969, p103; TURGOOSE S., 1982 a, p97-101.

<sup>340</sup> Minigrip™ bags.

<sup>341</sup> Stewart™ 'Seal fresh' boxes.

<sup>342</sup> Hanwell Datalogger rh-t bug in the cold and Meaco telemetry system at room temperature.

<sup>343</sup> WATKINSON D., LEWIS M., 2004, p88-102; WATKINSON D., LEWIS M., 2005, p241-252; THICKETT D., ODLYHA M., in press, 2006.

<sup>344</sup> 200g of silica gel per 1.8l or 2.25l PP box.

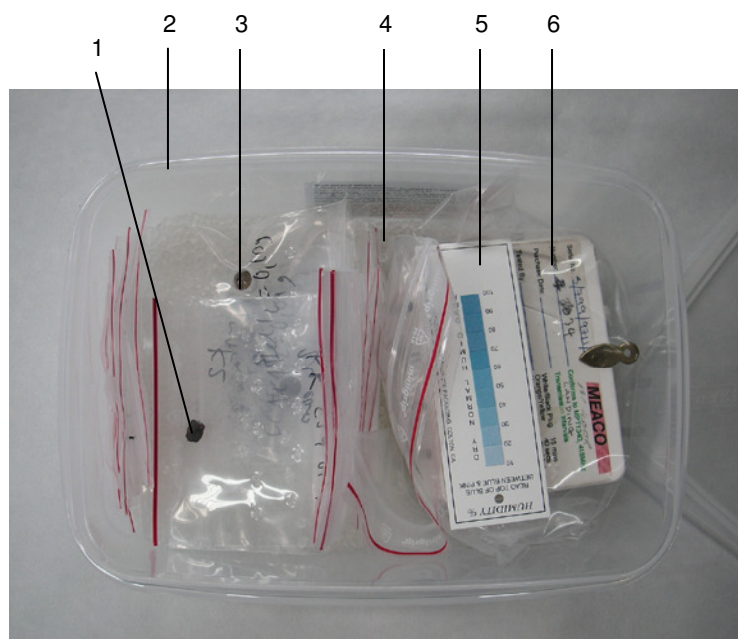
The third parameter to be examined was the temperature. Temperature seems to have an influence on the velocity of corrosion processes. In corrosion-friendly conditions higher temperatures enhance corrosion.<sup>345</sup> At low temperatures, corrosion can be slowed down. Again, half the samples were placed into a cold climate at 4 °C in a refrigerator and compared to samples left at room temperature (see table 1).

Many conservators apply dry storage to freshly excavated iron artifacts for short- and long-term storage. It was decided to take a look at dry storage compared to storage combining dryness and cold, as both approaches are used in Switzerland.

| Sample group | Nature of sample | Bags polyethylene (PE) open | Bags polyethylene (PE) closed | Temperature      | RH                        |
|--------------|------------------|-----------------------------|-------------------------------|------------------|---------------------------|
| D1           | Synthetic        |                             | Closed                        | Room temperature | Uninfluenced              |
| E1           | Synthetic        |                             | Closed                        | 4 °C             | Uninfluenced              |
| F1           | Synthetic        |                             | Closed                        | Room temperature | Dry (silica gel, 0-5% RH) |
| G1           | Synthetic        |                             | Closed                        | 4 °C             | Dry (silica gel, 0-5% RH) |
| H1           | Synthetic        | Open                        |                               | Room temperature | Uninfluenced              |
| I1           | Synthetic        | Open                        |                               | 4 °C             | Uninfluenced              |
| K1           | Synthetic        | Open                        |                               | Room temperature | Dry (silica gel, 0-5% RH) |
| L1           | Synthetic        | Open                        |                               | 4 °C             | Dry (silica gel, 0-5% RH) |
| D2           | Archaeological   |                             | Closed                        | Room temperature | Uninfluenced              |
| E2           | Archaeological   |                             | Closed                        | 4 °C             | Uninfluenced              |
| F2           | Archaeological   |                             | Closed                        | Room temperature | Dry (silica gel, 0-5%RH)  |
| G2           | Archaeological   |                             | Closed                        | 4 °C             | Dry (silica gel, 0-5% RH) |
| H2           | Archaeological   | Open                        |                               | Room temperature | Uninfluenced              |
| I2           | Archaeological   | Open                        |                               | 4 °C             | Uninfluenced              |
| K2           | Archaeological   | Open                        |                               | Room temperature | Dry (silica gel, 0-5% RH) |
| L2           | Archaeological   | Open                        |                               | 4 °C             | Dry (silica gel, 0-5% RH) |

Table 1: Setup of samples in groups D, E, F, G, H, I, K, L.

<sup>345</sup> Reaction rates increase as temperature is raised.



- 1: Archaeological sample in resealable PE Minigrip™ bag provided with holes
- 2: Stewart™ PP box
- 3: Synthetic powder sample in resealable PE Minigrip™ bag provided with holes
- 4: Silica gel
- 5: Humidity-indicating strip
- 6: Datalogger (Meaco)

Figure 48: Setup of samples in a PP box with added silica gel (group K1/K2).

The synthetic powder samples were placed in small round plastic containers<sup>346</sup>.

The archaeological samples (nails) were cut in small pieces of approximately 2cm using a metal saw. Pictures of the nails were taken before the experimental work started.



Figure 49: Cutting the archaeological nails using a metal saw was more difficult than expected...

Each group of synthetic powder samples consisted of three samples per month over a five-and-a-half months test period (sample analysis every month). Archaeological samples were put to the test for either three or five-and-a-half months (two to three samples) before being taken out.

<sup>346</sup> Plastic tops 8mm diameter x 10mm height supplied by SAMCO, United Kingdom, [www.samco.co.uk](http://www.samco.co.uk), June 2006.

| Sample group | Amount of silica gel added <sup>347</sup> | Volume of PP box | Type of datalogger |
|--------------|---|------------------|--------------------|
| D1/D2        |   | 2.25l            | Meaco              |
| E1/E2        |   | 1.8l             | Hanwell rh-t bug   |
| F1/F2        | 200g (at 0-5% RH)                         | 2.25l            | Meaco              |
| G1/G2        | 200g (at 0-5% RH)                         | 1.8l             | Hanwell rh-t bug   |
| H1/H2        |   | 2.25l            | Meaco              |
| I1/I2        |   | 1.8l             | Hanwell rh-t bug   |
| K1/K2        | 200g (at 0-5% RH)                         | 2.25l            | Meaco              |
| L1/L2        | 200g (at 0-5% RH)                         | 1.8l             | Hanwell rh-t bug   |

Table 2: Indications on amount of silica gel added to the different types of Stewart<sup>TM</sup> PP boxes and on dataloggers used.



Figure 50: Packed samples and datalogger (rh-t bug from Hanwell) ready to go into the refrigerator.



Figure 51: Stewart<sup>TM</sup> boxes in the refrigerator.

#### 4.4.2 Oxygen-free storage of samples using the RP-System<sup>TM</sup>

Corrosion occurs when oxygen and humidity are present (see chapter 2.1.2). Lowering the oxygen level could slow down or inhibit corrosion occurring on freshly excavated iron artifacts. It was therefore decided to test two oxygen absorbers on their capacity of preventing the formation of akaganéite ( $\beta$ -FeOOH) in the previously described samples. One of the absorbers (RP-K) would only act on the oxygen concentration in the enclosure and the second (RP-K) would also lower the RH.

Oxygen-free storage was carried out using the Revolutionary Preservation System<sup>TM</sup> from Mitsubishi Gas Chemical Company. All samples were placed into bags made from ESCAL<sup>TM</sup> high-barrier film (see chapter 3.3.4).

<sup>347</sup> 20kg/1m<sup>3</sup> silica gel are recommended for conditioning (THOMSON G., 1977, p88). For the 1.8l box a minimum amount of 0.036kg and for the 2.25l box 0.045kg of silica gel would be required. In the present work an excess of 0.2kg was added to assure a very dry climate over the experimental period of five-and-a-half months.





Figure 52: Bags for experiments made from ESCAL™ high barrier film.



Figure 53: CRISS CROSS Universal Heat Sealing Machine used for making seals on the ESCAL™ bags.

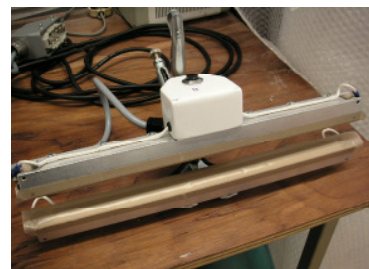


Figure 54: Heat-sealing jaws used when sealing ESCAL™ barrier film.

The bags (see figure 52) were closed in two different ways (see table 3). Either on all sides with heat seals using a CRISS CROSS Universal Heat Sealing Machine (see figure 53)<sup>348</sup> or closed on the last side with a very airtight clip from Mitsubishi Gas Chemical Company and provided with the RP-System™. The first packaging method would test a long-term approach, as objects could be definitely sealed. The clipped bags would test the possibility to apply the RP-System™ as a short-term and temporary storage method used on site to give objects protection until arrival in the laboratory.

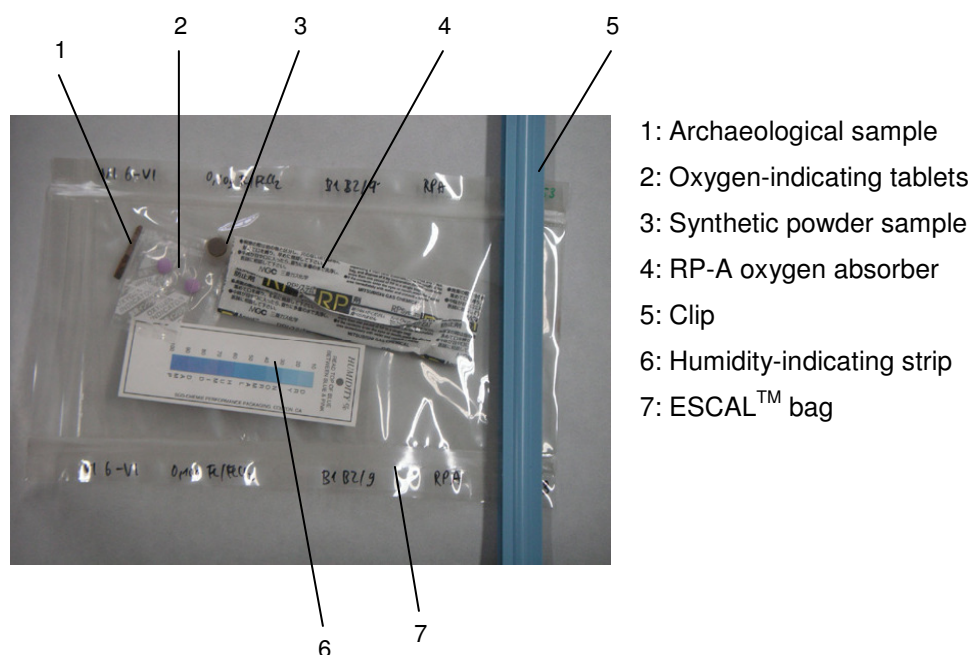


Figure 55: Test setup for samples packed with an RP-A oxygen absorber. The bag is closed with a clip (test group B1/B2).

Two oxygen absorbers from the RP-System™ were tested and compared (see chapter 3.3.2). The RP-A oxygen absorber lowers the oxygen content to near zero and the RH below 10%. RP-K has the same performances as RP-A, but does not affect the RH.

<sup>348</sup> Heat-sealing was performed with a weld setting at position 3 (117 °C, which is very close to 118 °C, the melting temperature of LLDPE, the heat-sealable layer of ESCAL™) and cool setting at 6 (MC PHAIL D., LAM E., DOYLE A., 2003, p100-104).

Monitoring of the system was carried out using RH strips and oxygen-indicating tablets<sup>349</sup> (two per enclosure). Oxygen levels were measured for one series (with the clips) using a Mapcheck oxygen meter from Systech Instruments Ltd. (provided with a needle) at the end of the test period. For the series with fully heat-sealed bags, the GSS450 Oxygen Analyser from Gas Sensor Solutions was used and monitoring through the bags was made possible over the whole testing period using ruthenium sensors.<sup>350</sup>

| <b>Sample group</b> | <b>3 heat seals + clip or fully heat-sealed</b> | <b>Nature of sample</b> | <b>RP-A absorber (for 300 ml of air)</b> | <b>RP-K absorber (for 300 ml of air)</b> | <b>Oxygen measurement technique used</b>                   |
|---------------------|---|-------------------------|--|--|--|
| A1                  | Clip  | Synthetic               | No absorber                              | No absorber                              | Mapcheck oxygen meter (needle) at the end of test          |
| A2                  | Clip  | Archaeological          | No absorber                              | No absorber                              | Mapcheck oxygen meter (needle) at the end of test          |
| B1                  | Clip  | Synthetic               | RP-A                                     |  | Mapcheck oxygen meter (needle) at the end of test          |
| B2                  | Clip  | Archaeological          | RP-A                                     |  | Mapcheck oxygen meter (needle) at the end of test          |
| C1                  | Clip  | Synthetic               |  | RP-K                                     | Mapcheck oxygen meter (needle) at the end of test          |
| C2                  | Clip  | Archaeological          |  | RP-K                                     | Mapcheck oxygen meter (needle) at the end of test          |
| AX1                 | Fully heat-sealed                               | Synthetic               | No absorber                              | No absorber                              | GSS450 Oxygen Analyser (monitoring over whole test period) |
| BX1                 | Fully heat-sealed                               | Synthetic               | RP-A                                     |  | GSS450 Oxygen Analyser (monitoring over whole test period) |
| CX1                 | Fully heat-sealed                               | Synthetic               |  | RP-K                                     | GSS450 Oxygen Analyser (monitoring over whole test period) |

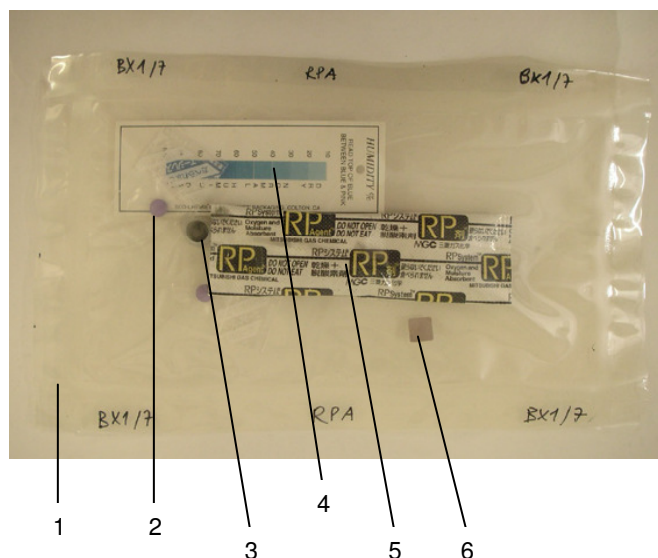
Table 3: Setup for groups A, B, C, AX, BX, CX.

Synthetic and archaeological samples were packed in the way described in table 3. Six groups of samples were set up. Group A, B and C were set up for a period of five-and-a-half months, groups AX, BX and CX for three months.<sup>351</sup> Archaeological samples were put to the test for either three or five-and-a-half months before being taken out in groups A, B and C. Synthetic samples were analysed monthly in all groups.

<sup>349</sup> Oxygen-indicating tablets from Mitsubishi Gas Chemical Company.

<sup>350</sup> See Chapter 3.3.5 for details on oxygen monitoring.

<sup>351</sup> Series AX, BX and CX were launched later when doubts on the efficiency of the clips used for closing the anoxic enclosures arose.



- 1: ESCAL™ bag
- 2: Oxygen-indicating tablet
- 3: Synthetic powder sample
- 4: Humidity-indicating strip
- 5: RP-A oxygen absorber
- 6: Ruthenium sensor (SensiSpot)

Figure 56: Test setup for samples packed with an RP-A oxygen absorber. The bag is closed with four heat seals (test group BX1).

All ESCAL™ barrier film bags from group A, B and C were tested on leakage. This was done using a D-TEK™ Select Refrigerant Leak Detector from INFICON, spraying a refrigerant gas into the bags, closing them and checking for possible outflow with the leak detector. Used bags showed no leakage through seals and clip before starting tests.

The ESCAL™ bags from groups AX, BX and CX were checked for leakage with the GSS450 Oxygen



Figure 57: Leak detector used for making sure that the ESCAL™ bags showed no leakage before tests started. (www.inficon.com, June 2006).

Analyser after termination of the setup, as the reading is direct and can be repeated over the whole testing period. No leakage occurred once the samples were packed and the oxygen content was down to zero.

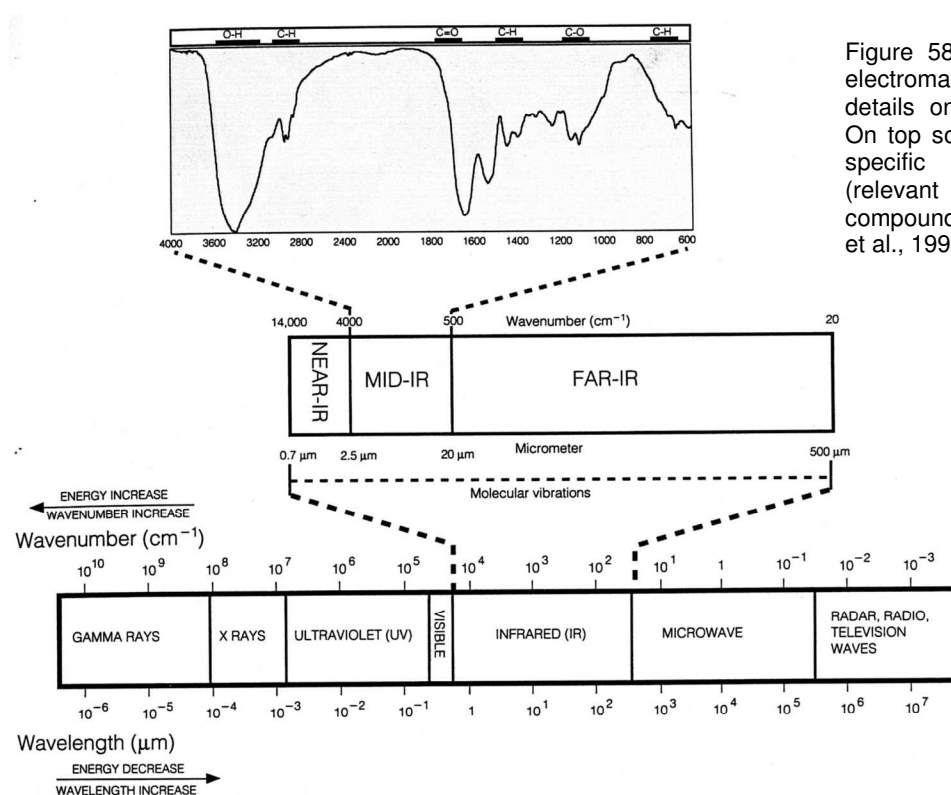
## 4.5 Analytical techniques

Changes occurring in the powder samples as well as in the corrosion layers of the archaeological nails can be observed using different techniques. Major colour changes and changes in volume can be observed visually with the naked eye or using a microscope. More precise results on the quality of the corrosion products forming can be obtained using XRD and FT-IR. In this work FT-IR was also used to quantify the amount of akaganéite ( $\beta$ -FeOOH) formed.



### 4.5.1 Fourier-transform infrared spectroscopy (FT-IR) analysis

Working with Infrared Spectroscopy we are interested in the wavelength range of 1mm - 1 $\mu$ m ( $10^{-1}$  –  $10^{-4}$ cm), the infrared region of electromagnetic radiation. Quanta of this radiation can interact with organic as well as inorganic compounds.<sup>352</sup> Infrared Spectroscopy is used to examine the molecular vibrations.<sup>353</sup> Molecular vibrations can occur as symmetrical stretching, asymmetrical stretching and bending. A dipole moment needs to be present in the molecule or to be induced. A molecule will only show vibrations if a dipole is present. Looking at the spectra obtained with FT-IR, we see information about the type of the oscillating molecule or group on the x-axis (wavelength axis in  $\text{cm}^{-1}$ ), and the intensity or absorbance on the y-axis. Using Infrared Spectroscopy allows us to work with a very low amount of sample (1-2mg is enough).<sup>354</sup>



FT-IR (standard transmission) was previously used by Thickett for monitoring of akaganéite ( $\beta$ -FeOOH) formation from the same type of synthetic samples as used in this work.<sup>355</sup>

Typical absorption band positions for akaganéite ( $\beta$ -FeOOH) have been indicated by Schwertmann, Cornell and Murad et al. in the following regions (intensities in  $\text{cm}^{-1}$ ): 3480 (bulk OH stretch), 3390 (OH-stretching band), 1630 ( $\text{H}_2\text{O}$ -bending band), 1025-1095 (weak, OH deformation), 790-850 (interaction of  $\text{H}_2\text{O}$  molecules with the hollandite tunnels or O-H...O bending vibrations), 650-690

<sup>352</sup> FERRETTI M., 1993, p33.

<sup>353</sup> REGUER S., 2005, p54.

<sup>354</sup> FERRETTI M., 1993, p36.

<sup>355</sup> THICKETT D., *unpublished*, 2003, p5.

(asymmetric Fe-O stretch), 490 and 420 (symmetric Fe-O-Fe stretch).<sup>356</sup> In the present work, we refer primarily to the region of 790-850 and for confirmation to 650-690 to detect the presence of akaganéite ( $\beta$ -FeOOH). These regions have shown to give a high level of certainty about the compounds' presence. The absorption band at  $848\text{cm}^{-1}$  would be used for quantification in this paper.

| Absorption region in $\text{cm}^{-1}$ | Strength/Intensity (s=strong, w=weak) <sup>357</sup> | Vibration  |
|---------------------------------------|--|--|
| 3723, 3686, 3659                      | very weak  | Surface OH groups  |
| 3460-3480<br>3487                     | s  | Bulk OH stretch<br><i>Bulk OH stretch</i>  |
| 3391                                  | s  | <i>OH stretching band</i>  |
| 1630                                  | s  | <i>H<sub>2</sub>O bending band</i>   |
| 1025-1095<br>1096<br>1050             | w  | OH deformation<br><i>OH deformation</i><br><i>OH deformation</i>   |
| 790-840                               |  | Asymmetric Fe-O stretch  |
| 848                                   | s  | <i>Interaction of H<sub>2</sub>O molecules with the hollandite tunnels or O-H...O bending vibrations</i> |
| 818                                   | w  |  |
| 650-690                               |  | Asymmetric Fe-O stretch  |
| 699                                   | s  | <i>Asymmetric Fe-O stretch</i>   |
| 650                                   |  | <i>Asymmetric Fe-O stretch</i>   |
| 490                                   |  | <i>Asymmetric Fe-O-Fe stretch</i>  |
| 400-410<br>420                        | s  | Asymmetric Fe-O-Fe stretch<br><i>Asymmetric Fe-O-Fe stretch</i>  |

Table 4: Infrared absorption bands for akaganéite ( $\beta$ -FeOOH) mentioned in the relevant literature (Cornell/Schwertmann (1996)<sup>358</sup> and Murad *et al.* (2000)<sup>359</sup>.

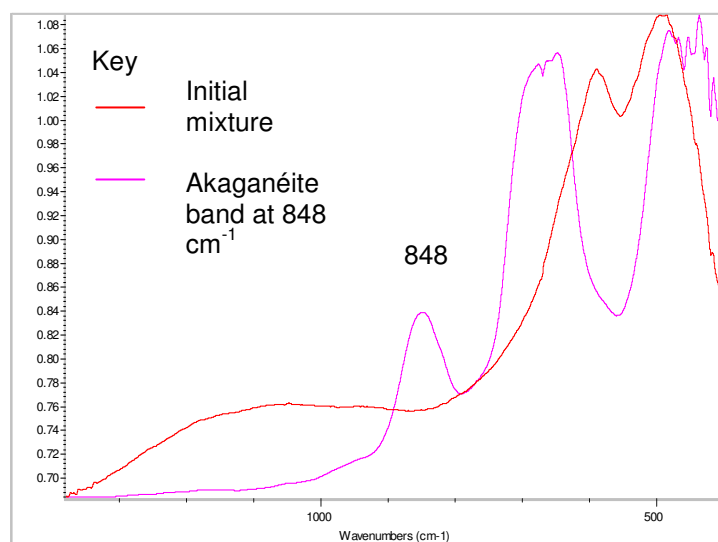


Figure 59: As akaganéite ( $\beta$ -FeOOH) forms, the characteristic absorption band at  $848\text{cm}^{-1}$  is clearly visible whereas in our initial powder mixture it is not present.

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

<sup>356</sup> CORNELL R. M., SCHWERTMANN U., 1996, p134-135; MURAD E., BISHOP J. L., 2000, p716-721.

<sup>357</sup> Strong (s) absorption bands were defined as above 50% of the strongest absorption, middle (m) bands as between 25 – 50% and weak (w) bands as below 25%.

<sup>358</sup> CORNELL R. M., SCHWERTMANN U., 1996, p134-135.

<sup>359</sup> MURAD E., BISHOP J. L., 2000, p716-721.

Analysis was carried out using a Perkin Elmer 2000 FT-IR. The potassium bromide (KBr) pellet technique was applied. Sample size was of 0.006g (6mg) in 0.3g (300mg) KBr. It was found that 0.012g (12mg) of sample matter introduced too much noise in the spectra, whereas 0.003g (3mg) seemed to be a less ideal amount of sample in terms of detecting the required information. The sample and the KBr were ground to a fine powder using an agate pestle and mortar. The powder obtained was double pressed to 10 tonnes. This was done with a 13mm die and hand press (Perkin-Elmer). The disc obtained was approximately 0.1mm thick. Analysis was performed by collecting 32 scans in a wavelength range of  $400\text{-}4000\text{cm}^{-1}$  at  $4.0\text{cm}^{-1}$  resolution. Working with 32 scans was found to give satisfactory quality spectra.

Before the examination of the synthetic samples used in the test series could start, reference material had to be produced to determine the detection limit of the FT-IR equipment.

Akaganéite ( $\beta\text{-FeOOH}$ ) was produced by heating 100ml of 0.3M iron(III) chloride ( $\text{FeCl}_3$ ) at  $70^\circ\text{C}$  in a sealed glass flask for 48 hours (see figure 60). The precipitate was collected by centrifuging (see figure 61), washed four times in the centrifuge, with freshly deionised water<sup>360</sup> and then left to dry in the air.<sup>361</sup>

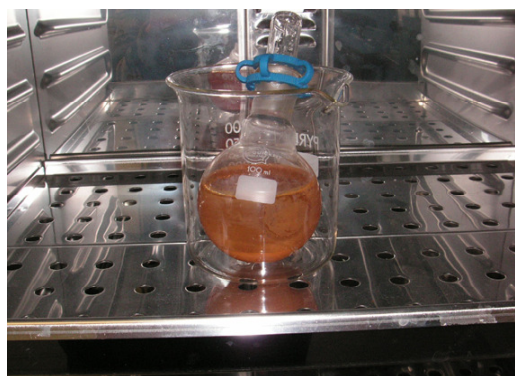


Figure 60: 3M Iron(III) chloride while heated at  $70^\circ\text{C}$  for 48 hours.



Figure 61: Iron(III) chloride hydrate after heating, ready for centrifugation.

The detection limit was found to be 0.1mg (0.0001g) akaganéite ( $\beta\text{-FeOOH}$ ) in 6mg (0.006g) mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ) in a 300mg (0.3g) KBr disc (1.66% akaganéite,  $\beta\text{-FeOOH}$ , in the disc). This meant that below this amount of the compound, it would be difficult to say for sure it was present.

$\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ , one of the compounds to produce our powder samples, was examined. 0.03g (30mg)  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  was mixed with 0.27g (270mg) KBr to obtain a powder of 300 mg in weight and ground using an agate pestle and mortar. The powder obtained was double pressed to 10 tonnes. This was done with a 13mm die and hand press (Perkin-Elmer). The disc obtained was approximately 0.1mm thick. Analysis was performed by collecting 32 scans in a wavelength range of  $400\text{-}4000\text{cm}^{-1}$ . The disc was then cut in half, KBr was added up to a total weight of 0.3g. The new disc was analysed in the same way and this procedure repeated ten times to observe changes in the FT-IR spectra and to determine interesting regions in terms of characterisation of the compound.

<sup>360</sup> 18.2M $\Omega$ .

<sup>361</sup> THICKETT D., *unpublished*, 2003, p5.

Observation of these spectra showed interesting absorption band regions at  $2220\text{cm}^{-1}$  (a well visible, rather broad band of small size<sup>362</sup>), a middle-sized band at  $582\text{cm}^{-1}$  and a band, a bit stronger than the previous one, at  $485\text{cm}^{-1}$  (see figure 63). Also a characteristic split absorption band with peaks at  $1640\text{cm}^{-1}$  and  $1610\text{cm}^{-1}$  was well visible (see figure 62). Comparing these spectra to those from the synthetic powder samples in the tests, it would be interesting to see if any band disappeared if akaganéite ( $\beta\text{-FeOOH}$ ) was to form. This would then mean that iron chloride tetrahydrate ( $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ) disappears to make room for akaganéite ( $\beta\text{-FeOOH}$ ).

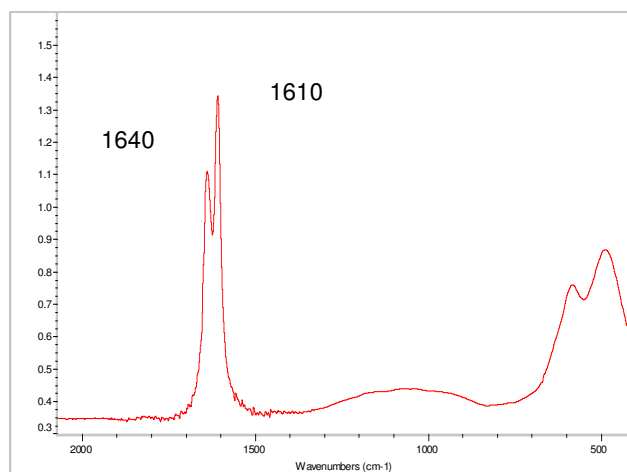


Figure 62: Characteristic split absorption band with two peaks at  $1640\text{cm}^{-1}$  and  $1610\text{cm}^{-1}$  for iron chloride tetrahydrate ( $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ).

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

A freshly prepared sample of equal amounts of (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ ) was analysed with both FT-IR and XRD to determine the characteristics of the initial powder mixture used afterwards in the experimental phase (see also chapter 4.5.2).

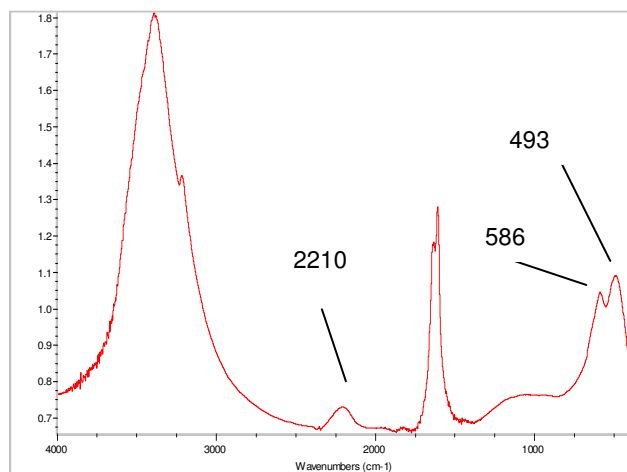


Figure 63: FT-IR spectrum of the initial powder mixture (iron and iron chloride tetrahydrate). Typical bands for iron chloride tetrahydrate are located in the region of  $2210\text{cm}^{-1}$ ,  $586\text{cm}^{-1}$  and  $493\text{cm}^{-1}$  (see description above).

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

<sup>362</sup> For definition of the size of absorption bands, see table 4.

### 4.5.2 X-ray diffraction (XRD) using a powder diffractometer

The term diffraction concerns the interaction of a type of wave with a material whose unit cell dimensions are comparable to the wavelength in question. Variations in the amplitude or phase of the wave can be produced by the concerned material. This causes a phenomenon called interference, which may be constructive or destructive (waves in phase or in opposition). Using X-rays, these can interact with the tested material. If the material is crystalline and we use a monochromatic beam, then constructive interference occurs if Bragg's law<sup>363</sup> is satisfied:

$$n\lambda = 2d\sin\theta$$

$n$  = integer number

$\theta$  = diffraction angle

$\lambda$  = wavelength

$d$  = distance between crystalline planes

Matter partly absorbs or transmits X-rays.<sup>364</sup>

*„Each peak, or reflection, in the diffraction pattern corresponds to X-rays diffracted from a specific set of planes in the specimen, and these peaks are of different heights (intensities). The intensity is proportional to the number of X-ray photons of a particular energy that have been counted by the detector for each angle  $2\theta$ .”<sup>365</sup>*

As a result we obtain a diffractogram.<sup>366</sup>

Many peaks can be present for a single material, each peak standing for one crystallographic plane. From the diffractogram we can read about the shape and size of the unit cell. It is possible to detect the presence and abundance of a material in the sample. If using a diffractometer, the sample and detector rotate during data collection (see figure 64).<sup>367</sup>

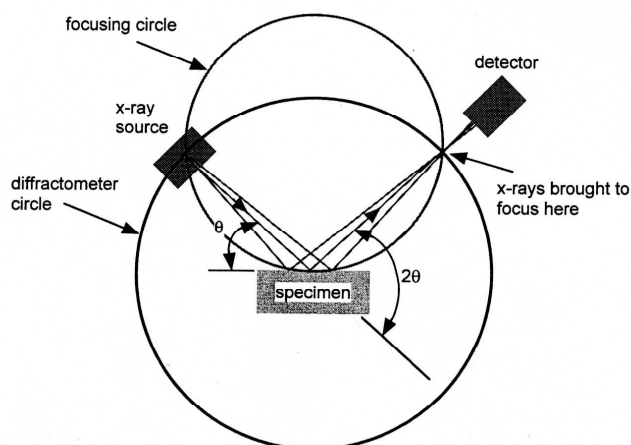


Figure 64: X-ray diffractometer and its geometry. (SURY-ANARAYANA C., 1998, p64).

XRD was carried out with a Philips

1830/1840. Monochromatic X-rays were produced by an X-ray tube with a copper target (Co-K $\alpha$ ,  $\lambda=1.79$ ). Working parameters were at 40kV (kilovolt) and 40mA (milliampere). Samples were ground in an agate mortar and displayed regularly on a glass plate covering a surface of 1cm<sup>2</sup> (using industrial methylated spirit IMS left to evaporate before analysis). Analysis was carried out on the diffractometer

<sup>363</sup> Bragg's law relates the angles  $\theta$ , the wavelength of the rays  $\lambda$  and the lattice spacings  $d_{hkl}$ . A plot of the observed diffraction intensity against the Bragg angle  $\theta$  gives the X-ray pattern of a powdered phase (CORNELL R. M., SCHWERTMANN U., 1996, p165.).

<sup>364</sup> Absorbing of X-rays by matter can be in two different ways: by scattering and by true absorption. Scattering can take place in all directions. This energy is not transmitted to the detector and so is said to be absorbed.

<sup>365</sup> SURYANARAYANA C., NORTON M. G., 1998, p81.

<sup>366</sup> Plot of intensity of diffracted X-ray versus  $2\theta$ .

<sup>367</sup> FERRETTI M., 1993, p39-40.

with a start angle ( $^{\circ}2\theta$ ) of 6.000 and an end angle ( $^{\circ}2\theta$ ) of 100.000. Scan time was 15 minutes and 40 seconds, time per step was 0.5 seconds. The maximum d-value ( $\text{\AA}$ ) was 17.0912 and minimum 1.16766. Obtained spectra were compared with the identification reference library from the International Centre for Diffraction Data (ICDD) and self-produced reference spectra for the initial powder mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ).



Figures 65 – 67: Preparation of a powder sample to be analysed with XRD using an agate mortar to grind the mixture and a glass plate for display.

Obtained spectra were compared with the identification reference library from the ICDD by superposing reference spectra with the spectra of the analysed materials. As soon as three major peaks of the reference library spectrum overlapped with the samples' spectrum, the so found compound was suspected to be present. ICDD would not always suggest the presence of a certain compound. Therefore manual identification was carried out.

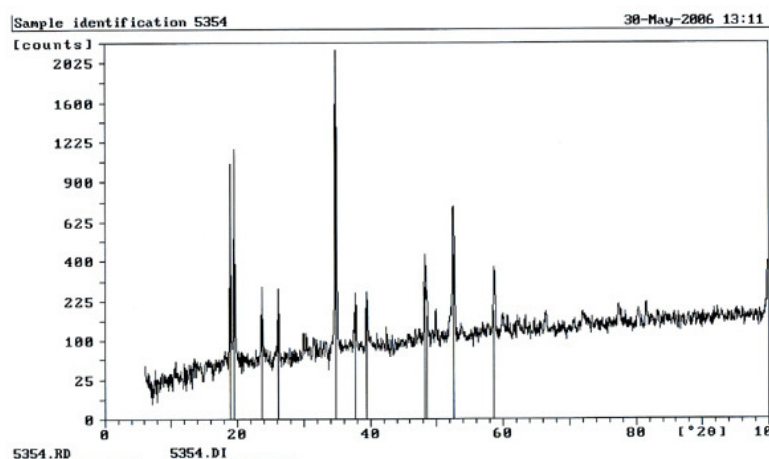


Figure 68: X-ray diffractogram for the initial powder mixture (same amounts of iron and iron chloride tetrahydrate).<sup>368</sup> Comparing with the ICDD file (16-0123 for iron chloride tetrahydrate) we see that the three strongest indicated peaks are well visible at 18.910, 19.510 and 26.180, ( $^{\circ}2\theta$ ) respectively.<sup>369</sup>

Three different ICDD files for akaganéite ( $\beta\text{-FeOOH}$ ) have been used to compare the powder samples of the tests with. In the following table the three major peaks of these references are indicated.

<sup>368</sup> Distinctive peaks for our mixture are located at (angle  $^{\circ}2\theta$ ): 18.910, 19.510, 23.670, 26.180, 34.820, 37.745, 39.445, 48.565, 58.650 (for iron chloride tetrahydrate) and 52.540 (for iron).

<sup>369</sup> ICDD file 16-0123 for iron chloride tetrahydrate indicates the following d-values (in decreasing importance) for the compound: 3.97, 5.50, 5.33, 3.01, 2.78, 2.20, 2.18 and 2.13. Using Bragg's law, one can easily transform those numbers to obtain the values for  $2\theta$ .

| File ICDD   | d-values | 2 $\theta$ (°) |
|---|----------|----------------|
| 13-0157:  | 7.40 (x) | 14.0147        |
| Akaganéite syn  | 3.31 (x) | 31.05377       |
| FeO(OH, Cl)   | 1.64 (x) | 62.57045       |
| 42-1315:  | 7.47 (x) | 13.8863        |
| Akaganéite-M  | 2.55 (9) | 40.2725        |
| Fe <sub>8</sub> (O, OH) <sub>16</sub> Cl <sub>1.3</sub> ) | 3.35 (7) | 30.6846        |
| 34-1266:  | 3.33 (x) | 30.868         |
| Akaganéite-M, syn   | 2.55 (6) | 40.2725        |
| FeO(OH)   | 7.47 (4) | 13.8863        |

Table 5: International Centre for Diffraction Data (ICDD) information on akaganéite ( $\beta$ -FeOOH).<sup>370</sup>

### 4.5.3 Microscopy

The synthetic samples and the archaeological iron nails were examined using an optical microscope (Leica DML) when they came out of their packaging system. In reflected light the surface of the powders and nails could be analysed visually. The work was carried out at a magnification of 50-100x in dark field mode.<sup>371</sup> Pictures (digital images) were taken and written records made to monitor the appearance of the powders monthly and of the nails after three and five-and-a-half months.

Changes in colour, in the distribution of components in the powder samples, in volume and structure could be observed with the help of the microscope and the naked eye (no colorimetric analysis was carried out and observations were based on personal perception).

The microscope proved to be easy to use and provided principal indications, so it was not necessary to resort to more expensive techniques. The microscope could be used by conservators to monitor changes on the surface of iron artifacts.

### 4.5.4 Oxygen monitoring

Packing samples in an anoxic environment, a way had to be found to monitor the oxygen level in the bags. For samples packed in ESCAL<sup>TM</sup> bags closed with a clip (see table 3, groups A, B, C) the oxygen content was measured at the end of each test period the powders were taken out. This was done using an oxygen meter (Mapcheck<sup>372</sup> from Systech Instruments Ltd.) equipped with a needle to pierce the bag and extract a certain amount of the gases present in the system. A patch was placed onto the pierced area. The needle pierced through the patch, which has the ability to close completely (in theory) after the measurement. It was possible to read the percentage of oxygen.

<sup>370</sup> ICDD database.

<sup>371</sup> Eyepieces: 10x; objectives: 5x, 10x.

<sup>372</sup> The range of the instrument for oxygen was 0.001 % - 100 % with a response time of <5 seconds and an accuracy of +/- 0.5 % of reading (above 10 %) and +/- 2 % of reading (below 2 %) respectively. The instrument uses stabilized zirconia (ZrO<sub>2</sub>), capable of conductivity to oxygen ions when a difference of oxygen partial pressure exists across a cell. The cell where this is to occur is heated to a minimum temperature of 600 °C (Systech Instruments Ltd., Mapcheck Instruction Manual, 07/03/01).





Figure 69: Using an oxygen meter provided with a needle to pierce the anoxic enclosure and extract gas. A patch is placed on the pierced area.



Figure 70: Oxygen-indicating tablets from Mitsubishi Gas Chemical Company.

Two oxygen-indicating tablets (from Mitsubishi Gas Chemical Company) were introduced into each package for all groups and the colour change (violet-pink) observed. The tablets should be violet as soon as oxygen is present (above 0.5%) and turn pink when oxygen is absent (less than 0.1% oxygen).

For the second series of tests (see table 3, groups AX, BX and CX) a new monitoring system was used (Oxygen Analyser GSS450 from gas Sensor Solutions, see figure 71).<sup>373</sup> A printed sensor (called SensiSpot) containing a ruthenium-complex was introduced into the transparent bag before sealing. The ruthenium fluoresces when exposed to the light from the light emitting diode (LED). If oxygen is present, it quenches the fluorescence. The instrument measures this fluorescence. Oxygen levels could be read throughout the testing period by illuminating the sensor and reading the amount of the reemitted light on a graph on the computer (the more light reemitted by the sensor, the less oxygen present).<sup>374</sup>



Figure 71: GSS450 Oxygen Analyser with optical head, detector and computer where data is read instantly. (Photo: [www.gss.ie](http://www.gss.ie), June 2006).

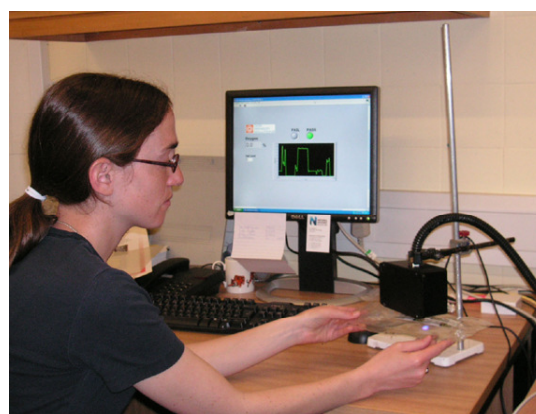


Figure 72: Real time measuring of the oxygen level in an anoxic enclosure using the GSS450 Oxygen Analyser.

<sup>373</sup> The producers indicate a detection limit for oxygen of 0.005 % - 0.3 % and accuracy of  $\pm 0.1$  %.

<sup>374</sup> The Oxygen Analyser is composed of an optical head using a light emitting diode (LED) to illuminate the sensor (SensiSpot). When the sensor (SensiSpot) reemits light, it is detected using photodiodes. This information has to be fed into an electronic circuitry where the signals are converted into oxygen concentration values. Specific software as well as calibrations of instruments for the reading and recording of the data is provided by Gas Sensor Solutions (Gas Sensor Solutions, [www.gss.ie](http://www.gss.ie), 10/03/2006; personal communication with Chris Collins, Natural History Museum, London, 13/03/2006).



