



FACULTY OF SCIENCES

Department of Analytical Chemistry

A STUDY OF THE ELECTROLYTIC REDUCTION OF
CORRODED LEAD OBJECTS
AND
THE APPLICATION, CHARACTERIZATION AND TESTING
OF A PROTECTIVE LEAD CARBOXYLATE COATING

Bart Schotte

Thesis submitted in fulfilment of the requirements
for the degree of Doctor in Science: Chemistry

Promotor: Prof. Dr. A. Adriaens
Copromotor: Prof. Dr. M.G. Dowsett
Copromotor: Prof. Dr. L. Vincze

Academic year 2006-2007



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*Science may set limits to knowledge,
but should not set limits to imagination.*

Bertrand Russell

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Part I

General introduction, corrosion and
conservation, applied techniques

Chapter 1

General introduction on lead

This chapter starts with the description of the historical and present use of lead. This is followed by a discussion on the corrosion of lead in all its aspects, starting from the basic principles to the different corrosion forms observed on lead substrates. The chapter concludes with an overview of treatment methods applied on corroded lead objects.

1.1 Brief historical survey and present applications

Lead was one of the first used metals, due to its low melting point [1]. Indeed, lead artefacts are amongst the oldest metallic objects discovered. The oldest dated artefact was found in Çatalhöyük in Turkey and was dated to 6500 BC [2]. The soft, malleable and ductile metal was also used by the ancient Egyptians for the construction of statues and pipelines, but also for ceramic glazes, sinkers in fishing nets and ornaments [2]. Related products as lead carbonate and lead oxide were used as pigments in face powders, rouges and mascara [3]. The ancient Greeks extracted lead for several applications as pipelining and roofing material [2].

Chapter 1

The extraction of lead from its ore at ancient Greece (Laurion) is well described in the literature [4]. The Romans produced tons of lead for little objects such as pewter cups, plates, pitchers, pots and pans and other household artefacts, but also for their water conducting system. They were aware that lead could cause serious health problems, even madness and death. However, they were so fond of its diverse uses that they did not recognize the hazards [2].

During the middle ages, lead was used for small hand tools, but also for the construction of sarcophagi and canalizations [5]. Stained glass or leaded glass was placed in many cathedrals and churches [2]. The metal was also alloyed with other elements such as tin for the production of pilgrim medallions, communion tokens, coins [5] and ceramic glazes [2].

From the 15th to the 19th century, lead was used as a construction material. Many magnificent buildings of that time still stand under their original lead roof [2]. Another important application was the production of lead and pewter organ pipes because of their excellent sound characteristics [6]. Communion tokens were used from the 17th century on as tickets of admission of Holy Communion and were made of lead and lead alloys [7].

Contemporary applications of lead and lead alloys include their use for lead-accumulators (primary use) associated with the automobile industry, shielding material against electromagnetic waves, sound deadening, ammunition, cable sheathing and construction materials (sheet, pipe, solder, wool for caulking) [8].

It is clear that lead had many important applications throughout history. Due to the limited corrosion rate of lead and lead alloys, a 'lead heritage' has been well preserved.

1.2 The metal lead

Lead is a bluish-white lustrous metal. It is very soft, dense, highly malleable, ductile and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to the air. Lead can be easily alloyed with many other metals, forming low melting-point alloys, which can be cast into many shapes [8].

Regarding their composition, antiquities were generally made of very impure lead. However, a non-exhaustive literature survey shows that the reported compositional data must be critically viewed, as in most cases the samples are either not representative, or the procedure for determining the lead content is not specified [1]. It is nonetheless interesting to examine general tendencies. From the statistical distribution of artefacts, according to their lead content presented in Figure 1.1, three main compositional groups are discerned [1]. Most analyzed objects fall into the group of high lead content. In literature, they are often (and probably equivocally) referred to as 'pure lead', although, as noted before, they certainly contain minor elements, forming a precipitated second phase (Figure 1.1a). Another group includes artefacts containing about 40% lead, which generally corresponds to alloys of low melting point: dendrites of α -phase (lead rich) surrounded by the eutectic, which includes naturally the β -phase, rich in the other element, is a very common structure in these cases (Figure 1.1b). Finally, there is the case of leaded alloys, most particularly bronzes, in which lead is added in a low content to improve properties for casting and machine manipulation. Once again, due to the immiscibility of elements, lead is normally found in more or less fine globules dispersed in the alloy matrix (Figure 1.1c) [1].

A practical example of the effects of alloying is the recently observed corrosion of organ pipes (renaissance and early baroque) in churches in Belgium, France, Italy, the Netherlands and Portugal [6]. These pipes contain a small percentage of tin (1.5-2%) to harden the pipes and to increase their luster. The phenomenon did not occur with organ pipes from the same time period in British churches, which contain up to 20% tin. The reason for the different composition was that Europe's tin sources were located in Cornwall, with

the result that it was much cheaper in Britain [6].