## 5 RESULTS

The chapter is subdivided into three parts. The first one will give the results obtained testing dry and dry/cold storage. The second part deals with the results of experiments with oxygen-free environments and a third part gives some additional results that were found to be of interest in the course of this work. Each part recapitulates the initial question for which an answer was to be found.

FT-IR, XRD and optical microscopy were applied to the powder samples. Results for the archaeological samples can be found only in those parts where visual and microscopic observation was applied, as the amount of material used turned out to be too small for analysis on FT-IR and XRD. Raman spectroscopy was used for some synthetic powder samples to get complementary answers to questions that occurred when working with FT-IR. These observations can be found in the section on additional results.

For details on the samples groups see chapter 4 (tables 1 and 3). Precise data recorded over the test period as well as most calculations can be found in annex I (CD-R).

### 5.1 Problem 1: Dry and cold storage

#### *Recapitulation*

How does storage in a cold, dry or cold/dry environment affect the formation of akaganéite ( $\beta$ -FeOOH) in our powder mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ )? And how do our archaeological samples (Roman nails) react in this storage climate?

#### **5.1.1 General observations**

##### **5.1.1.1 Powder samples**

When taking the powders out of their enclosure at the end of a testing period, differences in the sample groups in appearance were visible to the naked eye. At first, colour changes were observable: some powders still showed the initial grey to grey-green colour, but some had changed to become either very orange-brown or slightly more brown than orange. Powders that hadn't visibly changed in colour were the ones that later – using analytical techniques – did not show akaganéite ( $\beta$ -FeOOH) or only very little of it. The more orange the powders became (always with a touch of brown), the more akaganéite ( $\beta$ -FeOOH) would be detected.



Figure 73: Powder samples stored in closed PE bags in a PP box at room temperature (group D1) after four months became orange-brown in colour.



Figure 74: The colour of powder samples stored in a dry climate in PE bags provided with holes, in a PP box at room temperature (group K1), did not show any colour change after four months. The samples remained grey-green.

Another observation could be made: where akaganéite ( $\beta$ -FeOOH) was forming, the volume of the powder increased. The plastic containers in which the powders were filled became fuller and fuller right up to the top.

#### 5.1.1.2 Archaeological samples

Five archaeological samples showed active corrosion after five-and-a-half months in some of the enclosures. Zones of active corrosion occurred on nails stored without any climate control in PE bags placed into PP boxes (groups D1 and H1) as well as samples stored cold in PE bags with holes (group I1).

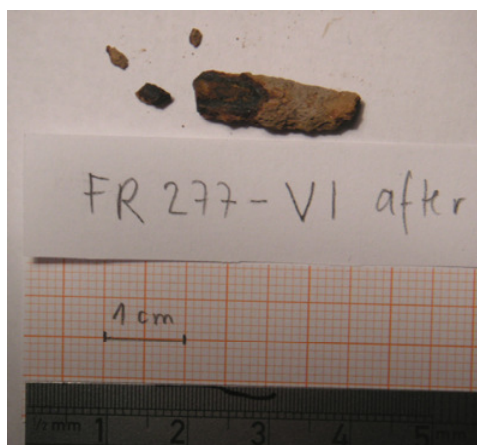


Figure 75: Archaeological sample stored at room temperature in a closed PE bag placed in a PP box (group D1) after 5.5 months: spalling of the outer layers due to active corrosion is visible.



Figure 76: Storage for 5.5 months in uncontrolled climates (here group H1, PE bags with holes at room temperature) causes the sample to fall apart.

## 5.1.2 Observations under the microscope

### 5.1.2.1 Powder samples

As mentioned in chapter 5.1.1.1 the colour of the powders changed as akaganéite ( $\beta$ -FeOOH) developed. But also, when looking at the powders under an optical stereomicroscope (Leica DML), the shape of the crystals and size of particles had changed in some of the samples. When akaganéite ( $\beta$ -FeOOH) formed, the particles in general became smaller. The bigger whitish iron chloride tetrahydrate crystals ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) that were visible in the initial powder mixture and the very small graphitic iron (Fe) particles disappeared to turn into an orange powdery substance where not much difference could be seen between the initial components.

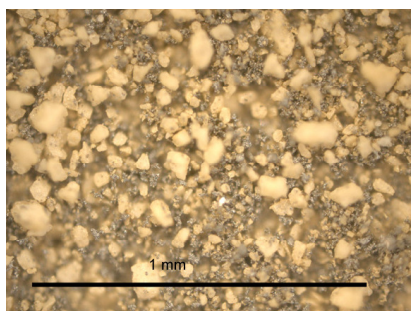


Figure 77: Powder without akaganéite ( $\beta$ -FeOOH) after 4 months in a dry and cold climate (group L1): the iron chloride crystals as well as the iron particles are distinct and visible.

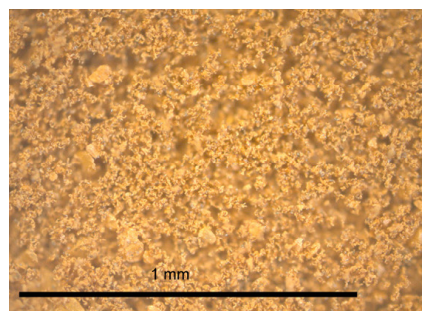


Figure 78: 'Spaghetti-like' spindles when akaganéite ( $\beta$ -FeOOH) occurs in a cold climate with no RH control (group I1, 4 months).

This powder seemed very uncongested and had an appearance of 'spaghetti-like' spindles. Sometimes, when transformation to akaganéite ( $\beta$ -FeOOH) was not completed, Fe-particles were visible attached to the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -crystals and to the orange spindle-structure. Powders with no akaganéite ( $\beta$ -FeOOH) remained dark grey-green and the whitish crystals of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were apparent as well as the graphitic iron particles.

### 5.1.2.2 Archaeological samples

As can be seen in the figures below, active corrosion could be determined on some nails using a Leica DML microscope in reflected light and dark field mode. Corrosion seemed to be in a stable state for samples stored dry. Here the earthy layers showed some cracks, probably due to desiccation.

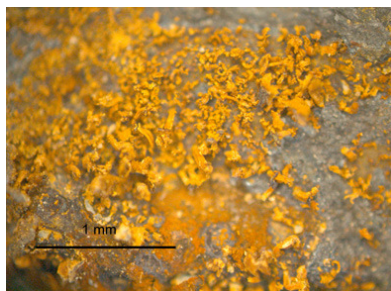


Figure 79: Active corrosion on archaeological sample (FR 277-VI) after 5.5 months in an uncontrolled climate in a closed PE bag (group D2).

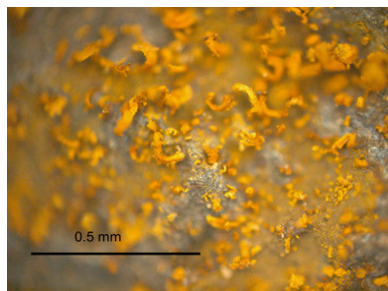


Figure 80: Sample (FR 277-VI) after 5.5 months (group D2) where the small orange 'sausages' of active corrosion are visible.

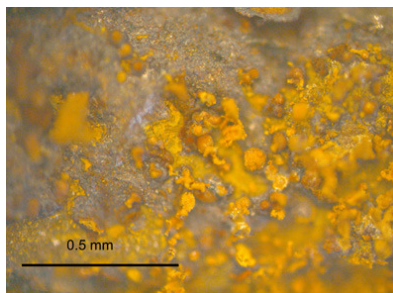


Figure 81: Nail (FR 254-01-VI) where small round craters filled with orange and red-orange corrosion are visible (cold storage with uninfluenced RH, group I2).

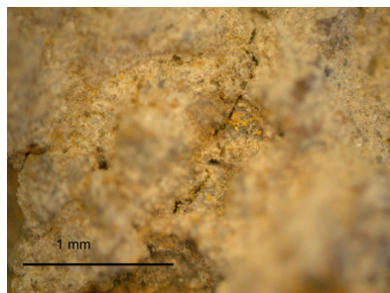


Figure 82: Sample after 5.5 months in a closed PE bag stored dry with silica gel (group F2): the earthy layer shows some cracks.

### 5.1.3 Analytical results for the synthetic powder samples

#### 5.1.3.1 Absolute amount of akaganéite ( $\beta$ -FeOOH) in the samples after five-and-a-half months

All the reference groups (D1, E1, H1, I1) where the RH was uninfluenced showed akaganéite ( $\beta$ -FeOOH) already after the first month, confirmed by FT-IR (often not visible in XRD, after this short period). During the first three months, groups E1 and I1 (samples stored cold) developed much less akaganéite ( $\beta$ -FeOOH) than their equivalents stored at room temperature. When the refrigerator broke down during the fourth month, the samples quickly developed the same amount in akaganéite ( $\beta$ -FeOOH) as in the groups at room temperature (D1 and H1). After five-and-a-half months, the amount of iron converted in the groups stored in closed PE bags was over 90%. Providing the PE bags with holes was followed by a smaller amount of akaganéite ( $\beta$ -FeOOH). This confirmed the suitability of the chosen sample material as being reactive and showing the desired transformation when stored in an unfriendly environment.

Samples stored in a dry climate at 0-5% RH (groups F1, G1, K1, L1) showed almost no or no akaganéite ( $\beta$ -FeOOH) after five-and-a-half months. Dry storage in the cold seemed to produce slightly less akaganéite ( $\beta$ -FeOOH) than storage at room temperature. It did not become clear whether it was of any importance to close the PE bags or to provide them with holes.<sup>375</sup>

<sup>375</sup> It might be that a remainder of moisture in the closed PE bag could react quicker with the powders than if the bag had holes and the desiccation could equilibrate more quickly.

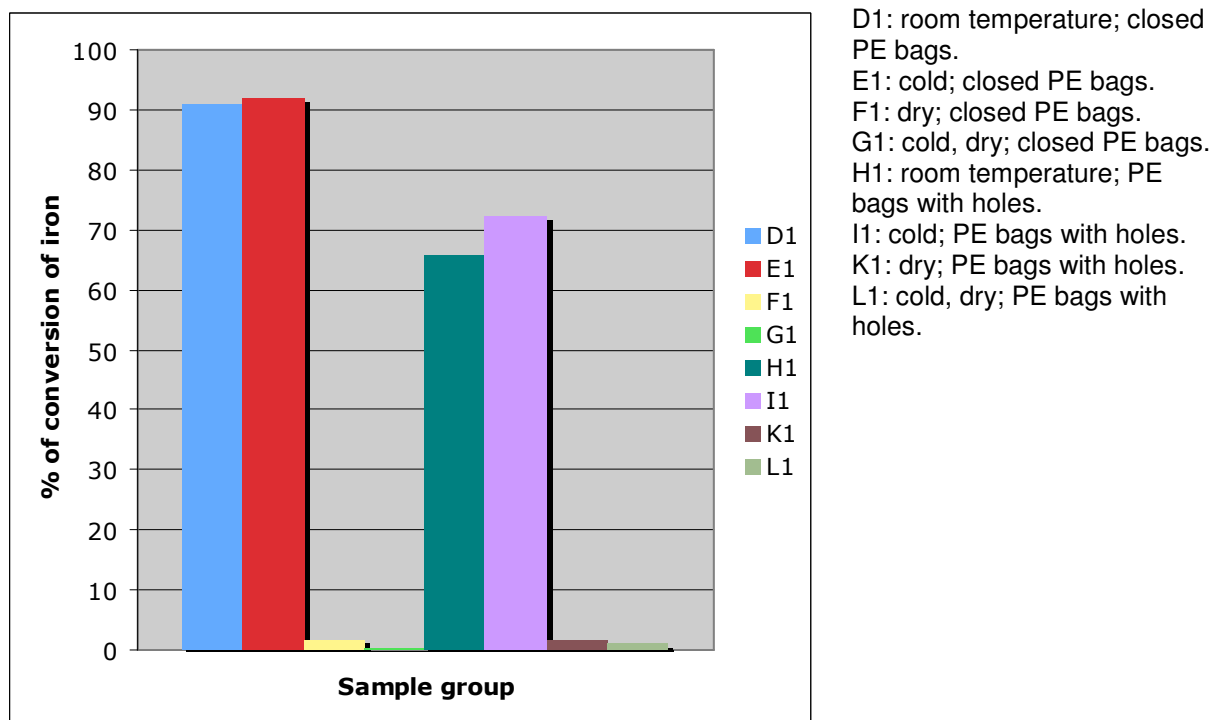


Figure 83: Percentage of iron converted to akaganéite ( $\beta$ -FeOOH) after 5.5 months of experimentation.

### 5.1.3.2 Comparison of all sample groups: evolution of the relative amount of akaganéite ( $\beta$ -FeOOH)

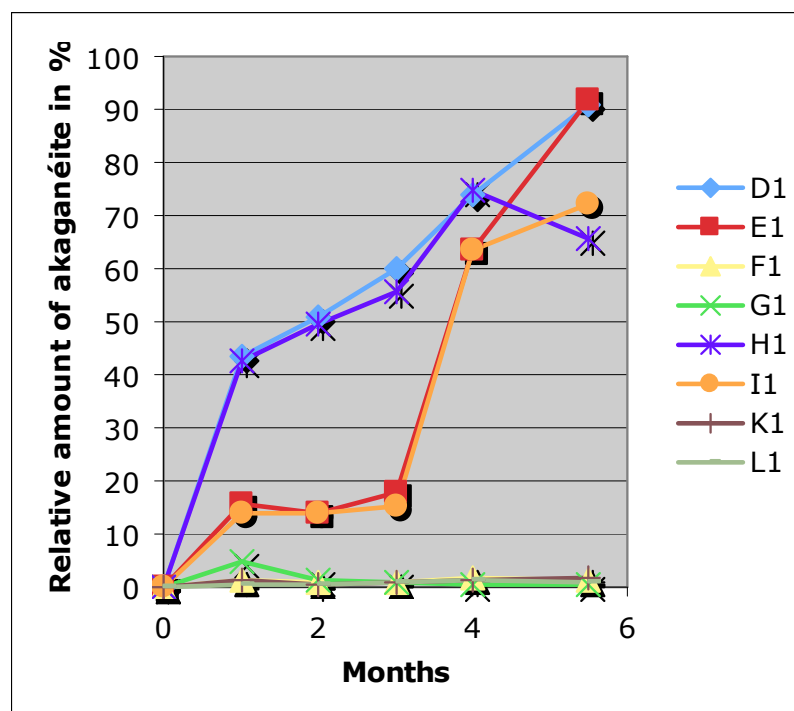


Figure 84: Evolution of akaganéite ( $\beta$ -FeOOH) in the sample groups (percentage of akaganéite ( $\beta$ -FeOOH) in the potassium bromide (KBr) discs used for FT-IR).

The decline in the amount of akaganéite ( $\beta$ -FeOOH) in group H1 after 5.5 months might be due to a difference in the sample material for this specific month or to some imprecise weighing.

Figure 84 shows the evolution of akaganéite ( $\beta$ -FeOOH) in all sample groups.<sup>376</sup> The effect of the cold can clearly be seen. However, samples stored in the cold developed a massive amount of akaganéite ( $\beta$ -FeOOH) during the fourth month.<sup>377</sup> The benefit of dry storage is evident, and the addition of cold seems to be negligible as it does not seem to add much supplementary benefit to dry storage.<sup>378</sup>

### 5.1.3.3 Detection of akaganéite ( $\beta$ -FeOOH): differences observed using Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD)

FT-IR is sensitive to very low amounts of akaganéite ( $\beta$ -FeOOH) in the powder mixture used. XRD is less sensitive and often does not reveal akaganéite ( $\beta$ -FeOOH) in the spectrum, whereas it was well visible using FT-IR. It became obvious that one can detect even the slightest amount of akaganéite ( $\beta$ -FeOOH) by means of FT-IR.

The following figures show FT-IR and XRD spectra in contrast (figures 85 and 86): in FT-IR akaganéite ( $\beta$ -FeOOH) was visible even if there is only approximately 1% in the mixture. XRD did not always reveal the akaganéite ( $\beta$ -FeOOH), even if the peak height in FT-IR already indicates a fairly high amount present.<sup>379</sup>

As soon as an important amount of akaganéite ( $\beta$ -FeOOH) was observable in the powder samples, the compound was identifiable in both FT-IR and XRD (using first manual identification for XRD and later, as the amount increased, the compound was identified by the identification program).<sup>380</sup>

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<sup>376</sup> The relative amount of akaganéite ( $\beta$ -FeOOH) in the potassium bromide (KBr) pellet used for FT-IR.

<sup>377</sup> This was probably due to a break-down of the refrigerator.

<sup>378</sup> Addition of dry silica gel prevented the formation of akaganéite ( $\beta$ -FeOOH). Only if samples were packed in closed PE bags and the package placed into the cold (group G1) was a small amount of akaganéite ( $\beta$ -FeOOH) detected (4.7%, as can be seen for month 1 in the graph). For all other groups with silica gel, the amount of akaganéite ( $\beta$ -FeOOH) did not exceed 1.5%.

<sup>379</sup> It was found that below an amount of 10% akaganéite ( $\beta$ -FeOOH) in the powder mixture, the compound was not detected by XRD using manual identification. When using only the identification program that brings up possible compounds in the mixture, the amount had to be even more important (above 50% of akaganéite,  $\beta$ -FeOOH, in the mixture).

<sup>380</sup> Manual identification in XRD was possible with amounts of akaganéite ( $\beta$ -FeOOH) of about 10% - 15% in the mixture. Clearly with an amount of 60% akaganéite ( $\beta$ -FeOOH) in the mixture, the XRD identification program listed the compound as present. FT-IR already showed the compound when it amounted to as little as 1-2%.



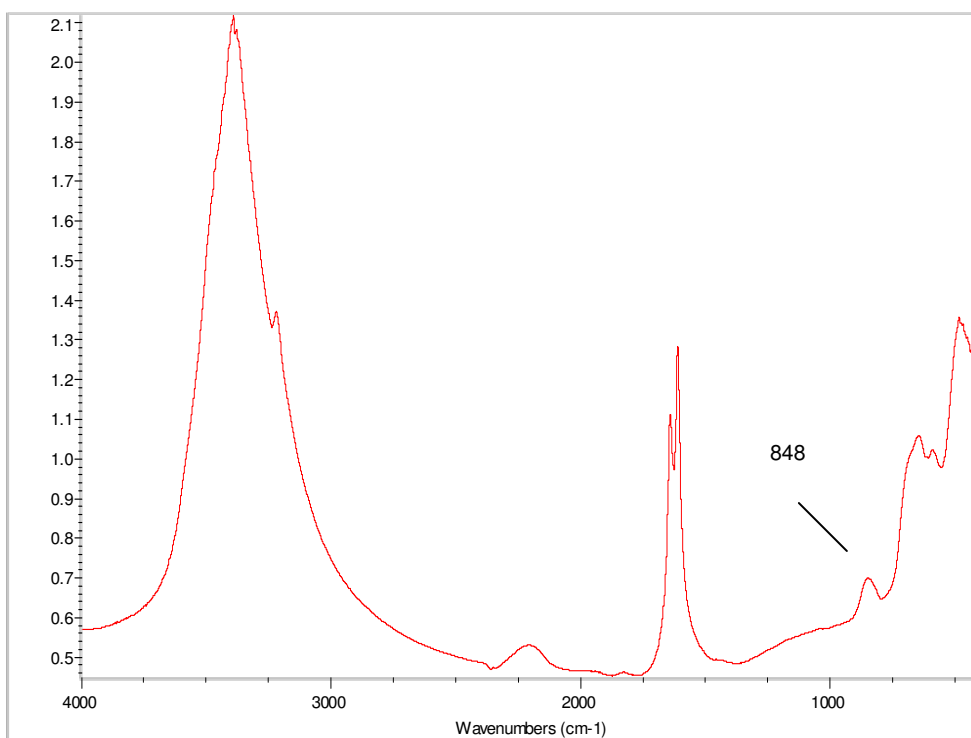


Figure 85: After one month of storage in the cold without influencing the RH, the sample (group I1) packed in a PE bag with holes clearly showed akaganéite ( $\beta$ -FeOOH) using FT-IR as a method of analysis.

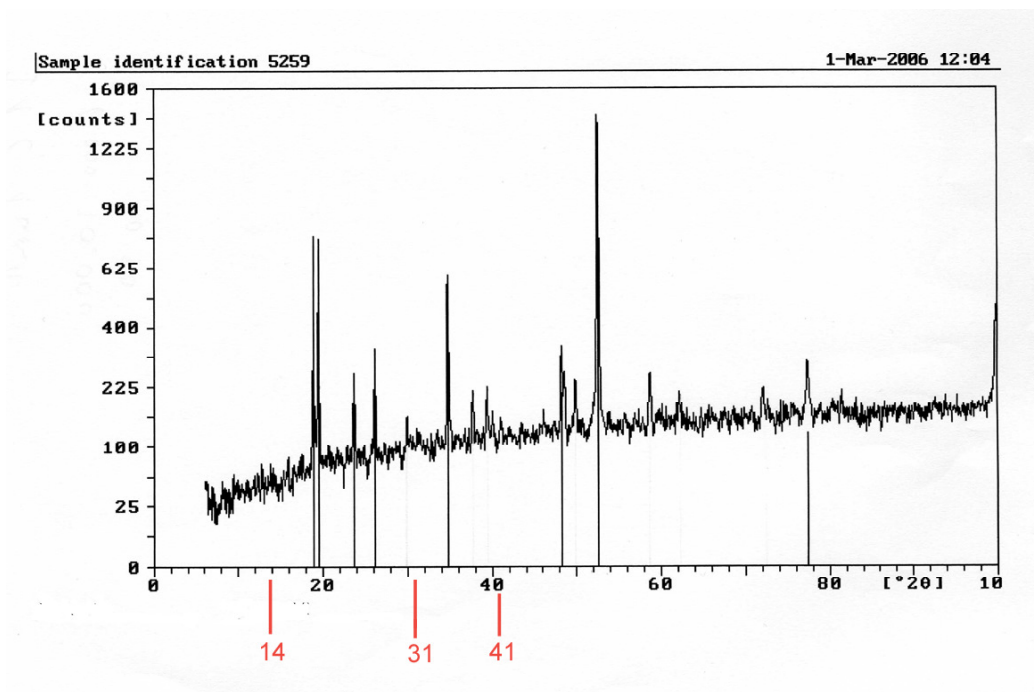


Figure 86: XRD did not show the presence of akaganéite ( $\beta$ -FeOOH) in the sample from group I1 even if the amount was already quite important (at least 10% in the mixture). Typical peaks for akaganéite ( $\beta$ -FeOOH), which should be well visible, would be situated at 14°, 31° and 41° ( $2\theta$ ), marked in red.

#### 5.1.3.4 Differences in the height of the Fourier-transform infrared spectroscopy (FT-IR) absorption band at $848\text{cm}^{-1}$

The absorption band at  $848\text{cm}^{-1}$  was found to be a very good indicator of the presence of akaganéite ( $\beta\text{-FeOOH}$ ) in the samples. This band was used to take a closer look at our sample groups.

Samples stored without desiccant (silica gel), already formed akaganéite ( $\beta\text{-FeOOH}$ ) after short periods. The compound was present in the FT-IR spectra after the first month of experimentation. Taking the FT-IR spectra for these sample groups after two months enabled us to observe that the amount of akaganéite ( $\beta\text{-FeOOH}$ ) formed was less when putting samples in the cold than when leaving them at room temperature. This is characterised by differences in the peak height (see figure 87). Whether the resealable PE bags were entirely closed or provided with holes made no relevant difference.

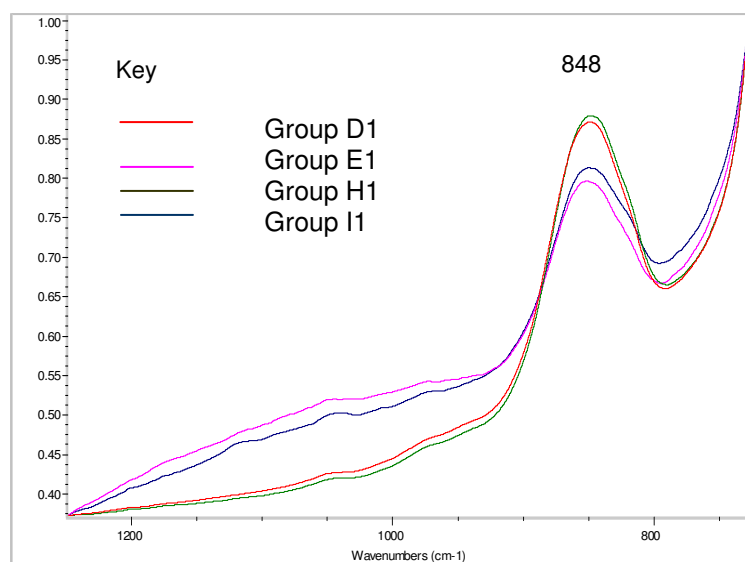


Figure 87: After two months, the absorption band at  $848\text{cm}^{-1}$  was more significant for samples stored at room temperature (groups D and H) than when stored in the cold (groups E and I).

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

Things became more complicated when looking at the FT-IR spectra of the samples stored with silica gel. The region at  $848\text{cm}^{-1}$  shows almost no absorption band for those groups (F1, G1, K1, L1). But still there seems to be a slight difference when compared to the spectrum of the initial mixture (see figure 88). The peak height here shows akaganéite ( $\beta\text{-FeOOH}$ ) at a percentage of  $0.5 - 1.4\%$ , which is also extremely close to the detection limit evaluated previously for the FT-IR equipment (see chapter 4.5.1). Over the whole testing period the FT-IR spectra for groups F1, G1, K1 and L1 showed this slight, very weak band in the specified region.



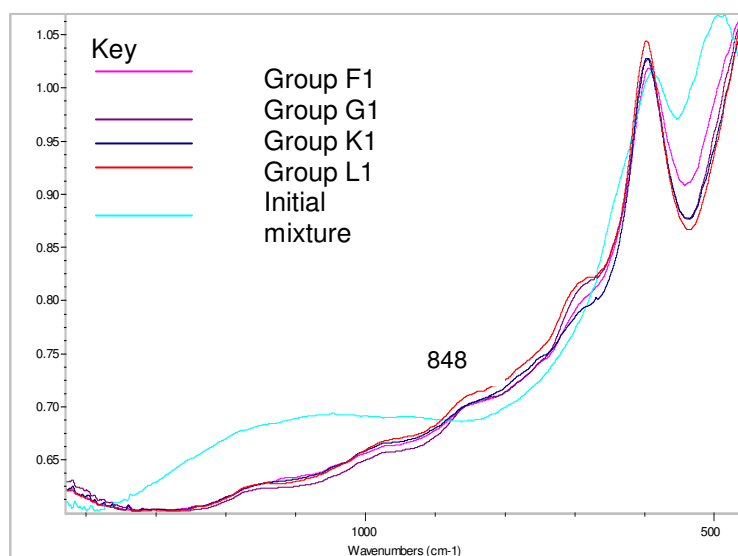


Figure 88: After two months the differences in all the groups with added silica gel (F1, G1, K1, L1) in terms of akaganéite ( $\beta$ -FeOOH) formation were negligible. The amount formed proved to be very low, as can be seen in the spectrum to the left when compared with the initial mixture.

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

## 5.2 Problem 2: Oxygen-free storage of samples

### Recapitulation

How does storage in an anoxic environment at a low RH affect the formation of akaganéite ( $\beta$ -FeOOH) in our powder mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ )? Would it make any difference to leave the RH unaffected in this anoxic climate? And how do our archaeological samples (Roman nails) behave in this storage climate?

### 5.2.1 General observations

#### 5.2.1.1 Powder samples

As mentioned in chapter 5.1.1.1 the powders changed visibly in colour (see figures 89 and 90) and volume when akaganéite ( $\beta$ -FeOOH) formed. The same observations were made here as in the previous section concerning the formation of akaganéite ( $\beta$ -FeOOH) in the reference samples (group A1 and AX1 where oxygen was present). Where no or an infinitesimal amount of akaganéite ( $\beta$ -FeOOH) formed (oxygen-free dry storage, group B1, BX1) the powders remained unchanged in appearance. A slight colour change towards darker brown-grey tones was observed for groups C1 and CX1 (oxygen-free storage with uninfluenced RH). In this sample group some powders became quite dark whereas the others remained lighter in colour.<sup>381</sup>

<sup>381</sup> Two different effects were observed in the same sample group, where samples were stored identically (darker and lighter brown-grey).

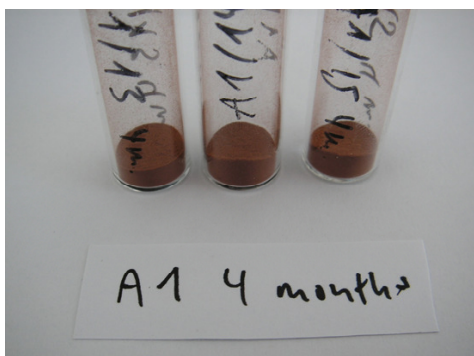


Figure 89: Powder samples stored without oxygen absorber: volume increase and orange-brown colour of the samples.

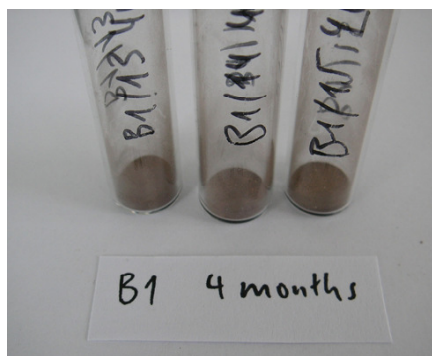


Figure 90: Oxygen-free dry storage: no volume and colour change of the powder is visible.

### 5.2.1.2 Archaeological samples

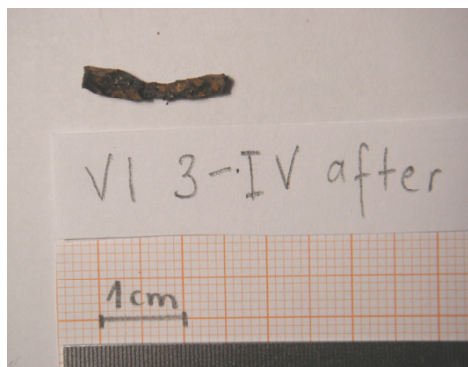


Figure 91: Archaeological sample (VI 3-IV) showing corrosion after storage in an ESCAL<sup>TM</sup> bag for 3 months (sample group A2 where oxygen was present).

Three nails in group A1 (no oxygen absorber added) seemed to corrode and showed some dark orange corrosion after three and five-and-a-half months in the enclosures. On one of these nails the corrosion showed circular holes in the surface of the nail (VI 3-IV). However, FT-IR could not confirm any akaganéite ( $\beta$ -FeOOH).

The nails stored in the anoxic enclosures did not show any active corrosion.

## 5.2.2 Observations under the microscope

### 5.2.2.1 Powder samples

The powders stored in an anoxic environment using the RP-A oxygen absorber lowering the RH did not show any transformation in their appearance (see figures 96 and 97). Using the absorber RP-K (uninfluenced RH) seemed to make the iron (Fe) particles in the mixture adhere slightly more to the iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) crystals, as can be seen in the following pictures (figures 92 and 93). Those powders also became darker as can be seen in figures 94 and 95 (grey) than the ones stored dry without oxygen (groups B1 and BX1). The samples without any absorber became very orange-brown and the particle size decreased. The  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -crystals and Fe-particles began to 'disappear' and 'spaghetti-like' spindles formed (see chapter 5.1.2.1).

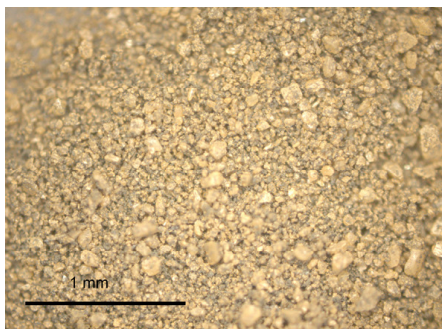


Figure 92: Powder sample after 1 month storage using the RP-K oxygen absorber in fully sealed bags (group CX1).

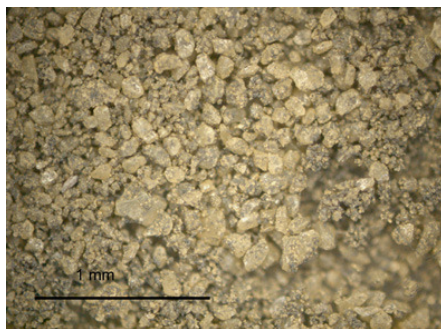


Figure 94: After three months, the powders looked darker and grey when using anoxic storage without influencing the RH (sample group CX1, RP-K absorber).

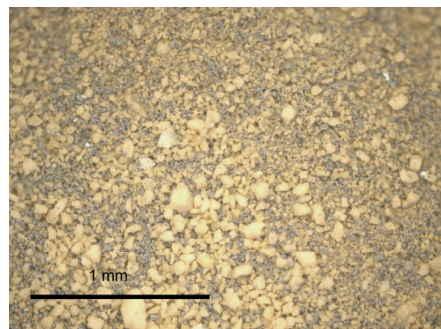


Figure 96: Using oxygen-free dry storage did not change the appearance of the powder sample after 1 month testing period (sample group BX1, RP-A absorber).

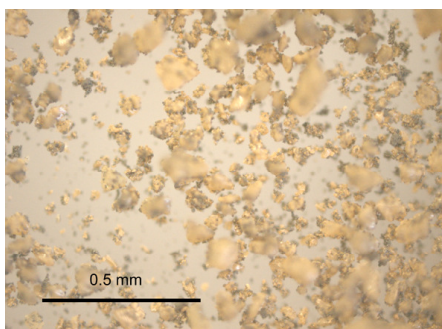


Figure 93: The iron particles in the powder mixture of group CX1 using the RP-K absorber adhere slightly more to the whitish iron chloride tetrahydrate crystals than in group BX1, where dry anoxic enclosures were tested.

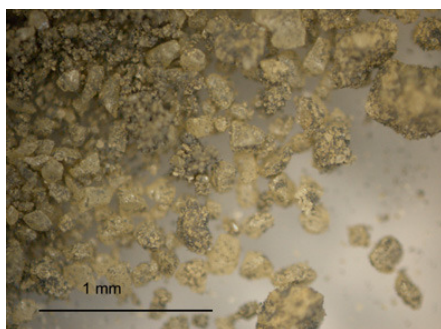


Figure 95: The white crystals were fully surrounded by small iron particles after three months (compare with image to the left).

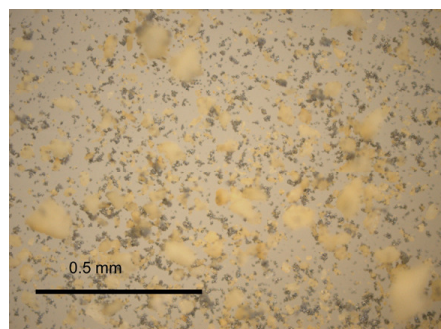


Figure 97: Detached iron and iron chloride tetrahydrate particles in sample group BX1 (dry oxygen-free storage).

### 5.2.2.2 Archaeological samples

Some corrosion seemed to take place on three nails where no oxygen absorber had been used. Unfortunately, FT-IR could not confirm the presence of akaganéite ( $\beta$ -FeOOH), as the amount of powder on the sample usable for analysis was too small. The following pictures (figures 98 and 99) show some areas on one of the nails (VI 3-II). Cracks in the earthy layer as well as some corrosion layers on nails stored in dry anoxic enclosures might have been caused by desiccation (figures 100 and 101).



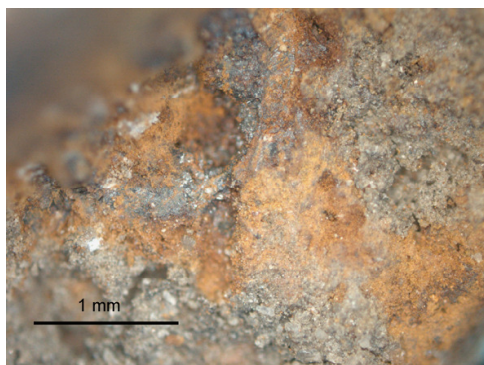


Figure 98: Nail (VI 3-II) after storage in an ESCAL™ bag without oxygen absorber. Stable corrosion is visible.



Figure 99: Zone of active corrosion on the same sample, see on the left, figure 98 (VI 3-II), after three months.

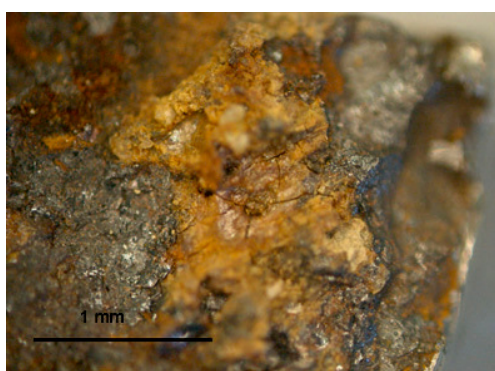


Figure 100: Storage in dry anoxic enclosures causes cracking in the corrosion layers of the sample (VI 6-IV).



Figure 101: Desiccation might be the origin of cracks in corrosion layers as well as earthy layers in the sample from left (sample VI 6-IV).

### 5.2.3 Analytical results for synthetic powder samples

#### 5.2.3.1 Absolute amount of akaganéite ( $\beta$ -FeOOH) in the samples after five-and-a-half months

Where the synthetic powder samples were packed in an anoxic and dry climate (absorber RP-A), no or only a negligible amount of akaganéite ( $\beta$ -FeOOH) formed after five-and-a-half months (fully sealed bags performed better than the ones with clips). Using the oxygen absorber RP-K (no influence taken on the RH) brought changes to the powders (see chapter 5.2.3.3). Packing samples without any absorber seemed to develop either more or less akaganéite ( $\beta$ -FeOOH).<sup>382</sup> Figure 102 shows the amount of akaganéite ( $\beta$ -FeOOH) formed after five-and-a-half months for enclosures without any absorber and for those where the RP-A absorber was tested (oxygen-free dry climate).<sup>383</sup> The anoxic

<sup>382</sup> This was probably dependant on the RH and leakage of bags. The higher the RH was, the more akaganéite ( $\beta$ -FeOOH) was formed. The bags with clips had a higher leakage rate than the fully sealed ones.

<sup>383</sup> Quantification has been carried out for the groups where bags were closed with a clip. The fully heat-sealed enclosures were not used for quantification, as the weighing of samples during preparation was not accurate enough.

enclosures where the RH was influenced are not included in the figure, as some questions remained on the corrosion product that had developed (see chapter 5.2.3.3).

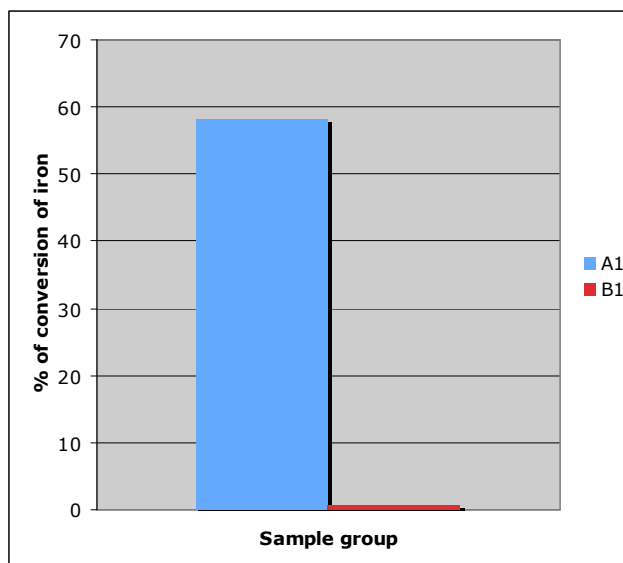


Figure 102: Amount (in %) of iron converted to akaganéite ( $\beta$ -FeOOH) after 5.5 months for groups A1 and B1.

### 5.2.3.2 Comparison of all sample groups: evolution of the relative amount of akaganéite ( $\beta$ -FeOOH)

Leaving the powder samples in a dry anoxic climate produces negligible amounts of akaganéite ( $\beta$ -FeOOH). If no oxygen absorber at all is introduced to the package, the amount of akaganéite ( $\beta$ -FeOOH) is significant.<sup>384</sup>

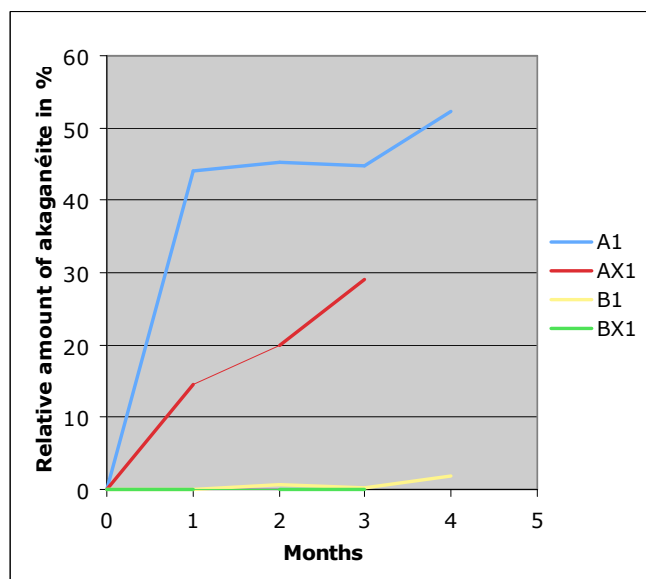


Figure 103: Evolution of the relative amount (in %) of akaganéite ( $\beta$ -FeOOH) in KBr discs (the line is thin where no data was available). Group C1 and CX1 (RP-K absorber) have not been included as the results were not entirely clear (see chapter 5.2.3.3).

<sup>384</sup> As can be seen in figure 103, the amount of akaganéite ( $\beta$ -FeOOH) in group AX1 is smaller than in group A1. This might be due to differences in the RH as well as to the air exchange rate that it higher for clipped bags than for fully sealed ones.

### 5.2.3.3 RP-A and RP-K oxygen absorbers: the differences

The environment using RP-A oxygen absorber showed an oxygen level of 0.0 % and a RH between 0.5 – 7.2 %.<sup>385</sup> Using the RP-K absorber also led to 0.0 % oxygen in the enclosures but the RH was between 25 – 40 %.<sup>386</sup>

XRD showed the presence of iron (Fe), iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and iron chloride dihydrate ( $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ) when using RP-A.

For storage of powder samples with RP-K, iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) were detected with XRD.

FT-IR showed no or only a negligible amount of akaganéite ( $\beta\text{-FeOOH}$ ) when using the absorber RP-A.<sup>387</sup>

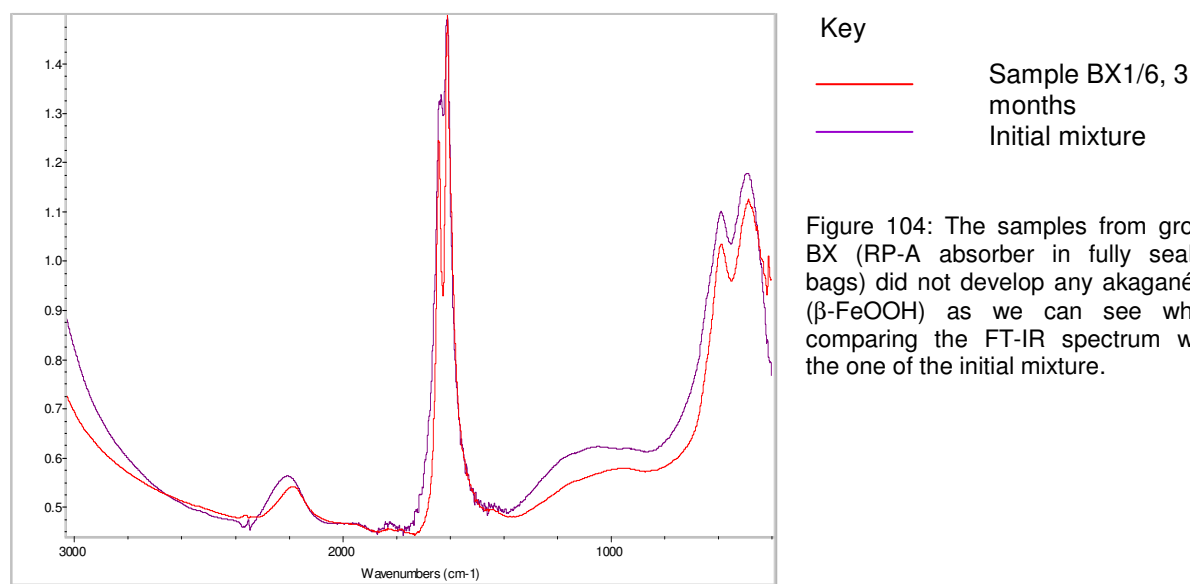


Figure 104: The samples from group BX (RP-A absorber in fully sealed bags) did not develop any akaganéite ( $\beta\text{-FeOOH}$ ) as we can see when comparing the FT-IR spectrum with the one of the initial mixture.

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

Two different types of FT-IR spectra were observed when working with the RP-K absorber. This coincided with the powders being either quite dark (grey-brown) or lighter. Some spectra, for the darker powders, showed four distinct absorption bands ( $888\text{cm}^{-1}$ ,  $817\text{cm}^{-1}$ ,  $765\text{cm}^{-1}$  and  $727\text{cm}^{-1}$ ) whereas others, the lighter powders, only three ( $817\text{cm}^{-1}$ ,  $765\text{cm}^{-1}$  and  $727\text{cm}^{-1}$  with the band at  $888\text{cm}^{-1}$  missing), see figure 105. Where four bands of interest were present, iron(III) chloride ( $\text{FeCl}_3$ ), or one of its hydrated forms, as well as goethite ( $\alpha\text{-FeOOH}$ )<sup>388</sup> and some akaganéite ( $\beta\text{-FeOOH}$ )<sup>389</sup> might have formed (see figure 106).<sup>390</sup> For spectra with three bands, possibly akaganéite,

<sup>385</sup> Measurements were taken with an RH-meter (S1 Sword Hygrometer from Rotronic, UK) which provided results within a range of 0.5 – 7.2% RH. These results are not precise, but served to check that the absorber was working (the RH has to be below 10%).

<sup>386</sup> The quite important range in RH (25 – 40%) might be due to the initial RH when packing samples (some were packed in January and some in April). The powder samples are also capable to pick up moisture. All these parameters influence the RH in the enclosures.

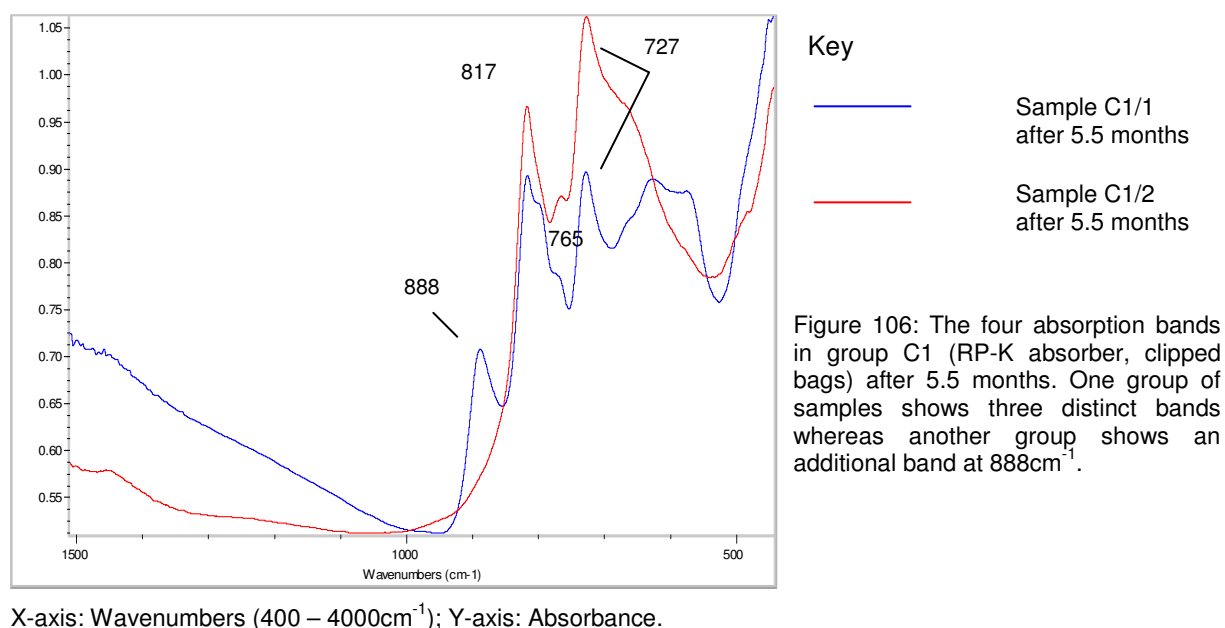
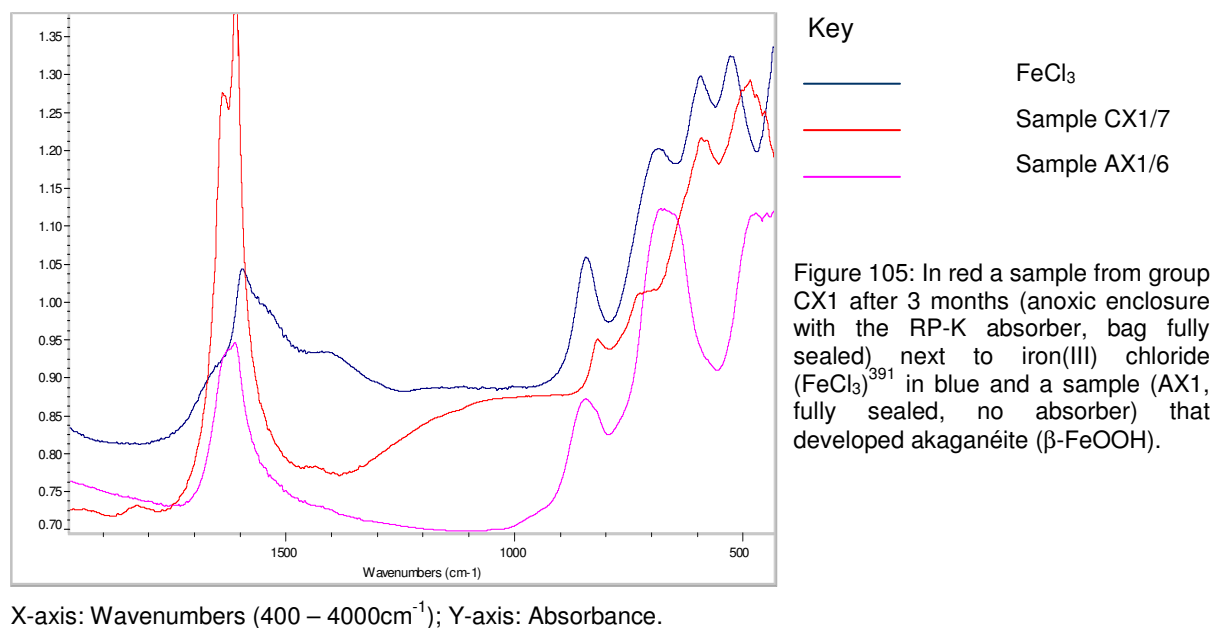
<sup>387</sup> Negligible amounts (approximately 0.2 – 0.6%) were sometimes visible, which is extremely close to the detection limit of the equipment.

<sup>388</sup> Regions that could correspond are  $900\text{cm}^{-1}$ ,  $798\text{cm}^{-1}$  and  $625\text{cm}^{-1}$ .

<sup>389</sup> The band at  $817\text{cm}^{-1}$  could correspond to akaganéite ( $\beta\text{-FeOOH}$ ).

<sup>390</sup> We compared the spectra obtained with reference spectra from David Thickett (English Heritage) obtained for  $\text{FeCl}_3$  and ( $\alpha\text{-FeOOH}$ ).

$\beta$ -FeOOH (in the absorption region of  $817\text{cm}^{-1}$ ) and some form of iron(III) chloride ( $\text{FeCl}_3$ ) were present.

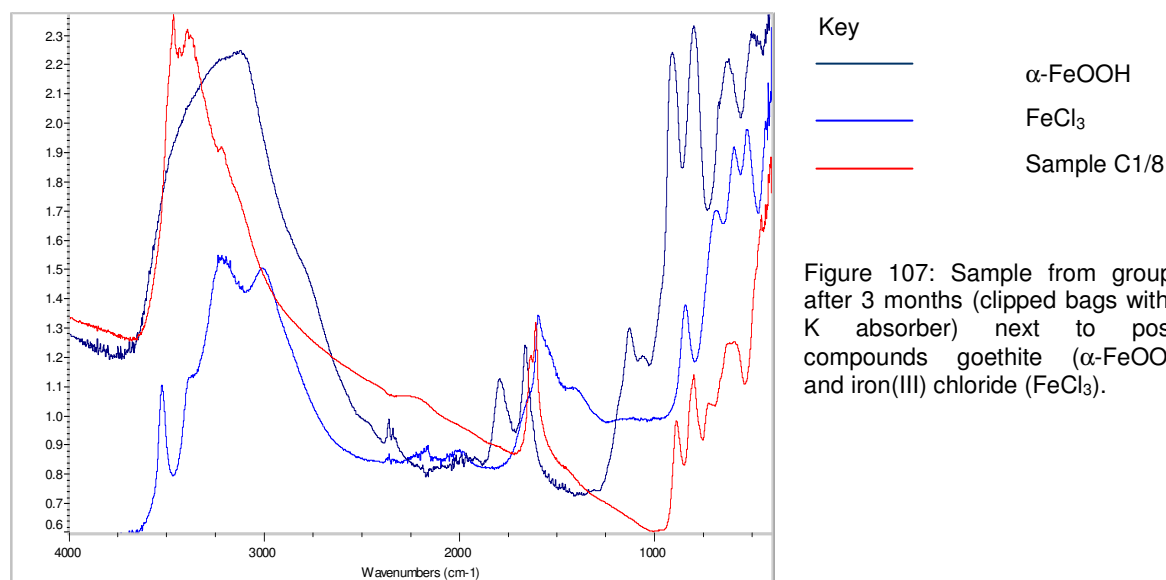


Analysis carried out using XRD did not clarify the questions as none of the hypothesis when working with FT-IR could be confirmed. The amount of the corrosion product concerned in the sample might have been too small to be detected using this technique.

It can be said that the formation of iron(III) chloride is a step forward in the oxidation of the iron ( $\text{Fe}^{2+}$  becomes  $\text{Fe}^{3+}$  on oxidation) and part of the transformation reaction that leads from iron to akaganéite ( $\beta$ -FeOOH). It has also been mentioned that goethite ( $\alpha$ -FeOOH) can form out of akaganéite ( $\beta$ -

<sup>391</sup> This reference spectrum was obtained by David Thickett, English Heritage, and kindly made available.

FeOOH). This had previously been observed on archaeological material.<sup>392</sup> However, the reactions that occurred in the powders when using RP-K absorbers were not fully understood at this point. Further research was needed to examine the questions. It was therefore decided to use Raman spectroscopy which can sometimes give complementary information to FT-IR spectra. The results can be found in chapter 5.3.3.



X-axis: Wavenumbers (400 – 4000cm<sup>-1</sup>); Y-axis: Absorbance.

#### 5.2.3.4 Detection of akaganéite (β-FeOOH): differences observed using Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD)

As mentioned previously XRD is less sensitive in detecting small amounts of akaganéite (β-FeOOH) than is FT-IR. In the sample groups where oxygen absorbers were used, no akaganéite (β-FeOOH) was ever detected with XRD. But FT-IR showed some interesting details as can be seen in the following figure (108), where samples from group CX1 were analysed (RP-K oxygen absorber).

<sup>392</sup> Personal communication with David Thickett, English Heritage, June 2006.

<sup>393</sup> This reference spectrum was obtained by David Thickett, English Heritage, and kindly made available.



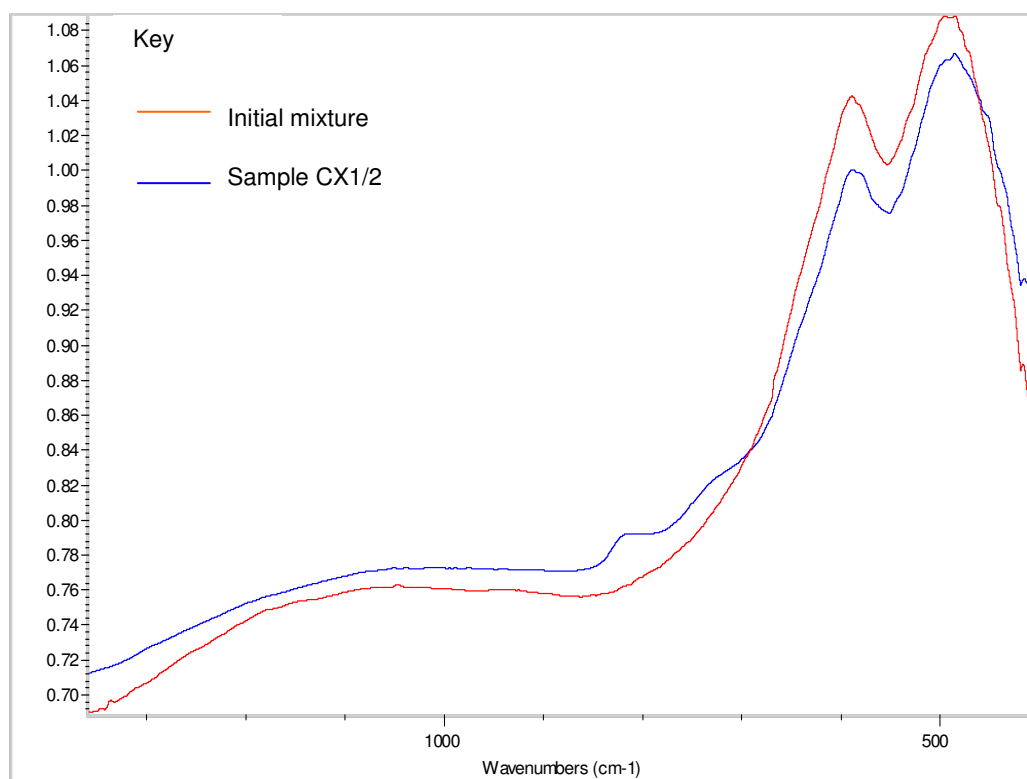


Figure 108: Where the sample was stored with an RP-K absorber and the bags fully sealed, some changes occurred in the powders as can be seen in the FT-IR spectrum.

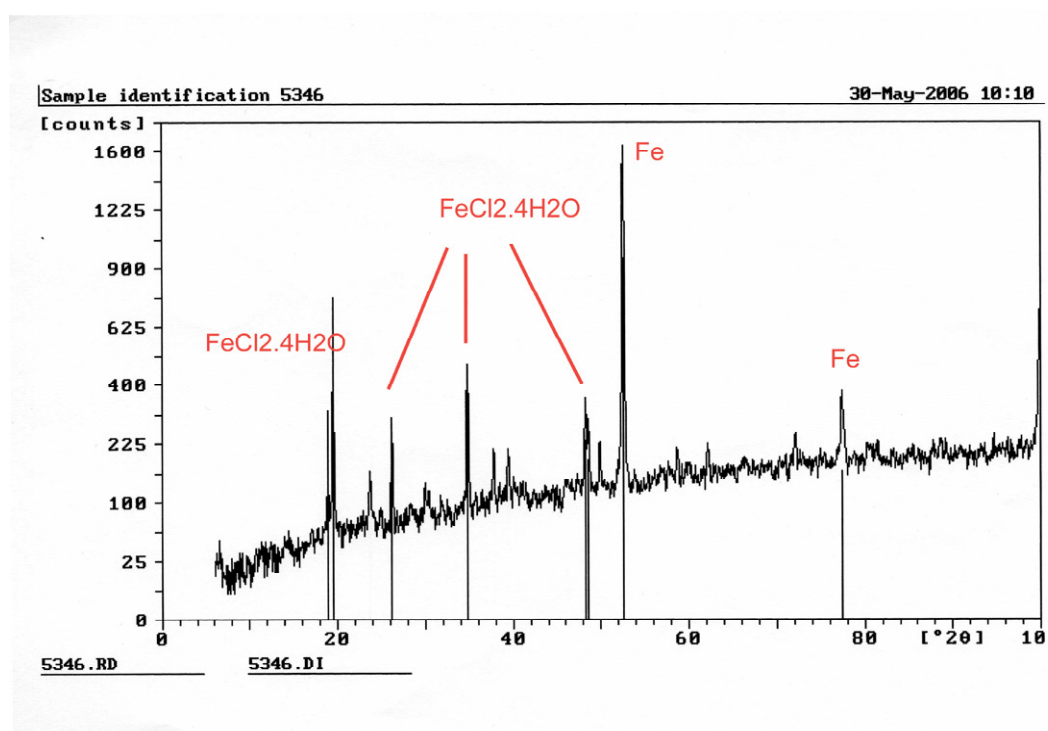


Figure 109: The XRD spectrum from the sample above does not show any compounds other than our initial mixture.

## 5.3 Further results

### 5.3.1 Other corrosion products detected in the synthetic powder samples using X-ray diffraction (XRD)

Using XRD not only revealed the presence of the two initial compounds mixed for our initial mixture, which were iron (Fe)<sup>394</sup> and iron chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O)<sup>395</sup>. When working with dry environments (when silica gel was added to the storage climate or the 'drying' oxygen absorber RP-A was used), iron chloride dihydrate<sup>396</sup> (FeCl<sub>2</sub>·2H<sub>2</sub>O) usually formed (see figure 110), as water was removed. This second form is said to be more stable than FeCl<sub>2</sub>·4H<sub>2</sub>O.<sup>397</sup>

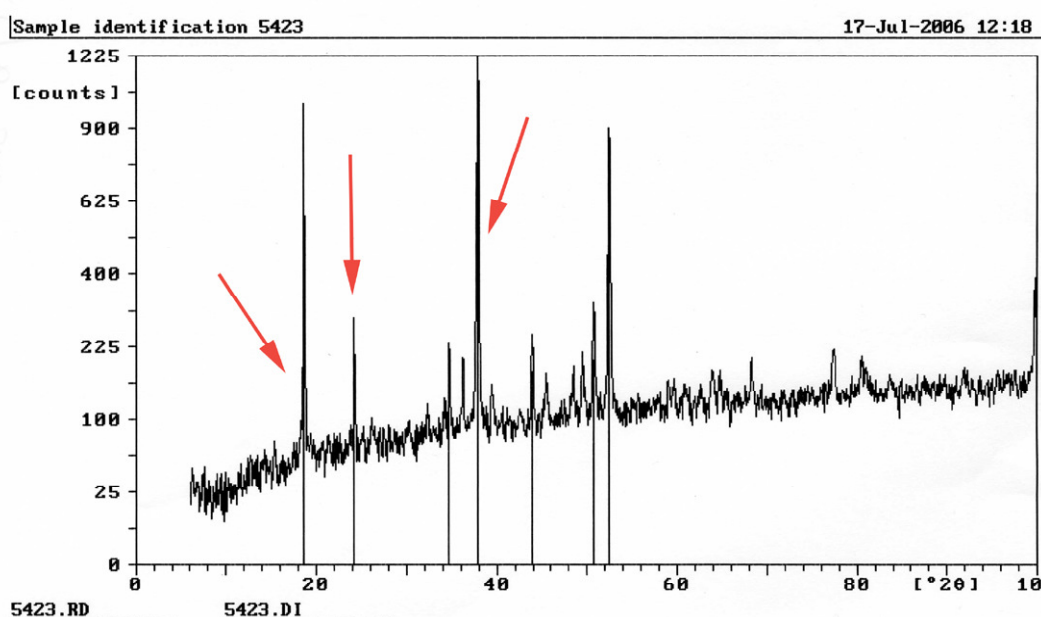


Figure 110: A sample stored in dry anoxia shows the presence of the iron chlorides FeCl<sub>2</sub>·4H<sub>2</sub>O and FeCl<sub>2</sub>·2H<sub>2</sub>O. FeCl<sub>2</sub>·2H<sub>2</sub>O is visible in the region of 18.640°, 24.215° and 37.905° (2θ), see red arrows. This corresponds to the d-values 5.5, 4.27, 2.76, given by the ICDD database for iron chloride dihydrate.

In some circumstances iron chloride heptahydrate (2FeCl<sub>3</sub>·7H<sub>2</sub>O), also called iron (III) chloride 7-water, was indicated as having formed. This reaction takes place under oxidising conditions. The iron ions Fe<sup>2+</sup> in the iron chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O) are oxidised and become Fe<sup>3+</sup>. This reaction – Fe(II) that becomes Fe(III) – can be a step forward to akaganéite (β-FeOOH) formation.<sup>398</sup> 2FeCl<sub>3</sub>·7H<sub>2</sub>O formed in samples exposed to the cold (sample group I1) and in samples packed in

<sup>394</sup> International Centre for Diffraction Data (ICDD) database reference: 06-0696 (iron syn.).

<sup>395</sup> Ibid.,: 16-0123 (iron chloride hydrate).

<sup>396</sup> Ibid.,: 01-0210 (iron chloride hydrate), 25-1040 (Rokühnite, syn.) and 33-0646 (Rokühnite).

<sup>397</sup> Iron chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O) contains enough water to support electrolytic corrosion compared to iron chloride dihydrate (FeCl<sub>2</sub>·2H<sub>2</sub>O) that does not contain enough to do so (WATKINSON D., LEWIS M., 2004, p93).

<sup>398</sup> Personal communication with David Thickett, English Heritage, 25/06/2006.

ESCAL<sup>TM</sup> barrier film (groups A1 and AX1). However, this corrosion product did not seem to be present every month, thus indicating transformation to other corrosion products.<sup>399</sup>

### 5.3.2 Fourier-transform infrared spectroscopy (FT-IR): visible decrease in iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) as akaganéite ( $\beta\text{-FeOOH}$ ) forms

As mentioned in chapter 4.5.1, iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) shows some typical absorption bands in FT-IR spectra.

As akaganéite ( $\beta\text{-FeOOH}$ ) formed during the experimental phase, these typical bands for  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  changed. In the beginning, the rather small band at  $2220\text{cm}^{-1}$  got broader. The more akaganéite ( $\beta\text{-FeOOH}$ ) formed there, the more this band disappeared. The middle-sized band at  $582\text{cm}^{-1}$  was also present in the first phase of formation of akaganéite ( $\beta\text{-FeOOH}$ ) next to the bigger band at  $650\text{cm}^{-1}$  (typical for akaganéite,  $\beta\text{-FeOOH}$ ), see figure 111. But, as soon as a certain amount of akaganéite ( $\beta\text{-FeOOH}$ ) formed, this band did not show any more. The band at  $2220\text{cm}^{-1}$  proved to be present for longer than the one at  $582\text{cm}^{-1}$ , which disappeared much more quickly during akaganéite ( $\beta\text{-FeOOH}$ ) formation.<sup>400</sup> It also became apparent, that the two absorption bands at  $1640\text{cm}^{-1}$  and  $1610\text{cm}^{-1}$ , which were well split and strong for mixtures that had not changed during experimentation, became united in one band at about  $1620\text{cm}^{-1}$  as akaganéite ( $\beta\text{-FeOOH}$ ) became important (see figure 112).

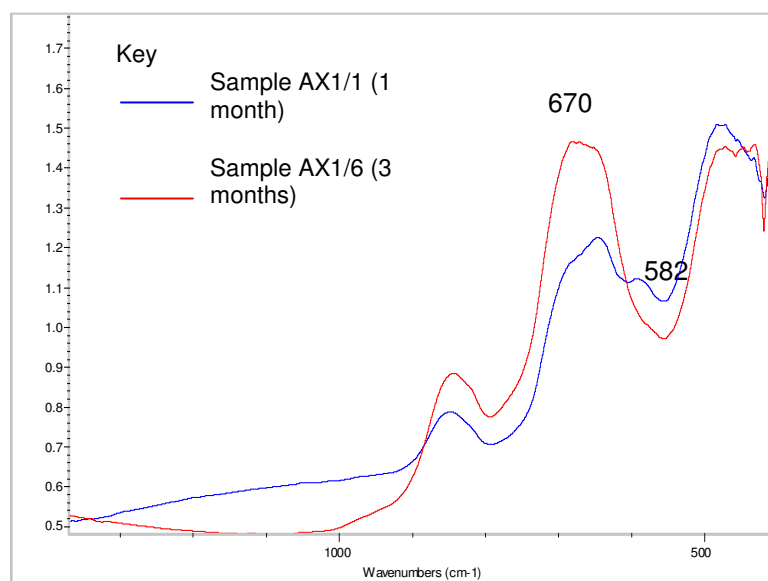
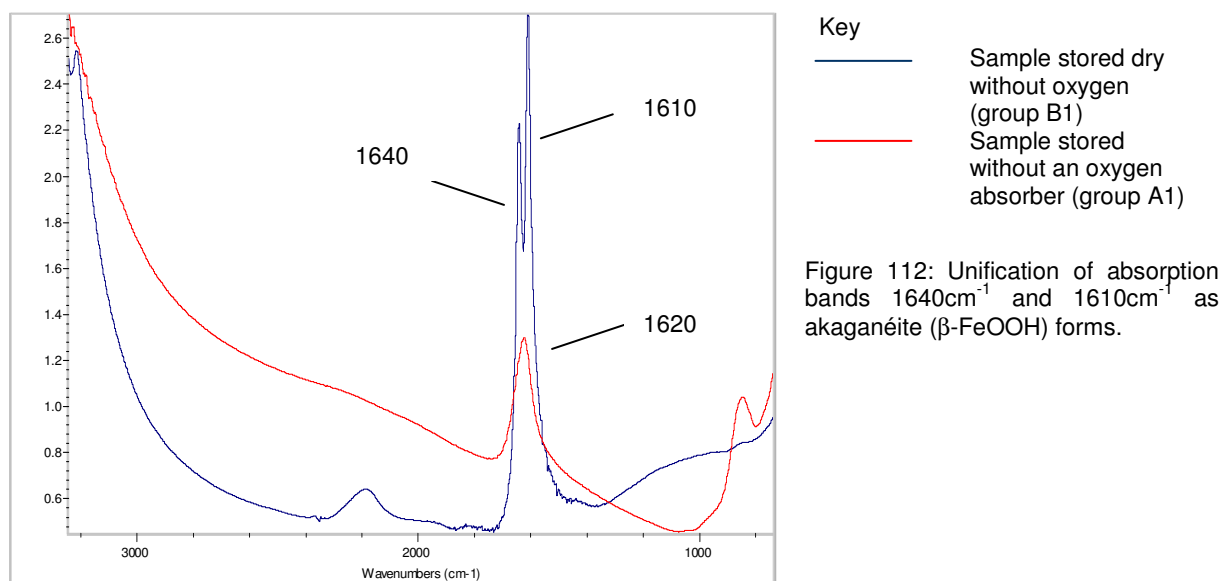


Figure 111: As akaganéite ( $\beta\text{-FeOOH}$ ) forms, the initial band of iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) at  $582\text{cm}^{-1}$  slowly disappears and leaves space for a band in the region of  $670\text{cm}^{-1}$ . After 1 month we can still see this first band in the sample stored without an absorber in a fully sealed bag (blue line). After 3 months, we see only the band at about  $670\text{cm}^{-1}$  as the amount of akaganéite ( $\beta\text{-FeOOH}$ ) becomes significant.

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

<sup>399</sup> Iron (III) chloride 7-water / iron chloride heptahydrate ( $2\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$ ) appeared in the beginning of the experimentation (during the first three months for group I1 and during the first month for groups A1 and AX1).

<sup>400</sup> It was decided that iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) should be visible on the FT-IR spectra down until the absorption band was a minimum of three times above the baseline noise.



X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

### 5.3.3 Raman spectroscopy: complementary confirmation of results from Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD)

As the results from the sample groups C1 and CX1 where the oxygen absorber RP-K was used were not entirely clear, it was decided to analyse some samples using Raman spectroscopy. This analytical technique can sometimes give complementary information on FT-IR spectra.

Where the amount of akaganéite ( $\beta\text{-FeOOH}$ ) was extremely low but visible in FT-IR (and probably extremely close to the detection limit) some Raman spectra were obtained to get a more precise idea and to see whether akaganéite ( $\beta\text{-FeOOH}$ ) was present.

When working with Raman spectroscopy, very small amounts of samples are sufficient: a single crystal is enough. This is an advantage as we can analyse the different compounds in a mixture.

The sample is illuminated by a monochromatic beam of light (using a laser beam). Inelastic scattering of the incident light can occur (a very small percentage of the light,  $<<1\%$ , is scattered in this way) and this is known as Raman scattering (whereas most of the incident light is scattered by elastic collision with the molecules of the sample, known as Rayleigh scattering). Raman scattering occurs when incident photons gain or lose a small amount of energy by interaction with the sample. These small energy exchanges are measured by Raman spectroscopy.<sup>401</sup> With Raman spectroscopy we can thus measure the energy of light scattered by a sample.

The scattering of electromagnetic radiation by the molecules of a solid leads to Raman spectra.<sup>402</sup> The spectrum shows on the X-axis the wavenumber/ $\text{cm}^{-1}$  and the intensity on the Y-axis.

When working with Raman spectroscopy, we look at the so-called Raman effect: it is the inelastic scattering of photons by molecules.<sup>403</sup> A change in vibrational, rotational or electronic energy can be

<sup>401</sup> Personal communication with Tracey Chaplin, 01/08/2006.

<sup>402</sup> CORNELL R. M., SCHWERTMANN U., 1996, p135.

<sup>403</sup> <http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>, 31/07/2006.

the consequence of Raman scattering.<sup>404</sup> The energies of the incident and the scattered photons are different and this difference is measured. Both Raman and infrared spectroscopy measure the vibrational energies of molecules but are based on different theories. To observe infrared-active vibrational motion, the dipole moment of the molecule must change. Whereas for a Raman-active vibration, the polarizability of the molecule has to change.<sup>405</sup> Changes in the polarization of the system are produced by active Raman vibrations.<sup>406</sup> The two techniques complement each other as they tell us different things about the examined molecules.<sup>407</sup>

A Renishaw System 1000 Ramascope equipped with a helium-neon ion laser ( $\lambda=632.8$  nm) was used for analysis. References from the relevant literature<sup>408</sup> as well as reference materials<sup>409</sup> were used for identification.

Raman spectroscopy was used for samples from group C1 (powders after five-and-a-half months in

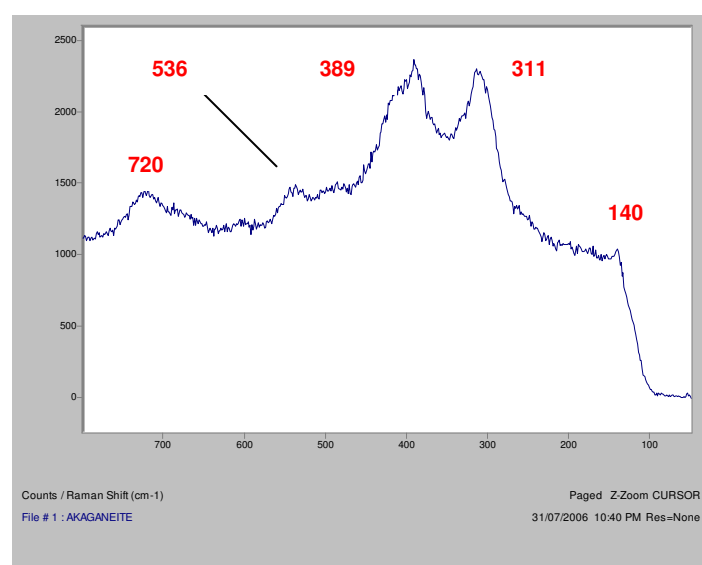


Figure 113: Spectrum from our synthetically produced akaganéite ( $\beta$ -FeOOH)<sup>410</sup> with some typical band positions in red (the small band at  $140\text{cm}^{-1}$  might well come from a rest of  $\text{FeCl}_3$  used for the production of the material).

anoxic storage using the RP-K absorber). As stated in chapter 5.2.3.3 there were two slightly different FT-IR spectra occurring for the samples stored with the RP-K absorber. Moreover the colour of one group of samples was darker than for the samples of the second group. For the first group (darker in colour and with four FT-IR bands of interest) goethite ( $\alpha$ -FeOOH), a form of iron(III) chloride ( $\text{FeCl}_3$ ) and some akaganéite ( $\beta$ -FeOOH) were considered as possible compounds. For the second group, where the powders were lighter in colour and showed three interesting

bands on FT-IR spectra, iron(III) chloride ( $\text{FeCl}_3$ ) and akaganéite ( $\beta$ -FeOOH) were cited. In the powder mixtures different crystals were analysed. There was a visible difference between yellow-orange crystals and dark grey crystals.

For the darker samples (that had shown four bands of interest using FT-IR) the yellow-orange crystals proved to be composed of a mixture of goethite ( $\alpha$ -FeOOH), akaganéite ( $\beta$ -FeOOH) and iron(II)

<sup>404</sup> <http://www.kosi.com/raman/resources/tutorial/index.html>, 31/07/2006.

<sup>405</sup> <http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>, 31/07/2006.

<sup>406</sup> CORNELL R. M., SCHWERTMANN U., 1996, p135.

<sup>407</sup> <http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>, 31/07/2006.

<sup>408</sup> CORNELL R. M., SCHWERTMANN U., 1996, p135; BOUCHARD M., SMITH D. C., 2003, p2263; DE FARIA D. L. A. et al., 1997, p873-878.

<sup>409</sup> The following compounds were analysed and Raman spectra obtained for comparison.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ : Iron(III) chloride hexahydrate, ACS, 97.0 – 102.0%, from Alfa Aesar A Johnson Matthey;  $\text{FeCl}_2$ : Iron(II) chloride (metals basis), 99.5%, from Alfa Aesar A Johnson Matthey;  $\alpha$ -FeOOH: Iron(III) hydroxide, alpha, from Alfa Aesar A Johnson Matthey;  $\beta$ -FeOOH.

<sup>410</sup> See chapter 4.5.1 for the production of the reference material.

chloride ( $\text{FeCl}_2$  from the initial  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) with mainly goethite ( $\alpha\text{-FeOOH}$ ), as can be seen in figure 114.

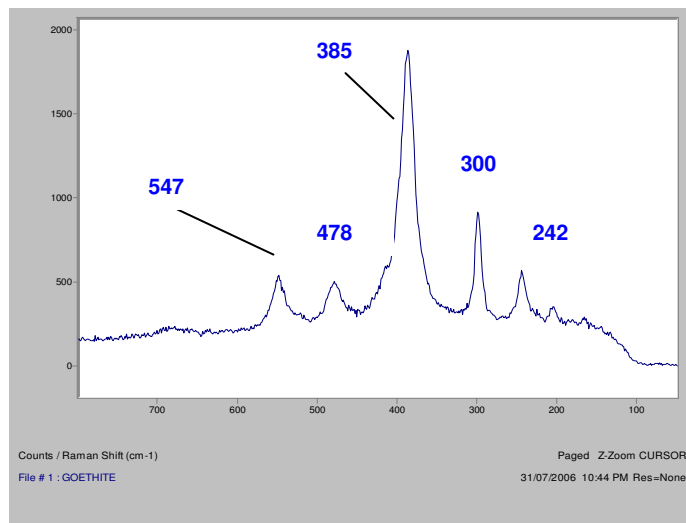
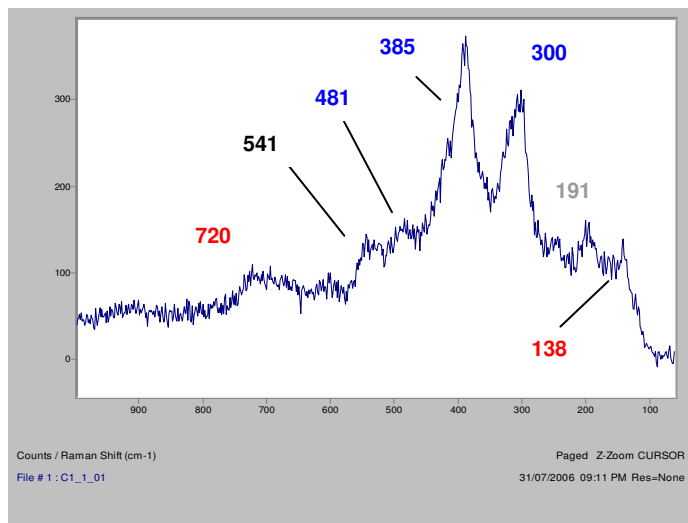


Figure 114: A yellow-orange crystal from a dark sample from group C1. In blue the bands that correspond to goethite ( $\alpha\text{-FeOOH}$ ), red the bands that could correspond to akaganéite ( $\beta\text{-FeOOH}$ ) and grey the typical band of iron(II) chloride ( $\text{FeCl}_2$ ).

Figure 115: A Raman spectrum from the reference goethite ( $\alpha\text{-FeOOH}$ ) with typical band positions in blue.

When analysing dark crystals in the darker mixture, a form of iron(III) chloride ( $\text{FeCl}_3$ ) was for the greatest part detected (see figure 116). The iron(III) chloride might be present in one of its hydrated forms or as  $\text{FeCl}_3$ . Some goethite ( $\alpha\text{-FeOOH}$ ) and akaganéite ( $\beta\text{-FeOOH}$ ) were detected too as present in the mixture.

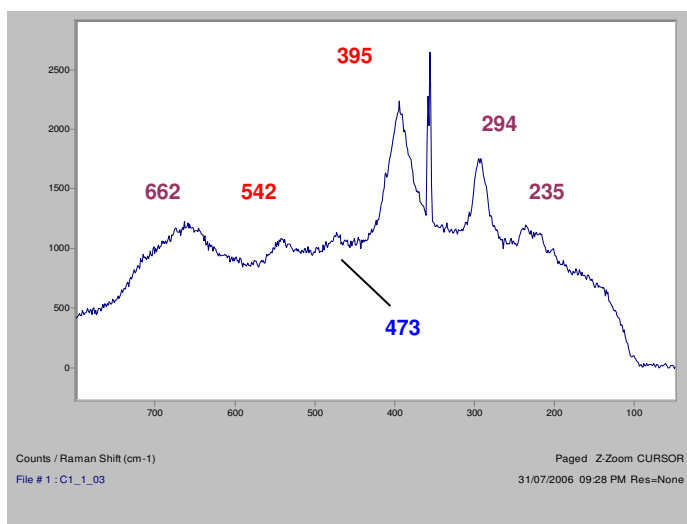


Figure 116: A dark crystal from the darker powder mixture (group C1) shows the presence of some species containing iron(III) chloride ( $\text{FeCl}_3$ ), marked in purple. Red is used for akaganéite ( $\beta\text{-FeOOH}$ ) bands and blue for goethite ( $\alpha\text{-FeOOH}$ ). (The band at  $\sim 360\text{cm}^{-1}$  was caused by a cosmic ray and can be ignored).

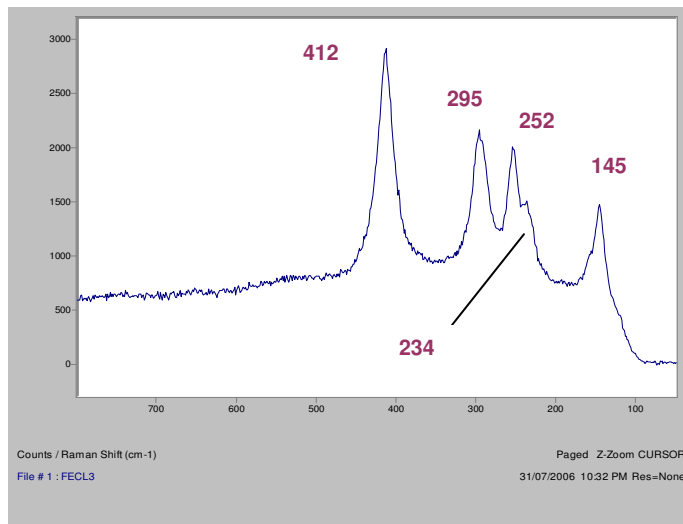


Figure 117: The spectrum of the reference material iron(III) chloride 6-water ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , also called iron(III) chloride hexahydrate).

The lighter samples (which had previously shown three bands of interest in FT-IR and were thought to show the presence of akaganéite,  $\beta$ -FeOOH and iron(III) chloride) revealed similar results. The yellow-orange crystals were composed of a mixture of probably akaganéite ( $\beta$ -FeOOH), goethite ( $\alpha$ -FeOOH) and iron(II) chloride ( $\text{FeCl}_2$  from the initial  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), as can be seen in figure 118. This time goethite ( $\alpha$ -FeOOH) did not seem to be present in a more important amount than the other two compounds.

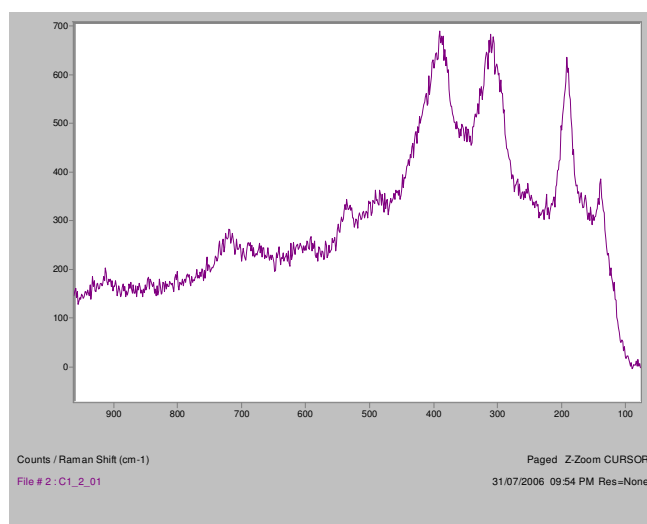
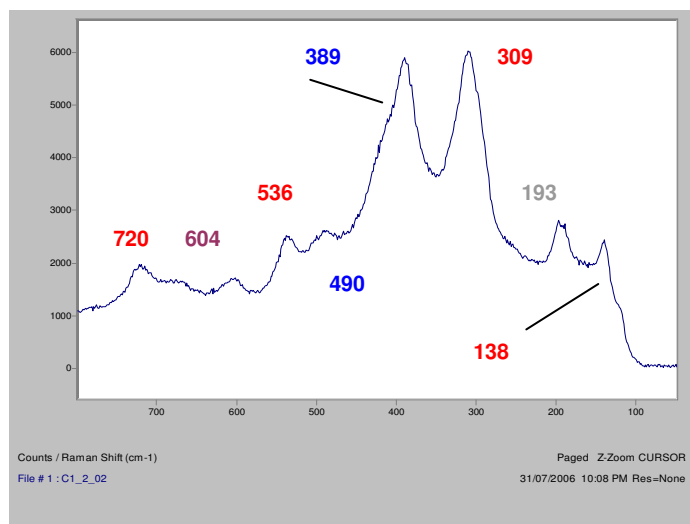


Figure 118: A yellow-orange crystal from the lighter powder mixture (sample C1/2 that had shown three bands of interest in FT-IR) shows the presence of akaganéite,  $\beta$ -FeOOH (in red), goethite,  $\alpha$ -FeOOH (in blue), iron(II) chloride,  $\text{FeCl}_2$  (in grey) and some iron(III) chloride,  $\text{FeCl}_3$  (in purple).

Figure 119: Another yellow-orange crystal from the same sample (lighter powder) as on the left shows a similar result on the Raman spectrum.

The dark crystals clearly showed the presence of iron(III) chloride ( $\text{FeCl}_3$ ) in one of its forms (it could not be ascertained if this was in hydrated state) and some akaganéite ( $\beta$ -FeOOH), as seen in figure 120.