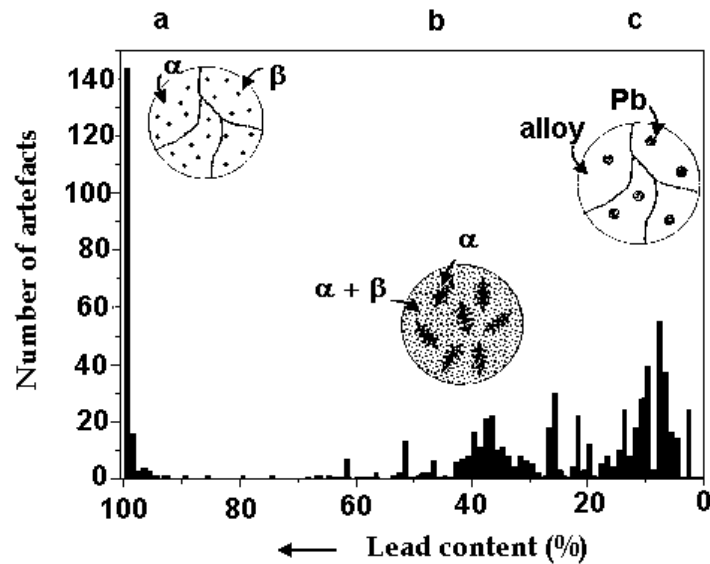


Figure 1.1: Distribution of lead artefacts according to their lead content (from [1]). Three compositional groups can be observed: (a) high lead content, the structure of which consists of a lead-rich matrix (α) with precipitates of a second, minor element-rich phase (β); (b) intermediate lead content, corresponding to low melting point alloys, used in the as-cast condition, revealing lead-rich (α) dendrites in an eutectic ($\alpha + \beta$); (c) low lead content, exemplified by copper-base leaded alloys, where lead is segregated in the form of fine globules.

1.3 Corrosion of lead

1.3.1 Basic principles (from [9])

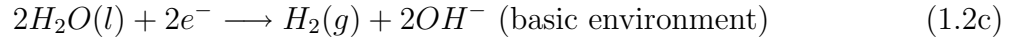
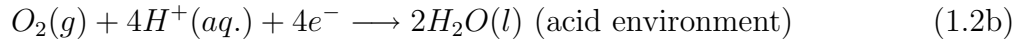
Corrosion is an electrochemical process which attacks the metal in a humid environment. The most visible effects of corrosion are due to the oxidation of the metal (M). However, this is only the net anodic reaction of the total corrosion process. The oxidation reaction must be compensated by a reduction reaction, which takes up the released electrons and

reacts cathodically. The oxidation reaction of a metal and the most possible reduction reactions are respectively shown in expressions 1.1 and 1.2a-c.

Oxidation of M:



Possible reduction reactions:



The metal ions as observed on corroded objects, in general, are mostly hydrated, solvated, form complex ions or insoluble metal compounds.

1.3.2 Thermodynamic properties (from [10])

A corrosion reaction is only spontaneous if the Gibbsfree energy ΔG is smaller than 0. The changes in free energy are related to the corresponding equilibrium potential (E_0) of the corrosion reaction $\Delta G = -nFE_0 < 0$, where n is the number of electrons transferred in the reaction, F Faraday's constant (96485 C mol^{-1}) and E_0 , for a spontaneous process, should be larger than 0. The standard equilibrium potential is defined as the potential of a metal M in a solution of its ion M^{n+} of unit activity one, at 298 K and at atmospheric pressure. The standard electrode potentials of the most frequent electrochemical reactions where lead is involved are given in Table 1.1.

Because the reactions indicated by (a) and (b) have standard potentials more positive than the corrosion reaction of lead (c) (see Table 1.1), they can all drive the oxidation of lead. The electrode potentials which are quoted are standard values, and change with the pH of the medium.

Table 1.1: Standard electrode potentials in H_2O at 298 K (from [11]).

Electrodereaction	E_0 (V) against standard hydrogen electrode
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	1.700
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.685
$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$	1.455
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (a)	1.229
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	0.980
$PbO_2 + H_2O + 2e^- \longrightarrow PbO + 2OH^-$	0.248
$2H^+ + 2e^- \longrightarrow H_2$ (b)	0.000
$Pb^{2+} + 2e^- \longrightarrow Pb$ (c)	-0.126
$PbCl_2 + 2e^- \longrightarrow Pb + 2Cl^-$	-0.268
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	-0.356
$Pb(OH)_2 + 2H^+ + 2e^- \longrightarrow Pb + 2H_2O$	-0.408
$PbCO_3 + 2e^- \longrightarrow Pb + CO_3^{2-}$	-0.506
$PbO + H_2O + 2e^- \longrightarrow Pb + 2OH^-$	-0.580

A thermodynamic discussion of corrosion, however, only indicates whether a tendency to corrode exists. A classical method to present the possible corrosion behavior of a metal is the use of potential pH-diagrams (next section).