No akaganéite ( $\beta$ -FeOOH) was detected using Raman spectroscopy in the samples from groups B1 (samples after a test period of five-and-a-half months) and BX1 (samples after three months), where dry anoxia was tested. The peak visible in figure 121 is the one that stands for iron(II) chloride (of our initial  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), figure 122.

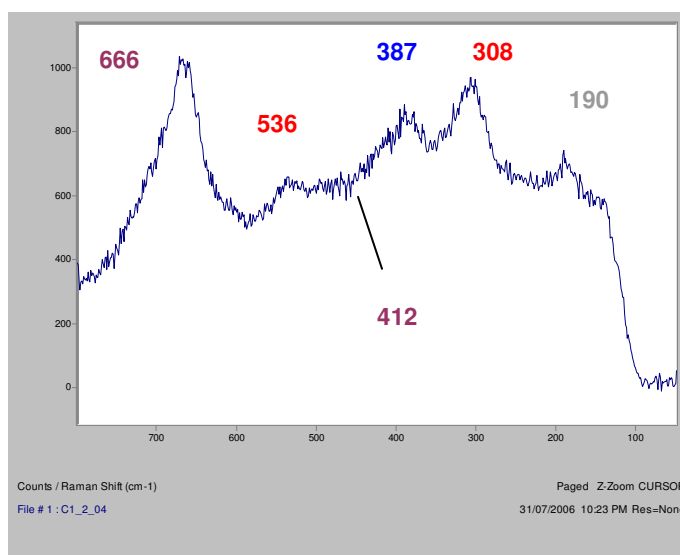


Figure 120: A dark crystal from the lighter sample (C1/2, with previously three bands of interest in FT-IR) showed the presence of, for the greatest part, a form of iron(III) chloride (in purple) and akaganéite,  $\beta$ -FeOOH (in red). Blue stands for goethite ( $\alpha$ -FeOOH), and grey for iron (II) chloride ( $\text{FeCl}_2$ ).

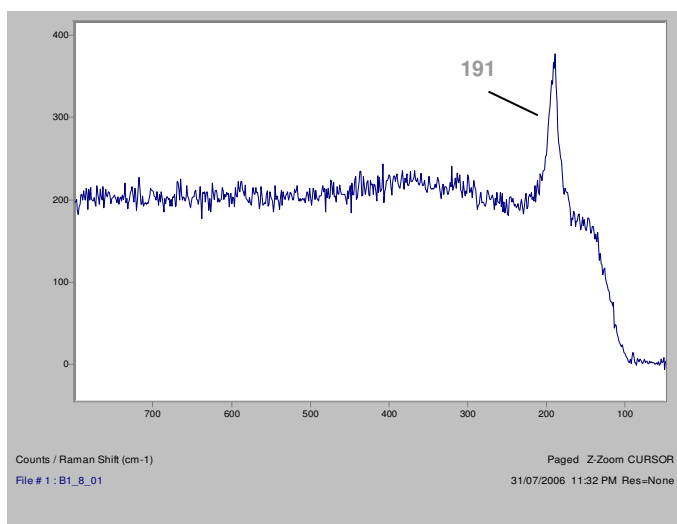


Figure 121: Raman spectrum obtained from a sample stored in dry anoxia for 5.5 months (group B1). No akaganéite ( $\beta$ -FeOOH) was detected. The band at  $191\text{cm}^{-1}$  is typical for iron(II) chloride ( $\text{FeCl}_2$ ).

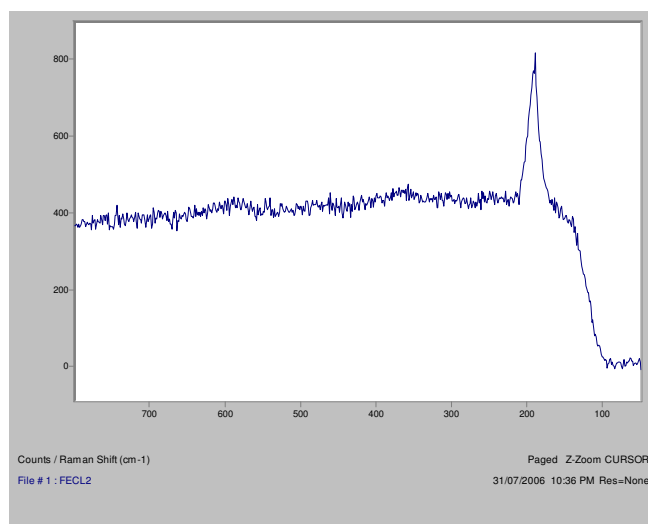


Figure 122: Reference material iron(II) chloride ( $\text{FeCl}_2$ ): the typical band at  $191\text{cm}^{-1}$  is well visible.

This confirms that the amount of akaganéite ( $\beta$ -FeOOH) in these groups can be neglected. In the FT-IR spectra of these samples the presence of akaganéite ( $\beta$ -FeOOH) was always very close to the detection limit. We measured amounts of 0.5 – 2 % akaganéite ( $\beta$ -FeOOH) in the potassium bromide (KBr) disc for FT-IR in almost all sample groups (B, F, G, K, L). Compared to Raman spectroscopy where we can analyse a single crystal, FT-IR analyses a mixture of all compounds present. When confirming the results on Raman equipment, we pinpointed single crystals of different appearance and in this case the akaganéite ( $\beta$ -FeOOH) did not show.

### 5.3.4 Amount of oxygen absorbed by the RP-A oxygen absorber

The oxygen absorbers used in this work are sold for a volume of 300ml air (the absorber removes the oxygen in these 300ml of air). It has previously been mentioned that the absorber usually has a higher absorption capacity than what it is sold for (see chapter 3.3).<sup>411</sup> To determine how much oxygen one absorber (RP-A) really absorbs, the following test was carried out.

A sachet of RP-A (we used the ones for 300ml) was cut in half and divided between two glass flasks of 500ml volume each, which were then closed. One RP-A bag was placed in a third glass flask of 500ml volume. As references, two 500ml glass flasks were included without an absorber. The oxygen content in the glass flasks was measured three hours after the test set-up, then again one and three days later.<sup>412</sup> This was carried out using the GSS450 Oxygen Analyser and ruthenium sensors placed in the glass flasks. Afterwards the amount of oxygen removed in each glass flask was calculated (see table 6).

<sup>411</sup> MAEKAWA S., ELERT K., 2003, p44.

<sup>412</sup> It was found that the oxygen absorber needed a maximum of three days for full reaction, which means lowering the oxygen contents in the enclosures as far as possible.



| Setup  | Oxygen (in %) in the glass flask after three hours | Oxygen (in %) in the glass flask after one day | Oxygen (in %) in the glass flask after three days | Oxygen removing capacity for volume of air (in ml). The oxygen in the following volumes (of air) can be removed |
|--|--|--|---|---|
| Glass flask 1 (500ml) with half an RP-A oxygen absorber (for 300ml air). | 19.5   | 17.7   | 15.2  | 268.765 <sup>413</sup>  |
| Glass flask 2 (500ml) with half an RP-A oxygen absorber (for 300ml air). | 19.9   | 16.1   | 15.8  | 239.709   |
| Glass flask 3 (500ml) with an RP-A oxygen absorber (for 300ml air).      | 18.1   | 10.0   | 9.1   | 564.165   |
| Glass flask 4 (500ml) without oxygen absorber.                           | 21.6   | 22.2   | 19.8  |   |
| Glass flask 5 (500ml) without oxygen absorber.                           | 20.7   | 20.7   | 19.5  |   |

Table 6: Calculation of the oxygen absorption capacity of RP-A oxygen absorbers.

With this test it can be observed that the average of half an RP-A absorbing sachet (for 300ml of air) can absorb the oxygen from a volume of 263.52ml of air.<sup>414</sup> On average, one entire RP-A sachet, sold for 300ml of air, could absorb the oxygen from a volume of 527.04ml of air.<sup>415</sup> This confirms the statement by the producer that the absorber has a higher capacity than what it is sold for.

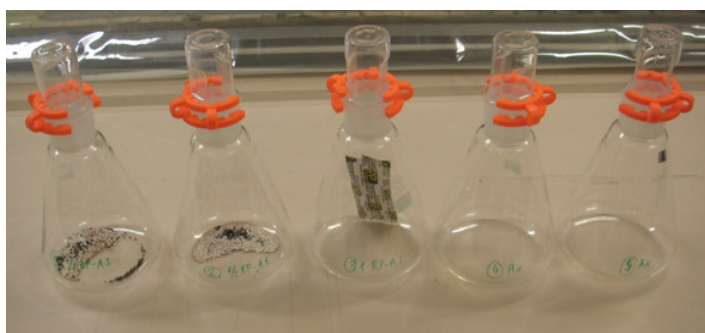


Figure 123: Test setup for the measurement of the oxygen absorbing capacity of the RP-A oxygen absorber. Two glass flasks of 500ml with half an absorber, one flask with an entire absorber and two glasses without any absorber.

<sup>413</sup> The calculation was as follows: the average from glass flasks 4 and 5 (without any absorber) was calculated : 20.75% oxygen. Then the amount of oxygen removed from the 500ml of air in flask 1 was determined (20.75% - 15.2% = 5.55%). With the oxygen absorber we aim for an oxygen level of 0.1% in the environment: so in theory we would have needed to remove 20.65% oxygen from glass flask 1. We use this value to calculate the oxygen absorption capacity of the RP-A sachet used in flask 1. We divide the real amount of oxygen removed in the flask by the value it should have removed in theory and multiply it by 1000 to obtain the volume of air that the oxygen could be removed from.  $(5.55/20.65) \times 1000 = 268.765\text{ml}$ . Half an RP-A sachet (for 0.5x300ml air, that means 150ml air) could thus remove the oxygen from 268.765ml of air.

<sup>414</sup> Average of flasks 1, 2 and 3.

<sup>415</sup> Average of flasks 1, 2 and 3, then multiplied by two.

### 5.3.5 Prediction of life-times of the tested storage systems


It is important to know how long our storage methods last. This means how long it will take until we have to consider changing the silica gel we added to keep our objects dry or the oxygen absorber to keep an anoxic environment.

#### 5.3.5.1 Working with plastic containers and silica gel

If we consider storing our archaeological iron in a dry enclosure, we could place the objects into a plastic box (of a certain trademark) and add dry silica gel to keep the contents dry.<sup>416</sup> The box though is placed in an environment where the RH might not be very low. Let us suppose an average of 50%. The RH in the box will grow higher and higher over the time, towards the external RH as air and moisture can get into the box. Three ways of inflow are possible: temperature change, pressure and simple diffusion. The most important one is the diffusion of air through the seals and cracks.<sup>417</sup>

This rise (or decay) in RH is exponential and characterised by a half-time. The hygrometric half-time depends on the air leakage rate of the box (air changes per day<sup>418</sup>) and the buffering material (here silica gel) placed into the box.<sup>419</sup>

Three boxes were tested for the time they would, after addition of silica gel (5% RH), keep a dry climate (not exceeding 15% RH advised for safe storage of archaeological iron where no active corrosion could develop<sup>420</sup>).<sup>421</sup>

| Tested box: trademark   | Air exchange rate (AER) <sup>422</sup> | Life-time <sup>423</sup> (RH level of box $\leq 15\%$ ) <sup>424</sup> |
|---|--|--|
| Stewart <sup>TM</sup> 'Seal fresh' (polypropylene PP) <sup>425</sup><br> | 0.65ac/d (air changes/day)             | 248 days<br>(approximately 8 months)                                   |

<sup>416</sup> We use 20kg/m<sup>3</sup> silica gel for conditioning.

<sup>417</sup> THOMSON G., 1977, p87.

<sup>418</sup> See annex II for calculation of air exchange rate.

<sup>419</sup> THOMSON G., 1977, p87.

<sup>420</sup> TURGOOSE S., 1982 a, p100.

<sup>421</sup> For our calculations of the time until the silica gel has to be renewed we used the following formula for the half-time:  $t_{1/2} = 4MB/N$ ; where  $t_{1/2}$  = 'hygroscopic half-time' of case and contents, M= dry weight of buffer in case/case volume, B='specific moisture reservoir' of buffer (moisture in kg/g for a 1% RH rise), N= number of air changes per day (THOMSON G., 1977, p93; personal communication with David Thickett, English Heritage, 25/06/2006). See annex I, CD-R, for details.

<sup>422</sup> See annex II for calculation of air exchange rates.

<sup>423</sup> See annex I, CD-R, for details on calculations.

<sup>424</sup> Time until the silica gel has to be changed: initial RH of the gel is 5% and it has to be changed when 15% is reached in the box.

<sup>425</sup> Stewart<sup>TM</sup> boxes from Azpack Limited, United Kingdom.



|   |                            |                                       |
|---|----------------------------|---------------------------------------|
| Curver™ (lid polyethylene PE and bottom polypropylene PP) <sup>426</sup><br> | 0.61ac/d (air changes/day) | 264 days<br>(approximately 9 months)  |
| Rondo™ (lid polyethylene PE and bottom polypropylene PP) <sup>427</sup><br>  | 0.28ac/d (air changes/day) | 575 days<br>(approximately 19 months) |

Table 7: Air exchange rates (AER) and life-times for three plastic boxes (Stewart™, Curver™, Rondo™).

As can be seen from the table above the Rondo™ box performs best with a life-time of 575 days (if the external RH is of 50%).<sup>428</sup>

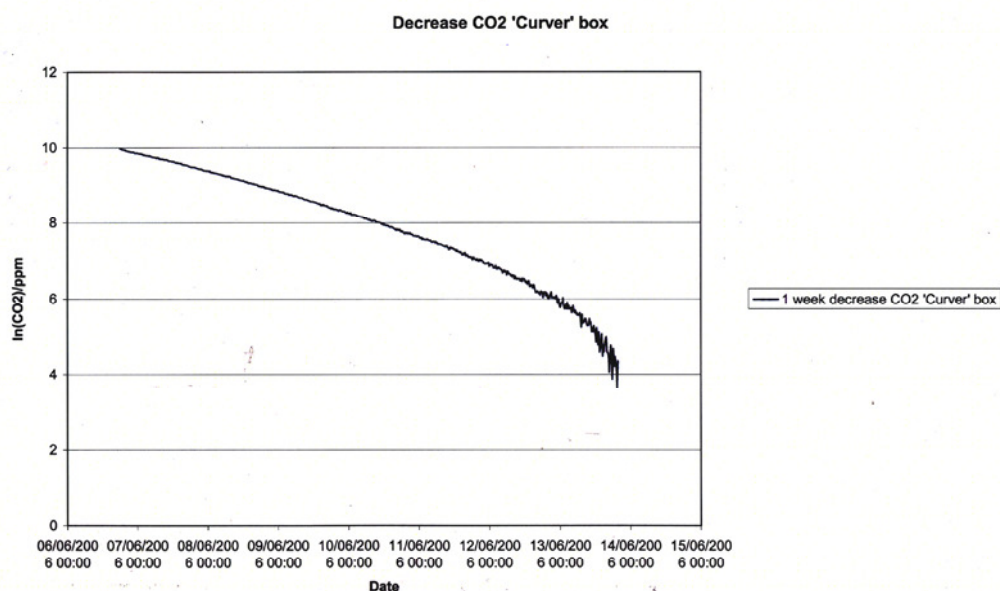


Figure 124: The decrease of carbon dioxide (CO<sub>2</sub>) in the Curver™ box measured with a Carbon Dioxide Meter (Vaisala) over a week. The data was used to determine the air exchange rate (AER).

<sup>426</sup> Curver™ boxes from Rubbermaid (Curver Kunststoff GmbH), Germany or Semadeni AG, Switzerland.

<sup>427</sup> Rondo™ boxes from Rotho Kunststoff AG, Switzerland.

<sup>428</sup> With an external RH of 60% the life-time for the Rondo™ box would be of 459 days, with 70% external RH it would be of 382 days (see annex I, CD-R).

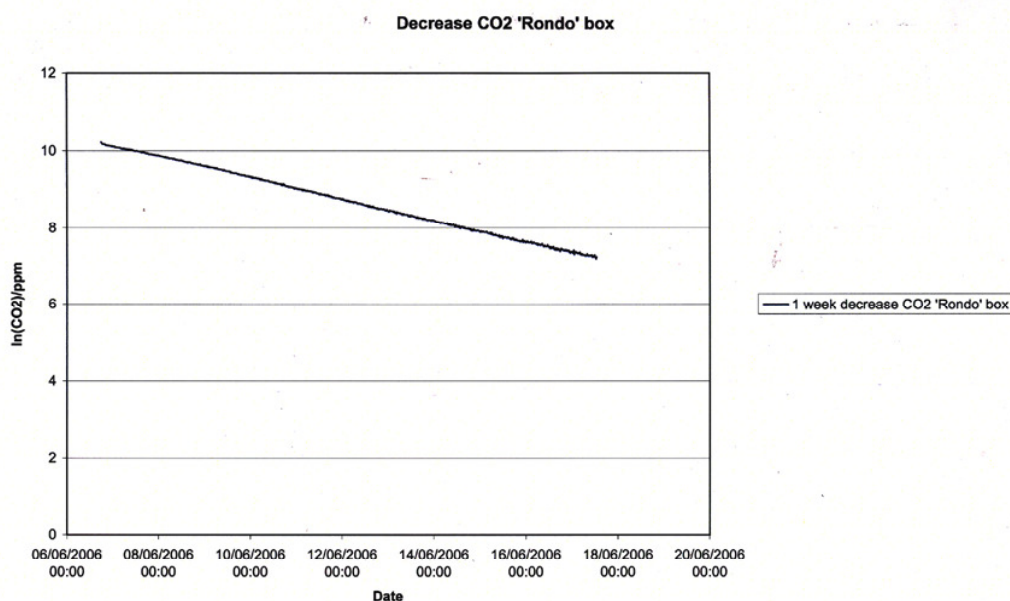


Figure 125: The decrease in carbon dioxide (CO<sub>2</sub>) is more regular for the Rondo™ box than the Curver™ box (previous figure) and Rondo™ has a lower air exchange rate (AER) than Curver™.

### 5.3.5.2 Working with the RP-System™

At present, we do not know how long anoxic enclosures really last as applications only started in the last few years. People have mentioned life-times of decades, most often about twenty years.<sup>429</sup>

If choosing to store objects using anoxic enclosures we have to consider some parameters that will influence the life-time of the system: the quality of the high barrier film (and its degradation over time), the quality of the heat seals or the clips, the oxygen absorption capacity of the oxygen absorber and the storage environment (temperature and RH that surround the enclosures).

There are two ways of calculating the life-time of the system. One takes into account the air exchange rate (AER) of the bag (and therefore the quality of the seals) whereas the other works with the oxygen transmission rate (OTR) of the plastic. This second calculation does not take into account leakage through the seals (which obviously will give a longer life-time, as we surely have leakage through seals). The first calculation would therefore be more precise as the sealed enclosures made of ESCAL™ film leak. The leakage is very little compared to other enclosure as the plastic boxes<sup>430</sup> like Stewart™ but has to be taken into account.

<sup>429</sup> Christoph Waller, Long Life for Art, states that the life-time could be of some decades until the barrier film would break down (personal communication, 16/08/2006). Chris Collins, Natural History Museum, stated a benchmark for ESCAL™ film of 20 years (personal communication, march 2006). Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, said the RP sachets should stay effective once opened for at least 20 years (personal communication, 26/06/2006).

<sup>430</sup> The plastic boxes have a higher AER than the ESCAL™ bags as leakage through the seals is more important.

If we use the AER for our calculation we have to take the following parameters into account. The AER of the bag itself<sup>431</sup>, the quantity of oxygen the oxygen absorber can absorb<sup>432</sup> and the quantity of moisture the buffer in the absorber can pick up if working with RP-A (the absorber that lowers the RH). A bag with all sides heat-sealed will last longer than a bag closed with a clip on the last side as the clip lets more air pass in than the heat seals.

Working with the OTR we have to multiply this value by the area of our container. Then we have to know how much oxygen absorption potential is in the bag (the number and the size of the oxygen absorbers). This will give us a minimum oxygen-free time.<sup>433</sup>

In this work we give some indications of life-times for anoxic enclosures based on the calculation using the OTR of the ESCAL<sup>TM</sup> film. However, this method is not the best suited: as it does not take into account the leakage through seals or clips. But measuring the AER turned out to be problematic as it seems to be questionable to use carbon dioxide (CO<sub>2</sub>) as a tracer gas working with sealed ESCAL<sup>TM</sup> bags. This gas is unlikely to behave in the same way as oxygen, when considering permeation through the film (see chapter 3.3.3 and annex II).

The OTR for ESCAL<sup>TM</sup> barrier film is reported as 0.05cc/m<sup>2</sup>/day (at 25 °C and 60% RH). The values of ESCAL<sup>TM</sup> film are measured on a film of 0.11mm thickness.<sup>434</sup>

The oxygen absorption capacity of an RP-A sachet sold for a volume of 300ml of air was actually seen to be higher than this. Such a sachet could absorb the oxygen in 527.04ml of air in average (see chapter 5.3.4). We have seen that even if the oxygen absorption capacity of the RP-A oxygen absorber was exhausted in a specific enclosure, the RH stayed at low levels for longer. This means that the climate inside the bag remained dry even if the oxygen level was already approaching 10% or more. The moisture buffer in the RP-A sachet seems therefore to remain active longer than its oxygen absorbing part. We can thus say we have a specific life-time for the enclosure in terms of low oxygen levels, but the packed iron objects are probably still out of danger of corrosion even if the oxygen level rises, as the RH stays low longer.<sup>435</sup> This gives us a longer life-time of our enclosure.

For the calculation taking into account the OTR we need to know the area of the enclosure. Supposing we would like to get a volume of one litre, the surface area could be approximately 0.0833m<sup>2</sup>. The oxygen passing through this area per day would then be of 0.00416cc.<sup>436</sup> If we know, that one RP-A sachet (for 300ml air) can actually absorb the oxygen from 527.04ml air, this gives a quantity of oxygen of 110.6784ml assuming air is composed of 21% oxygen. For our bag we take 3 RP-A bags (each for 300ml air). The life-time is then, as can be seen in the following table, 79816.15 days (218.67 years). However, this value is not realistic as the leakage through the seals is not taken into account. And the degradation of the barrier film is also an aspect to take into account. There is a need for further research upon that point. We could consider flushing bags with nitrogen to obtain an

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<sup>431</sup> Leakage can mainly occur through the seals (or in addition through the clip) and through the film itself (the three ways of inflow of air stated by Thomson are also valid for this storage method: temperature change, pressure and simple diffusion; see chapter 5.3.5.1). (THOMSON G., 1977, p87.).

<sup>432</sup> See chapter 5.3.4.

<sup>433</sup> Personal communication with Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, 26/06/2006.

<sup>434</sup> MAEKAWA S., ELERT K., 2003, p20-27; COLLINS C., unpublished, 1999, p6.

<sup>435</sup> The present work has shown the efficiency of dry storage to prevent active corrosion.

<sup>436</sup> Knowing that per m<sup>2</sup> the oxygen passing through is of 0.05cc/day.

oxygen-free environment and then measure the increase in the oxygen level using the GSS450 Oxygen Analyser (see chapter 4.5.4). Of course measurements would take a long time, as one cannot expect a quick increase in oxygen. The life-time of an anoxic ESCAL<sup>TM</sup> enclosure is probably, as stated by many conservators, closer to the twenty years than to the 100 – 200 years calculated using the OTR of ESCAL<sup>TM</sup> film: because the seals leak (a little) and the plastic film itself degrades (due to the influence of humidity, light or oxygen).

In this section we use simple bags: this means that if objects are double-bagged with oxygen absorbers in the inner and outer layers, the life-time of the inner bag becomes much longer.<sup>437</sup> Also the probability of leaks is reduced.<sup>438</sup>

| <b>Volume of enclosure</b> | <b>Number of RP-A sachets</b> | <b>Calculation<br/>Oxygen absorbing<br/>capacity of<br/>absorber(s) / oxygen<br/>passing through the<br/>area per day</b> | <b>Life-time (days) to<br/>change of oxygen<br/>absorber</b> |
|----------------------------|-------------------------------|---|--|
| 1000ml                     | 3 RP-A (each for 300ml air)   | $(3 \times 110.6784) / 0.00416$   | 79816.15 days<br>(218.67 years)                              |
| 300ml                      | 1 RP-A (for 300ml)            | $110.6784 / 0.002$  | 55339.2 days (151.61 years)                                  |

Table 8: Some calculations of life-times for anoxic enclosures based on the OTR of the ESCAL<sup>TM</sup> barrier film.

<sup>437</sup> Personal communication with Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, 26/06/2006.

<sup>438</sup> Personal communication with David Thickett, English Heritage, London, 22/08/2006.

## 6 DISCUSSION

### 6.1 Materials and packaging methods used: some comparisons

For the first series of samples we raised the question if it would make a difference closing or leaving open the resealable PE bags. Slightly better results were obtained in terms of preventing akaganéite ( $\beta$ -FeOOH) formation when the PE bags were provided with holes. However, the differences were very small, in the order of 1% difference in the amount of akaganéite ( $\beta$ -FeOOH) in the powders. In the first hours and days after packing the samples, the climate in the PP boxes mixes and equilibrium is reached in the PE bags placed in the PP boxes. It might be that mixing, and so the achievement of dryness due to added silica gel, is faster when the PE bags are left open.

Some reflections have to be made on the packaging method when using oxygen absorbers. This work has compared packing in bags provided with either four heat seals or three heat seals and one clip to close the last side. The first method could be applied as a long-term model whereas the second one could be used in the short term (for packing objects on site while they wait for further treatment). The clips have shown to increase the air exchange rate (AER) in the bags. Therefore the life-time of the system will be shorter compared to an all-sealed bag.<sup>439</sup> The time period tested showed the clips and seals to last for five-and-a-half months, while the oxygen level stayed at zero over this time.

For oxygen monitoring, the oxygen-indicating tablets provided by Mitsubishi Gas Chemical Company cannot be used for the long term. Their shelf life is far too short (guaranteed six months) and their reliability too poor. The colour change does not occur every time it should and sometimes takes up to several weeks. The tablets can be added to the package in the beginning (always more than one tablet) to have a rough idea of what happens in the bag. But they cannot be taken as 100% reliable.

The oxygen monitoring system tested (GSS450 Oxygen Analyser) was easy to use, but also revealed some problematic aspects. The sensors used (SensiSpot) are probably sensitive to high RH and high temperatures.<sup>440</sup> Their life-time and stability has to be submitted to further research. The readings with the GSS450 Oxygen Analyser did not always give coherent results. A certain error value has to be taken into account.<sup>441</sup>

### 6.2 Problems encountered during experimental work

For the samples packed in plastic boxes, no major problems occurred in terms of packaging. The refrigerator where half the samples were stored broke down during the fourth test month and this had an important influence on the synthetic powder samples: where not stored with silica gel, the samples developed an important amount of akaganéite ( $\beta$ -FeOOH). Where silica gel was added, the dry atmosphere prevented akaganéite ( $\beta$ -FeOOH) formation even when temperature rose as the refrigerator broke down.

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<sup>439</sup> The oxygen absorber will last less long as more oxygen diffuses into the bag.

<sup>440</sup> POLLARD T., *unpublished*, 2006, p32.

<sup>441</sup> Pollard indicates a minimum error value of 0.5% to be taken into account (POLLARD T., *unpublished*, 2006, p30).

Some problems occurred during this research that showed clearly what the crucial aspects were when making anoxic enclosures.

It is extremely important to choose the right sealing temperature if making bags from ESACL™ high barrier film. This temperature was not known when the first test series was launched.<sup>442</sup> All the used bags had tested negatively on leakage using a leak detector (see chapter 4.4.2). Nonetheless it was found that some bags were leaking (due to the wrong sealing temperature) and so the oxygen absorbers quickly lost efficiency. The synthetic powder samples in those bags eventually developed akaganéite ( $\beta$ -FeOOH) and could not be used for comparison. Some doubts arose as well on the performance of the clips in keeping the enclosures free of oxygen access. As those problems and questions occurred it was decided that another test series should be launched with fully heat-sealed bags and using the by then known heat-sealing temperatures.<sup>443</sup> Contacts were made then with the Natural History Museum (NHM), London, which kindly invited us to use facilities and materials for another test series.

Another problematic aspect was the monitoring of the oxygen contents in the anoxic enclosures. The indicating tablets (from Mitsubishi Gas Chemical Company and provided with the RP-System™) turned out to be unreliable. Far too many indicators did not turn pink within hours, but only within days or weeks. Some stayed violet even though the oxygen level was shown zero. Re-using the indicators turned out to be impossible, and a too long exposure to oxygen would not let the indicators turn pink again in an anoxic environment. Problems were also encountered using an oxygen meter provided with a needle to take measurements (see chapter 4.5.4). Sometimes the amount of air left in the anoxic enclosures was too little for a decent reading (as the bags lose about 20% of volume due to the scavenging of oxygen). In this case, only one measurement could be taken and no errors were allowed in the piercing of the bag. The use of the GSS450 Oxygen Analyser (see chapter 4.5.4) proved to be easy. But sometimes the readings were not consistent. One has to consider an error value of at least 0.5%.<sup>444</sup>

As money was an aspect to take into account during the test series, we had to use opened and resealed bags containing the oxygen absorbers. It is said that if resealing the bag containing the absorbers, they would become less efficient with each re-opening.<sup>445</sup> So some test bags contained absorbers that were probably a bit less efficient, which might not pose a problem for the short time of this research, but would become a factor if anoxic enclosures are applied on a long-term basis.

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<sup>442</sup> The sets on the heat sealer were adjusted at that moment following experience and advice by a conservation scientist who had worked with the RP-System™. It has to be said that the heat sealer could not be adjusted in terms of temperature but only on a graduation from 1 - 10 (the higher the number, the higher the – unknown – temperature...).

<sup>443</sup> Weld setting should be at 3 (117°C, which is very close to 118°C, the melting temperature of LLDPE) and cool setting at 6 if using a CRISS CROSS Universal Heat Sealing Machine (MC PHAIL D., LAM E., DOYLE A., 2003, p96-104).

<sup>444</sup> POLLARD T., unpublished, 2006, p13.

<sup>445</sup> Personal communication with Chris Collins, Natural History Museum, London, June 2006



### 6.3 Reflections on the quantity of akaganéite ( $\beta$ -FeOOH) detected using Fourier-transform infrared spectroscopy (FT-IR)

When working with FT-IR a very small amount of akaganéite ( $\beta$ -FeOOH) in the sample is enough to show up as absorption bands on the spectrum. As most of the samples revealed an – even if very small – absorption band in the region of  $848\text{cm}^{-1}$ , answers to this had to be found, as some samples should not have formed akaganéite ( $\beta$ -FeOOH) following the corrosion theories. Reasons for this could be as follows: The time between sample preparation and their packaging could be of some importance (the setup for experimental work took one day during which the powder mixture was exposed to the room climate and some reactions could take place). It took all enclosures some time to get to their equilibrium and this time interval could be of some concern.<sup>446</sup> When the synthetic powder samples were collected for analysis, they were stored in a closed PP box with added dry silica gel (at 5% RH) to prevent the reactive powders to change during transport. It was also decided to start analysis on FT-IR and after this to go on with XRD, as this technique is less sensitive. Due to the 3-4 hour time interval<sup>447</sup> between collection and analysis of the samples (which were located in two different places and not close to the facilities with analytical equipment<sup>448</sup>), the synthetic powder mixtures could still react and form a small amount of akaganéite ( $\beta$ -FeOOH). This means that when reading the results, all groups can possibly show akaganéite ( $\beta$ -FeOOH), even the ones where there should not be any (dry oxygen-free storage, dry storage and dry/cold storage where the amount of akaganéite,  $\beta$ -FeOOH, is extremely small). Raman spectroscopy however showed no akaganéite ( $\beta$ -FeOOH) in the sample groups stored dry without oxygen when FT-IR spectra showed smallest amounts of 0.5 – 2% (very close to the detection limit). This is possibly due to the fact that FT-IR gives an ‘overview’ of the whole mixture and with Raman spectroscopy we can pinpoint single crystals in the mixture.

The increasing amount of the relative percentage (%) of akaganéite ( $\beta$ -FeOOH) in the potassium bromide (KBr) pellets used for FT-IR has already been shown (see chapters 5.1.3.2 and 5.2.3.2). Results were based on a relative amount, as the powders were not weighed accurately over the first four months when coming out of the enclosures (this would have been necessary to give precise quantitative indications). Precise weighing was only done after the last test period at five-and-a-half months to give an accurate indication on how much akaganéite ( $\beta$ -FeOOH) had really formed in the synthetic powder mixture (see chapters 5.1.3.1 and 5.2.3.1).

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<sup>446</sup> The RH usually dropped within a day but the oxygen level took longer (about three days). It seemed that for anoxic storage, the interval of three days to get an oxygen percentage of zero was too long to prevent corrosion in the powder samples. Using RP-A where the RH dropped within hours probably prevented reactions until the oxygen was lowered.

<sup>447</sup> Once the potassium bromide (KBr) to make the discs for analysis on FT-IR became wet and means to dry it had to be found. This took two days (heating the KBr in an oven at  $120^{\circ}\text{C}$ ) and interrupted analysis after the fourth month (and is visible in the results: e.g. the amount of akaganéite ( $\beta$ -FeOOH) in the sample group B1 and BX1 is higher than under normal circumstances). KBr is very sensitive to high RH and this was a problem working at a laboratory where RH was high during the summer.

<sup>448</sup> Some samples were placed at the Natural History Museum, London, and some at Ranger’s House, English Heritage, in Greenwich. Oxygen measurements for the second group had to be performed at the British Museum in Central London before bringing all samples to Birkbeck College, located in Central London, where FT-IR analysis could be carried out. XRD was carried out at Fort Cumberland, English Heritage, Portsmouth.

## 6.4 Open question: corrosion products formed in samples stored with the oxygen absorber RP-K (sample group C1 and CX1)

It seemed that when using oxygen absorbers RP-K the corrosion process in our synthetic powder samples was not stopped. Nevertheless it was not fully understood what reactions occurred. The powders showed different amounts of akaganéite ( $\beta$ -FeOOH), some form of iron(III) chloride ( $\text{FeCl}_3$ ), goethite ( $\alpha$ -FeOOH) and iron(II) chloride (from the initial  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), identified and confirmed both by FT-IR and Raman spectroscopy.

We have observed that the oxygen level within anoxic enclosures drops to zero within approximately two to three days (for both tested oxygen absorbers) whereas if the RP-A absorbers for a dry climate are used, the RH drops within hours. This might be a possible explanation for the differences observed for those absorbers: whereas the RH was lowered very quickly, no reaction occurred in the powder samples. Where the RH remained the same, the time interval of two to three days for all oxygen to be removed might have been enough for some reactions to occur. This would indicate that the key factor for stopping the corrosion reactions is the RH, as even a very small amount of oxygen seems to be enough for the corrosion reactions to occur.

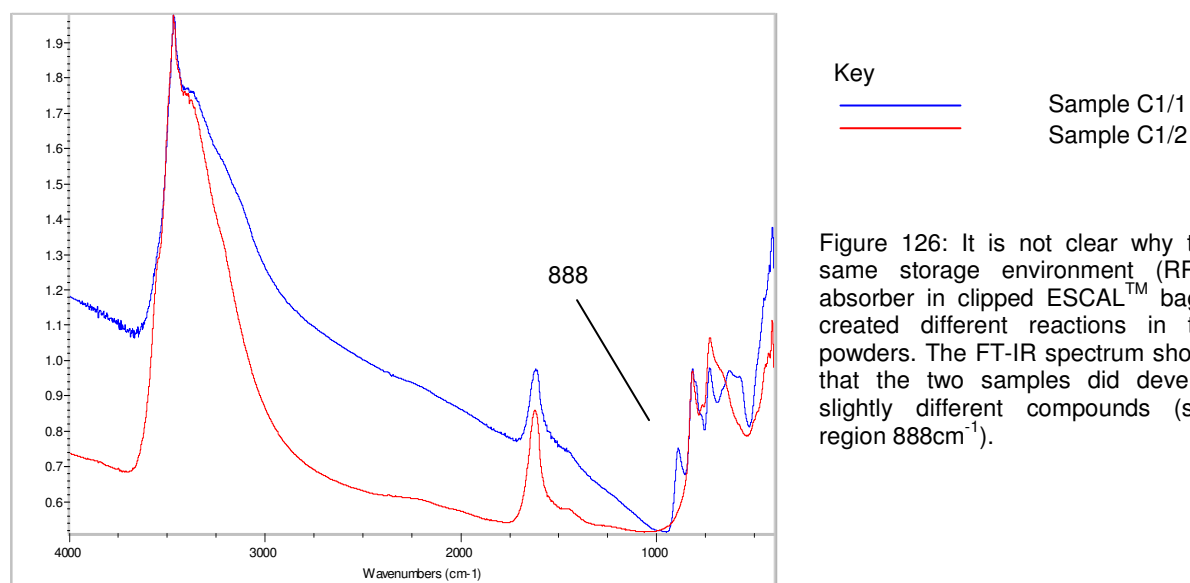


Figure 126: It is not clear why the same storage environment (RP-K absorber in clipped ESCAL<sup>TM</sup> bags) created different reactions in the powders. The FT-IR spectrum shows that the two samples did develop slightly different compounds (see region  $888\text{cm}^{-1}$ ).

X-axis: Wavenumbers ( $400 - 4000\text{cm}^{-1}$ ); Y-axis: Absorbance.

## 6.5 Relative humidity: its affect on the produced amount of akaganéite ( $\beta$ -FeOOH)

Comparing the amount of akaganéite ( $\beta$ -FeOOH) formed in groups A1 and AX1 (samples packed in ESCAL<sup>TM</sup> barrier film) showed certain differences. Group A1 (clipped bags) had formed 44% of akaganéite ( $\beta$ -FeOOH) after one month whereas group AX1 (all-sealed bags) only 14%.<sup>449</sup> This might

<sup>449</sup> Relative amount of akaganéite ( $\beta$ -FeOOH) in the potassium bromide (KBr) pellet used for Fourier-transform Infrared Spectroscopy (FT-IR).

be due to differences in the RH.<sup>450</sup> For group A1 the RH was slightly higher in the bags (35% RH) than in group AX1 (20-30% RH).<sup>451</sup> Another aspect might be the leakage of bags. The bags with clips showed a higher air exchange rate (AER) than the fully heat-sealed ones. This means more oxygen comes into the bags and is available for reactions with the powder sample.<sup>452</sup>

## 6.6 Problems encountered working with the archaeological samples

The work with 'real' material, here the archaeological nails, turned out to be difficult. Cross sections of the nails were produced in the beginning of this work to confirm the presence of chlorides in the corrosion layers. Scanning Electron Microscopy (SEM) was used for this purpose, but no conclusive results were obtained and it remained unclear if any chlorides were present in the nails.<sup>453</sup> As access to SEM was not possible after this one time, it was decided to follow the evolution in the corrosion behaviour of the nails by means of XRD and FT-IR. Both techniques turned out to need more material for sampling than was available on the nails. In the end the decision was made to base observations on visual examination. Still, only a few nails showed active corrosion (in the uncontrolled environments). This might be due to the absence or very small amount of chlorides present in the sample material as well as to the fact that the chlorides are often not directly accessible to water and oxygen. However, the need remains to test the examined storage methods with 'real' freshly excavated artifacts.

## 6.7 Transfer: from the synthetic powder samples to real archaeological iron artifacts

Akaganéite ( $\beta$ -FeOOH) is a voluminous corrosion product and its formation causes stress in the iron object to cracks, and eventually to a break-down of the object. The physical damage caused is in line with the volume expansion of akaganéite ( $\beta$ -FeOOH). This is probably the most important aspect when an object suffers from active corrosion. It has been said that for some objects even a relatively small amount of akaganéite,  $\beta$ -FeOOH (1% by weight) in an archaeological iron could cause physical damage.<sup>454</sup> The more akaganéite ( $\beta$ -FeOOH) present, the more likely the damage appears.

As could be seen testing the synthetic powder mixture, akaganéite ( $\beta$ -FeOOH) appeared very quickly when exposing the samples to air and moisture.<sup>455</sup> This probably means that on excavation the first hours and days are crucial for efficient packaging, as oxygen and moisture get access to the active species in the excavated iron objects and this abruptly provokes corrosion reactions within the objects.

<sup>450</sup> The synthetic powder samples have an ability to pick up water vapour.

<sup>451</sup> As the moment of packing was not the same, the RH on the day the tests were set up was different and this influenced the initial RH in the bags. Readings were done with humidity-indicating strips, and at the end of a test period RH was measured with a portable RH-meter.

<sup>452</sup> The powder samples react with the oxygen present and depletion in oxygen in the ESCAL<sup>TM</sup> bags without an oxygen absorber was detectable over the test period.

<sup>453</sup> For the samples from the site in the canton of Fribourg, mainly magnetite ( $\text{Fe}_3\text{O}_4$ ) was detected, whereas for the samples from Vindonissa goethite ( $\alpha$ -FeOOH) was dominant as a corrosion product.

<sup>454</sup> Personal communication with David Thickett, English Heritage, London, 25/06/2006; THICKETT D., ODLYHA M., 2005, p565-571.

<sup>455</sup> The powder mixture of iron (Fe) and iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) was exposed to 52% RH and akaganéite ( $\beta$ -FeOOH) formed after a short period of one day.

Consider an iron object that weighs 100g and initially has 1g of iron chloride solution in it. If this solution fully converts upon exposure to air and moisture to form akaganéite ( $\beta$ -FeOOH), then damage would be expected and has been observed at these levels. If we consider our synthetic powder mixture and say that out of 100g initial mixture (that would correspond to the iron chloride solution in our fictive object) formed 1g akaganéite ( $\beta$ -FeOOH) in the tests, we might say that under the same conditions of storage, our iron object would have formed 0.01g of akaganéite ( $\beta$ -FeOOH). The best storage methods formed between 0.1 and 0.7g akaganéite ( $\beta$ -FeOOH) in the powders, which is even less and probably can be considered to present a very low risk of damage.

However, further research is needed to define critical and minimal amounts of akaganéite ( $\beta$ -FeOOH) causing damage to the archaeological iron artifacts.

## 7 POSSIBLE APPLICATIONS

This chapter shows a possible application of the use of anoxic enclosures on a large scale referring to the work carried out at the Natural History Museum (NHM) in London. A second part goes into details comparing the two tested storage methods on their costs.

### 7.1 A related case study: The Natural History Museum London

The Natural History Museum (NHM) Palaeontology Department in London has a collection of nine million specimens. Many of these objects are subject to deterioration by oxidation (e.g. pyrite specimens, see chapter 3.2.1). For the past three years, the NHM has carried out research into anoxic storage at the Palaeontology Department.<sup>456</sup> Using anoxic storage 8,000 – 10,000 highly delicate specimens are to be packed and preserved for the future. This would avoid expensive treatments, which often have to be repeated when objects prove instable. Oxygen-free storage seems for many specimens a safer way of long-term preservation. The NHM plans to pack pyrite, amber, meteorite and a few organic specimens in anoxic enclosures.

The project is to pack objects using the RP-System™ from Mitsubishi Gas Chemical Company. The bags are made of ESCAL™ barrier film and the oxygen absorbers RP-K and RP-A are used. Sometimes, the absorber is taken out of its sachet and pillow-like containers formed, which give the specimen a foothold. Monitoring of the oxygen level in the bags is carried out by placing a ruthenium sensor (SensiSpot)<sup>457</sup> in the enclosure and taking measurements with the 450GSS Oxygen Analyser yearly.<sup>458</sup> The packing of the collection should take two to three years. If afterwards a specimen has to undergo research (e.g. CAT scans, Computerised (Axial) Tomography, a technique often used by the researchers at the NHM), this can be done while leaving it in its enclosure, as it has no effect on the analysis.

The NHM also uses temporary anoxic enclosures (bags closed with clips) for work on site with oxidising materials. Within twenty-four hours the so packed specimens are brought from the field to the laboratory for long-term storage.

Even though the financial investment for materials is heavy in the beginning<sup>459</sup> (and packing needs staff), it becomes small in the long term, as enclosures and absorbers do not have to be replaced very often.<sup>460</sup> Assessment by direct oxygen monitoring is carried out every year and as soon as higher oxygen levels are detected in a bag, the absorber can be renewed.

However, Chris Collins, head of conservation at the NHM has some concerns. He would like to obtain a more stable barrier film than ESCAL™ in which he fears the instability in the long term of the

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<sup>456</sup> The department of Mineralogy has been using anoxic enclosures for some specimens for the last six years.

<sup>457</sup> Gas Sensor Solutions Ltd., Ireland.

<sup>458</sup> Gas Sensor Solutions Ltd. will soon bring a handheld oxygen analyser on the market, which will make it easy for the curators to walk through the collection and take measurements.

<sup>459</sup> The cost for the setup of anoxic enclosures and all materials (oxygen monitoring, heat sealer, barrier film, oxygen absorbers) is estimated at approximately £15,000, this not including staff.

<sup>460</sup> The long-term expectation is to place objects into enclosures for periods up to 20 years. (Chris Collins at „The Use of Oxygen-Free Environments in the Care of Historic & Artistic Materials“, Conservation Seminar, National Museum Wales, Cardiff, 16 March 2006).

poly(vinyl alcohol) (PVAL) layer.<sup>461</sup> He pointed out that the materials used for anoxic enclosures did not come from the field of conservation but from the food industry and may not be designed for the long-term use in conservation. But already the technology seems to work and has proven efficient in the short term. The sensors (SensiSpot) used for oxygen monitoring will need some further examination, as their stability in the long term is doubted. Collins sees the fact that anoxic enclosures are cost effective in the long term (as expensive and repeated treatments can be abandoned) as very positive.



Figure 127: Specimens at the NHM are placed in acid-free boxes before these are packed in anoxic enclosures.



Figure 128: Specimens in anoxic enclosures, with bags specially designed for the NHM project.

## 7.2 Cost comparison: dry versus oxygen-free storage

An important aspect when planning storage for the short and long term is cost. Let us take a look at the two systems we examined during this research project. Costs do not only occur for materials. Monitoring is another aspect and this has to be carried out by staff that has to be paid. In this chapter we have tried to give some indications on the initial investments one has to consider if applying any of the two tested methods. In terms of cost of staff, we can only give some indications on how regularly the storage systems have to be monitored.

Let us consider dry storage first and then move to anoxic enclosures. The life-time of these two have been detailed elsewhere (chapter 5.3.5) and we refer to this data.

### 7.2.1 Dry storage using *Rondo™* boxes

The number of objects to be packed is 70 small iron finds, packed in resealable PE bags with holes and placed into a single labelled 8l box. PE foam is added into the resealable bags to protect the objects.<sup>462</sup> The monitoring consists of changing the desiccant every 19 months (see chapter 5.3.5.1).

<sup>461</sup> Chris Collins states a 20-year benchmark for ESCAL™ film (personal communication, march 2006).

<sup>462</sup> Number chosen based on packing of objects in Augusta Raurica by Maria Luisa Fernandez, Treatment laboratory for archaeological finds, Augusta Raurica, Switzerland, July 2006.

| <b>Materials</b> <sup>463</sup>                                   | <b>Cost per piece</b>  | <b>Total cost (for 70 objects)</b> |
|---|--|------------------------------------|
| Rondo <sup>TM</sup> box (8l) <sup>464</sup>                       | CHF 8.12   | CHF 8.12                           |
| Desiccant (Rubingel, 60g bags) <sup>465</sup>                     | CHF 1.18   | CHF 3.54                           |
| PE bags 100 x 125mm (Minigrip <sup>TM</sup> ) <sup>466</sup>      | CHF 0.51 (CHF 5.15 for 100 bags)   | CHF 3.60                           |
| PE foam <sup>467</sup> (thickness 3mm)                            | (Roll 380mm x 175m: CHF 69.00)<br>a) 400mm x 200mm (for covering box): CHF 0.07<br>b) 90mm x 120mm (for support in PE bag): CHF 0.03 | a) CHF 0.07<br>b) CHF 2.10         |
| Relative humidity-indicating strips <sup>468</sup> (cobalt-free). | CHF 2.00   | CHF 2.00                           |
| Label (standard for archives) <sup>469</sup> 60 x 100mm           | CHF 0.05 per label   | CHF 0.05                           |
| Total cost  |  | CHF 19.48                          |

Table 9: Cost estimations for dry storage.

This method is simple in its application and staff needs little training. The cost is low in the short term, but as silica gel has to be renewed quite frequently, it is costly over time. Staff has to be paid for monitoring and regularly changing the silica gel, which is probably the most problematic aspect with regard to this method. Museums and laboratories are often short of staff. If the silica gel does not get changed when needed, corrosion is likely to occur as the gel loses its efficiency.

### 7.2.2 Oxygen-free storage using the RP-System<sup>TM</sup>

The number of objects to be packed is again 70 small iron finds, packed individually (bag size: 150 x 250mm). Monitoring: No real numbers are available on how often one has to change the oxygen absorber if using simple bags as the use of the RP-System<sup>TM</sup> is very recent.<sup>470</sup> If double bags with oxygen absorbers are used in the outer and inner bag, replacing of absorbers in the outer bag can be done less frequently and the objects in the inner bag are not affected (see chapter 8.1).<sup>471</sup>

<sup>463</sup> Information provided by Maria Luisa Fernandez, treatment laboratory for archaeological finds, Roman town of Augusta Raurica, Switzerland, July 2006.

<sup>464</sup> Prodingen Verpackung AG, Genuastr. 15, CH-4142 Münchenstein, Switzerland.

<sup>465</sup> Available for example at: Zeochem AG, Seestrasse 108, CH-8707 Uetikon, Switzerland or Hänsseler AG, Industriestrasse 35, CH-9101 Herisau, Switzerland.

<sup>466</sup> Semadeni AG, Tägetlistrasse 35-39, Postfach, CH-3072 Ostermundigen 1, Switzerland.

<sup>467</sup> Prodingen Verpackung AG, Genuastr. 15, CH-4142 Münchenstein, Switzerland.

<sup>468</sup> Long life for art, Christoph Waller, Im Bückle 4, D-79288 Gottenheim, Germany.

<sup>469</sup> Scheitlin-Papier AG, Industriestr. 20, CH-9302 Kronbühl, Switzerland.

<sup>470</sup> Chris Collins, Natural History Museum, London, has specimens packed in ESCAL<sup>TM</sup> bags for more than ten years using RP-K oxygen absorbers and claims they are still well protected as no visual change can be observed in the objects.

<sup>471</sup> Items can be double-bagged, which makes the system last longer (personal communication with Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, 26/06/2006).

| Materials  | Cost per piece                      | Total cost <sup>472</sup> |
|--|-------------------------------------|---------------------------|
| Heat sealer (Model Joke SZ 380/8) <sup>473</sup>                 | CHF 2025.00                         | CHF 2025.00               |
| ESCAL <sup>TM</sup> barrier film <sup>474</sup>                  | 1m = CHF 23.90 (10m = CHF 199.20)   | 6m = ~CHF 143.40          |
| RP-3A oxygen absorber <sup>475</sup>                             | CHF 1.38 (100 sachets = CHF 138.65) | CHF 97.05                 |
| Relative humidity-indicating strips <sup>476</sup> (cobalt-free) | CHF 1.59                            | CHF 111.60                |
| GSS450 Oxygen Analyser <sup>477</sup>                            | CHF 5654.00                         | CHF 5654.00               |
| SensiSpot (sensor) <sup>478</sup>                                | CHF 0.25                            | CHF 17.50                 |
| Clips <sup>479</sup> 500mm (cut into half)                       | CHF 9.50 (10 Clips = CHF 89.25)     | CHF 315.60                |
| Total cost for all   |                                     | CHF 8364.15               |

Table 10: Cost estimations for dry anoxic storage.

With this method, the initial investment is very considerable in terms of materials as well as training of the staff (as packing takes some time to be learned properly). Once the objects are packed, they don't have to be re-opened for a long time to change oxygen absorbers.<sup>480</sup>

The cost of the materials seems very high. But we have to take into consideration that the machines are amortised with each bag produced. If we take a life-time of the machines of ten years and pack 1000 objects each year, the additional cost will be of only CHF 0.7 per bag.

<sup>472</sup> Usually costs get lower when ordering big quantities of materials.

<sup>473</sup> Long life for art, Christoph Waller, Im Bückle 4, D-79288 Gottenheim, Germany.

<sup>474</sup> Ibid.

<sup>475</sup> Ibid.

<sup>476</sup> Ibid.

<sup>477</sup> Gas Sensor Solutions Ltd., The Invent Centre, Glasnevin, Dublin, Ireland.

<sup>478</sup> Ibid.

<sup>479</sup> Conservation by Design Ltd, Bedford, United Kingdom.

<sup>480</sup> No precise indication on this time period is available. Most people who work with the RP-System<sup>TM</sup> claim it stays protective and active for 10 – 20 years.



## 8 CONCLUSIONS

### 8.1 Conclusions

Best results in prevention of active corrosion (akaganéite,  $\beta$ -FeOOH) in the submitted samples were observed using either dry storage or oxygen-free dry storage. The experimentation took five-and-a-half months, so the long-term conclusions have to be made with respect to the rather short test period. However, it seems that the first moments after excavation are crucial for the prevention of active corrosion. Therefore the storage method needs to be efficient in this first period after excavation and maintained afterwards.

The analytical techniques used in this work showed to be complementary. XRD showed to be a good tool to confirm the presence of main crystalline compounds in a mixture. But it was only possible to detect a compound in the mixture when present in amounts above 10%. FT-IR appeared to be most useful for the detection of akaganéite ( $\beta$ -FeOOH) even if only present in very small amounts. Raman spectroscopy was best used to confirm results from both other techniques and to obtain clarity upon the different compounds in the mixture.

Dry storage seems to be most efficient if packing objects in resealable PE bags that are left opened and placing them into an adequate plastic box.<sup>481</sup> Dry silica gel can be used as a desiccant.

Dry storage in the cold does not seem to bring advantages over simple dry storage. Furthermore, there is always a risk that the refrigerator breaks down. Placing objects into the cold (when no RH control is available) seems to produce less akaganéite ( $\beta$ -FeOOH) than leaving them at room temperature. Still, it has to be considered, that cold storage is energy-consuming and costly.

Applying dry storage needs little training. The method is cheap to set up but staff needs to replace silica gel in the boxes regularly to keep the dry climate (depending on the plastic boxes this can be every eight to nineteen months).

Oxygen-free storage is most efficient when using the RP-A oxygen absorber (anoxia and dryness) and fully sealed bags (made from ESCAL<sup>TM</sup> high barrier film). No akaganéite ( $\beta$ -FeOOH) forms. Using the oxygen absorber RP-K, which does not influence the RH, seems to pose some problems, as corrosion reactions are not stopped. It could be the time between packing the samples and the moment when all oxygen is absorbed by the absorber which is of importance. This oxygen lowering process can take up to three days. If the RH is lowered by the RP-A absorber, this takes only hours and can stop reactions even before the oxygen content is down to zero. The RP-K absorber does not lower the RH and the remaining moisture might react with the remaining oxygen up to the moment that the oxygen level is low enough.

Setting up oxygen-free storage using the RP-System<sup>TM</sup> is costly and in the beginning needs some training. But once objects packed, they can stay in their enclosures for a long time without having to

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<sup>481</sup> From the three tested trademarks Rondo<sup>TM</sup>, Stewart<sup>TM</sup> and Curver<sup>TM</sup>, the first one showed the best results in terms of life-time of the silica gel (it also had the smallest air exchange rate, AER).

change the oxygen absorbers. The absorbers are said to remain active for about twenty years.<sup>482</sup> The weak factor is the barrier film used (heat-sealed or clipped), which can never be 100% tight, even if air exchange rates (AER) are extremely low. And the plastic barrier film will itself degrade over the time. One could consider to double bag the objects, using oxygen absorbers both in the inner and outer bag. The absorber in the outer bag could then easily be changed every few years to prevent external oxygen entering the inner bag. Oxygen access to the inner bag would also be lowered, which increases its properties.<sup>483</sup>

We have tested two possibilities of making anoxic enclosures. One uses a clip to close the last side after packing the object, the other bag is fully heat-sealed. Both approaches perform well in the short term. Considering that the bag with the clip has a higher air exchange rate, AER (due to air coming through the clip) than the fully heat-sealed one, the first method should not be used for long-term storage. The efficiency of the oxygen absorber will be exhausted much quicker than in the fully heat-sealed bag. The clips are a good option for on-site packaging, as bags can be prepared in advance and objects only have to be placed into them before closing. No heat-sealing equipment has to be available on site. Once the objects arrive in the laboratory, they can then be packed definitely for the long term.

Conservators often mention that oxygen-free storage is not adapted for archaeological artifacts because the objects have to be studied, examined and drawn and therefore taken off their enclosures. The use of ESCAL<sup>TM</sup> barrier film allows examination through the bag to a certain extent, but does not seem fully satisfactory upon that point. Still, packing objects using anoxic enclosures remains very efficient in the prevention of active corrosion and the loss of the object. We could therefore consider packing our excavated iron finds on site using dry oxygen-free storage. This would instantly protect the artifacts and in the same time the drying process would start. On arrival in the laboratory, when examination and drawing of the objects starts, a switch to dry storage could be opted for, when dealing with objects susceptible to be on display or often examined. For objects that return to the stores for many years, dry oxygen-free storage is a real option, as little monitoring is requested.

The efficiency of dry storage and its easiness in application was proved with this work. It remains a very good option for storage of archaeological iron even if very regular monitoring and change of silica gel has to be considered.

Two domains remain problematic. One is the packaging of very large artifacts. Often plastic storage containers are not big enough. Producing ESCAL<sup>TM</sup> barrier film bags of big sizes is possible and one can consider using either dry silica gel or oxygen absorbers for conditioning. The second domain concerns objects with organic remains. They have to be handled with care. If the remains are in a mineralized state, dry oxygen-free storage can be considered. But if they are not mineralized, this approach cannot be recommended because of the drying out of the artifact. We have tested the oxygen absorber RP-K that does not affect the RH to see whether this could be an option for storage of iron with organic remains. This absorber has to be studied further for this purpose as the results still

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<sup>482</sup> Personal communication with Jerry Shiner, Microclimate Technologies International / Keepsafe Systems, 26/06/2006.

<sup>483</sup> Ibid.

raise questions about the prevention of corrosion of the iron. For these artifacts damp packing to imitate burial conditions might still be the most adequate method to be used for the moment.

## **8.2 Perspectives and further work**

For iron artifacts there is still no stabilisation treatment 100 % efficient in the prevention of active corrosion. So we can understand the approach of some conservators who say it is still better to have a good storage method and wait for the development of better treatment methods. This approach can also come from the conviction that it is primordial to leave all traces on the object and that treatments would alter the information contained within the object. If we choose to follow the path of preventive conservation there remains work to do when talking about storage methods. This project has shown that prevention of active corrosion can be achieved by acting on the RH and on the oxygen level surrounding the artifact. The materials used for dry storage are well known and satisfactorily used in conservation. This is not the case for materials used with anoxic storage. Here we need to find cheaper materials that can be adjusted to the field of conservation and meet our needs. Better and cheaper high barrier films would be welcome. The monitoring systems for oxygen levels within enclosures need further development and study. Once we are able to measure the oxygen percentage through our enclosures with satisfactory results the application of anoxic storage will become more interesting. Also some research needs to be carried out to determine exact life-times for anoxic storage by finding an accurate way to measure the air exchange rate (AER) of the enclosures (an adequate tracer gas needs to be found as the use of carbon dioxide, CO<sub>2</sub>, showed to be problematic). This is important if we want to take into consideration the leakage through seals and film of the bags. Basing life-time calculations on the oxygen transmission rate (OTR) is questionable, as the factor of leakage is neglected (see chapter 5.3.5.2). The existing tools need to be further developed and adjusted to the use in the museum environment. The oxygen absorber RP-K from the RP-System™ tested in the present work needs further understanding regarding the corrosion products that can be formed in the packed material.

Storing archaeological iron with the prevention of active corrosion is possible: the methods exist and if carried out correctly, the artifacts can be conserved for the long term. We therefore need to put a lot of effort in the monitoring of our collections and change materials when necessary to guarantee the long-term survival of our collections.

## 9 REFERENCES

### 9.1 Note on illustrations, figures and tables

Information on the contents and origin of the illustrations, figures and tables is given in the captions. If no source is mentioned, the illustrations, figures and tables were created by the author. If another source was used, this is indicated in brackets.

### 9.2 Cited references

ABE Y., KONDOH Y.

Oxygen absorbers. In: Aaron L. Brody (Ed.). Controlled/modified atmosphere/vacuum packaging of foods. Food & Nutrition Press, Inc. Trumbull, Connecticut 06611, USA, 1989, p149-158.

AGELESS®: Oxygen Absorber preserving product purity, integrity and freshness. MGC Mitsubishi Gas Chemical Company, Inc., 1994.

AILOR W. H.

Handbook of Corrosion Testing and Evaluation. Wiley, New York, 1971.

ARGEMI M., GONZALO D., PUGES M., MASPOCH L., MOUREY W., ALONSO M.

Long-term conservation of heritage in transformed atmospheres. In : Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux. Draguignan-Figanières, France, 27 – 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p245-247.

ARGO J.

The treatment of corrosion with amines. In: Conservation News. United Kingdom Institute for Conservation of Historic and Artistic Works, Vol. 17, 1982, p7-9.

ARRHENIUS O.

Conservation of old rusty iron objects and protection against further destruction. In: Conservation of old rusty iron objects: reduction of rust with hydrogen gas. Swedish Corrosion Institute, Bulletin No. 61E, 1973, p2-7.

ARRHENIUS O., BARKMAN L., SJÖSTRAND E.

Conservation of old rusty iron objects: reduction of rust with hydrogen gas. Swedish Corrosion Institute, Bulletin No. 61E, 1973.

ASHLEY-SMITH J., MONCRIEFF A. J.

Experience with Silica Gel for Controlling Humidity in Showcases. In: Preprints of the 7<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Copenhagen, 10 – 14 September 1984, International Council of Museums, 1984, p84.17.1-5.

BAILEY S. W., BANKS H. J.

A Review of Recent Studies of the Effects of Controlled Atmospheres on Stored Product Pests. In: J. Shejbal (Ed.). Controlled Atmosphere Storage of Grains. Developments in Agricultural Engineering 1. An International Symposium held from 12 – 15 May 1980, Castalgandolfo, Italy, Elsevier Scientific Publishing Company, 1980, p101-118.

BARKMAN L.

Corrosion and Conservation of Iron. In: Conservation in Archaeology and the Applied Arts. Preprints of the Contributions to the Stockholm Congress, 2-6 June 1975, IIC, London, 1975, p169-172.

BECKER H.

RP System™, ein neues Verpackungsmaterial für korrosionsempfindliche Materialien. In: Arbeitsblätter für Restauratoren. Heft 1, Gruppe 21, Magazinierung, 1999, p72-76.

BERNAL J. D., DASGUPTA D. R., MACKAY A. L.

The oxides and hydroxides of iron and their structural inter-relationships. In: Clay Minerals Bulletin. Vol. 4, 1959, p15-30.

BORN H.

Bergung und Aufbewahrung als wichtige Konservierungsvoraussetzung bei Metallfunden. In: Arbeitsblätter für Restauratoren. Heft 2, Gruppe 20, Bergungstechnik, 1982, p54-61.

BOUCHARD M., SMITH D. C.

Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass. In: Spectrochimica Acta. Part A, Vol. 59, 2003, p2247-2266.

BROKERHOF A. W.

Low-oxygen treatment and solarisation of the Probona iconostasis: Alternative pest control methods in the field. In: Bridgland J. (Ed.). Preprints of the 12<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Lyon, 29 August – 3 September 1999, International Council of Museums, James & James (Science Publishers) Ltd., Lyon, 1999, p14-20.

BROMELLE S.

The Russell and Abney Report on the Action of Light on Water Colours. In: Studies in Conservation. Vol. 9, No. 4, 1964, p140-151.

BULST W. A.

L'Oro del Ghiberti. Restauri alla Porta del Paradiso. In: Kunstchronik: Monatsschrift für Kunstwissenschaft, Museumswesen und Denkmalpflege. Zentralinstitut für Kunstgeschichte in München, 39. Jahr, Heft 4, April 1986, p125-126.

CALVER A., HOLBROOK A., THICKETT D., WEINTRAUB S.

Simple methods to measure air exchange rates and detect leaks in display and storage enclosures. In: Verger I. (Ed.). Preprints of the 14<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, The Hague, 12 – 16 September 2005, James & James (Science Publishers) Ltd., The Hague, 2005, p597-609.

CARRIÓ V., STEVENSON S.

Assessment of materials used for anoxic microenvironments. In: Townsend, J. H., Eremin, K., Adriaens A. (Eds.). Conservation Science 2002. Papers from the Conference held in Edinburgh, Scotland, 22 – 24 May 2002, Archetype Publications Ltd., London, 2003, p32-38.

CHILDS C. W., GOODMAN B. A., PATERSON E., WOODHAMS F. W. D.

The Nature of Iron in Akaganéite ( $\beta$ -FeOOH). In: Australian Journal of Chemistry. Vol. 33, 1980, p15-26.

CHRISTENSEN B. B.

Obsolete Method of Iron Conservation? In: Archaeologica Lundensia. Investigationes de Antiquitatibus Urbis Lundae, III, Res Medievales, Ragnar Blomqvist, Kulturhistoriska Museet, Lund, 1968, p299-301.

COLLINS C.

Barrier Films. In: Geological Conservation Unit, University of Cambridge, *unpublished*, 1999, p1-11.

Conservation of Iron. Clarke R. W., Blackshaw S. M. (Eds.). National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982.

CORNELL R. M., SCHWERTMANN U.

The Iron Oxides. Structure, Properties, Reactions, Occurrence and Uses. VCH Verlagsgesellschaft, Weinheim, Germany, 1996.

CRONYN J. M.

The Elements of Archaeological Conservation. Routledge, London, 1990.

CURISTER S.

Control of Air in Cases and Frames. In: Technical Studies in the Field of Fine Arts. Vol. 5, No. 2, 1936, p109-116.

DANIEL V., LAMBERT F. L.

Ageless™ Oxygen Scavenger: Practical Applications. In: WAAC Newsletter. Vol. 15, No. 2, May 1993, p12-14.

DANIEL V., MAEKAWA S., PREUSSER F. D.

Nitrogen Fumigation: A Variable Alternative. In: Bridgland J. (Ed.). Preprints of the 10<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Washington, DC, 22 – 27 August, 1993, p863-867.

DANIELS V. D., PASCOE M. W., HOLLAND L.

Plasma Reactions in the Conservation of Antiquities. In: The Conservation and Restoration of Metals. Proceedings of the symposium held in Edinburgh, 30 – 31 March 1979, Scottish Society for Conservation and Restoration, 1979, p61-69.

DAY J.

Practical application of the Revolutionary Preservation (RP) System® for marcasite. In: Verger I. (Ed.). Preprints of the 14<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, The Hague, 12 – 16 September 2005, James & James (Science Publishers) Ltd., The Hague, 2005, p435-441.

DE FARIA D. L. A., VENANCIO SILVA S., DE OLIVEIRA M. T.

Raman Microspectroscopy of Some Iron Oxides and Oxyhydroxides. In: Journal of Raman Spectroscopy. Vol. 28, 1997, p873-878.

DEGRIGNY C., DURIVAUT L., CHEVALIER B., DARRIET B.

Réalisation et caractérisation d'éprouvettes base fer simulant l'altération des objets archéologiques. PCR 'Fer chlorures', Institut de Chimie de la Matière Condensée de Bordeaux, Arc'Antique Laboratoire de Restauration et de Recherche sur les objets d'art de Nantes, Septembre 1999.

EICHHORN P.

Eisenkonservierung und –restaurierung am Württembergischen Landesmuseum. In: Arbeitsblätter für Restauratoren. Heft 1, Gruppe 1, Eisen, 1975, p74-80.

ELERT K., MAEKAWA S.

Anwendung von Sauerstoffabsorbieren in Museen. In: Restauero. Zeitschrift für Kunsttechniken, Restaurierung und Museumsfragen. Heft 5, 2000, p348-354.

EMMERLING J.

Die Verwendung von Komplexon III in der Museumswerkstatt. In: Arbeitsblätter für Restauratoren. Heft 1, Gruppe 16, Materialien, 1969, p3-6.

ENTWISTLE R. M.

The More Cheese the Stronger It Is: The Life and Work of George Nathan Maynard. In: Oddy A., Smith S. (Eds.). Practice – Future Prospects. The British Museum Occasional Paper. No. 145, London, 2001, p67-73.

ERIKSEN E., THEGEL S.

Conservation of Iron Recovered from the Sea. Tojhusmuseets Skrifter 8, Copenhagen, 1966.

ERSFELD J., BLECK R.-D.

Zum Problem der Entsalzung metallener Fundobjekte. In: Restaurierung und Museumstechnik. Museum für Ur- und Frühgeschichte Thüringens, Nr. 4, Weimar, 1981, p23-61.

EVANS U. R.

An Introduction to Metallic Corrosion. Edward Arnold Ltd., London, 1948.

EVANS U. R.

The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications. Edward Arnold Ltd., London, 1960.

EVANS U. R.

The Corrosion of Metals. Edward Arnold Ltd., London, 1924.

EVANS U. R., TAYLOR C. A. J.

Critical Humidity for Rusting in the Presence of Sea Salt. In: British Corrosion Journal. University of Cambridge, Vol. 9, No. 1, Cambridge, 1974, p26-28.

FEITKNECHT W., GIOVANOLI R., MICHAELIS W., MÜLLER M.

Über die Hydrolyse von Eisen(III)Salzlösungen. I. Die Hydrolyse der Lösungen von Eisen(III)chlorid. In: Helvetica Chimica Acta. Vol. 56, Nr. 8, 1973, p2847-2856.

FERRETTI M.

Scientific Investigations of Works of Art. ICCROM – International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, 1993.

FRANCE-LANORD A.

La conservation du casque mérovingien de Baldenheim. In: Cahiers d'Archéologie et d'Histoire d'Alsace. La Société pour la Conservation des Monuments historiques d'Alsace, No. 130, 1949, p277-280.

GALLAGHER K. J.

The Atomic Structure of Tubular Subcrystals of  $\beta$ -Iron (III) Oxide Hydroxide. In: Nature. Vol. 226, 1970, p1225-1228.

GALLAGHER K.J., PHILLIPS D.N.

Hydrogen exchange Studies and proton transfer in beta-iron (III) oxyhydroxide. In: Chimia. Vol. 23, 1969, p465-470.

GERWIN W.

Die Korrosion archäologischer Eisenfunde im Boden – Zusammenhänge mit Bodeneigenschaften. In: Arbeitsblätter für Restauratoren. Heft 1, Gruppe 19, Naturwissenschaftliche Untersuchungen, 1999, p173-182.

GILBERG M.

Inert Atmosphere disinfestation using Ageless® Oxygen Scavenger. In: Grimstad K. (Ed.). Preprints of the 9<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Dresden, German Democratic Republic 26 – 31 August 1990, p812-814.

GILBERG M.

The effects of low oxygen atmospheres on museum pests. In: Studies in Conservation. Vol. 36, 1991, p93-98.

GILBERG M.

The Storage of Archaeological Iron under Deoxygenated Conditions. In: Newsletter: Metals Working Group. ICOM Committee for Conservation, No.1, July 1, 1985, p3.

GILBERG M., GRATAN D.

Oxygen-free Storage using Ageless Oxygen Absorber. In: Preventive Conservation: Practice, Theory and Research. Preprints of the Contributions to the Ottawa Congress, 12 – 16 September 1994, International Institute for Conservation of Historic and Artistic Works, 1994, p177-180.

GILBERG M. R., SEELEY N. J.

The alkaline sodium sulphite reduction process for archaeological iron: a closer look. In: Studies in Conservation. Vol. 27, No. 4, November 1982, p180-184.

GILBERG M. R., SEELEY N. J.

The Identity of Compounds Containing Chloride Ions in Marine Iron Corrosion Products: A Critical Review. In: Studies in Conservation. Vol. 26, 1981, p50-56.

GREIFF S., BACH D.

Eisenkorrosion und Natriumsulfidentsalzung: Theorie und Praxis. In: Arbeitsblätter für Restauratoren. Heft 2, Gruppe 1, Eisen, 2000, p319-339.

HANSEN E. F.

Protection of Objects from Environmental Deterioration by Reducing Their Exposure to Oxygen. In: Shin Maekawa (Ed.). Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998, p16-25.

HÖPFNER M.

Passive Konservierung grosser Mengen archäologischer Eisensfunde. In: Arbeitsblätter für Restauratoren. Heft 2, Gruppe 21, Magazinierung, 1999, p77-82.

JAKOBSEN T.

Iron Corrosion Theories and the Conservation of Archaeological Iron Objects in the 19<sup>th</sup> Century with an Emphasis on Scandinavian and German Sources. In: Daniels V (Ed.). Early Advances in Conservation. British Museum Occasional Paper. No. 65, Department of Conservation, London, 1988.

KEENE S., ORTON C.

Stability of Treated Archaeological Iron: an Assessment. In: Studies in Conservation. Vol. 30, 1985, p136-142.

KELLER P.

Vorkommen, Entstehung und Phasenumwandlung von  $\beta$ -FeOOH in Rost. In: Werkstoffe und Korrosion. Vol. 20, 1969, p102-108.

KELLER P.

Eigenschaften von  $(\text{Cl, F, OH})_{<2}\text{Fe}_8(\text{O,OH})_{16}$  und Akaganéit. In: Neues Jahrbuch für Mineralogie. Abhandlungen. Band 113, Heft 1, Stuttgart, 1970, p29-49.

KENTTÄMAA M.

Das elektrolytische Reinigungsverfahren bei der Konservierung von im Boden gefundenen Metallgegenständen. In: Suomen Muinaismuistoyhdistyksen Aikakauskirja. Finska Fornminnesföreningens Tidskrift. XLII, Helsinki, 1938, p3-30.

KISHAN H., MAEKAWA S.

Preservation of the Original Documents of the Constitution of India. In: Maekawa S. (Ed.). Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998, p62-67.

KNIGHT B.

A Review of the Corrosion of Iron from Terrestrial Sites and the Problem of Post-Excavation Corrosion. In: The Conservator. No. 14, 1990, p37-43.

KNIGHT B.

The Stabilisation of Archaeological Iron: Past, Present and Future. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). Metal 95. Proceedings of the International Conference on Metals Conservation. Semur en Auxois, 25 – 28 September 1995, James & James (Scientific Publishers) Ltd., 1997, p36-40.

KNIGHT B.

Why do some iron objects break up in store? In: Clarke R. W., Blackshaw S. M. (Eds.). Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p50-55.



KRAUSE E.

Ein neues Verfahren zur Conservirung der Eisen-Alterthümer. In: Zeitschrift für Ethnologie. Organ der Berliner Gesellschaft für Anthropologie, Ethnologie und Urgeschichte, Vierzehnter Band, Berlin, 1882, p533-538.

KREFTING A.

Om nogle Metaller Oxydation ved noitrale Saltes Medvirken. In: Christiania Videnskabs-Selskabs Forhandling for 1892. No. 16, p3-13.

KÜHN H.

The Effect of Oxygen, Relative Humidity and Temperature on the Fading Rate of Watercolors. Reduced Light-Damage in a Nitrogen Atmosphere. In: Thomson G. (Ed.). Preprints of the Contributions to the London Conference on Museum Climatology. London, 18 – 23 September 1967, The International Institute of Conservation of Historic and Artistic Works, 1967, p79-85.

LAMBERT F. L., DANIEL V., PREUSSER F. D.

The Rate of Absorption of Oxygen by Ageless<sup>TM</sup>: the Utility of an oxygen Scavenger in Sealed Cases. In: Studies in Conservation. Vol. 37, 1992, p267-274.

Light and Humidity: Safeguarding Historic Collections. Short Course Programme, *unpublished*, English Heritage, London, 1 – 3 November 2004, p22.

LOCKETT K., MCKENZIE B.

Anoxic framing investigations at Tate to date. In: Rayner J., Kosek J. M., Christensen B. (Eds.). Art on Paper: Mounting and Housing. Archetype Publications Ltd., The British Museum, London, 2005, p67-74.

MACDONALD WELCH S.

Open-minded storage: a box-maker's perspective on housing art on paper. In: Rayner J., Kosek J. M., Christensen B. (Eds.). Art on Paper: Mounting and Housing. Archetype Publications Ltd., The British Museum, London, 2005, p42-47.

MACKAY A. L.

β-Ferric Oxyhydroxide. In: Mineralogical Magazine. Vol. 32, No. 250, 1960, p545-557.

MACKAY A. L.

β-Ferric oxyhydroxide – akaganéite. In: Mineralogical Magazine. Vol. 33, 1962, p270-280.

MC PHAIL D., LAM E., DOYLE A.

The Heat Sealing of ESCAL® Barrier Films. In: The Conservator. No. 27, 2003, p96-104.

MAEKAWA S. (Ed.) (1998 a)

Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998.

MAEKAWA S. (1998 b)

Conservation of the Royal Mummy Collection at the Egyptian Museum. In: Maekawa S. (Ed.). Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998, p10-14.

MAEKAWA S. (1998 c)

Design and Construction of the GCI's Hermetically Sealed Display and Storage Case. In: Maekawa S. (Ed.). Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998, p40-54.

MAEKAWA S., ELERT K.

Large-scale Disinfestation of Museum Objects using Nitrogen Anoxia. In: Bridgland J. (Ed.). Preprints of the 11<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Edinburgh, Scotland, 1 – 6 September 1996, James & James (Science Publishers) Ltd., 1996, p48-53.

MAEKAWA S., ELERT K.

The Use of Oxygen-Free Environments in the Control of Museum Insect Pests. Tools for Conservation, The Getty Conservation Institute, Los Angeles, 2003.

Mapcheck Instruction Manual. Systech Instruments Ltd., 07/03/01.

MATHIAS C.

Examination of the Interaction Between Ferrous Metals and the Archaeological Burial Environment for a Seventeenth-Century Plantation Site. In: Parisi C. (Ed.). Proceedings of the 6<sup>th</sup> International Conference on "Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage". Rome, 17-20 May 1999, Italian Society for Non-Destructive Testing Monitoring Diagnostics, Ministry of Cultural Heritage and Activity, Central Institute for Restoration, Vol. 3, Rome, 1999, p1841-1855.

MATHIAS C., RAMSDALE K., NIXON D.

Saving archaeological iron using the Revolutionary Preservation System. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4-8 October 2004, p28-42.

MEIER M., TEGGE C.

Verpackung in Stickstoffgas – eine neue Methode zur Lagerung von archäologischen Funden. In: Berichte zur Denkmalpflege Niedersachsen. 16. Jahrgang, Heft 4, 1996, p148-151.

MURAD E., BISHOP J. L.

The infrared spectrum of synthetic akaganéite,  $\beta$ -FeOOH. In: The American Mineralogist: journal of the Mineralogical Society of America. Vol. 85, 2000, p716-721.

NEFF D., DILLMANN P., BELLOT-GURLET L., BERANGER G.

Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system. In: Corrosion Science. Vol. 47, 2005, p515-535.

NICHOLSON C., RITZENTHALER M. L.

The Declaration of Independence, the United States Constitution and Bill of Rights: scientific basis and practice of encasement. In: Rayner J., Kosek J. M. and Christensen B. (Eds.). Art on Paper: Mounting and Housing. Archetype Publications Ltd., The British Museum, London, 2005, p75-80.

NORTH N. A.

Conservation of metals. In: C. Pearson (Ed.). Conservation of Marine Archaeological Objects. Butterworth & Co., 1987, p207-232.

NORTH N. A.

Corrosion products on marine iron. In: Studies in Conservation. Vol. 27, No. 2, 1982, p75-83.

NORTH N. A., PEARSON C. (1975 a)

Alkaline sulfite reduction treatment of marine iron. In: Preprints of the 4<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Venice, 13 – 18 October 1975, International Council of Museums, 1975, p75/13/3.1-14.

NORTH N. A., PEARSON C. (1975 b)

Investigations into methods for conserving iron relics recovered from the sea. In: Conservation in Archaeology and the Applied Arts. Preprints of the Contributions to the Stockholm Congress, 2 – 6 June 1975, IIC, London, 1975, p173-181.

NORTH N. A., PEARSON C.

Washing Methods for Chloride Removal from Marine Iron Artifacts. In: Studies in Conservation. Vol. 23, 1978, p174-186.

NUTTGENS F., TINKER Z.

The Conservation of Rubberised Textiles: Two Case Histories. In: The Conservator. No. 24, 2000, p24-38.

ODDY W. A., HUGHES M. J.

The Stabilization of 'Active' Bronze and Iron Antiquities by the Use of Sodium Sesquicarbonate. In: *Studies in Conservation*. Vol. 15, 1970, p183-189.

ORGAN R. M.

The Safe Storage of Unstable Glass. In: *Museums Journal*. Vol. 56, February 1957, p265-272.

PLENDERLEITH H. J.

The Conservation of Antiquities and Works of Art: Treatment, Repair, and Restoration. London Oxford University Press, 1956.

POLLARD T.

An Investigation into the Use of *Escal®* in Anoxic Enclosures. Major Project Report, *unpublished*, London, May 2006.

POST J. E., BUCHWALD V. F.

Crystal structure refinement of akaganéite. In: *American Mineralogist*. Vol. 76, No.1 and 2, 1991, p272-277.

POST J. E., HEANEY P. J., VON DREELE R. B., HANSON J. C.

Neutron and temperature-resolved synchrotron X-ray powder diffraction study of akaganéite. In: *American Mineralogist*. Vol. 88, No. 1, 2003, p782-788.

Powder Diffraction File. Alphabetical Indexes: Inorganic Phases. Sets 1-44. International Centre for Diffraction Data, Pennsylvania, USA, 1994.

PURINTON N., IRVING J.

Argon-filled containers for the display of paper. In: Rayner J., Kosek J. M. and Christensen B. (Eds.). *Art on Paper: Mounting and Housing*. Archetype Publications Ltd., The British Museum, London, 2005, p81-85.

RATHGEN F.

Die Konservierung von Altertumsfunden. II. und III. Teil: Metalle und Metallegierungen, organische Stoffe. Handbücher der staatlichen Museen zu Berlin. 2. Auflage, Berlin und Leipzig, 1924.

REBIERE J., MOUREY W., FRANCOISE J., SIDOT E.

Interaction métal-environnement : Application à des milieux confinés. In : *Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux*. Draguignan-Figanières, France, 27 – 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p248-252.

REFAIT PH., GENIN, J.-M. R.

The oxidation of ferrous hydroxide in chloride-containing aqueous media and Pourbaix diagrams for green rust I. In: *Corrosion Science*. Vol. 34, 1993, p797-819.

REGUER S.

Phases chlorées sur les objets archéologiques ferreux corrodés dans les sols: caractérisations et mécanismes de formation. Thèse, Présentée pour obtenir le grade de docteur en sciences de l'Université de Paris XI Orsay, 2005.

Available online at [www-drecam.cea.fr/1ps/TheseReguer/index.htm](http://www-drecam.cea.fr/1ps/TheseReguer/index.htm), 02/2006.

REGUER S., DILLMANN P., MIRAMBET F., BELLOT-GURLET L.

Local and structural characterisation of chlorinated phases formed on ferrous archaeological artefacts by  $\mu$ XRD and  $\mu$ XANES. In: *Nuclear Instruments and Methods in Physics Research. Article in Press*, Elsevier, 2005, p1-5.

Available online at [www.sciencedirect.com](http://www.sciencedirect.com), 11/2005.

RINUY A., SCHWEIZER F. (1982 a)

Entsalzung von Eisenfunden mit alkalischer Sulfitlösung. In: *Arbeitsblätter für Restauratoren*. Heft 1, Gruppe 1, Eisen, 1982, p160-174.

RINUY A., SCHWEIZER F. (1982 b)

Application of the alkaline sulphite treatment to archaeological iron: a comparative study of different desalination methods. In: Clarke R. W., Blackshaw S. M. (Eds.). Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p44-49.

ROSENBERG G. A.

Antiquités en fer et en bronze. Leur transformation dans la terre contenant de l'acide carbonique et des chlorures et leur conservation. Copenhagen, Gyldendalske Boghandels Sortiment, 1917.

RUST M. K., KENNEDY J. M.

The Feasibility of Using Modified Atmospheres to Control Insect Pests in Museums. Final Report Contract No. GF/RUST/89, July 1, 1989 – December 12, 1991, GCI Scientific Program Report, March 1993, The Getty Conservation Institute, 1993.

SALIN E., FRANCE-LANORD A.

Rhin et Orient: Le Fer à l'Epoque Mérovingienne. Etude Technique et Archéologique. Paris, 1943.

SALIN E., FRANCE-LANORD A.

Le Cimetière Mérovingien de Varangéville. In: De Boccard E. (Ed.). Gallia. Fouilles et Monuments Archéologiques en France Métropolitaine, Tome IV, 1946, p261-267.

SALZER T.

Zur Conservierung von Eisen-Alterthümern. In: Dr. Krause G. (Hrsg.). Chemiker-Zeitung. Central-Organ für Chemiker, Techniker, Fabrikanten, Apotheker, Ingenieure. Nr. 38, Jahrgang 11, Cöthen, Mai 1887, p574.

SCHARFF W., ARNOLD CH., GERWIN W., HUESMANN I., MENZEL K., PÖTZSCH A., TOLKSDORF-LIENEMANN E., TRÖLLER-REIMER A.

Schutz archäologischer Funde aus Metall vor immissionsbedingter Schädigung. Materialhefte zur Archäologie in Baden-Württemberg. Landesdenkmalamt Baden-Württemberg, Verband der Landesarchäologen in der Bundesrepublik Deutschland E. V., Heft 57, 2000.

SCHMIDT-OTT K.

Applications of low pressure plasma treatment at the Swiss National Museum and assessment of the results. In : Zeitschrift für Archäologie und Kunstgeschichte. Band 54, Heft 1, 1997, p45-49.

SCHMIDT-OTT K., BOISSONNAS V.

Low-pressure hydrogen plasma : an assessment of its application on archaeological iron. In: Studies in Conservation. Vol. 47, No. 2, 2002, p81-87.

SCHWEIZER F.

Stabilization of RH in exhibition cases: an experimental approach. In: Froment D. (Ed.). Preprints of the 7<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Copenhagen, 10 – 14 September 1984, International Council of Museums, 1984, p84.17.50-84.17.53.

SCHWERTMANN U., CORNELL R. M.

Iron Oxides in the Laboratory. Preparation and Characterization. WILEY-VCH, Weinheim, Second, Completely Revised and Extended Edition, 2000.

SCOTT A.

The Cleaning and Restoration of Museum Exhibits. Report upon Investigations conducted at the British Museum, Department of Scientific and Industrial Research, Bulletin No. 5, Published by His Majesty's Stationery Office, London, 1921.

SCOTT A.

The Cleaning and Restoration of Museum Exhibits. Third Report upon Investigations conducted at the British Museum, Department of Scientific and Industrial Research, London, 1926.

SCOTT A.

Deterioration and Restoration, with especial Reference to Metallic Exhibits. In: The Museums Journal. The Museums Association, Vol. 33, No. 1, London, 1933, p4-8.

SCOTT D. A.

Iron and Steel in Art: Corrosion, Colourants, Conservation. *In press*, Archetype Publications Ltd., 2006.

SCOTT D. A., SEELEY N. J.

The Washing of fragile Iron Artifacts. In: Studies in Conservation. Vol. 32, 1987, p73-76.

SEASE C.

Sir William Flinders Petrie : An Unacknowledged Pioneer in Archaeological Field Conservation. In: Oddy A. and Smith S. (Eds.). Past Practice – Future Prospects. The British Museum Occasional Paper. No. 145, London, 2001, p183-188.

SELWITZ CH., MAEKAWA S.

Inert Gases in the Control of Museum Insect Pests. Getty Conservation Institute, 1998.

SELWYN L.

Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p294-306.