1.3.3 Potential - pH diagram

On a basis of thermodynamics (i.e. the Nernst equation), so-called Pourbaix diagrams can be constructed. These diagrams show the stability of species as a function of potential and pH. Although many basic assumptions must be considered in their derivation, such diagrams can provide valuable information for the study of corrosion phenomena [9].

Several regions can be distinguished on the diagram: immunity, which means that the metal is stable; corrosion, which means that a soluble metal compound is stable and passivation, which means that a low solubility metal compound is stable and forms a passive film on the surface [11].

The Pourbaix diagrams below represent the lead-water (Figure 1.2a) and lead-water-carbonate (Figure 1.2b) systems at ambient temperature. The dotted lines indicate the stability region of aqueous environment. Figure 1.2 shows that lead will corrode when no passive film is formed. In the presence of carbonate species (Figure 1.2b), the metal will be passivated in the pH region of 5-12. This implies that atmospheric corrosion, where carbonate species are present from equilibrium with carbon dioxide, will be limited very soon after passivation [11].

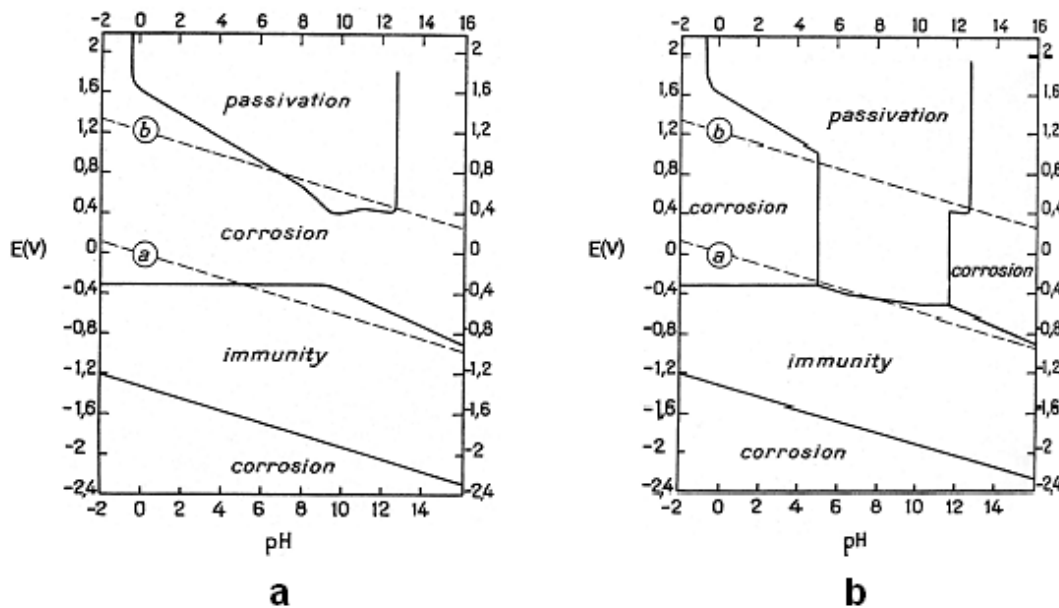


Figure 1.2: Pourbaix diagrams of (a) lead-water and (b) lead-water-carbonate systems (from [11]).

Some limitations of such diagrams include the fact that no information on corrosion kinetics is provided and that the diagrams are valid only for specific temperature and pressure conditions. They are also constructed for selected concentrations of ionic species and only consider pure substances [11].

1.3.4 Kinetics of the corrosion reaction (from [12])

The theoretical approach to the corrosion reaction may be based on the Butler-Volmer (BV) equation of the oxidant and reductant systems. A simplified situation describes a system which contains one corroding metal and one electron acceptor. The BV equations of the metal (M) and electron acceptor (EA) are respectively given in Equations 1.3 and 1.4 and plotted in Figure 1.3.

$$\text{For M: } I_M = I_{0,M} \{ e^{\alpha_{a,M}} - e^{-\alpha_{k,M} f \eta_M} \} \quad (1.3)$$

$$\text{For EA: } I_{EA} = I_{0,EA} \{ e^{\alpha_{a,EA}} - e^{-\alpha_{k,EA} f \eta_{EA}} \} \quad (1.4)$$

Where $I_{M/EA}$ is the netto oxidation/reduction current, $I_{0,M/EA}$ is the exchange current density, $\alpha_{a,M/EA}$ and $\alpha_{k,M/EA}$ the anodic and cathodic transfer coefficients, f is $\frac{F}{RT}$ and η_M equals $E - E_{e,M/EA}$ with $E_{e,M/EA}$ the equilibrium potentials, respectively from the metal and the electron acceptor.