SELWYN L. S., LOGAN J. A.

Stability of Treated Iron: A Comparison of Treatment Methods. In: Bridgland J. (Ed.). Preprints of the 10<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Washington, DC, 22 – 27 August, 1993, p803-807.

SELWYN L. S., SIROIS P. J., ARGYROPOULOS V.

The corrosion of excavated archaeological iron with details on weeping and akaganéite. In: Studies in Conservation. Vol. 44, No. 4, 1999, p217-232.

SHASHOUA Y.

Ageless® oxygen absorber: From theory to practice. In: Bridgland J. (Ed.). Preprints of the 12<sup>th</sup> Triennial Meeting. ICOM Committee for Conservation, Lyon, 29 August – 3 September 1999, International Council of Museums, James & James (Science Publishers) Ltd., Lyon, 1999, p881-887.

STÅHL K., NIELSEN K., JIANG J., LEBECH B., HANSON J. C., NORBY P., VAN LANSCHOT J.

On the akaganéite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artefacts. In: Corrosion Science. Vol. 45, 2003, p2563-2575.

Standards in the Museum Care of Archaeological Collections. Museums and Galleries Commission, Volume 1, London, 1992.

STOLOW N.

The Microclimate: A Localized Solution. In: Museum News. Vol. 56, No. 2, 1977, p52-63.

SURYANARAYANA C., NORTON M. G.

X-Ray Diffraction: A Practical Approach. Plenum Press, New York, 1998.

The Use of Oxygen-Free Environments in the Care of Historic & Artistic Materials. Conservation Seminar, National Museum Wales, Cardiff, 16 March 2006.

THICKETT D.

Analysis of Iron Corrosion Products with Fourier Transform Infra-red and Raman Spectroscopies. In: Proceedings of the Sixth Infrared and Raman Users Group Conference (IRUG6). Florence, Italy, March 29<sup>th</sup>-April 1<sup>st</sup>, 2004, p85-102.

THICKETT D.

Post-Excavation Changes to Archaeological Iron Objects. Characterisation and Preparation of Standard Materials. Report, *unpublished*, Birkbeck College, London, 2003.

THICKETT D., ODLYHA M.

Application of thermomagnetometry to corrosion studies of archaeological iron. In: Journal of Thermal Analysis and Calorimetry. Vol. 80, 2005, p565-571.

THICKETT D., ODLYHA M.

Assessment of Dry Storage Microenvironments for Archaeological Iron. In: The Conservation of Archaeological Materials: Current Trends and Future Directions. Postprints to the Conference held in Williamsburg, VA, Nov. 13 – 17, 2005, *Article in press*, November 2006.

THOMSON G.

Stabilization of RH in exhibition cases: hygrometric half-time. In: Studies in Conservation. Vol. 22, No. 2, 1977, p132-140.

TURGOOSE S.

Corrosion and Structure: Modelling the Preservation Mechanisms. In: Evidence Preserved in Corrosion Products: New Fields in Artifact Studies. Occasional Papers. United Kingdom Institute for Conservation of Historic and Artistic Works, No. 8, 1989, p30-32.

TURGOOSE S. (1982 a)

Post-Excavation Changes in Iron Antiquities. In: Studies in Conservation. Vol. 27, No. 3, 1982, p97-101.

TURGOOSE S. (1982 b)

The nature of surviving iron objects. In: Clarke R. W., Blackshaw S. M. (Eds.). Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p1-7.

TURGOOSE S.

Structure, Composition and Deterioration of Unearthed Iron Objects. In: Current Problems in the Conservation of Metal Antiquities. International Symposium on the Conservation and Restoration of Cultural Property, October 4 – October 6, 1989, Tokyo National Research Institute of Cultural Properties, Tokyo, Japan, 1993, p35-53.

VALENTIN N.,

Preservation of Historic Materials by Using Inert Gases for Biodeterioration Control. In: Shin Maekawa (Ed.). Oxygen-Free Museum Cases. Research in Conservation, The Getty Conservation Institute, 1998, p26-38.

VALENTIN N., LINDSTROM M., PREUSSER F.

Microbial control by low oxygen and low relative humidity environment. In: Studies in Conservation. Vol. 35, 1990, p222-230.

VEPREK S., ECKMANN CH., ELMER J. T.

Recent Progress in the Restoration of Archaeological Metallic Artifacts by Means of Low Pressure Plasma Treatment. In: Schweizer F., Villiger V. (Hrsg.). Methoden zur Erhaltung von Kulturgütern. Forschungsergebnisse aus dem nationalen Forschungsprogramm 16 des Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung, Verlag Paul Haupt Bern und Stuttgart, Bern, 1989, p171-180.

VEPREK S.

A New Method for the Restoration of Archaeological Metallic Artifacts by Means of Low Pressure Plasma Treatment: the Development and Present Status. In: Current Problems in the Conservation of Metal Antiquities. International Symposium on the Conservation and Restoration of Cultural Property, October 4 – October 6, 1989, Tokyo National Research Institute of Cultural Properties, 1993, p71-88.

VERINK E. D.

Simplified Procedure for Constructing Pourbaix Diagrams. In: Corrosion. National Association of Corrosion Engineers (NACE), Vol. 23, December, 1967, p371-373.

WATKINSON D.

An assessment of lithium hydroxide and sodium hydroxide treatments for archaeological ironwork. In: Clarke R. W., Blackshaw S. M. (Eds.). Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p28-43.

WATKINSON D., LEWIS M. T.

Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects. In: Studies in Conservation. Vol. 50, No. 4, 2005, p241-252.

WATKINSON D., LEWIS M. T.

SS Great Britain iron hull: modelling corrosion to define storage relative humidity. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p88-102.

WATKINSON D., NEAL V.

First Aid for Finds. RESCUE, The British Archaeological Trust, United Kingdom Institute for Conservation of Historic and Artistic Works (UKIC), Archaeology Section, Third Edition, London, 1998.

WIHR R.

Elektrolytische Metallentsalzung. In: Arbeitsblätter für Restauratoren. Heft 2, Gruppe 1, Eisen, 1972, p31-48.

ZUCCHI F., MORIGI G., BERTOLASI V.

Beta Iron Oxide Hydroxide Formation in Localized Active Corrosion of Iron Artifacts. In: Floyd Brown B., Burnett H. C., Chase W. T., Goodway M., Kruger J., Pourbaix M. (Eds.). Corrosion and Metal Artifacts – A Dialogue Between Conservators and Archaeologists and Corrosion Scientists. National Association of Corrosion Engineers, 1977, p103-105.

## 9.3 Communications

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THICKETT D., Conservation Scientist, English Heritage (EH), London, United Kingdom.

## 9.4 Consulted internet links

<http://carbon.cudenver.edu/public/chemistry/classes/chem4538/raman.htm>, 31/07/2006.

<http://www.cwall.de/oxygen.htm>, 14/10/2005.

<http://www.conservation-by-design.co.uk>, 29/06/2006.

<http://www.gss.ie>, 28/06/2006.

<http://www.hanwell.com/rht-bug-c.html>, 08/02/2006.

<http://www.inficon.com>, 16/11/2005.

<http://www.keepsafe.ca/escal.shtml>, 15/12/2005.

<http://www.kosi.com/raman/resources/tutorial/index.html>, 31/07/2006.

<http://www.meaco.com>, 26/06/2006.

[http://www.twi.co.uk/j32k/protected/band\\_3/ksab003.html](http://www.twi.co.uk/j32k/protected/band_3/ksab003.html), 13/02/2006.

<http://www.vaisala.com>, 29/06/2006.

## 9.5 Further reading

ABD EL HALEEM S. M., ABD EL AAL A.

Pitting Corrosion Currents on Steel in Relation to the Concentration of Inhibitive and Corrosive Anions under Natural Corrosion Conditions. In: British Corrosion Journal. Vol. 14, No. 4, 1979, p226-230.

ALEXANDER B. J., FOLEY R. T.

Corrosion Products of Iron Dissolution- Dependence on Anions in Solution. In: Corrosion. Vol. 32, No. 6, June 1976, p297-302.

ALONSO C., CASTELLOTE M., ANDRADE C.

Chloride threshold dependence of pitting potential of reinforcements. In: Electrochimica Acta. Vol. 47, 2002, p3469-3481.

ARGO J. A.

A Qualitative Test for Iron Corrosion Products. In: Studies in Conservation. Vol. 26, No. 4, 1981, p140-142.

ARGO J. A.

On the Nature of "Ferrous" Corrosion Products on Marine Iron. In: Studies in Conservation. Vol. 26, No. 1, 1981, p42-44.

ARGYROPOULOS V., ANGELINI E., DEGRIGNY C.

Innovative conservation approaches for monitoring and protecting ancient and historic metals collections from the Mediterranean Basin. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p43-52.

ARGYROPOULOS V., SELWYN L. S., LOGAN J. A.

Developing a Conservation Treatment Using Ethylenediamine as a Corrosion Inhibitor for Wrought Iron Objects Found at Terrestrial Archaeological Sites. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). Metal 95. Proceedings of the International Conference on Metals Conservation. Semur en Auxois, 25 – 28 September 1995, James & James (Scientific Publishers) Ltd., 1997, p153-158.

ASAKURA S., NOBE K.

Electrodissolution Kinetics of Iron in Chloride Solutions. In: Journal of the Electrochemical Society. Vol. 118, No. 1, 1971, p13- 22.

BARKER B. D., KENDELL K., O'SHEA C.

The Hydrogen Reduction Process for the Conservation of Ferrous Objects. In: Clarke R. W., Blackshaw S. M. (Eds.). Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p23-27.

BARKMAN L.

Corrosion and conservation of iron. In: Conservation of old rusty iron objects: reduction of rust with hydrogen gas. Swedish Corrosion Institute, Bulletin No. 61E, 1973, p14-33.



BARTOLINI M., COLOMBO B., MARABELLI M., MARANO A., PARISI C.

Non-destructive Tests for the Control of Ancient Metallic Artifacts. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). *Metal 95. Proceedings of the International Conference on Metals Conservation, Semur en Auxois, 25 – 28 September 1995*, James & James (Scientific Publishers) Ltd., 1997, p43-49.

BEAUDOIN A., CLERICE M.-C., FRANCOISE J., LABBE J.-P., LOEPER-ATTIA M.-A., ROBBIOIA L. Corrosion d'Objets Archéologiques en Fer après Déchloration par la Méthode au Sulfite Alcalin; Caractérisation Physico-Chimique et Rétraitement Electrochimique. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). *Metal 95. Proceedings of the International Conference on Metals Conservation, Semur en Auxois, 25 – 28 September 1995*, James & James (Scientific Publishers) Ltd., 1997, p170-177.

BECKER H., ROMUSSI M.

Entwicklung und Anwendungspraxis eines Schutzsystems für empfindliche Auflagerungen auf Eisenobjekten während der Plasmabehandlung. In: *Arbeitsblätter für Restauratoren. Heft 2, Gruppe 1, Eisen*, 2000, p311-318.

BERTHOLON R.

La limite de la surface d'origine des objets métalliques archéologiques. Caractérisation, localisation et approche des mécanismes de conservation. Thèse pour obtention de Doctorat en Archéologie, Université de Paris I – Pantheon-Sorbonne U.F.R. d'Art et d'Archéologie, soutenance le 20 décembre 2000.

BLACK J. W. B.

Choosing a conservation method for iron objects. In: Clarke R. W., Blackshaw S. M. (Eds.). *Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53*, London, 1982, p15.

BLACKSHAW S. M.

An appraisal of cleaning methods for use on corroded iron antiquities. In: Clarke R. W., Blackshaw S. M. (Eds.). *Conservation of Iron. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53*, London, 1982, p16-22.

BLAND P.A., KELLEY S.P., BERRY F.J., CADOGAN J. M., PILLINGER C. T.

Artificial weathering of the ordinary chondrite Allegan: Implications for the presence of Cl<sup>-</sup> as a structural component in akaganéite. In: *The American Mineralogist: journal of the Mineralogical Society of America*. Vol. 82, 1997, p1187-1197.

BOBICHON C., DEGRIGNY C., DALARD F., TRAN Q. K.

An electrochemical study of iron corrosion inhibitors in aqueous polyethylene glycol solutions. In: *Studies in Conservation*. Vol. 45, No. 3, 2000, p145-153.

BRESLE A.

The corrosion of steel and the dangerous chlorides. In: *Industrial Finishing and Surface Coatings*. Vol. 28, No. 335, 1976, p15-18.

BRIMBLECOMBE P., RAMER B.

Museum Display Cases and the Exchange of Water Vapour. In: *Studies in Conservation*. Vol. 28, 1983, p179-188.

BURKE J.

Vapor Barrier Films. In: *WAAC Newsletter*. Vol. 14, No. 2, May 1992, p13-17.

CALVER A.

The ventilation of enclosures to reduce internally generated pollutants and simple techniques to measure air exchange rates within enclosures: report on progress to date. In: *Presentation Abstracts from the 4<sup>th</sup> Meeting of the Indoor Air Pollution Working Group*. Copenhagen, 2001. Available on [http://www.iaq.dk/iap/iap2001/2001\\_06.htm](http://www.iaq.dk/iap/iap2001/2001_06.htm), 07/2006.

- CANTI M. G., DAVIS M.  
Tests and Guidelines for the Suitability of Sands to be used in Archaeological Site Reburial. In: Journal of Archaeological Science. Vol. 26, 1999, p775-781.
- CARLIN W., KEITH D., RODRIGUEZ J.  
Less is more: measure of chloride removal rate from wrought iron artefacts during electrolysis. In: Studies in Conservation. Vol. 46, No. 1, 2001, p68-76.
- CASSAR M., MARTIN G.  
The Environmental Performance of Museum Display Cases. In: Preventive Conservation: Practice, Theory and Research. Preprints of the Contributions to the Ottawa Congress, 12 – 16 September 1994, International Institute for Conservation of Historic and Artistic Works, London, 1994, p171-173.
- COLE I.S., MUSTER T. H., LAN D., GANTHER W. D.  
Some recent trends in corrosion science and their application to conservation. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p2-16.
- Comment reconnaître la corrosion active. Notes le l'ICC, Institut canadien de conservation, 9/1, 1989.
- CORNELL R. M., GIOVANOLI R.  
Transformation of akaganéite into goethite and hematite in the presence of Mn. In: Clays and Clay Minerals. Vol. 39, No. 2, 1991, p144-150.
- COSTAIN CH., LOGAN J.  
Survey of Iron Artifacts from Red Bay, Labrador, To Assess the Effectiveness of Various Iron Treatments. In: Newsletter: Metals Working Group. ICOM Committee for Conservation, No.1, July 1, 1985, p8-9.
- COSTAIN CH. G.  
Evaluation of Storage Solutions for Archaeological Iron. In: Journal of the Canadian Association for Conservation. Vol. 25, 2000, p11-20.
- CROOME H. L.  
Corrosion rate study of cannon at the Prince of Wales' fort. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p195-205.
- CULLITY B. D., STOCK S. R.  
Elements of X-Ray Diffraction. Third Edition, Prentice Hall, 2001.
- DEGRIGNY C., SPITERI L.  
Electrochemical monitoring of marine iron artefacts during their storage/stabilisation in alkaline solutions. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p315-331.
- DE GROOT I., DEGRIGNY C.  
Electrolytic stabilisation of a marine composite porthole and its framework. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p427-442.
- DERRICK M. R., STULIK D., LANDRY J. M.  
Infrared Spectroscopy in Conservation Science. Scientific Tools for Conservation, The Getty Conservation Institute, Los Angeles, 1999.
- DREWS M. J., DE VIVIES P., GONZALES N. G., MARDIKIAN P.  
A study of the analysis and removal of chloride in iron samples from the "Hunley". In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p247-260.
- EVANS U. R.  
Electrochemical mechanism of atmospheric rusting. In: Nature. Vol. 206, June 5, 1965, p980-982.

FELL V., WILLIAMS J.

Monitoring of archaeological and experimental iron at Fiskerton, England. In: Proceedings of Metal 2004. National Museum of Australia Canberra ACT, 4 – 8 October 2004, p17-27.

FENN J. D., FOLEY K.

Passivation of iron. In: Conservation in Archaeology and the Applied Arts. Preprints of the Contributions to the Stockholm Congress, 2 – 6 June 1975, IIC, London, 1975, p195-198.

GALBRAITH S. T., BAIRD T., FRYER J. R.

Structural Changes in  $\beta$ -FeOOH Caused by Radiation Damage. In: Acta Crystallographica. Vol. 35, 1979, p197-200.

GALLIANO F., GERWIN W., MENZEL K.

Monitoring of metal corrosion and soil solution at two excavation sites and the laboratory. In: Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux. Draguignan-Figanières, France, 27 – 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p87-91.

GERWIN W., SCHARFF W., BAUMHAUER R.

Corrosive decay of archaeological metal finds from different soils and effects of environmental pollution. In: Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux. Draguignan-Figanières, France, 27 – 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p100-105.

GONZALEZ-CALBET J. M., ALARIO-FRANCO M. A.

A thermogravimetric and electron microscopy study of the decomposition of akaganeite. In: Thermochimica Acta. Vol. 58, No. 1, October 1982, p45-51.

GONZALES-CALBET J. M., ALARIO-FRANCO M. A., GAYOSO-ANDRADE M.

The porous structure of synthetic akaganeite. In: Journal of Inorganic & Nuclear Chemistry. Vol. 43, No. 2, 1981, p257-264.

GOODBURN-BROWN D.

The Effect of Various Conservation Treatments on the Surface of Metals from Waterlogged Sites in London. In: Roy A., Smith P. (Eds.). Archaeological Conservation and its Consequences. Preprints of the Contributions to the Copenhagen Congress, 26 – 30 August 1996, The International Institute for Conservation, London, 1996, p59-64.

GRAHAM M. J., COHEN M.

Analysis of Iron Corrosion Products Using Mössbauer Spectroscopy. In: Corrosion. National Association of Corrosion Engineers (NACE), Vol. 32, No. 11, November 1976, p432-438.

GRATTAN D. W., GILBERG M.

Ageless oxygen absorber: chemical and physical properties. In: Studies in Conservation. Vol. 39, 1994, p210-214.

GREEN L. R., BRADLEY S.

An Investigation of Strategies for the Long-term Storage of Archaeological Iron. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). Metal 95. Proceedings of the International Conference on Metals Conservation, Semur en Auxois, 25 – 28 September 1995, James & James (Scientific Publishers) Ltd., 1997, p305-309.

GREEN L. R., THICKETT D.

Testing materials for use in storage and display of antiquities – a revised methodology. In: Studies in Conservation. Vol. 40, No. 3, 1995, p145-152.

GÜNZLER H., GREMLICH H.-U.

IR Spectroscopy: An Introduction. Wiley-VCH, Weinheim, 2002.

HANSEN J.

Conservation of Iron Artefacts in Norway with an Emphasis on the Boiling Method used in Christiania 1870-1884. In: Oddy A., Smith S. (Eds.). *Past Practice – Future Prospects*. The British Museum Occasional Paper. No. 145, London, 2001, p95-102.

HARRISON P.

The Conservation of Archaeological Iron with Amines. In: *Newsletter: Metal Working Group*. ICOM Committee for Conservation, No. 4, 1988, p10-13.

HJELM-HANSEN N., VAN LANSCHOT J., SZALKAY C. D., TURGOOSE S.

Electrochemical assessment and monitoring of stabilisation of heavily corroded archaeological iron artefacts. In: *Corrosion Science*. Vol. 35, No. 1-4, 1993, p767-774.

HORIE C. V., FRANCIS D. M.

A pilot study of moisture vapour transmission rate through Stewart's plastic boxes. In: *Conservation News*. Vol. 23, 1984, p13-17.

ISHIKAWA T., KATOH R., YASUKAWA A., KANDORI K., NAKAYAMA T., YUSE F.

Influences of metal ions on the formation of  $\beta$ -FeOOH particles. In: *Corrosion Science*. Vol. 43, 2001, p1727-1738.

ISHIKAWA T., KONDO Y., YASUKAWA A., KANDORI K.

Formation of magnetite in the presence of ferric oxyhydroxides. In: *Corrosion Science*. Vol. 40, 1998, p1239-1251.

JAKOBSEN T.

Iron Conservation at the National Museum of Copenhagen – Past and Present. In: *Preprints of the 7<sup>th</sup> Triennial Meeting*. ICOM Committee for Conservation, Copenhagen, 10 – 14 September 1984, International Council of Museums, 1984, p84.22.8-10.

JENKINS R., SNYDER R. L.

Introduction to X-ray Powder Diffractometry. *Chemical Analysis*. Vol. 138, John Wiley & Sons, Inc., 1996.

JOHNSTON J. H., LOGAN N. E.

A Precise Iron-57 Mössbauer Spectroscopic Study of Iron(III) in the Octahedral and Channel Sites of Akaganéite ( $\beta$ -Iron Hydroxide Oxide). In: *Journal of the Chemical Society. Dalton Transactions*. Inorganic Chemistry. Vol. 204, No. 1, 1979, p13-16.

KALMAN E., LAKATOS M., KARMAN F. H., NAGY F., KLENCZAR Z., VERTES A.

Mössbauer spectroscopy for characterization of corrosion products and electrochemically layers. In: *Corrosion Reviews*. Vol. 23, No. 1, 2005, p1-106.

KANEKO K.

Surface Chemistry of FeOOH Microcrystals. In: *Current Problems in the Conservation of Metal Antiquities*. International Symposium on the Conservation and Restoration of Cultural Property, October 4 – October 6, 1989, Tokyo National Research Institute of Cultural Properties, Tokyo, Japan, 1993, p55-70.

KEENE S.

Real-time Survival Rates for Treatments of Archaeological Iron. In: Scott D. A., Podany J., Considine B. B. (Eds.). *Ancient and Historic Metals*. The Getty Conservation Institute, 1994, p249-264.

KIBRYA R., SHASHOUA Y.

Evaluation of the suitability of polypropylene Stewart Plastic boxes. In: *Abstracts of internal Reports*. British Museum Department of Conservation, Conservation Research Group, 1995-1997.

KOEZUKA T.

Desalting of Iron Objects found in Inland Area by LiOH Method. In: Current Problems in the Conservation of Metal Antiquities. International Symposium on the Conservation and Restoration of Cultural Property, October 4 – October 6, 1989, Tokyo National Research Institute of Cultural Properties, Tokyo, Japan, 1993, p101-105.

KOTZAMANIDI I., SARRIS E., VASSILIOU P., KOLLIA C., KANIAS G. D., VAROUFAKIS G. J., FILIPPAKIS S. E.

Effect of heat treatment in reducing plasma environments on chloride ion removal and corrosion of oxidised steel artefacts. In: British Corrosion Journal. Vol. 34, No. 4, 1999, p285-291.

LANG J., MIDDLETON A.

Radiography of Cultural Material. Elsevier Butterworth-Heinemann, Second Edition, Oxford, 2005.

Le soin et le nettoyage du fer. Notes de l'ICC, Institut canadien de conservation, 9/6, 1995.

Le traitement du fer à l'acide tannique. Notes de l'ICC, Institut canadien de conservation, 9/5, 1990.

MC CAWLEY J. C.

Current Research into the Corrosion of Archaeological Iron. In: ICOM, Metals Group, 1984, p25-27.

MAEDA Y., MATSUO Y., SUGIHARA A., MOMOSHIMA N., TAKASHIMA Y.

Mössbauer studies of first-stage corrosion products on iron powder and corrosion products on highly corroded nails. In: Corrosion Science. Vol. 33, 1992, p1557-1567.

MATHIAS C.

A Conservation Strategy for a Seventeenth Century Archaeological Site at Ferryland, Newfoundland. In: Journal of the International Institute for Conservation – Canadian Group. Vol. 19, 1994, p14-23.

MAYNE J. E. O., TURGOOSE S.

Significance of the redox potential in the inhibition of the corrosion of iron by non-oxidising inhibitors in the pH range 5-13. In: British Corrosion Journal. Vol. 10, No. 1, 1975, p44-46.

MICHALSKI S.

Leakage prediction for buildings, cases, bags and bottles. In: Studies in Conservation. Vol. 39, 1994, p169-186.

MISAWA T., HASHIMOTO K., SHIMODAIRA S.

The mechanism of formation of iron oxide and oxyhydroxides in aqueous solutions at room temperature. In: Corrosion Science. Vol. 14, 1974, p131-149.

Mise en reserve des métaux. Notes de l'ICC, Institut canadien de conservation, 9/2, 1995.

MITOV I., PANEVA D., KUNEV B.

Comparative study of the thermal decomposition of iron oxyhydroxides. In: Thermochimica Acta. Vol. 386, 2002, p179-188.

MÜHLETHALER B., THEILER F., OSWALD N., GEISER R., PULVER W.

Methoden zur Konservierung von Bodenfunden aus Eisen in Verbindung mit organischen Materialien. In: Schweizer F., Villiger V. (Hrsg.). Methoden zur Erhaltung von Kulturgütern. Forschungsergebnisse aus dem nationalen Forschungsprogramm 16 des Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung, Verlag Paul Haupt Bern und Stuttgart, Bern, 1989, p165-169.

NEFF D., DILLMANN P., BELLOT-GURLET L., BERANGER G.

Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system. In: Corrosion Science. Vol. 47, 2005, p515-535.

NESTEROVA M., MOREAU J., BANFIELD J. F.

Model biomimetic studies of templated growth and assembly of nanocrystalline FeOOH. In: Geochimica et Cosmochimica Acta. Vol. 67, No. 6, p1177-1187.

NIEMEYER B.

"Investigative Conservation" – das Restaurierungskonzept des Ancient Monuments Laboratory/English Heritage zur Untersuchung grosser Fundkomplexe. In: Arbeitsblätter für Restauratoren. Heft 2, Gruppe 1, Eisen, 1994, p287-292.

NORTH N. A., PEARSON C.

Thermal decomposition of FeOCl and marine cast iron corrosion products. In: Studies in Conservation. Vol. 22, 1977, p146-157.

O'SHEA C., DAVIES B., KENDELL K., AKED S.

The Use of Hydrogen Reduction in Stabilizing Large Items of Iron Recovered from the Sea. In: Brommelle N. S., Thomson G. (Eds.). Science and Technology in the Service of Conservation. Preprints of the Contributions to the Washington Congress, 3 – 9 September, 1982, ICC, 1982, p126-129.

OSWALD N.

Konservierung von Bodenfunden aus Eisen und organischem Material – eine Projektarbeit des Schweizerischen Nationalfonds [1,2]. In: Conservation of Metals: Problems in the treatment of metal-organic and metal-inorganic composite objects. International Restorer Seminar, Veszprem, Hungary, 1 – 10 July, 1989, p27-31.

PEARSON C. (1972 a)

The preservation of iron cannon after 200 years under the sea. In: Studies in Conservation. Vol. 17, No. 3, 1972, p91-110.

PEARSON C. (1972 b)

Restoration of cannon and other relics from H. M. B. "Endeavour". In: Report 508. *Unclassified*, Department of Supply, Australian Defence Scientific Service, Defence Standards Laboratories, Maribyrnong, Victoria, June 1972.

PEARSON C. Editor

Conservation of Marine Archaeological Objects. Butterworth & Co., 1987.

POST J. E.

Rietveld Refinement of the Akaganeite Structure, using Powder X-Ray Diffraction Data. In: Geological Society of America. Vol. 20, Centennial Celebration, Abstracts with Programs, 1988, p102-103.

POURBAIX M.

Potential-pH Diagrams and Metallic Corrosion. In: Ailor W. H. (Ed.). Handbook of Corrosion Testing and Evaluation. Chapter 26, Wiley, New York, 1971, p661-687.

REBIERE J.

Conservation préventive des vestiges métalliques: une approche comparative des boîtes de stockage hermétiques. In: Conservation Restauration des Biens Culturels. A.R.A.A.F.U. Paris, No. 3, Paris, décembre 1991, p10-13.

REES-JONES S. G.

Some aspects of the conservation of iron objects from the sea. In: Studies in Conservation. Vol. 17, No. 1, 1972, p39-43.

REFAIT PH., GENIN J.-M. R.

The transformation of chloride-containing green rust one into sulphated green rust two by oxidation in mixed Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> aqueous media. In: Corrosion Science. Vol. 36, 1994, p55-65.

REFAIT PH., GENIN J.-M. R.

The mechanisms of oxidation of ferrous hydroxychloride  $\beta$ -Fe<sub>2</sub>(OH)<sub>3</sub>Cl in aqueous solution: the formation of akaganeite vs goethite. In: Corrosion Science. Vol. 39, 1997, p539-553.

REFAIT PH., ABDELMOULA M., GENIN J.-M. R.

Mechanisms of formation and structure of green rust one in aqueous corrosion of iron in the presence of chloride ions. In: Corrosion Science. Vol. 40, 1998, p1547-1560.

REFAIT PH., BENALI O., ABDELMOULA M., GENIN J.-M. R.

Formation of "ferric green rust" and/or ferrihydrite by fast oxidation of iron (II-III) hydroxychloride green rust. In: Corrosion Science. Vol. 45, 2003, p2435-2449.

RINUY A.

Vergleichende Untersuchungen zur Entsalzung von Eisenfunden. In: Arbeitsblätter für Restauratoren. Heft 1, Gruppe 1, Eisen, 1979, s130-140.

RINUY A., SCHWEIZER F.

Méthodes de conservation d'objets de fouilles en fer. Etude quantitative comparée de l'élimination de chlorures. In: Studies in Conservation. Vol. 26, No. 1, 1981, p29-41.

ROBINET L., THICKETT D.

A New Methodology for Accelerated Corrosion Testing. In: Studies in Conservation. Vol. 48, No. 4, 2003, p263-268.

ROSSO K. M., RUSTAD J. R.

Structures and energies of AlOOH and FeOOH polymorphs from plane wave pseudopotential calculations. In: The American Mineralogist: journal of the Mineralogical Society of America. Vol. 86, 2001, p312-317.

SATO N.

The stability of localized corrosion. In: Corrosion Science. Vol. 37, No. 12, 1995, p1947-1967.

SCHARFF W., BLUMER R.-D.

Wie kann man Eisenobjekte besser vor dem Zerfall schützen? In: Restauero. Zeitschrift für Kunsttechniken, Restaurierung und Muesumsfragen. Heft 5, 1994, p332-338.

SCHARFF W., HUESMANN I. A.

Accelerated Decay of Metal Soil Finds due to Soil Pollution. In: MacLeod I., Pennec S. L., Robbiola L. (Eds.). Metal 95. Proceedings of the International Conference on Metals Conservation, Semur en Auxois, 25 – 28 September 1995, James & James (Scientific Publishers) Ltd., 1997, p17-20.

SCHEINOST A. C., SCHWERTMANN U.

Color Identification of Iron Oxides and Hydroxysulfates: Use and Limitations. In: Soil Science Society of America journal: SSSAJ. Vol. 63, No. 5, 1999, p1463-1471.

SCHWERTMANN U., FECHTER H., TAYLOR R. M., STANJEK H.

A lecture and demonstration for students on iron oxide formation. In: Clays, Controlling the Environment. 10<sup>th</sup> International Clays Conference, Adelaide, Australia, July 18 to 23, 1993, CSIRO, 1995, p11-14.

SCOTT D. A.

Technology and Conservation of Iron.

Conference Reports, Notes on the Meeting held in Bristol, England, from 13.4.85 – 14.4.85. In: Newsletter: Metals Working Group. ICOM Committee for Conservation, No.1, July 1, 1985, p10-11.

SELWYN L.

Metals and Corrosion. A Handbook for the Conservation Professional. Canadian Conservation Institute, Ottawa, Canada, 2004.

SELWYN L. S., McKINNON W. R., ARGYROPOULOS V.

Models for chloride ion diffusion in archaeological iron. In: Studies in Conservation. Vol. 26, 2001, p109-120.

SELWYN L., ARGYROPOULOS V.

Removal of Chloride and Iron Ions from Archaeological Wrought Iron with Sodium Hydroxide and Ethlenediamine Solutions. In: Studies in Conservation. Vol. 50, 2005, p81-100.

SHASHOUA Y., THOMSEN S.

A Field Trial for the Use of Ageless in the Preservation of Rubber in Museums Collections. In: Saving the Twentieth Century: The Conservation of Modern Materials. Proceedings of a Conference, Symposium '91 – Saving the Twentieth Century, Ottawa, Canada, 15 – 20 September, 1991, Canadian Conservation Institute, 1993, p363-372.

SHEJBAL J. Editor

Controlled Atmosphere Storage of Grains. Developments in Agricultural Engineering 1. An International Symposium held from 12 to 15 May 1980, Castalgandolfo, Italy, Elsevier Scientific Publishing Company, 1980.

SIDOT E., MOUREY W., REBIERE J., FRANCOISE J.

Perspective thermochimique et cinétique de l'action d'absorbants de dioxygène sur la conservation des métaux. In: Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux. Draguignan-Figanières, France, 27 – 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p275-279.

SJÖSTRAND E.

Reduction of rust with hydrogen gas. In: Conservation of old rusty iron objects: reduction of rust with hydrogen gas. Swedish Corrosion Institute, Bulletin No. 61E, 1973, p8-13.

SPRIGGS J. A.

The Coppergate Helmet – A Holding Operation. In: Corrosion Inhibitors in Conservation. UKIC Occasional papers. No. 4, 1985, p33-34.

STAMBOLOV T., VAN DER RHEEDEN B.

Note on the removal of rust from old iron with thioglycolic acid. In: Studies in Conservation. Vol. 13, 1968, p142-144.

STAMBOLOV T., STÅHL K., NIELSEN K., JIANG J., LEBECH B., HANSON J. C., NORBY P., VAN LANSCHOT J.

On the akaganeite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artefacts. In: Corrosion Science. Vol. 45, 2003, p2563-2575.

STOLOW N.

Controlled Environment for Works of Art in Transit. Butterworth, London, 1966.

SZKLARSKA-SMIALOWSKA S.

Various Forms of Localised Corrosion in Iron and Steel: Common Features and Differences. In: British Corrosion Journal. Vol. 10, No. 1, 1975, p11-16.

TAMURA H., KAWAMURA S., HAGAYAMA M.

Acceleration of the oxidation of Fe<sup>2+</sup> ions by Fe(III)-oxyhydroxides. In: Corrosion Science. Vol. 20, 1980, p963-971.

TAYLOR R. M.

Influence of chloride on the formation of iron oxides from Fe(II) chloride. I. Effect of [Cl]/[Fe] on the formation of magnetite. In: Clays and Clay Minerals. Vol. 32, No. 3, 1984, p167-174.

THICKETT D., DAVID F., LUXFORD N.

Air Exchange Rate – the Dominant Parameter for Preventive Conservation? In: The Conservator. Vol. 29, 2005/6, p19-34.

TURGOOSE S.

The Corrosion of Archaeological Iron during Burial and Treatment. In: Studies in Conservation. Vol. 30, No. 1, 1985, p13-18.



TYLECOTE R. F., BLACK J. W. B.

The effect of hydrogen reduction on the properties of ferrous materials. In: *Studies in Conservation*. Vol. 25, No. 2, 1980, p87-96.

VISWANATHIAH M. N., TAREEN J. A. K., KRISHNA MURTHY K. V.

Differential thermal analysis of  $\beta$ -FeOOH (akaganéite). In: *The Indian Mineralogist*. Vol. 21, No. 1, 1980, p49-54.

WAGNER D. H. J., KROPP M., FISCHER W. R., KARS H.

A systematic approach to the evaluation of the corrosion load of archaeological metal objects. In: *Metal 98. Actes de la Conférence Internationale sur la Conservation des Métaux*. Draguignan-Figanières, France, 27 - 29 mai 1998, James & James (Science Publishers) Ltd., London, 1998, p80-86.

WALKER R.

The role of corrosion inhibitors in the conservation of iron. In: Clarke R. W., Blackshaw S. M. (Eds.). *Conservation of Iron*. National Maritime Museum, Greenwich, London SE109NF, Maritime Monographs and Reports, No. 53, London, 1982, p58-67.

WALLER R.

An Experimental Ammonia Gas Treatment Method for Oxidized Pyritic Mineral Specimens.

In: Grimstad K. (Ed.). *Preprints of the 8<sup>th</sup> Triennial Meeting*. ICOM Committee for Conservation, Sydney, Australia, 6 – 11 September, 1987, p623-630.

WATKINS S. C.

The Restoration Cycle: Conservation and Restoration of Metal Artefacts in the British Museum. In: *Conservation Restauration des Biens Culturels: Restauration, Dé-Restauration, Re-Restauration*. 4<sup>e</sup> colloque de l'A.R.A.A.F.U., Paris, 5 – 7 octobre, 1995, p223-233.

WATKINSON D.

Chloride Extraction from Archaeological Iron: Comparative Treatment Efficiencies. In: Roy A. and Smith P. (Eds.). *Archaeological Conservation and its Consequences*. Preprints of the Contributions to the Copenhagen Congress, 26 – 30 August, 1996, London, The International Institute for Conservation, 1996, p208-212.

WATKINSON D., TANNER M., TURNER R., LEWIS M.

ss Great Britain: teamwork as a platform for innovative conservation. In: *The Conservator*. Vol. 29, 2005/6, p73-86.

WECKLER B., LUTZ H. D.

Lattice vibration spectra. Part XCV. Infrared spectroscopic studies on the iron oxide hydroxides goethite ( $\alpha$ ), akaganéite ( $\beta$ ), lepidocrocite ( $\gamma$ ), and feroxyhite ( $\delta$ ). In: *European Journal of Solid State and Inorganic Chemistry*. Elsevier, Tome 35, No. 8-9, 1998, p531-544.

WEINTRAUB S.

Studies on the Behaviour of RH within an Exhibition Case. In: *Preprints of the 6<sup>th</sup> Triennial Meeting*. ICOM Committee for Conservation, Ottawa, 21 – 25 September 1981, International Council of Museums, 1981, p81.18.4.1-9.

WEINTRAUB S.

Demystifying Silica Gel. In: *Objects Speciality Group postprints*. American Institute for Conservation of Historic and Artistic Works, Objects Speciality Group, Vol. 9, 2002, p169-194.

WEIZHEN O., CHUNCHUN X.

Studies on Localized Corrosion and Desalination Treatment of Simulated Cast Iron Artifacts. In: *Studies in Conservation*. Vol. 50, 2005, p101-108.

WESTERN A. C.

The Conservation of Excavated Iron Objects. In: *Studies in Conservation*. Vol. 17, 1972, p83-87.

WHISTON C.

X-Ray Methods. Analytical Chemistry by Open Learning ACOL, John Wiley & Sons Publisher, London, 1987.

## **10 ANNEXES**

### **10.1 Annex I: CD-R (Excel tables related to the experimental work)**

(see attached CD-R at the end of the dissertation)

#### ***10.1.1 Plastic boxes***

**10.1.1.1 Air exchange rate Curver™ box**

**10.1.1.2 Air exchange rate Rondo™ box**

**10.1.1.3 Life-time plastic boxes**

#### ***10.1.2 Quantifications***

**10.1.2.1 Quantification akaganéite**

#### ***10.1.3 Results sample groups (FT-IR, XRD)***

**10.1.3.1 Results group A**

**10.1.3.2 Results group B**

**10.1.3.3 Results group C**

**10.1.3.4 Results group D**

**10.1.3.5 Results group E**

**10.1.3.6 Results group F**

**10.1.3.7 Results group G**

**10.1.3.8 Results group H**

**10.1.3.9 Results group I**

**10.1.3.10 Results group K**

**10.1.3.11 Results group L**

#### ***10.1.4 RP-A oxygen absorber***

**10.1.4.1 Oxygen-absorption capacity**

## 10.2 Annex II: Explanations on some calculations, dataloggers, methods and materials used (in alphabetical order)

### 10.2.1 Air exchange rate (AER) / Carbon dioxide meter

Product name: Vaisala GM 70 Carbon Dioxide Meter  
Company: Vaisala Ltd  
Tel.: +44 (0)1638 576200  
E-mail: uksales@vaisala.com  
Range and accuracy: 0-10'000 ppm +/- 20 ppm plus 2% of reading<sup>484</sup>

Calculation of the air exchange rate (AER) of an enclosure is important to predict life-times of desiccants or oxygen absorbers. It gives an indication on the tightness of the seals of the enclosure. The higher the AER of our enclosure, the quicker the desiccant or oxygen absorber has to be replaced because of exhaustion. The AER gives us indications on the leakage of the enclosure. Three contributions to leakage are possible: diffusion along gaps, infiltration through gaps and permeation through the enclosure material.<sup>485</sup>

One can use a carbon dioxide meter to measure the decrease in carbon dioxide (CO<sub>2</sub>) in an enclosure. A simple calculation then leads to our AER.

Application: One can breath into the enclosure (e.g. a bag), which is to be tested or use a carbon dioxide (CO<sub>2</sub>) cycle tyre inflator and cylinder to put a significant amount of CO<sub>2</sub> into the bag. The carbon dioxide meter is put into the bag to be tested and the bag is closed. Measurements take 24 hours at least. Then the data is downloaded.

The AER is the transfer from external air into and out of an enclosure. It is measured as air exchange per unit time.<sup>486</sup>

*„After introduction into a sealed enclosure, the concentration of the gas will decrease as air enters and leaves. If the driving forces for air exchange remain constant, the concentration of the tracer gas is found to decay exponentially against time. Plotting the natural logarithm of the exponential decay curve against time should result in a straight line, the slope of which is the AER in air changes per unit time.”*<sup>487</sup>

Equation for the calculation of the air exchange per unit time:<sup>488</sup>

$$N = [\ln(C_{\text{int}}^{t^0} - C_{\text{ext}}) - \ln(C_{\text{int}}^{t^1} - C_{\text{ext}})] / (t^1 - t^0) \quad \text{Equation 18}$$

<sup>484</sup> CALVER A., HOLBROOK A., THICKETT D., WEINTRAUB S., 2005, p601.

<sup>485</sup> Personal communication with David Thickett, English Heritage, London, 22/08/2006.

<sup>486</sup> CALVER A., HOLBROOK A., THICKETT D., WEINTRAUB S., 2005, p598.

<sup>487</sup> Ibid., p599.

<sup>488</sup> Ibid.

N = number of air changes

$C_{\text{int}}^{t^0}$  = internal concentration of tracer gas in enclosure at start

$C_{\text{ext}}$  = external concentration of tracer gas in room

$C_{\text{int}}^{t^1}$  = internal concentration of tracer gas in enclosure at end

$t^0$  = time at start (days)

$t^1$  = time at end (days)

ln = natural logarithm

Air exchange measurements on plastic boxes used for storage of archaeological material as well as on ESCAL<sup>TM</sup> barrier film bags were carried out in the present work using a Vaisala GM 70 Carbon Dioxide Meter. For plastic boxes the measurement of the AER has proven reliable. Results can be found in chapter 5.3.5.1.<sup>489</sup> However, for the bags made of ESCAL<sup>TM</sup> barrier film it remained unclear if carbon dioxide (CO<sub>2</sub>) was the best tracer gas to use. CO<sub>2</sub>-permeation through the film probably occurred as well as leakage through the seals. Additional permeation through the film would give different results as if leakage occurred only through the seals. We are only interested to measure the leakage of the seals. If it is the case that permeation of CO<sub>2</sub> occurs through film and leakage through seals, one should not consider the use of CO<sub>2</sub>-gas for the calculation of the AER of ESCAL<sup>TM</sup> film bags. The use of another method with oxygen as tracer gas might be more interesting.<sup>490</sup>

Instructions on how to use the Vaisala GM 70 Carbon Dioxide Meter and obtaining the air exchange rates (English Heritage, May 2006):

#### CO<sub>2</sub> logger Instructions

**Programme:** Start / All Programs / MI70 Link / MI70 Link

#### To Download:

- Connect the logger to the computer, turn the logger on
- (note it is best to charge the logger while downloading as the batteries tend to have run out)
- A box opens on logger screen with "Environment settings have an effect on CO<sub>2</sub> readings. Check the settings now? Yes / No", choose **No**
- Choose download file icon in software (looks like logger with red arrow)
- Opens new window with list of sets of data currently stored, highlight the set to download and choose **DOWNLOAD**
- The files can be deleted as it downloads by ticking box at bottom of download window, however if an error occurs the data is lost (files can also be deleted from the logger after downloading)
- Once downloaded opens another window with three tabs, first is the *information* tab, including a summary of the logger information and data
- The *chart* tab shows a graph of the data and the *data table* tab has the text view of the data
- Choose File / Save As/Export then the location for the data and save as an MI70 file
- Then choose File / Save As/Export and the same location for the data and same file name but save as a csv file.
- To delete the file either use the red X icon in the software or the menus on the logger. Once deleted the MI70 software can be shut down

<sup>489</sup> Personal communication with David Thickett, English Heritage, London, August 2006.

<sup>490</sup> CO<sub>2</sub> comports different from O<sub>2</sub> when looking at the diffusion of the gas along gaps and the permeation through the ESCAL<sup>TM</sup> film.

### To Graph:

- Open the csv file using EXCEL
- **To view full date:** double click on line between column headings for columns A and B
- In column B find the first value after the CO<sub>2</sub> was added (should be a noticeably large increase), click in column C next to this value
- Enter formula = **cell number – room reading** (eg =b3-400), then enter
- Click back on this cell and double click on the little square in the bottom right hand corner to fill the formula down column C
- In column D enter the formula = **ln (cell number)**, (eg =ln(c3)) for the first cell in column C
- Click back on this cell and double click on the little square in the bottom right hand corner to fill the formula down column D
- Leave the column highlighted and click on the chart icon
- In the Chart Wizard box step 1 choose an *XY (scatter)* graph, then **Next>**
- In the Chart Wizard box step 2 choose the *series* tab, add a name for the series, then choose the x values.
- This can be done by clicking on the spreadsheet icon and highlighting column A, using the heading bar, add the start cell number (for column D) next to the first letter A and the last cell number (for column D) to the last letter A (these can be found in the data range bar, before the series tab is used), then click on the icon at the end of the text bar to return to the chart wizard, then **Next>**
- In step 3 add titles and any axis information (y axis is normally *ln(CO<sub>2</sub>)*), then **Next>** and in step 4 choose the location of the graph (normally a new sheet) and **Finish**
- In order to determine the air exchange rate a regression line is required. Right click over the graph and choose **Source Data**, then the *series* tab
- In the series box choose **Add**, choose the spreadsheet icon next to the y values, then move to the spreadsheet choose the first cell for the straightest part of the data in column D and drag down to select 24 hours data, (or data in blocks of 24hours) choose the icon to go back to the chart wizard
- Then select the x values spreadsheet icon, choose the equivalent cells in column A and go back to the chart wizard, then **OK**
- There should now be a pink line sitting over part of the original line. Right click on these cells (to highlight just the pink line) and choose **Add Trendline**, this opens another window
- Choose a linear regression, in the *type* tab and under the *options* tab choose to *Display the equation on chart* and to *Display R squared value on chart*, then **OK**
- **The first number in the equation is the air exchange rate (the minus sign can be ignored as this indicates the direction of the slope of the line)**
- The R squared value gives an indication of the spread of the data (a number nearer to 1 means there is less spread)

### To Set Up:

- Turn the logger on
- A box opens on logger screen with “Environment settings have an effect on CO<sub>2</sub> readings. Check the settings now? Yes / No”, choose **No**
- Choose **Record**, **Record data** (using ► arrow), change the interval using **Set** (1s up to 12h are possible), then **OK**
- Scroll down to **Start/Stop recording**, then press **Start**
- Will tell you how much memory is available, choose **OK**

Carbon Dioxide Meter instructions (English Heritage, May 2006).

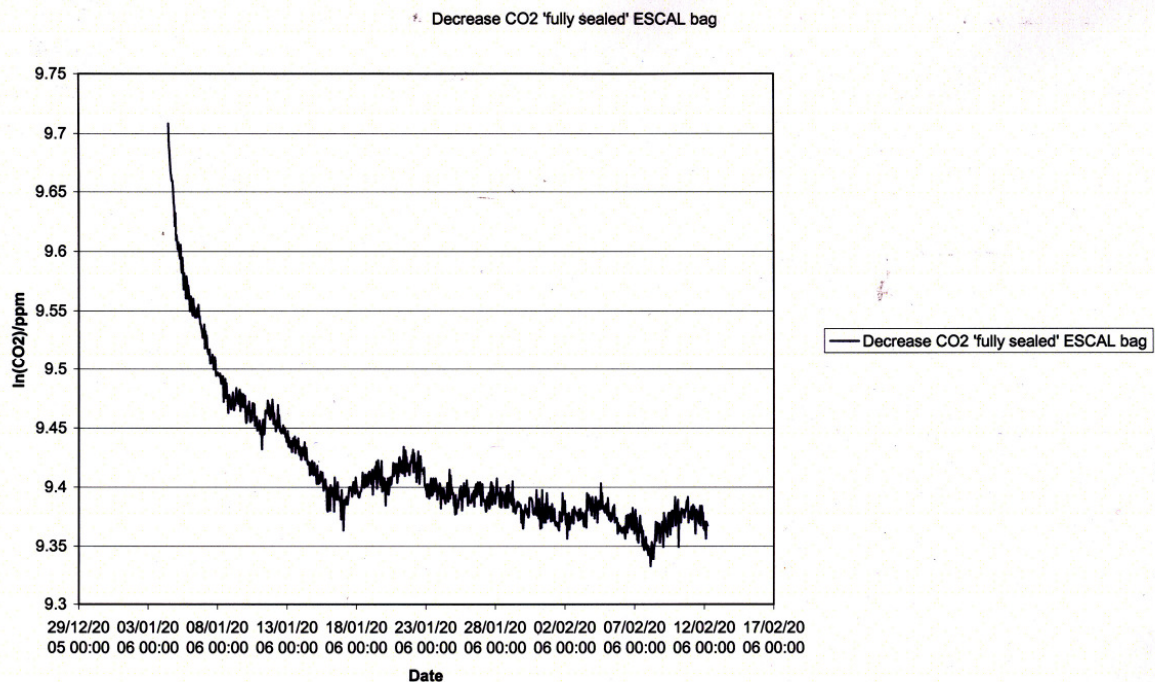


Figure 129: Decrease in carbon dioxide (CO<sub>2</sub>) in a fully sealed ESCAL<sup>TM</sup> bag, measured with a Vaisala GM 70 Carbon Dioxide Meter.

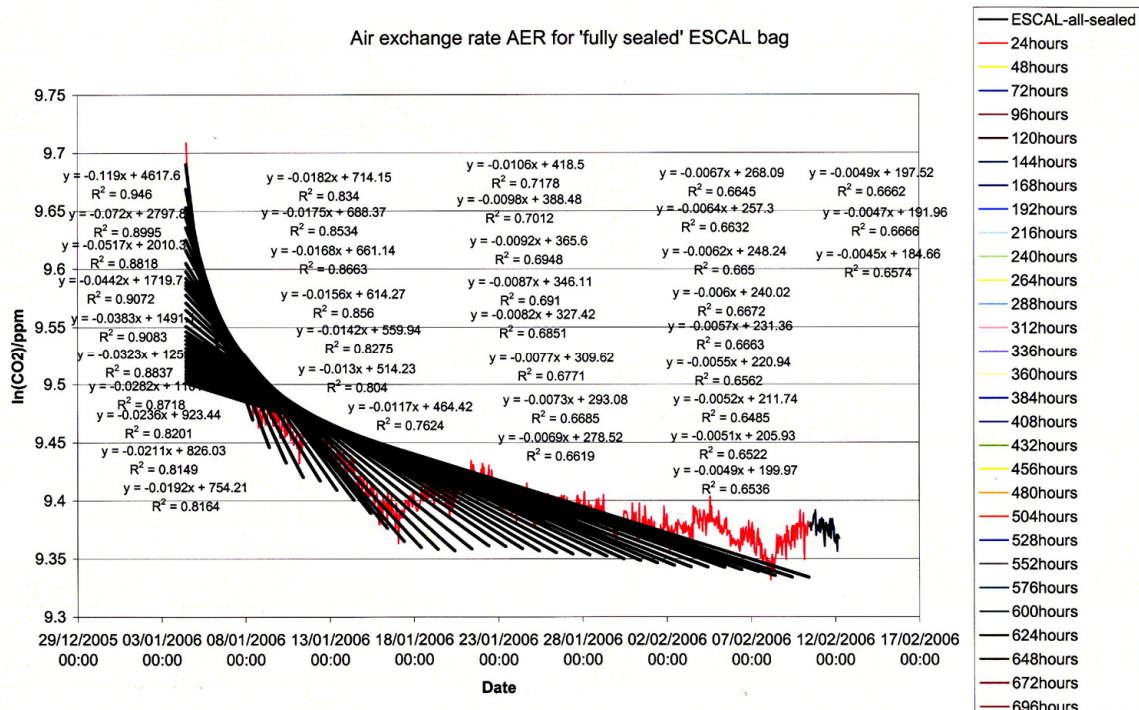


Figure 130: Some calculations of air exchange rates (AER) for a fully heat-sealed ESCAL<sup>TM</sup> bag, however doubtful as CO<sub>2</sub> was found to be problematic as tracer gas.



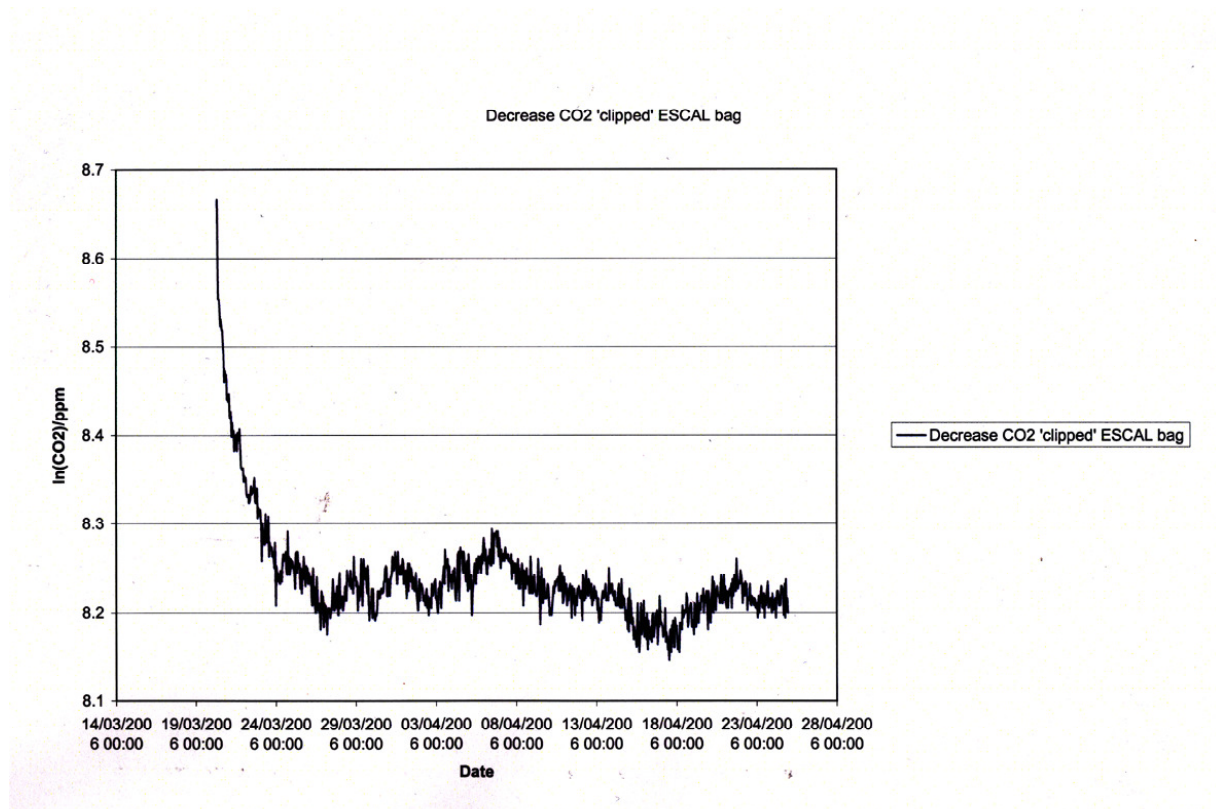


Figure 131: Decrease of CO<sub>2</sub> in an ESCAL<sup>TM</sup> bag when using a clip to close one side.

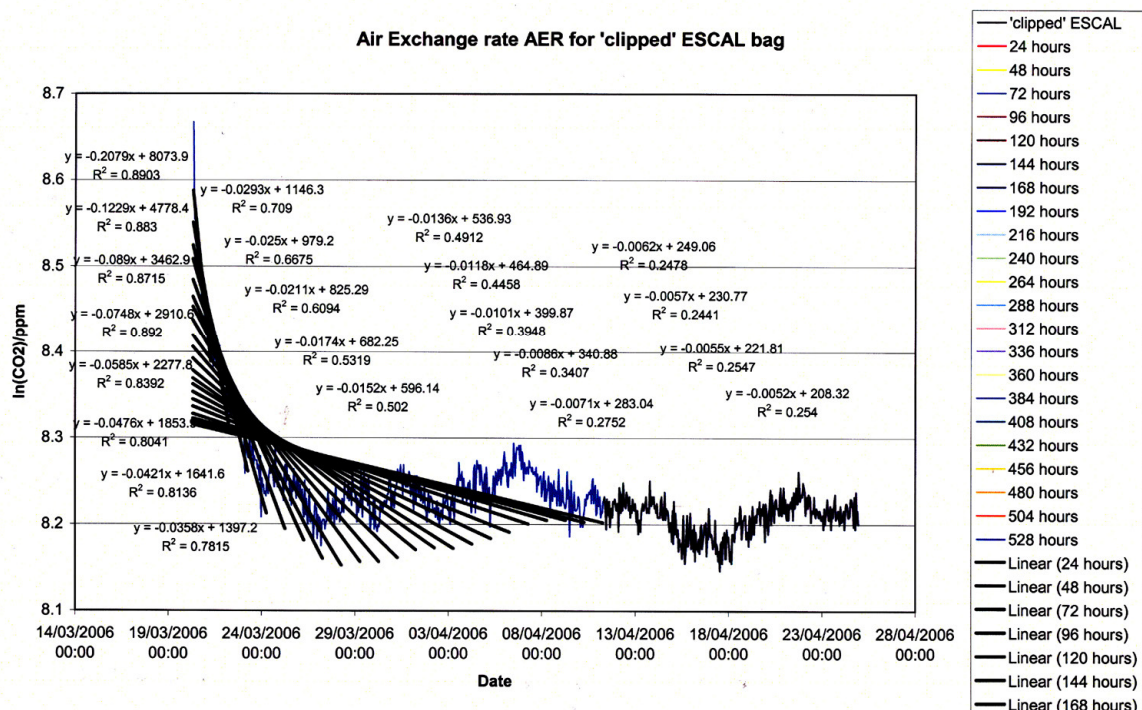


Figure 132: Some calculations of air exchange rates (AER) for an ESCAL<sup>TM</sup> bag closed with a clip on one side.



### **10.2.2 ESCAL<sup>TM</sup> barrier film**

|                               |   |
|-------------------------------|---|
| Company:                      | Mitsubishi Gas Chemical Company, Japan                          |
| Composition:                  | Co-extruded polypropylene; ceramic-coated PVA/PE <sup>491</sup> |
| Oxygen transmission rate:     | 0.05cc/m <sup>2</sup> /d  |
| Moisture vapour permeability: | 0.01g/m <sup>2</sup> /d   |
| Thickness:                    | 0.11mm  |

Costs (per metre, 100cm width):

Conservation by Design, United Kingdom (March 2006): £12.40 (per metre if buying 10m)

Long Life for Art Christoph Waller, Germany (March 2006): €15 (per metre)

### **10.2.3 Hanwell Datalogger: rh-t bug / Measurement of relative humidity and temperature**

Company: Hanwell Instruments Limited  
12-13 Mead Business Centre  
Mead Lane  
Hertford SG13 7BJ  
United Kingdom  
Tel.: +44 (0)870 443 1786

Product description:<sup>492</sup>

This datalogger reads temperatures and humidity levels at a given interval. To read the data, the system is connected to a computer and the data downloaded with the programme that Hanwell Instruments Limited provides.

|                     |   |
|---------------------|---|
| Dimensions:         | 110 x 67 x 23mm                         |
| Weight:             | 65g                                     |
| Power supply:       | 3.6 volt lithium batteries              |
| Battery life:       | Up to 5 years (depending upon use)      |
| Humidity sensor:    | Capacitive polymer                      |
| Temperature sensor: | Precision thermistor                    |
| Logging intervals:  | Programmable from 4 seconds to 18 hours |

#### ***Temperature***

|           |  |
|-----------|--|
| Range:    | -25°C to +80°C                           |
| Accuracy: | -25 to -5 +/-0.3°C<br>-5 to +50 +/-0.2°C |

<sup>491</sup> MACDONALD WELCH S., 2005, p43.

<sup>492</sup> [www.hanwell.com/rht-bug-c.html](http://www.hanwell.com/rht-bug-c.html), 08/02/2006.

+50 to +70 +/-0.3°C

+70 to +80 +/-0.4°C

#### *Humidity*

Range: 0 to 100% non condensing

Accuracy: +/- 2% over full range

### **10.2.4 Heat sealer / Sealing of plastic bags**

Product name: CRISS CROSS Universal Heat Sealing Machine

Company: Conservation by Design Limited, Bedford MK42 7AW, GB

Star Universal (Gosport) Ltd. (for repairs).

This heat sealer can be used for ESCAL<sup>TM</sup> barrier film. The two settings on the machine control weld and cooling time. The rest is programmed into the machine, which makes it a tool easy to use. This type of heat sealer separates the Power Unit and the weld jaws. The jaws are held together with a clamping system ('Mole Grip') and one can press a button situated on the jaws when ready to weld the material. The machine works by impulse welding. The jaws don't get very hot unless one puts the machine to a longer period of continuous use.<sup>493</sup>

The two films to be sealed together are put onto one another by pressure. A heated metal bar applies pressure to the two films, softens the plastic at the joint and forms a weld (impulse welding). The quality of the weld depends on the chosen parameters: bar temperature, weld pressure, weld time and cool time. The necessity for the heat to conduct through the film to the joint imposes a restriction on the thickness of material that may be welded. A practical limit of approximately 1mm exists.<sup>494</sup>

Best settings are: 3 (weld: 117°C); 6 (cool).<sup>495</sup>

Cost:

Conservation by Design Limited, United Kingdom (February 2006):

CRISS CROSS Remote Sealer Power Unit: £520

460mm remote jaws: £265

### **10.2.5 Iron chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O) powder**

Company: VWR International Ltd.

Poole BH15 1TD

United Kingdom

Detailed information:

Iron(II) chloride 4-hydrate (ferrous chloride)

<sup>493</sup> [www.conservation-by-design.co.uk](http://www.conservation-by-design.co.uk), 13/02/2006.

<sup>494</sup> [http://www.twi.co.uk/j32k/protected/band\\_3/ksab003.html](http://www.twi.co.uk/j32k/protected/band_3/ksab003.html), 13/02/2006.

<sup>495</sup> MC PHAIL D., LAM E., DOYLE A., 2003, p104.

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O} = 198.83 \text{ g/mol}$

Assay (manganometric)  $\geq 99.0\%$

### **10.2.6 Iron (Fe) powder**

Company: Fluka Chemie GmbH  
CH- 9471 Buchs  
Switzerland

Detailed information:

Iron 44890

Puriss. p. a.; Carbonyl-Iron powder;  $\geq 99.5\%$  (RT)

### **10.2.7 Leak detector / Leakage**

Working with enclosures to store objects we need to know about their performance in terms of leakage. The less an enclosure leaks, the less often we have to change our buffering material or oxygen absorber. A very simple test to get an idea of the performance of our enclosure is to use a leak detector.

Product name: D-TEK<sup>TM</sup> Select Refrigerant Leak detector

Company: INFICON  
Two Technology Place  
East Syracuse  
NY 13057  
USA  
reachus@inficon.com

The refrigerant leak detector uses an infrared absorption sensing cell sensitive only to refrigerants.<sup>496</sup> An infrared absorption filterometer is the centre of this technique. A sampling cell with an infrared source (emitter) is at one end and an infrared energy detector at the other with an optical filter in between. All refrigerants have an absorption spectrum in the range of 7.5-14 micrometers. The emitter creates a high-intensity stream of energy incorporating all wavelengths in the infrared spectrum. When this stream passes the optical filter, all wavelengths are blocked except those absorbed by refrigerants. If no refrigerant is present, then all the emitted energy strikes the detector. If there is refrigerant, some energy will be absorbed by it. Less energy reaches the detector and a signal is emitted.<sup>497</sup>

---

<sup>496</sup> The technique is based on infrared absorption sensors (CALVER A., HOLBROOK A., THICKETT D., WEINTRAUB S., 2005, p606).

<sup>497</sup> [www.inficon.com](http://www.inficon.com), 16/11/2005.

Tests carried out on ESCAL™ bags consisted in spraying some refrigerant into the bag, closing it with a clip and measuring possible leakage with the D-TEK™ Select Refrigerant Leak detector.<sup>498</sup>

### **10.2.8 Oxygen measurements**

1)

Product name: Mapcheck  
Company: Systech Instruments Ltd.  
Thame  
UK  
www.systech.co.uk  
Range: Oxygen: 0.001% - 100%  
Response time: < 5 seconds  
Accuracy: +/- 0.5% of reading (above 10%)  
+/- 2% of reading (below 2%)  
Reference gas: Air (20.9% oxygen)  
Ambient temp.: 0-40 °C

This instrument is equipped with a needle that takes the measurement. One can pierce into the bag in which we want to measure the percentage of oxygen. To do so, one puts a patch onto the place to pierce. The needle pierces through the patch, which has the ability to wholly close after the measurement. The instrument gives a direct reading of the percentage concentration of oxygen in the environment. This oxygen meter can measure oxygen concentration from 0.001% up to 100%. The instrument uses stabilized zirconia ( $ZrO_2$ ), capable of being conductive to oxygen ions when a difference of oxygen partial pressure exists across a cell. The cell where this is to occur is heated to a minimum temperature of 600 °C.<sup>499</sup>

2)

Product name: GSS450 Oxygen Analyser  
Company: Gas Sensor Solutions, Kevin Carty, Marketing and Sales Director  
Detection limit: Oxygen: 0.005% - 0.3%  
Accuracy: +/- 0.1%

Cost (Gas Sensor Solutions, March 2006):

GSS450 Oxygen Analyser: £6,000 (new portable version: £2,500, due for mid-2006)

SensiSpot: 10p (per piece)

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<sup>498</sup> The ESCAL™ bags were sealed on three sides and closed with a clip on the fourth side.

<sup>499</sup> Systech Instruments Ltd., Mapcheck Instruction Manual, 07/03/01.

This system works with the so-called SensiSpot, a printed sensor containing a ruthenium complex. This sensor is placed into the enclosure before sealing. With the GSS450 Oxygen Analyser one scans the sensor, which determines the oxygen concentration inside the bag. Illuminating the sensor causes the ruthenium complex to fluoresce. If oxygen is present, the fluorescence is quenched and the sensor will reemit less light. The amount of this reemitted light is therefore measured (the more the sensor reemits, the lower the oxygen content). The Oxygen Analyser is composed of an optical head using a light emitting diode (LED) to illuminate the sensor (blue light). When the sensor (SensiSpot) reemits light, it is detected using photodiodes. This information has to be fed into an electronic circuitry where the signals are converted into oxygen concentration values. Specific software as well as calibrations of instruments for the reading and recording of the data is provided by Gas Sensor Solutions.<sup>500</sup>

### **10.2.9 Oxygen transmission rate (OTR)**

*„The oxygen transmission rate of plastic films is measured by the standard method of the American Society for Testing Materials (ASTM 1999) wherein the film sample is mounted as the dividing barrier between two small chambers. Then pure nitrogen flows continuously through one chamber while oxygen flows through the other. Any oxygen permeating through the film into the nitrogen chamber is transported to a coulometric detector, producing an electrical current that is proportional to the amount of oxygen flowing into the detector per unit time. The ASTM oxygen transmission rate is measured by the volume of oxygen that moves through a sample of a film per square meter of film area each day ( $\text{cm}^3/\text{m}^2/\text{day}$ ), at 20 °C to 25 °C and 0% RH at the normal atmospheric pressure.“<sup>501</sup>*

*„In contrast, the permeability of a film is defined as dependent on the unit thickness of film. (Thus technically cannot be applied to a laminate. Laminates are not homogenous materials, and their properties are not necessarily uniform with an increase in thickness.) Nevertheless, if a film's permeability is multiplied by its thickness in mm or mil (0.001 in., i.e., 0.025mm), the result is approximately the OTR. [...] OTR is determined with air rather than 100% oxygen. Fortunately, the comparison is easy: simply dividing an OTR value in pure oxygen by 4.8 (because air is only 20.9% oxygen) gives its OTR in air.“<sup>502</sup>*

*„Permeability is the product of the permeance and the thickness of a film. Permeance is defined as the ratio of the gas transmission rate to the difference in partial pressure of the gas on both sides of the film. The gas transmission rate is the quantity of gas passing through a unit area of film per unit time.“<sup>503</sup>*

### **10.2.10 Radio telemetry system Meaco / Measurement of relative humidity and temperature**

Company: Meaco ([www.meaco.com](http://www.meaco.com))

<sup>500</sup> Gas Sensor Solutions, [www.gss.ie](http://www.gss.ie), 10/03/2006; personal communication with Chris Collins, Natural History Museum, London, 13/03/2006.

<sup>501</sup> MAEKAWA S., ELERT K., 2003, p26.

<sup>502</sup> Ibid.

<sup>503</sup> GILBERG M., GRATTAN D., 1994, p178.

Telemetry allows us to measure and report information remotely. The data here is transferred with the help of radio transmission.

The data is transmitted from the recording site to a computer located remotely. Data is then immediately accessible. The system can read over a long period, although batteries might to be changed from time to time.<sup>504</sup>

The Meaco system used records temperature and humidity at an interval of 20 minutes.

## 10.3 Annex III

### 10.3.1 Samples and their preparation

#### 10.3.1.1 Synthetic samples

The synthetic samples were produced mixing equal amounts of pure iron powder (Fe 99.5% purity from Fluka) and iron chloride hydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  99% purity from VWR International Ltd.). The sample weight was 0.1g.

#### 10.3.1.2 Archaeological samples

The archaeological samples (Roman nails) came from two Swiss excavations of the summer/autumn season of the year 2005 and arrived in London in December 2005.

The first Gallo-Romanic site is located in the canton of Fribourg (Bösingen Fendringenstrasse). The nails were found in a complex of a villa and are probably part of the remains of the Roman period of the site (end of 1<sup>st</sup> century BC until 3<sup>rd</sup> century AD). After excavation the nails were stored in plastic bags flushed with nitrogen.<sup>505</sup> The second site where samples were excavated is located in Vindonissa, canton of Aargau. The objects were excavated on the Windisch-Spillmannwiese site in 2005, V.003.1, position 102 (three nails per complex: 6653, 6654, 6655, 7288). The excavation took place between the 17<sup>th</sup> August and 5<sup>th</sup> October 2005. The site is located at the south gate of the legion camp Vindonissa. The objects were found in the top layers of the excavated ground and were dated as Roman (1<sup>st</sup> - 4<sup>th</sup> century AD). These nails were stored in resealable plastic bags after excavation. Upon arrival in London, pictures of the nails were taken and they were analysed visually under the microscope. No active corrosion was detected at that stage.

The nails were then cut into smaller pieces of around 2-3cm with a metal saw. These cut pieces were inserted to the experimentation after pictures were taken.



Figure 133: Synthetic powder sample weighed and placed into a plastic container to be placed into a test enclosure.

<sup>504</sup> Light and Humidity, Safeguarding Historic Collections, Short Course Programme, 2004, p22.

<sup>505</sup> Although the oxygen concentration was not equal to zero in the bags, but came to around 9-12%.



Figure 134: Archaeological samples (Bösingen, canton of Fribourg) before tests started.





Figure 135: Iron nails from the roman site Vindonissa, canton of Aargau.

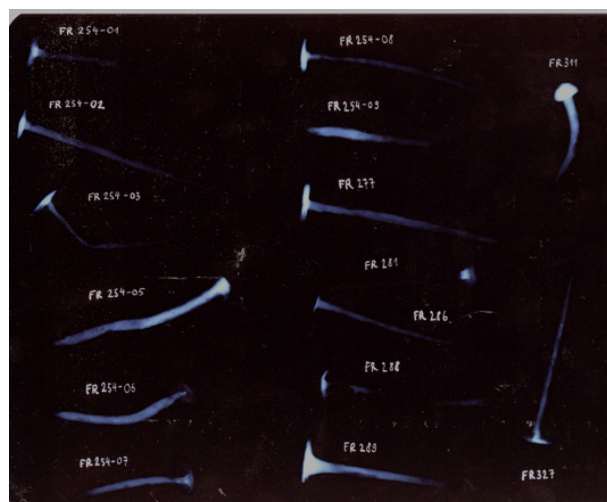


Figure 136: Before deciding which nails to take for experimental work it was ensured by the use of X-ray that metal remained in the samples (samples from the canton of Fribourg).

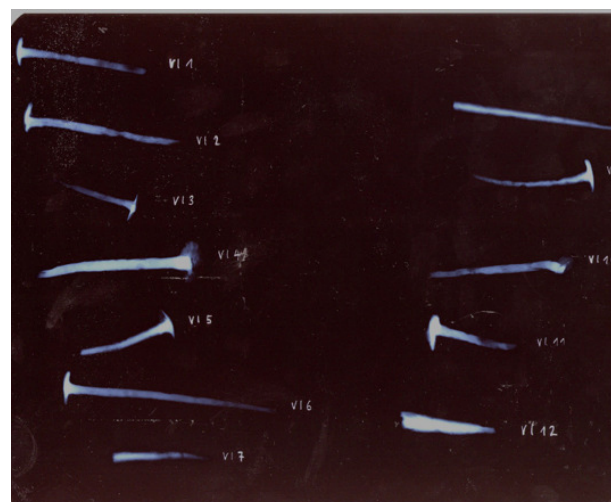


Figure 137: X-ray of the nails from Vindonissa before the tests began. Some metal remained in these Roman nails.



### 10.3.1.3 Correspondences

SAEF : Unité de valorisation  
laboratoire de conservation-restauration

Fiche d'intervention

Responsable: C. Buchiller  
Responsable: C. Benoit

| Fouille : BÖSINGEN FENDRINGENSTRASSE (BÖ-FEN) |               |         |          |          |              | Resp. fouille : | Jacques Monnier |            |
|---|---------------|---------|----------|----------|--------------|-----------------|-----------------|------------|
| Désignation                                   | No inf. suff. | secteur | Matériau | Interv.  | section (mm) | No FE           | Transmis à      | Date       |
| CLOU  | 254-01        | 205/41  | M/FE     | IP=SECT. | 4.3/4.5      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-02        | 205/41  | M/FE     | IP=SECT. | 3.2/3.4      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-03        | 205/41  | M/FE     | IP=SECT. | 3.6/3.7      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-04        | 205/41  | M/FE     | IP=SECT. | 6.3/6.4      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-05        | 205/41  | M/FE     | IP=SECT. | 5.0/5.3      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-06        | 205/41  | M/FE     | IP=SECT. | 4.9/5.0      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-07        | 205/41  | M/FE     | IP=SECT. | 3.5/4.1      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-08        | 205/41  | M/FE     | IP=SECT. | 4.2/4.4      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 254-09        | 205/41  | M/FE     | IP=SECT. | 5.0/5.2      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 277           | 205/41  | M/FE     | IP=SECT. | 3.8/4.0      | 2005/26-04      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 281           | 205/41  | M/FE     | IP=SECT. | 2.8/3.0      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 286           | 205/41  | M/FE     | IP=SECT. | 4.1/4.1      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 288           | 205/41  | M/FE     | IP=SECT. | 4.8/6.2      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 289           | 220/58  | M/FE     | IP=SECT. | 5.0/5.1      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 294           | 205/41  | M/FE     | IP=SECT. | 4.5/4.8      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 295           | 205/41  | M/FE     | IP=SECT. | 5.2/5.2      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 311           | 205/41  | M/FE     | IP=SECT. | 4.6/5.0      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 325           | 205/58  | M/FE     | IP=SECT. | 3.4/3.5      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 327           | 205/58  | M/FE     | IP=SECT. | 4.6/5.6      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |
| CLOU  | 328           | 205/58  | M/FE     | IP=SECT. | 4.6/4.8      | 2005/26-06      | HEAA-CR, S.G.   | 16.11.2005 |

Remarques : *IP=SECT. = Identification Ponctuelle de la section du clou*

List of the nails provided by the Archaeological Office of the Canton of Fribourg (Service Archéologique de l'Etat de Fribourg).



Direction de l'instruction publique,  
de la culture et du sport  
Direktion für Erziehung,  
Kultur und Sport

**Service archéologique**  
**Amt für Archäologie**

CANTON DE FRIBOURG / KANTON FREIBURG

13, Planche-Supérieure / Obere Matte  
1700 FRIBOURG / FREIBURG, le / den 21/11/2005

Madame Salomé Guggenheimer  
c/ English Heritage  
Londres

Tél. ++41 (0)26 351 22 22  
Fax ++41 (0)26 351 22 00  
E-mail SAEF@fr.ch

N/réf. cb  
U/Ref.

### **Clous pour test / étude corrosion**

Bonjour,

Suite à vos contacts avec notre labo- et plus précisément avec Cyril Benoît -, nous vous faisons parvenir ci-joint le lot de clous proposé provenant d'un chantier gallo-romain fouillé cette année, à savoir Bösinggen/Fendringen (BÖ-FEN, responsable : Jacques Monnier). Vous trouverez également, en plus de la documentation photo, quelques informations concernant le site en question. Les clous sont rangés par no.- d'inventaire dans des sachets sous azote.  
En vous souhaitant plein succès pour vos analyses et votre étude dont les résultats seront très intéressants à plus d'un titre, nous vous présentons nos salutations les meilleures

  
Carmen Buchiller  
Resp. unité valorisation

Annexes: - clous  
- doc. Photo  
- doc présentation du site

Letter from the Archaeological Office of the Canton of Fribourg (Service Archéologique de l'Etat de Fribourg) concerning the delivery of the archeological nails for sampling.

Depuis le 19<sup>e</sup> siècle, de nombreuses découvertes attestent la présence, à Bösing, d'une *villa rustica* d'époque romaine. Le terme *villa* désigne une exploitation agricole assez importante, comme on en connaît plusieurs centaines sur le Plateau suisse. Bösing appartient à la catégorie des grandes *villae*, puisque l'établissement devait couvrir une surface approchant les 8 hectares, à en juger par la répartition des trouvailles archéologiques.

Dans nos régions, les *villae* étaient divisées en deux parties : d'une part, la *pars urbana*, résidence du propriétaire, souvent richement décorées à la romaine par des fresques et des mosaïques, d'autre part, la *pars rustica*, zone productive de la *villa*, qui rassemblait des bâtiments économiques (granges, greniers, écuries, étables, ateliers artisanaux divers), mais aussi les habitations du personnel de la *villa*.

### Le bâtiment économique de la Fendringenstrasse

La fouille actuelle de la Fendringenstrasse, à environ 150 mètres au sud de la maison du propriétaire, concerne la partie productive (*pars rustica*) de la *villa*, une zone que les archéologues connaissent généralement moins bien que la *pars urbana*, souvent plus riche en vestiges. Les recherches ont débuté en avril 2005, motivée par la construction d'un bâtiment polyvalent (Mehrzweckgebäude), à côté de l'école. La surface à explorer d'ici le début des travaux s'élève à environ 3500 m<sup>2</sup>.

L'intérêt des recherches, outre une meilleure connaissance des zones productives des *villae*, réside dans la présence de nombreux vestiges antérieurs à l'époque romaine, qui attestent une présence humaine à Bösing bien plus ancienne qu'on ne le pensait jusqu'ici.

A l'origine, on peut imaginer le site comme une sorte de petit plateau parcouru par de petits ruisseaux. Un chenal de plus grandes dimensions, repéré dans la fouille sur une trentaine de mètres au moins, traversait la zone du sud au nord.

Les vestiges les plus anciens remontent à l'âge du Bronze final (vers 1000 avant J.-C.) ; il s'agit de quelques tombes à incinération, où les ossements brûlés étaient contenus dans une urne en céramique. Il s'agit des premières sépultures de ce type connues dans le district de la Singine. Un bracelet en bronze avait été déposé en offrande dans l'une des tombes.

D'autres traces d'une présence humaine antérieure à l'époque romaine remontent au *Second âge du Fer* (2<sup>e</sup>-1<sup>er</sup> siècle avant J.-C.). C'est à cette époque en effet que l'on répand au fond du chenal de grandes quantités de restes d'ossements animaux et de céramique à usage domestique (pots à provisions, écuelles), traces tangibles de la présence d'un habitat dans le secteur. A noter parmi la céramique la présence d'amphores (conteneurs) à vin, importées de la côte tyrrhénienne (occidentale) de l'Italie. Ces amphores sont la preuve concrète des échanges commerciaux qui existaient à cette époque entre les Helvètes, peuple indigène celtique, et le monde méditerranéen. Rappelons que notre pays sera intégré un peu plus tardivement dans l'Empire romain, sous le règne de l'empereur Auguste (fin du 1<sup>er</sup> siècle avant J.-C./début 1<sup>er</sup> siècle après).

A l'époque romaine, la zone semble occupée dès la période augusto-tibérienne, si l'on en croit la présence d'objets isolés (céramique surtout) et, surtout, une tombe à incinération, retrouvée dans le secteur des sépultures de l'âge du Bronze.

Toute la zone du plateau semble alors subir d'importants travaux de mise en valeur, avec l'aménagement d'une route en gros blocs de pierre, peut-être en relation avec une phase importante de défrichements. Les tombes plus anciennes de l'âge du Bronze sont alors soit recouvertes par les vestiges romains, soit profondément perturbées par les niveaux d'occupation (labours ?).

A l'ouest de la route, la zone du chenal connaît aussi de profonds bouleversements. Celui-ci semble avoir subi une ou plusieurs crues assez soudaines, qui ont laissé dans le chenal des grosses poches de sables et de galets charriés par le courant. Peu après cet événement, qui pourrait avoir eu lieu au



plus tard vers la fin du I<sup>er</sup> siècle avant J.-C., une présence humaine est perceptible dans la zone comprise entre le chenal et la route, à l'est. Certaines traces suggèrent qu'un premier bâtiment en bois a pu exister à cet endroit, mais il n'est pas encore possible de vérifier cette hypothèse. Dans la deuxième moitié du I<sup>er</sup> siècle de notre ère, la zone est partiellement nivelée pour permettre la construction d'un grand édifice (environ 18 x 12 m) reposant sur des fondations en pierre, non liées au mortier. Le bâtiment, dont les murs étaient vraisemblablement construits en matériaux légers (terre et/ou bois), était recouvert d'un toit en tuiles. Il abritait plusieurs locaux, dont la fonction est difficile à déterminer, vu le mauvais état de conservation des vestiges. La présence de scories de fer indique la présence du travail de ce métal dans le secteur ; peut-être le bâtiment abritait-il une forge dans l'une de ses pièces. Peu de vestiges subsistent à l'intérieur du bâtiment ; on peut citer la présence d'un gros bloc de schiste, qui pourrait avoir été travaillé et dont la fonction reste à déterminer. A cela s'ajoute un coffre constitué de 4 tuiles romaines à rebord (*tegulae*), qui pourrait abriter une petite sépulture d'enfant. Les recherches à venir permettront de vérifier l'hypothèse d'une tombe, enfouie à l'intérieur de l'édifice, contre un mur. Bien qu'il soit difficile d'expliquer cette coutume, on remarque que les sépultures d'enfants dans ou à proximité immédiate de bâtiments antiques est assez répandue dans le monde romain, y compris en « Suisse romaine » (d'autres occurrences sont connues dans les *villae* d'Orbe VD ou Neftenbach ZH, par exemple). A en juger par le mobilier archéologique retrouvé (céramique surtout), le bâtiment a eu une durée de vie assez limitée, puisqu'il semble avoir été détruit à la fin du II<sup>e</sup> siècle ou au début du III<sup>e</sup> siècle. La destruction n'a visiblement pas été causée par un incendie (absence de traces de feu), mais semble volontaire. Nous ignorons quelles sont les raisons qui ont poussé les habitants à démanteler le bâtiment, sur lequel on construit d'ailleurs un nouveau mur, d'orientation légèrement divergente, qui pourrait matérialiser le (nouveau ?) mur d'enclos de la *villa*.

A l'extrémité occidentale de la zone fouillée, en bordure immédiate de l'actuelle Fendringenstrasse, un chemin assez simple a été aménagé à l'époque romaine. D'après l'orientation, légèrement divergente, de ce chemin et de la route plus à l'est, on peut supposer que le carrefour entre ces deux voies devait se situer plus au nord, sous l'école actuelle, non loin d'un autre tronçon de route repéré devant les bâtiments actuels de l'administration communale.

Jacques Monnier

Documentation on the site where the archaeological samples were found in the canton of Fribourg, Switzerland.

Lic. phil. Judith Fuchs, Co-Leiterin Sammlung und Fundverwaltung  
Industriestrasse 3, 5200 Brugg  
Telefon 056 462 48 27/11  
Fax 056 462 48 15  
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Frau  
Salome Guggenheimer  
English Heritage  
23 Savile Row  
London W1S 2ET

United Kingdom

Brugg, 16. dezember 2005

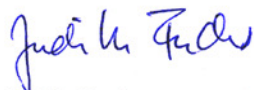
**Eisennägel aus Vindonissa für Ihre Untersuchungen**

Liebe Frau Guggenheimer

Anbei sende ich Ihnen 12 Eisennägel, bzw. Fragmente davon aus Vindonissa für Ihre Untersuchungen zur Bildung von Akaganeit im Rahmen Ihrer Diplomarbeit an der Haute école d'arts appliqués Arc La Chaux-de-Fonds. Die Nägel wurden bei uns dokumentiert und sind nun ein **Geschenk** an Sie. Wir nehmen zur Kenntnis und geben unser Einverständnis, dass sie bei den Untersuchungen zerstört werden.

Wir wünschen Ihnen viel Erfolg bei Ihren Forschungen und freuen uns, von Ihren Ergebnissen zu erfahren, wenn Sie Ihre Diplomarbeit abgeschlossen haben.

Mit freundlichen Grüssen  
**KANTONSARCHÄOLOGIE AARGAU**



Judith Fuchs

Letter from the Archaeological Office of the Canton of Aargau (Kantonsarchäologie Aargau) accompanying the gift of iron nails for testing.

De: Fuchs Judith BKSKA [Judith.Fuchs@ag.ch]

Date: jeu. 08/06/2006 06:52

À: Guggenheimer Salomé

Cc: Fellmann Regine BKSKA

Objet : AW: Eisennägel

Pièces jointes :

[Afficher sous forme de page Web](#)

Liebe Frau Guggenheimer

Hier die Angaben zu den 12 Nägeln bzw. Nagelfragmenten aus Windisch (AG)/Vindonissa, die wir Ihnen für Ihre Untersuchungen geschenkt haben:

Alle stammen von der Grabung Windisch - Spillmannwiese 2005, V.003.1, Position 102 (je drei aus den Fundkomplexen 6653, 6654, 6655 und 7288, geborgen zwischen 17. August und 5. Oktober 05). Die Grabung "Spillmannwiese" liegt im Umfeld des Südtores des Legionslagers von Vindonissa.

Pos. 102 beinhaltet die obersten Maschinenabträge, also die obersten, jüngsten Schichten. Die Nägel sind vermutlich alle römisch (1.-4. Jh. n. Chr.), in diesen Schichten lässt sich aber auch eine jüngere Datierung nicht ganz ausschliessen.

Ich hoffe, diese Angaben genügen Ihnen, und wünsche Ihnen weiterhin viel Erfolg bei Ihrer Arbeit.