The overall potential of the corroding system is a mixed potential, the corrosion potential E_{cor} . At this potential, the oxidation and reduction compensate and no net current flows (Figure 1.3). This implies that the corrosion current (I_{cor}), visualized in Figure 1.3, can be written as follows:

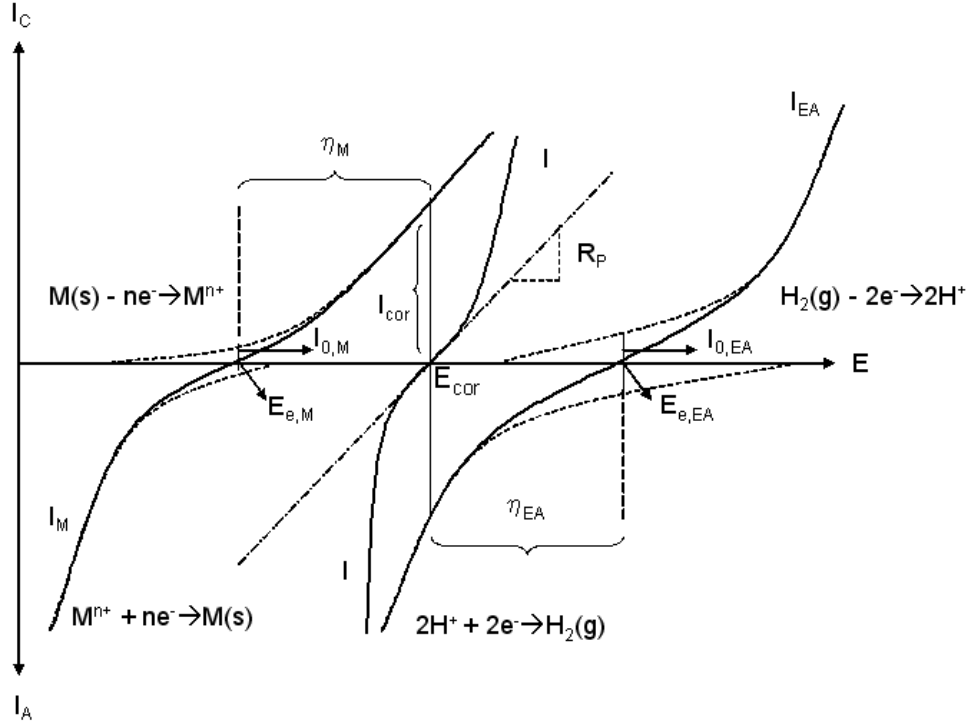


Figure 1.3: I-E curves with partial curves for M and EA. I_c and I_a , as given in the y-axis, are respectively from the cathodic and anodic current (from [13]).

$$I_{cor} = I_M = -I_{EA} \quad (1.5)$$

$$I_{cor} = I_{0,M} \{ e^{\alpha_{\alpha,M}(E_{cor}-E_{e,M})} - e^{-\alpha_{k,M}f(E_{cor}-E_{e,M})} \} \quad (1.6)$$

$$I_{cor} = I_{0,EA} \{ e^{\alpha_{\alpha,EA}(E_{cor}-E_{e,EA})} - e^{-\alpha_{k,EA}f(E_{cor}-E_{e,EA})} \} \quad (1.7)$$

In the specific case of lead, the oxidation most frequently results in the formation of the Pb^{2+} ion. The reduction reactions are mostly the conversion of O_2 and water. The reduction of protons to hydrogen gas, even in a strong acid environment, is kinetically unfavourable on lead substrates.

1.3.5 Types of corrosion observed on lead artefacts

A schematic diagram of the most common types of lead corrosion is shown in Figure 1.4. It is possible to distinguish two types: general and local corrosion [5]. Local corrosion can be a result of intergranular corrosion, due to a different energy partition on the grain boundaries. Local corrosion of lead can also be a result of specific conditions of relative humidity and the presence of organic compounds. These conditions are often present in exhibition cupboards, or in storage rooms of museums [14–17]. The organic substances described in literature are usually organic acid vapours released from many types of wood at relative humidity's above 50%. These vapours include formic acid ($CHOOH$), acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH) and tannic acid (complex formula not given), resulting from the hydrolysis of hemicelluloses [14]. It is known that oak wood is among the strongest organic acid emitters. For manufactured woods such as plywood, the vapours are produced by the oxidation of glue hardeners such as formaldehyde (CH_3CHO). Also the sticking materials often contain organic compounds which may evaporate. In well ventilated areas, the lead corrosion would not be affected. However, the limited air exchange in closed display cabinets can create a microclimate with high concentrations of organics (e.g. $\sim 6.10^{-6}$ to 2.10^{-4} m% of acetic acid [17]) [18].

Conservation scientists are aware of this problem and conferences are organized concerning indoor air quality in museums and storage conditions. Recently, COST [19–23], which supports European cooperation in the field of science and technology, dedicated a special network D42 on the indoor air quality of museum environments [24].

General corrosion

General corrosion is also referred to as uniform corrosion. The metal is consumed uniformly over the entire surface, and can precipitate in the form of insoluble salts such as cerussite ($PbCO_3$) and hydrocerussite ($2PbCO_3.Pb(OH)_2$) [25]. This protective layer drastically limits the corrosion speed, preventing further attack (see 1.3.3). The formation of this

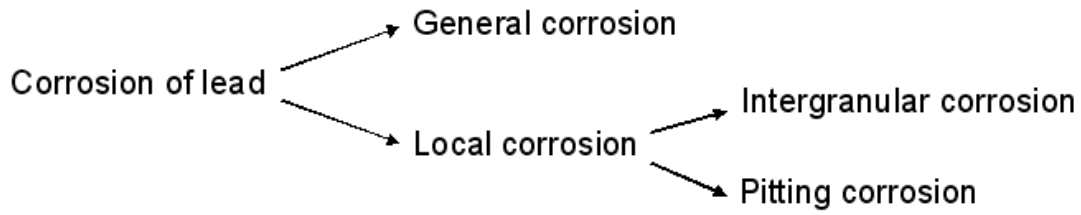


Figure 1.4: Scheme about the different corrosion forms on lead objects.

protective layer is the main reason why lead objects have been well preserved throughout history. This type of corrosion is observed when an object is exposed to the atmosphere or buried underground [26]. In most cases, this type of corrosion is associated with other types of corrosion. In Figure 1.5, a typical example of a uniformly corroded object is shown. This example corresponds to a lead adornment of a cupboard obtained from the National Museum of Denmark. The surface is covered uniformly with a corrosion layer, that causes a white appearance. This corrosion layer is often referred to as patina, meaning that it has an esthetical value.

Local corrosion

Intergranular corrosion

Intergranular corrosion is observed at the grain boundaries of the metal. It is a common phenomenon in metals and originates from the grains which build up the metal [1]. This is schematically shown in Figure 1.6a. The different composition of the core of the grain and the grain boundaries is subject to preferential corrosion attack along the boundaries. The energy of the boundaries is higher than that of the grain core because of the higher disorder [27]. A real example of intergranular corrosion is shown in Figure 1.6b, where the grain boundaries are preferentially covered by corrosion products. This intergranular corrosion is mostly the start of a severe corrosion with the formation of voluminous corrosion structures.

Pitting corrosion due to high relative humidity and presence of organic acids

Pitting corrosion, initiated by organic acids as formic, acetic and propionic acid, is often



Figure 1.5: General corrosion developed on a lead object. The details of the original object, even though covered by the uniform corrosion layer, remain clearly visible.

referred to as active corrosion [14]. The process is most clear for acetic acid (CH_3COOH) and proceeds in three steps, detailed below [14, 28].

1. Pit initiation

On bare lead surfaces, the pit initiation occurs at energetically preferable sites such as inclusions and grain boundaries [27]. On the other hand, uniformly corroded lead objects require local degradation of this layer before a pit can be created. The degradation is promoted under conditions of high relative humidity and in the presence of organic acids; the acids condense on the surface, thereby creating an aggressive medium locally wherein corrosion products (mainly lead carbonates) are dissolved [14, 28]. This process continues until the bare metal is reached [14]. At this point, a pit is created and a new phase in the process can be defined: pit growth [27].