Mit freundlichen Grüßen,  
Judith Fuchs

-----Ursprüngliche Nachricht-----

Von: Guggenheimer Salomé [<mailto:Salome.Guggenheimer@he-arc.ch>]

Gesendet: Sonntag, 4. Juni 2006 09:44

An: Fuchs Judith BKSKA

Betreff: Eisennägel

Liebe Frau Fuchs,  
vor einigen Monaten haben Sie mir Eisennägel für meine Diplomarbeit zur Verfügung gestellt. Könnten Sie mir bitte noch, ganz kurz kann das sein, ein paar Informationen geben zu Fundort und Datierung des Materials? Ich sollte das in meiner Arbeit erwähnen können. Sie haben mir damals geschrieben, die Nägel seien bei Ihnen dokumentiert.  
Besten Dank und freundliche Grüsse,  
Salome Guggenheimer

E-mail from Judith Fuchs in Brugg giving details upon the site where the nails used in the experimentation were excavated.

## 10.3.2 Tested storage systems: used materials

### 10.3.2.1. Dry, cold and dry/cold storage

Materials used were:

| Material / product         | Name  | Company                                     |
|----------------------------|---|---|
| Dataloggers <sup>506</sup> | Hanwell Datalogger rh-t bug   | Hanwell Instruments Limited, United Kingdom |
|                            | Meaco telemetry systems   | www.meaco.com                               |
| PE bags                    | Minigrip <sup>TM</sup> Sachets (PE-LD) 100 x 125mm                          | Semadeni AG, Semadeni (Europe) AG           |
| PP boxes                   | Stewart <sup>TM</sup> Boxes 'Seal fresh' (boxes of 1.8l and 2.25l)          | Azpack Limited, United Kingdom              |
| Samples                    | Iron powder <sup>507</sup>  | Fluka Chemie GmbH, Switzerland              |
|                            | Iron chloride hydrate <sup>508</sup> (FeCl <sub>2</sub> ·4H <sub>2</sub> O) | VWR International Ltd., United Kingdom      |
| Desiccant                  | Silica gel <sup>509</sup>   | Baltimore Chemicals Ltd., United Kingdom    |
| Relative humidity control  | Relative humidity-indicating strips   | Conservation by Design Ltd, United Kingdom  |

Table 11: Materials and equipment for tests on dry and dry/cold storage.

### 10.3.2.2. Oxygen-free storage

Materials used were:

| Material / product               | Name  | Company                                  |
|----------------------------------|---|--|
| Oxygen absorbers                 | RP-A and RP-K (for 300ml of air)  | Mitsubishi Gas Chemical Company, Japan   |
| High-barrier film                | ESCAL <sup>TM 510</sup>   | Mitsubishi Gas Chemical Company, Japan   |
| Oxygen-indicating tablets        | Indicating tablets 'Eye' for the RP-System <sup>TM</sup>                    | Mitsubishi Gas Chemical Company, Japan   |
| Clips                            | Clips for the use with the RP-System <sup>TM</sup>                          | Mitsubishi Gas Chemical Company, Japan   |
| Samples                          | Iron powder <sup>511</sup>  | Fluka Chemie GmbH, Switzerland           |
|                                  | Iron chloride hydrate <sup>512</sup> (FeCl <sub>2</sub> ·4H <sub>2</sub> O) | VWR International Ltd., United Kingdom   |
| Oxygen monitoring <sup>513</sup> | GSS450 Oxygen Analyser  | Gas Sensor Solutions, Ireland            |
|                                  | Mapcheck oxygen meter   | Systech Instruments Ltd., United Kingdom |

Table 12: Materials and equipment for tests on anoxic storage.

<sup>506</sup> See annex II for details on the equipment.

<sup>507</sup> Puriss. p. a.; Carbonyl-Iron powder; ≥ 99.5% (RT).

<sup>508</sup> Iron(II) chloride 4-hydrate (ferrous chloride), FeCl<sub>2</sub>·4H<sub>2</sub>O = 198.83 g/mol, assay (manganometric) ≥ 99.0%.

<sup>509</sup> 20kg/m<sup>3</sup> silica gel are needed for conditioning. For the 1.8l box a minimum amount of 0.036kg and for the 2.25l box 0.045kg of silica gel would be required. In the present work an excess of 0.2kg has been added to assure a very dry climate over the six months of the experimentation.

<sup>510</sup> Bag size was 150mm x 250mm.

<sup>511</sup> Puriss. p. a.; Carbonyl-Iron powder; ≥ 99.5% (RT).

<sup>512</sup> Iron(II) chloride 4-hydrate (ferrous chloride), FeCl<sub>2</sub>·4H<sub>2</sub>O = 198.83 g/mol, assay (manganometric) ≥ 99.0%.

<sup>513</sup> See annex II for details on the equipment.

### 10.3.3 Monitoring of test environments

The following figures show the RH and temperature levels of the period of the experimental work. The dataloggers used were Meaco and Hanwell instruments. For groups E and L (samples stored cold), no information could be obtained, probably because the batteries of the Hanwell loggers broke down due to the low temperatures.

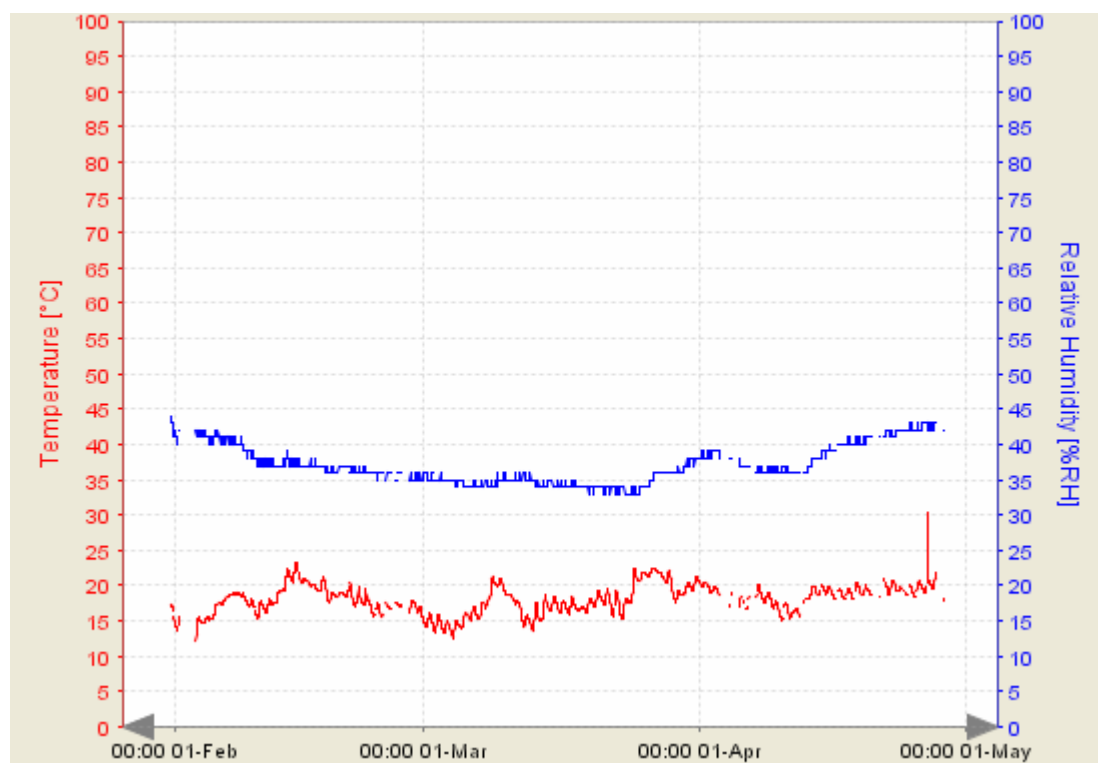


Figure 138: Relative humidity (%RH) and temperature (°C) for samples stored in closed PE bags (group D).



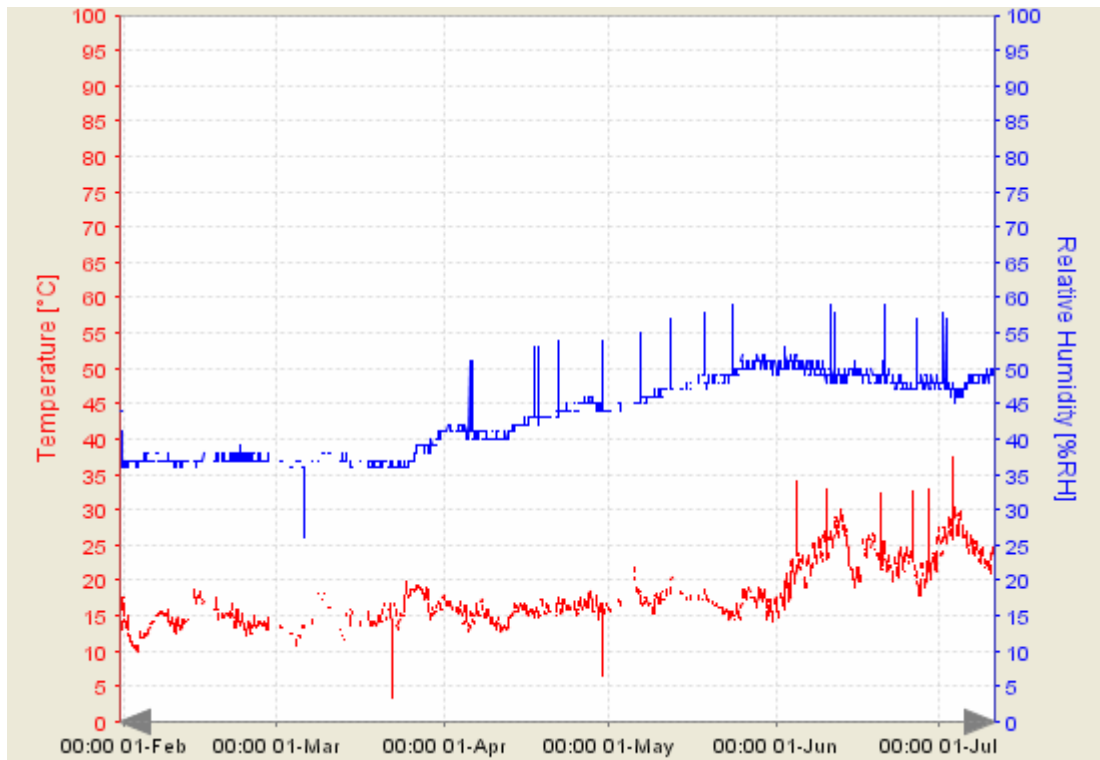


Figure 139: Relative humidity (%RH) and temperature (°C) for samples stored in PE bags with holes (group H).

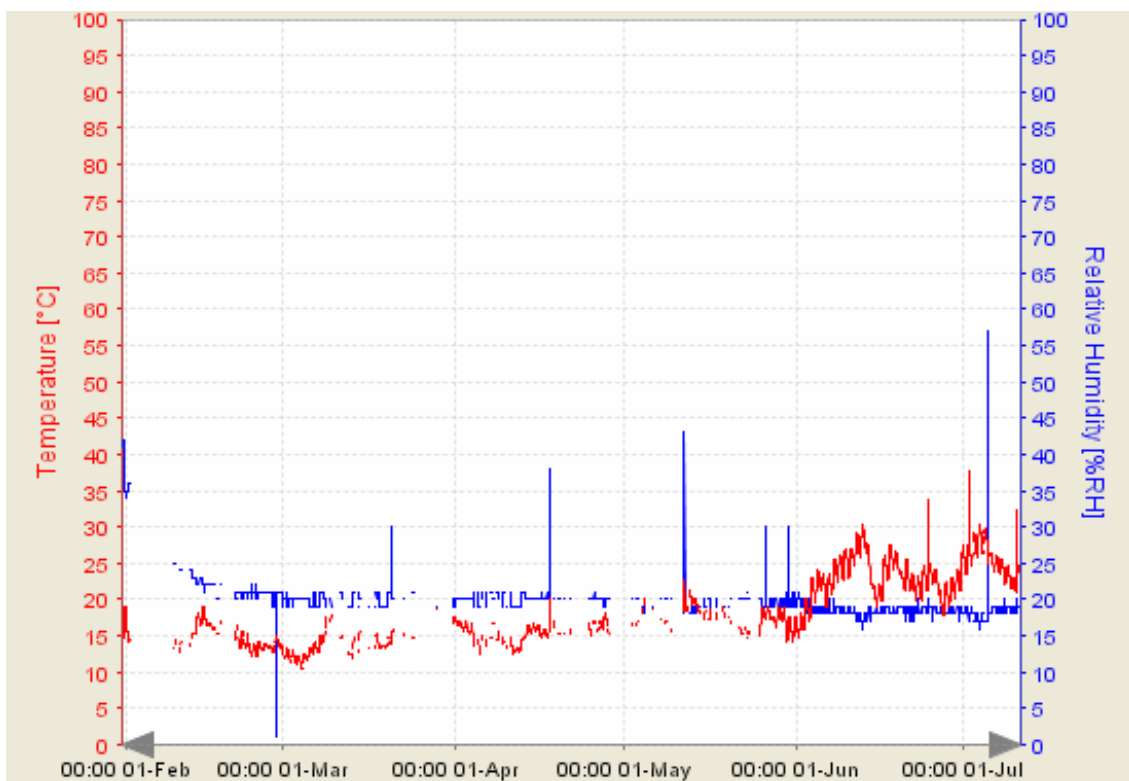


Figure 140: Relative humidity (%RH) and temperature (°C) for samples stored dry in closed PE bags (group F).

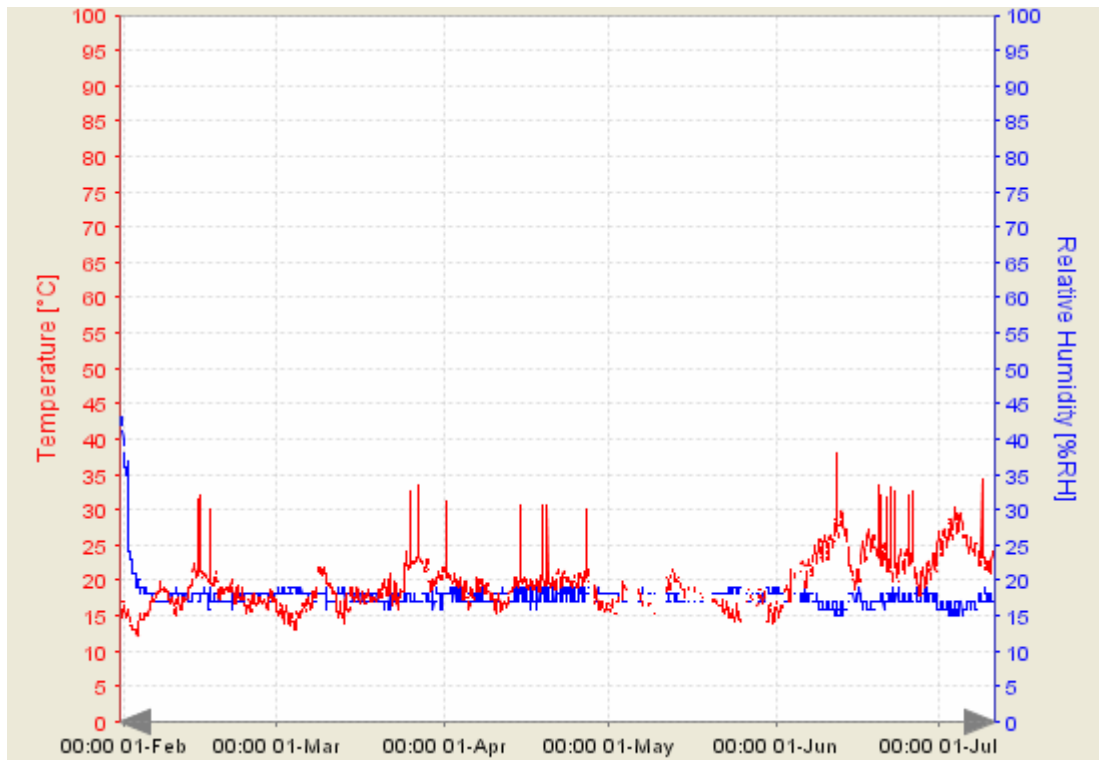


Figure 141: Relative humidity (%RH) and temperature (°C) for samples stored dry in PE bags provided with holes (group K).

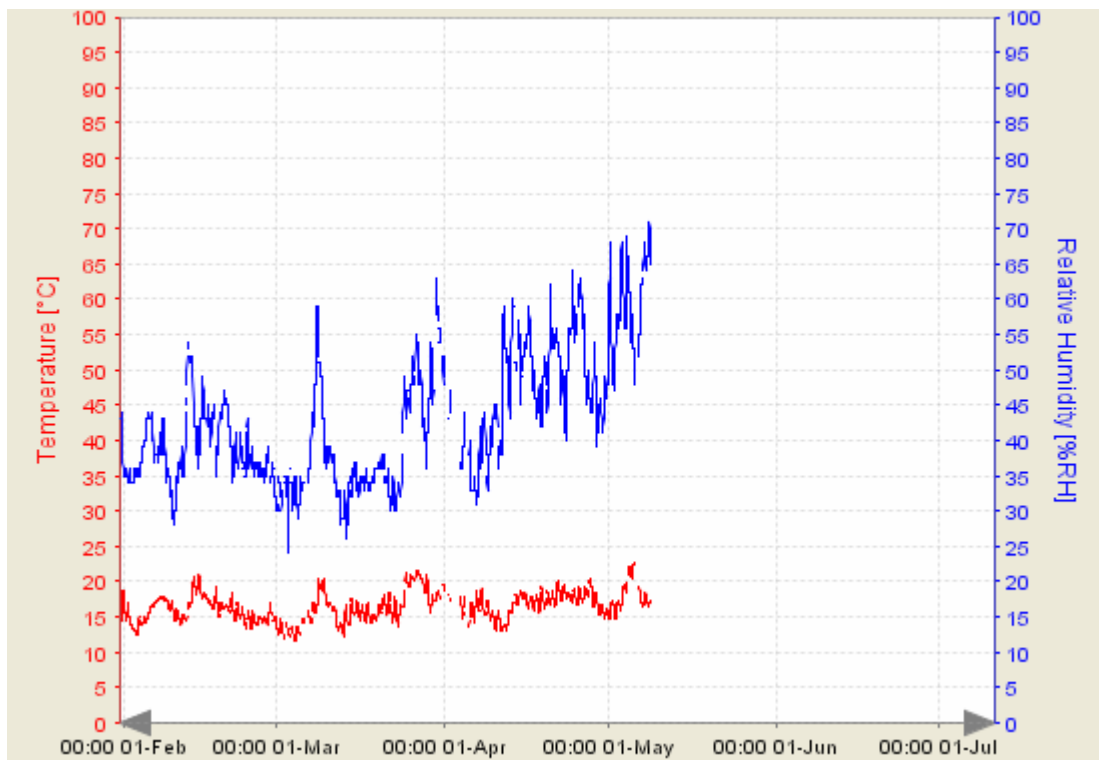
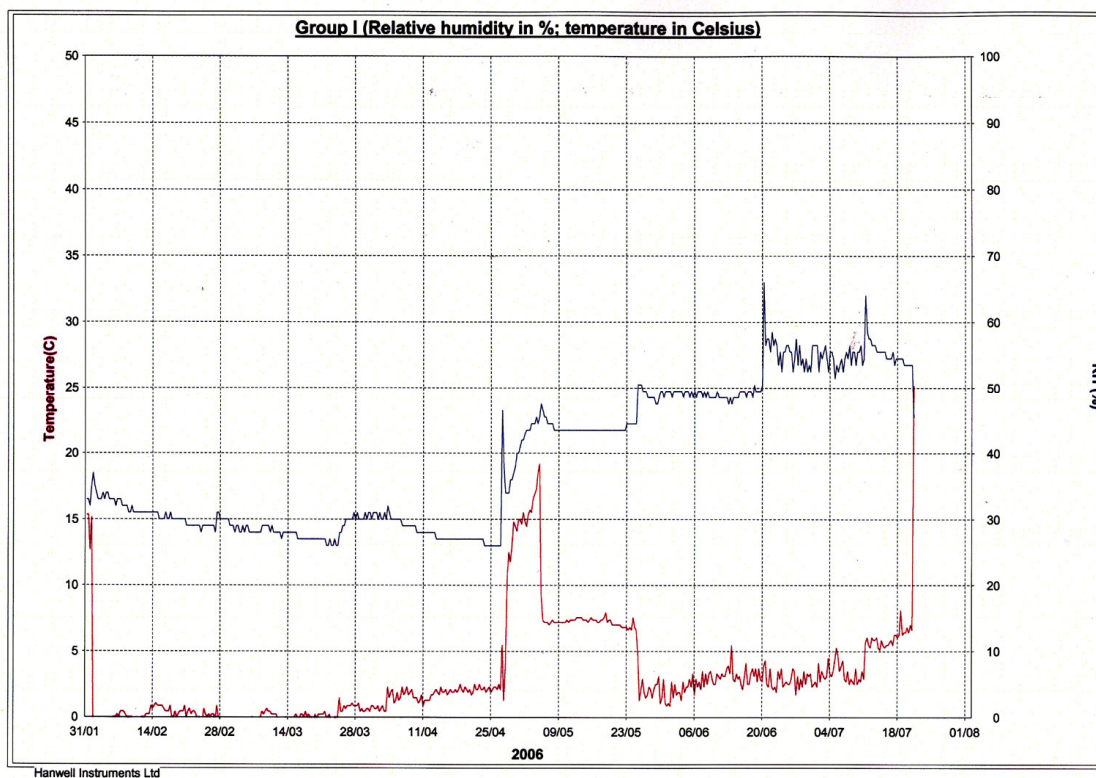
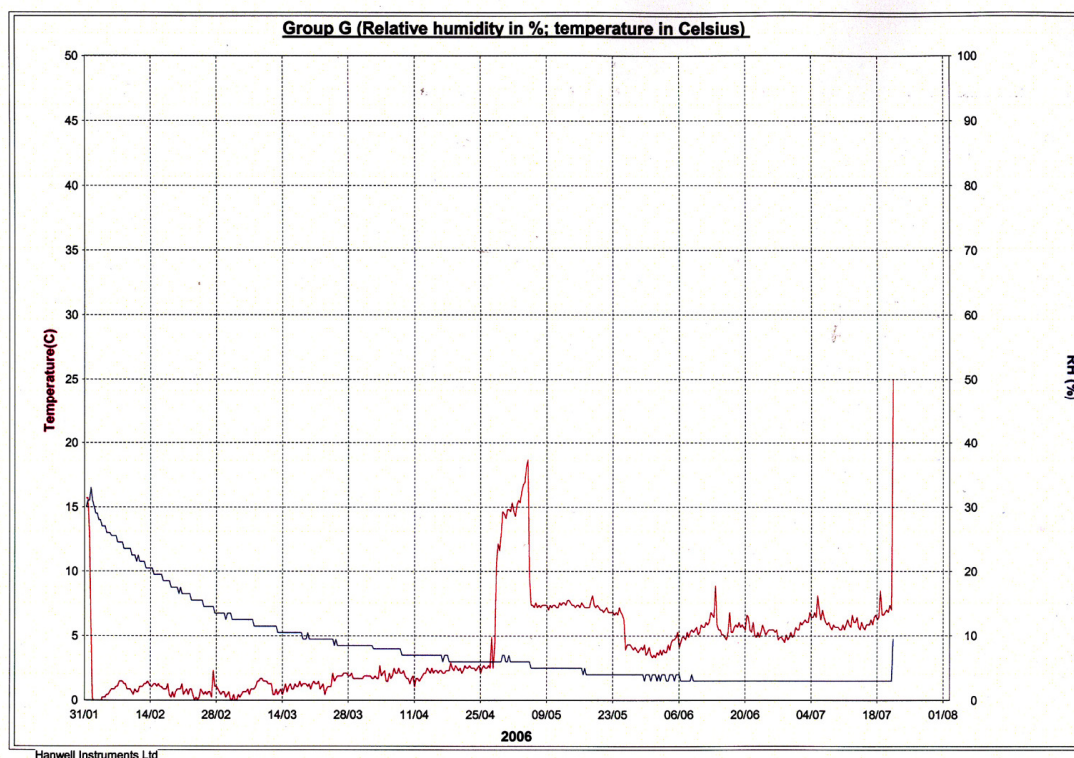


Figure 142: Climate at Ranger's House Painting Studio where the samples were stored. The logger failed during the test period.





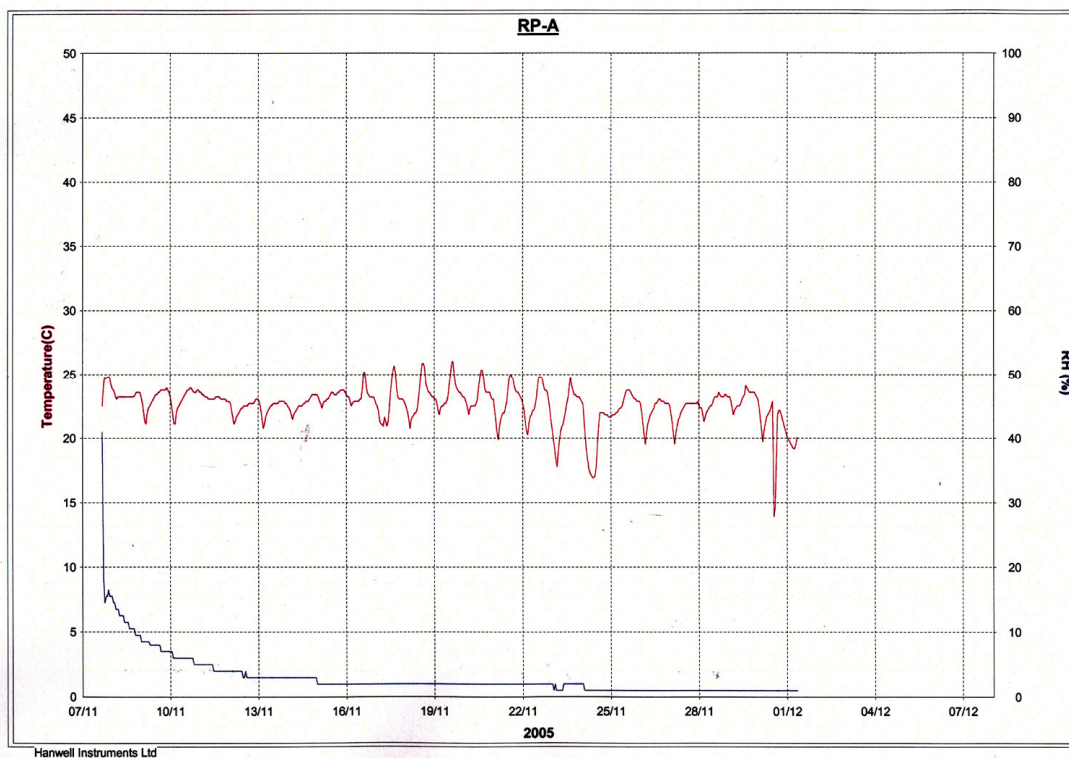


Figure 145: RH and temperature in an ESCAL™ bag (clipped) with the RP-A oxygen absorber. The RH quickly drops below 10%.

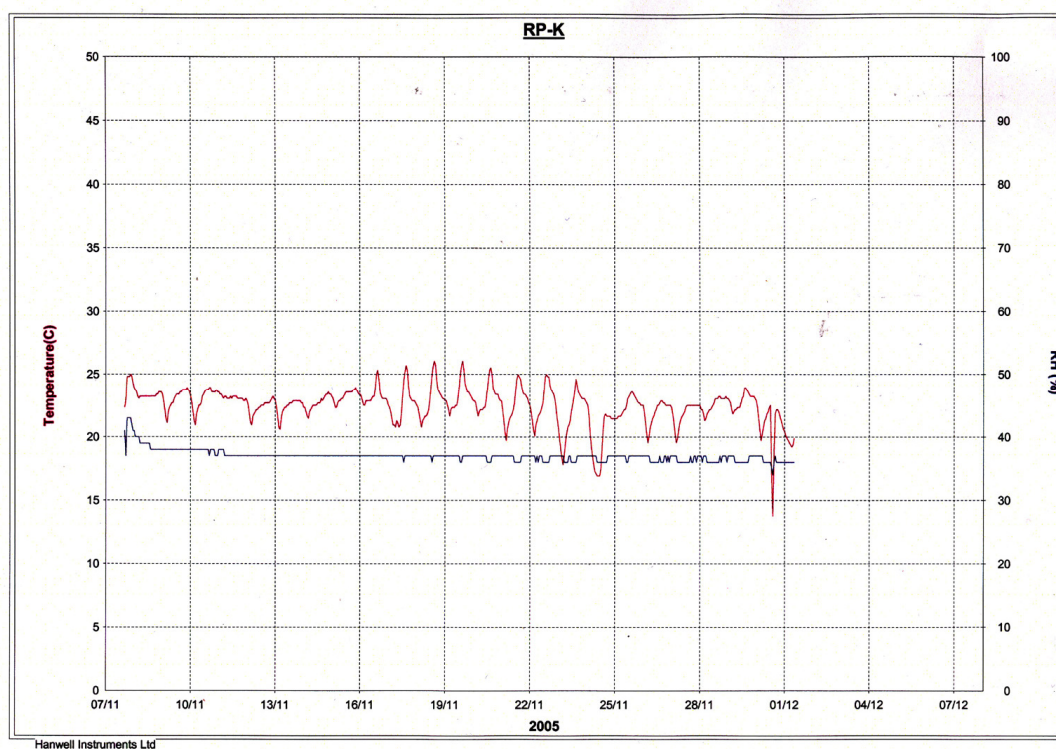


Figure 146: The RH, in blue, stays on the same level and is not affected when using the RP-K oxygen absorber.

## 10.4 Annex IV

### *10.4.1 Questionnaire on storage of archaeological iron in Switzerland*

#### 10.4.1.1 Questions

Questions to Swiss Laboratories in Conservation on the storage and treatment of freshly excavated iron:

**If possible, please give precise information about your approach.**

1. Does your institution regularly deal with freshly excavated iron artifacts? If yes, how many a year?
2. How are the iron artifacts stored after excavation? (Where possible, give some details).
  - a) In plastic boxes (Tupperware™ for example). Which boxes (trademarks) are used?
  - b) In sealed plastic bags or foils. Which bags/foils?
  - c) As a block (like in plaster, in foil, ...)?
  - d) Others: (please describe)?
3. Is the climate influenced during storage?
  - a) Cold storage (please describe how).
  - b) Dry storage (please describe how).
  - c) Oxygen-free storage (please describe how).
  - d) Others (please describe).
4. How long are the iron artifacts stored before a treatment begins?
5. Which treatments are applied? (for example immersion in alkaline sulphite, plasma, none).

### 10.4.1.2 Answers

| Question                    | Laboratory<br>(Canton)  | Laboratory<br>(Canton)  | Laboratory<br>(Canton)  | Laboratory<br>(Canton)  |
|-----------------------------|---|---|---|---|
|                             | Lausanne (VD)   | Sion (VD)   | Augusta Raurica<br>(BL)   | Neuchâtel (NE)  |
| <b>Iron finds per year:</b> | 300-500.  | 10-100.   | 1500-9000.  | 20-500.   |
| <b>Storage:</b><br>-boxes   |   | Various boxes (PE).   | -Box (Rondo™, PE/PP).<br>-Fragile objects on PE-foam (Alveolit™) in Plexiglas™ boxes placed in other boxes (Rondo™, PE/PP).<br>-Rako™ boxes (PP) for big finds.   |   |
| -bags                       | Bags Minigrip™ (PE).  | Object in bags Minigrip™ (PE) placed in the boxes (PE).                     | - Objects in resealable bags and paper bags on site.<br>- Objects placed into bags (PE) with holes, a layer of PE-foam (Alveolit™) protects the objects. The bags are placed into the boxes (Rondo™, PE/PP): long-term storage. | Bags Minigrip™ (PE), left open.   |
| -as a block (block lifting) | Sometimes, then put into refrigerator at 2°C.   | Used materials if a block is stored: aluminium foil, kitchen foil, plaster. | If occurring: object treated directly in the laboratory.  | Film (PE) put on object before plastering.                                |
| -others                     |   |   |   | Sometimes storage in film (PE) under vacuum.                              |
| <b>Climate:</b><br>-cold    | If long intervention on object before desalination: object placed in box (PE or PS) with lid or covering film (PE) and placed in cold at 2°C. | Objects arriving at the lab are stored in the refrigerator.                 |   | Very delicate objects sometimes put into cold as they wait for treatment. |
| -dry                        | Sometimes object in box (PS) with a separation (in one part object, in  |   | Silica Gel in boxes (Rondo™, PE/PP and Rako™, PP): RH   | After treatment if object is on exposition: RH controlled in              |

|                           |  |                                     |  |   |
|---------------------------|--|-------------------------------------|--|---|
|                           | other part desiccant), covered with lid, silica gel conditioned at 30% RH. Plans of a space where RH at 20%. |                                     | to be kept under 15%. Climate in store: 40% RH.  | showcases. Storage in RH controlled room (below 30%).   |
| -oxygen-free<br>-others   |  |                                     |  | No intervention on the surrounding climate before object treated (influence taken only if indicated). |
| <b>Time to treatment:</b> | 0-2 month.   | Weeks up to months.                 | 3-6 months.  | Days to years.  |
| <b>Treatment:</b>         | Alkaline sulphite.   | Alkaline sulphite if budget allows. | X-ray, photo, weighing, examination under microscope. Larger intervention only for specific exhibitions, research projects and publications. | Unveiling, alkaline sulphite, consolidation, protective wax.  |

| <b>Question</b>             | <b>Laboratory (Canton)</b>   | <b>Laboratory (Canton)</b>                     | <b>Laboratory (Canton)</b>  | <b>Laboratory (Canton)</b>   |
|-----------------------------|--|--|---|--|
|                             | <b>Bern (BE)</b>   | <b>Vaduz (Liechtenstein)</b>                   | <b>Chur (GR)</b>  | <b>Vindonissa (AG)</b>   |
| <b>Iron finds per year:</b> | 2000-5000.   | Fluctuant, following excavations.              | 400-500.  | 20-40 a week (for the years 2002-2005).  |
| <b>Storage:</b><br>-boxes   | Rako™ boxes (PP).  | Rako™ boxes (PP), Curver™ boxes (PE).          | Plexiglas™ boxes for special finds.   |  |
| -bags                       |  | Bags Minigrip™ (PE) in Rako™ boxes (PP).       | 1-10 objects in plastic bags (Polyfresh™, PE) closed with a plastified metal filament (bags are not closed hermetically, so no holes are made). | Bags Minigrip™ (PE).   |
| -as a block (block lifting) |  |  |   |  |
| -others                     | In cardboard boxes (acid-free), then in Rako™ boxes (PP) with lid (dust-free). | Big finds in bags made of ESCAL™ barrier film. | On site: objects air-dried for some days. Special finds in wrapping tissue in Plexiglas™-boxes.   | Finds selected for desalination are put into ESCAL™ barrier film bags with desiccant (Rubingel). |
| <b>Climate:</b>             | From 2006 onwards at 18°C  | Wet finds are placed into                      |   |  |

|                           |   |   |  |  |
|---------------------------|---|---|--|--|
| -cold                     | or less.  | refrigerator until photographed (1-5 days), then deep-freezing at -24 °C until treatment.   |  |  |
| -dry                      | From 2006 onwards at 28%.                                 | Dry objects in bags (Minigrip™, PE) in boxes (Curver™, PE) with Silica Gel, storage at room temperature. Big objects sealed in Escal™ barrier film. |  |  |
| -oxygen-free              |   |   |  |  |
| -others                   |   |   | Bags (PE) and boxes (Plexiglas™) put in cardboard boxes (not acid-free) until treatment. Objects in store: 18 °C, 40-50% RH. |  |
| <b>Time to treatment:</b> | 1-2 years.  | Months (especially for frozen objects it takes longer until treatment).   | 0-3 days for some objects. Can take up to 15 years to treatment. Most objects are not treated.                               | 5-20 months                                |
| <b>Treatment:</b>         | From 2006 onwards alkaline sulphite for chosen artifacts. | Alkaline sulphite.  | Rough unveiling, alkaline sulphite, fine unveiling, protective layer (Paraloid B72).   | X-ray, alkaline sulphite for chosen finds. |

| Question                    | Laboratory (Canton)  | Laboratory (Canton)   | Laboratory (Canton)                         |
|-----------------------------|--|---|---|
|                             | <b>Basel (BS)</b>  | <b>Fribourg (FR)</b>  | <b>Avenches (VD)</b>                        |
| <b>Iron finds per year:</b> | 735 (only the ones which came to the laboratory)   | 650   | 200   |
| <b>Storage:</b><br>-boxes   | Big boxes Captivair™, Rubbermaid™ (PE). Objects in small boxes (PS) from Semadeni Switzerland, then packed into the big boxes. |   | Boxes with membrane for very fragile finds. |
| -bags                       | Minigrip™ bags (PE).   | In Minigrip™ bags, PE (closed) after excavation. Then 3 days later arriving in lab. | Sealed bags.                                |



|                                  |   |  |   |
|----------------------------------|---|--|---|
|                                  |   | In lab: in sealed films of 2 layers (PA/PE, 20/70).  |   |
| -as a block (block lifting)      | Very rare (only for fragile finds), then in plaster, aluminium and foil (PE).   | Sealed film around the plastered block.  | If necessary.   |
| -others                          | Long-term storage for some objects (large weapons) in ESCAL <sup>TM</sup> barrier film.   |  | In Minigrip <sup>TM</sup> bags (PE).                      |
| <b>Climate:</b><br>-cold<br>-dry |   |  |   |
|                                  | Desiccant (Rubingel) in the boxes to keep the RH low.   | Oxygen-free bags placed in 25-35% RH, 20-28°C environment.   |   |
| -oxygen-free                     | RP-System <sup>TM</sup> (RP-A) for some treated objects only (large weapons).   | Extraction of oxygen from the bag, nitrogen flushing with help of low pressure.  | In sealed bags flushed with nitrogen.                     |
| -others                          | Stores: 20°C and 30%RH.   | Oxygen-free bags placed in 25-35% RH, 20-28°C environment.   | Stores: slight fluctuations in HR and temperature levels. |
| <b>Time to treatment:</b>        | 3 months to 8 years. Usually 6 months to 2 years.   | 3 months or more.  | 2 months to 10 years.                                     |
| <b>Treatment:</b>                | Unveiling and object then dried in an oven. Impregnation in Paraloid B72 in 3% toluene under vacuum. Decision, which object is treated and to what extend based on X-rays made of every object. | Some objects treated with alkaline sulphite. In the past some objects were treated with low plasma hydrogen reduction. | Either alkaline sulphite or no treatment.                 |

Table 13: Answers to the questions sent to Swiss conservation laboratories on the topic of storage and treatment of archaeological iron.

## **10.5 Annex V**

### ***10.5.1 Suppliers of materials and equipment (alphabetical order)***

#### **CRISS CROSS Universal Heat Sealing Machine**

*Conservation by Design Limited*

*Bedford MK42 7AW*

*United Kingdom*

*Star Universal (Gosport) LTD (for repairs)*

#### **Curver™**

*Polyethylene/polypropylene boxes*

*Rubbermaid (Curver Kunststoff GmbH)*

*An der Taft 63*

*63303 Dreieich*

*Germany*

*Or*

*Semadeni AG, Semadeni (Europe) AG*

*Tägetlistrasse 35-39*

*Industriezone Obere Zollgasse*

*3072 Ostermundigen*

*Switzerland*

#### **D-TEK™ Select Refrigerant Leak detector**

*INFICON*

*Two Technology Place*

*East Syracuse*

*NY 13057*

*USA*

*reachus@inficon.com*

#### **Fourier-transform infrared spectroscopy (FT-IR)**

*Perkin Elmer 2000 FT-IR*

#### **GSS450 Oxygen Analyser**

*Gas Sensor Solutions Ltd.*

*The Invent Centre*

*Glasnevin*

*Dublin 9*

*Ireland*

*www.gss.ie*

**Hanwell Dataloggers**

Hanwell Datalogger: rh-t bug

*Hanwell Instruments Limited*

*12-13 Mead Business Centre*

*Mead Lane*

*Hertford SG13 7BJ*

*United Kingdom*

*www.hanwell.com*

**Iron (Fe)**

Purity: 99.5%

*Fluka Chemie GmbH*

*9471 Buchs*

*Switzerland*

**Iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ )**

Purity: 99.0%

*VWR International Ltd.*

*Poole BH15 1TD*

*United Kingdom*

**Iron(II) chloride ( $\text{FeCl}_2$ )**

Purity: 99.5%

*Alfa Aesar A Johnson Matthey Company*

*30 Bond Street*

*Ward Hill, MA 01835*

*USA*

**Iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )**

Purity: 97.0 – 102.0%

*Alfa Aesar A Johnson Matthey Company*

*30 Bond Street*

*Ward Hill, MA 01835*

*USA*

**Iron(III) hydroxide, alpha ( $\alpha$ - $\text{FeOOH}$ , goethite)**

*Alfa Aesar A Johnson Matthey Company*

30 Bond Street  
Ward Hill, MA 01835  
USA

**Mapcheck (oxygen meter)**

Systech Instruments Ltd.  
Thame  
United Kingdom  
[www.systech.co.uk](http://www.systech.co.uk)

**Meaco (Radio Telemetry System)**

1 Cobbet Park  
Moorfield Road  
Slyfield Industrial Estate  
Guildford  
Surrey GU1 1RU  
United Kingdom  
[www.meaco.com](http://www.meaco.com)

**Minigrip™ polyethylene sachets**

100 x 125mm  
Semadeni AG, Semadeni (Europe) AG  
Tägetlistrasse 35-39  
Industriezone Obere Zollgasse  
3072 Ostermundigen  
Switzerland

**Plastic containers for samples**

Samco Silicone Products Ltd.  
Secton Court  
Veasey Close  
Nuneaton  
Warwickshire CV11 6RT  
United Kingdom  
[www.samco.co.uk](http://www.samco.co.uk)

**Raman spectroscopy**

Renishaw System 1000 Ramascope

**Relative humidity-indicating strips**

*Conservation by Design*

*Bedford MK42 7AW*

*United Kingdom*

*www.conservation-by-design.co.uk*

**Rondo™**

Polyethylene/polypropylene boxes

*Rotho Kunststoff AG*

*5303 Würenlingen*

*Switzerland*

Or

*Migros Distribution*

*Switzerland*

**RP-System™****ESCAL™**

**Indicating tablets ‘eye’ for RP-System™**

**Clips**

*Mitsubishi Gas Chemical Company*

*Japan*

*http://www.mgc.co.jp*

Distribution in Europe for small quantities (Germany):

*Long Life for Art*

*Christoph Waller*

*Im Bückle 4*

*79288 Gottenheim*

*Germany*

*Tel +49 (0)7665 940390*

*Fax +49 (0)7665 940391*

Distribution in Europe for small quantities (United Kingdom)

*Conservation by Design*

*Bedford MK42 7AW*

*United Kingdom*

*www.conservation-by-design.co.uk*

**S1 Sword Hygrometer**

*Rotronic Instruments (UK) Ltd*

*Unit 1a Crompton Fields*

*Crompton Way*

*Crawley  
West Sussex RH10 9EE  
United Kingdom*

**Silica Gel**

*Baltimore Chemicals Ltd  
Innovations House  
Jacksons Business Park  
Wessex Road  
Bourne End  
Bucks SL8 5DT  
United Kingdom  
[www.baltimorechemicals.co.uk](http://www.baltimorechemicals.co.uk)*

**Stewart™ Boxes 'Seal fresh'**

*1.8l and 2.25l polypropylene boxes  
Azpack Limited  
12 Kernan Drive  
Swingbridge Trading Estate  
Loughborough  
Leicestershire LE11 5JF  
United Kingdom*

**Vaisala GM 70 Carbon Dioxide Meter**

*Vaisala Ltd  
Tel.: +44 (0)1638 576200  
E-mail: [uksales@vaisala.com](mailto:uksales@vaisala.com)*

**X-ray diffraction (XRD)**

*Philips 1830/1840  
Nederlandse Philips Bedrijven B.V.  
Lelyweg 1  
7602 EA Almelo  
The Netherlands*