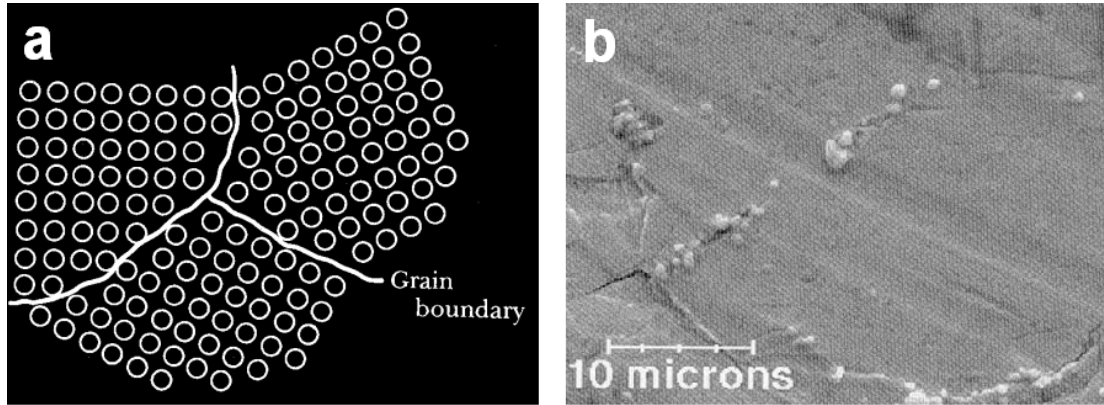
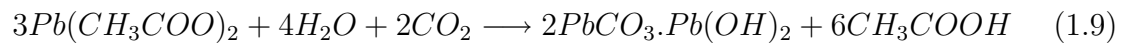


Figure 1.6: Schematic presentation of grains and grain boundaries in a metal (a) and SEM image illustrating granular corrosion observed on lead objects (b) (from [1]).

2. Pit growth

Independent of the pit initiation, the pit will grow by the accelerated corrosion of the metal [27]. The fast oxidation produces a local surplus of positive charges, provoking a migration of negative ions into the pit. These ions are mainly carbonates, acetates and hydroxides originating respectively from carbon dioxide, acetic acid and moisture. These reactions all occur in the liquid phase [28].

The recombination of these ions forms complex carbonates and acetates. The reactions for the formation of hydrocerussite are given in Equations 1.8 and 1.9 [14].



The pit growth, in the specific case of a uniformly corroded object, proceeds from the interface of the metal and the (uniform) corrosion layer. The corrosion products, as a result of the pit growth, are formed underneath the uniform layer and consist of lead carbonates and lead acetates [14].

3. Deterioration

The proceeding pit growth results in the formation of thick corrosion patches at the metal interface. The uniformly corroded layer, which is still on top, may crack as a result of the volume expansion of the pit and loses its adherence to the newly developed corrosion layer. This phenomenon is well observed in Figure 1.7, which shows the surface appearance of a corroded object with multiple pits. Some remainings of the uniformly corroded layer are indicated by the dashed line. The volume expansion of the pits is well observed where the uniform layer has fallen off, visible as bulges around the dashed lines.

The proceeding deformation and loosening of original material makes it difficult to read the original inscriptions. If this process is not stabilized, the object will disintegrate completely [14].

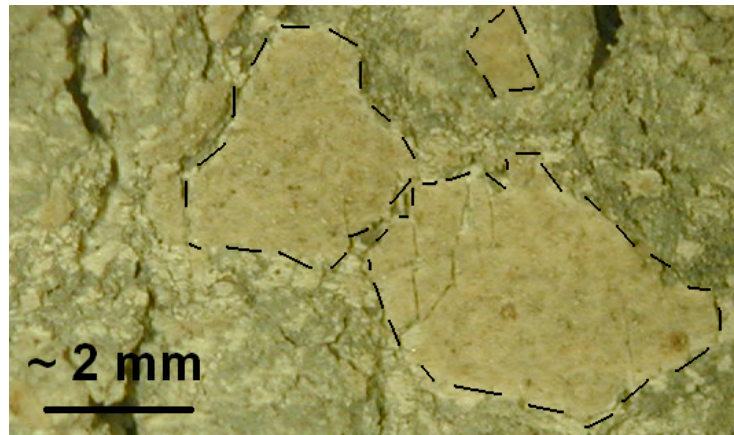


Figure 1.7: Result of pitting corrosion observed on lead objects. The newly formed corrosion at the metal/corrosion interface provokes cracks in the originally uniform corrosion layer. Some remainings of the initial coverage are surrounded by dashed lines.

The overall process of active (or pitting) corrosion is schematically shown in Figure 1.8.

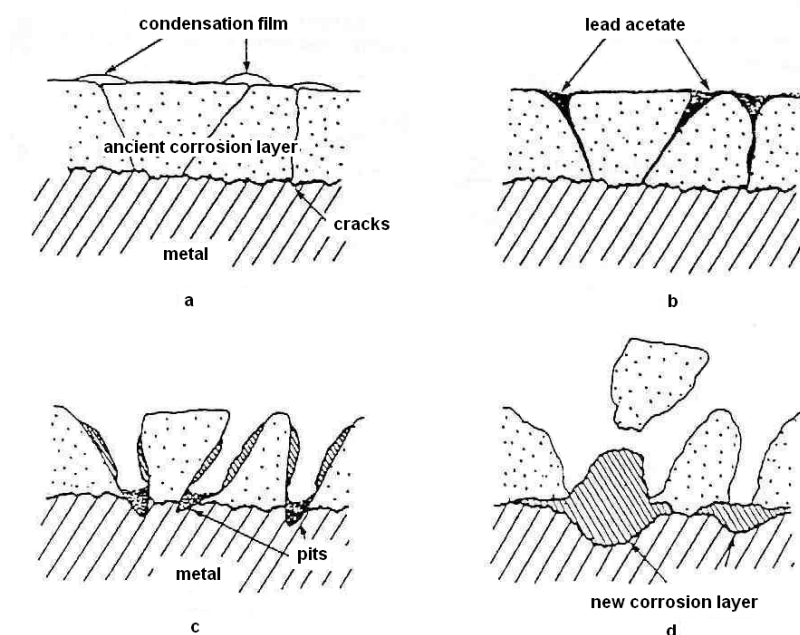


Figure 1.8: Schematic of active (or pitting) corrosion (from [14]).

1.3.6 Commonly observed lead corrosion products

Commonly observed corrosion products on lead objects and their chemical formula are listed in Table 1.2.

1.4 Treatment procedures *

The treatment procedures for lead objects described in the literature can be classified either as cleaning or as stabilization treatments. While the cleaning aims at revealing the remaining metal covered by a thin and protective corrosion layer, the stabilization treatments are performed to preserve part of the corrosion layer maintaining the original surface.

*This material formed the basis for a publication: B. Schotte and A. Adriaens. Treatments for corroded lead artefacts: an overview. *Studies in Conservation*, 51:1-8, 2006.

Table 1.2: Commonly observed lead corrosion products and their chemical formulas (from [16]).

Compound	Chemical formula
cerussite	$PbCO_3$
hydrocerussite	$2PbCO_3.Pb(OH)_2$
lead acetate oxide hydrate	$Pb(CH_3CO_2)_2.2PbO.H_2O$
lead formate	$Pb(CHO_2)_2$
lead formate hydroxide	$Pb(CHO_2)(OH)$
litharge	$\alpha-PbO$
massicot	$\beta-PbO$
plumbonacrite	$6PbCO_3.3Pb(OH)_2.PbO$

1.4.1 Cleaning

In 1924, Jenkinson [29] described the corrosion on leaden bullae, which are lead seals used to validate parchments, consisting of a product which was referred to as white lead or hydrocerussite ($2PbCO_3.Pb(OH)_2$). The humid and acidic storage condition of the leaden bullae seemed to be the cause of the formation of white lead, which is a corrosion product as a result of active corrosion. Their conservation treatment consisted of thorough mechanical brushing, first with white spirit (colourless liquid derived from petroleum distillation; it is used as a solvent, in paints and varnishes) and ether to degrease the surface, then with diluted HCl (8 %), then with diluted NH_3 (8 %) for neutralization, followed by rinsing with distilled water, and final drying by means of white spirit. Since this treatment is a cleaning protocol, the main purpose was the removal of the corrosion products. Whether or not the original surface was kept intact has not been described by the author. Although hydrochloric acid is an efficient solvent for removing most of the corrosion products, it may initiate the dissolution of the remaining lead.

In 1953, another cleaning method was proposed by Organ [30]. According to the author,

the method was progressive in the sense that no solvent action was needed. The treatment was based on the ion exchange between a synthetic resin (Amberlite IR 120 or Zeo-Karb 225) and the corrosion product hydrocerussite. In a recipient, the corroded lead piece was surrounded with the resin and filled with hot distilled water (Figure 1.9). The corrosion products dissolve and the resin takes up the Pb^{2+} ions, cleaning the surface. The CO_3^{2-} ion disappears then as CO_2 from the recipient. During the treatment, which could last for three days, the sample and resin were stirred using a copper rod to remove any gas bubbles. It was not suitable to leave the object in the solution during the night. Thus every evening, the object was removed and dried in air. The final step of the treatment was to dry the object thoroughly, either in an oven at 110°C or by an industrial blower, and to brighten it using a glass brush. Whether or not the objects treated were corroded actively was not mentioned in the paper, but since the interaction between the resin and the corrosion products appeared on the surface itself, the author was probably dealing with stable corrosion layers. An advantage of the method is the possibility of regeneration of the ion-exchange resin. To achieve this, the resin was first washed with $NaNO_3$, which exchanges the Pb^{2+} ions by Na^+ ions. Then, the Na^+ ions were exchanged with H^+ ions using HCl . This procedure is safer than regenerating the resin using the strongly oxidizing acid HNO_3 . This simple method was used successfully to remove lead carbonate, but it was never proven to be useful for the removal of other lead corrosion compounds. No other reference has been found in which this method was used.

Caley (1955) [26] examined and cleaned 56 stable objects from the Athens Agora. The excavated objects were protected by a stable corrosion layer. He described the corrosion products very precisely, and concluded that the main component was a lead carbonate (it was not determined whether it was cerussite ($PbCO_3$) or hydrocerussite ($2PbCO_3.Pb(OH)_2$). He proposed the following cleaning process. The objects were to be soaked in cold dilute HCl (1:10 diluted with distilled water) and immersed till no further visual change was apparent. This solvent was used for the conversion of lead carbonates and oxides into lead chlorides. Then the objects were soaked in hot distilled water for a few minutes, to

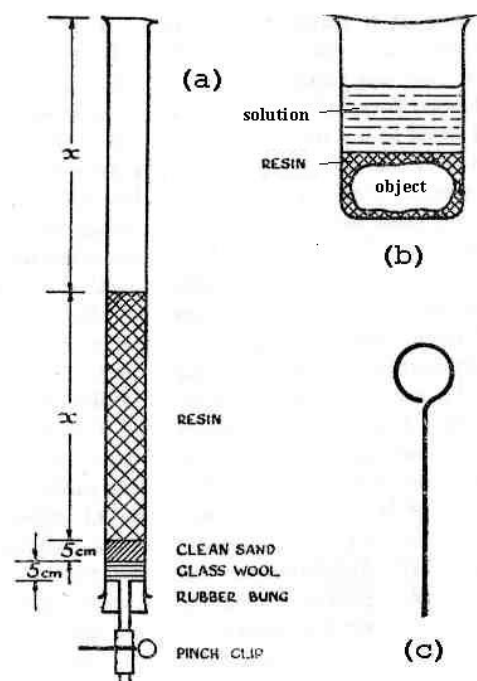


Figure 1.9: Setup of the cleaning treatment method proposed by Organ: (a) regeneration of the resin, (b) treatment of a corroded object and (c) copper stirrer [30].

wash away the lead chlorides formed, and to remove the acid in the corrosion layer. This action was followed by placing the objects in a dilute solution (10 %) of ammonium acetate (NH_4OAc) to remove the lead dioxide, that was not dissolved in the HCl solution, as well as some unconverted lead oxides. This solution was heated to $60^\circ C$, since the reaction is very slow at room temperature. The use of NH_4OAc was also meant to neutralize the residual acid. Afterwards the objects were soaked in cold, air-free distilled water and dried to the air, or soaked in 95 % alcohol before drying. The method was scientifically founded, and cleaned the surface well.

Another method was studied by Kuhn (1960) [31], and re-evaluated by Watson (1976) [32], which was based on the use of the chelating agent ethylene-diamine-tetra-acetic acid (EDTA). In this particular case, an EDTA-solution (10 % w/v) was used for the complexation of Pb^{2+} , originating from the corrosion products. The method was described

for a leaden bullae and a lead plate, covered with some active encrustations of basic lead carbonates. The objects were soaked in the EDTA-solution until all visible corrosion had dissolved. This could last from several hours to one day. If needed, typically in the case of severely corroded objects, the solution could be refreshed. The objects were then washed in tap water for one day. It was well known from laboratory tests that it was preferable to use tap water instead of distilled water, because the latter causes undesirable lead dissolution. In a next stage the objects were dipped in ethanol and covered by a thin layer of linseed oil. Afterwards, a paraffin coating was applied on the objects. The author also mentioned that where the objects were already treated (e.g. covered with a coating), any existing protective layer, had to be dissolved first in alcohol or benzol. This method is very effective for complex corrosion crusts, as the solution dissolves the crust. A disadvantage of the EDTA-procedure is, however, that the solution also attacks the bare metal, which can be a negative aspect in case the corrosion is not uniform. Watson therefore worked with more dilute solutions of EDTA (5 %) [32]. If severe local corrosion appeared, a more concentrated 10 % solution was used as well. He showed that EDTA will not dissolve all corrosion products, such as litharge (PbO). In case the removal of litharge was necessary, the object could be treated by 10 % NH_4OAc , as proposed earlier by Caley. The relative ease and the low costs of this treatment are strong advantages, implying a potential use for bigger objects as well [33, 34]. It should be mentioned that the use of actively corroded objects, as described above, to study the effects of EDTA is inappropriate. EDTA dissolves existing corrosion layers, and cleans the surface. Therefore, it should only be used for the removal of stable corrosion layers.

Spier [35] investigated the use of ultrasonic cleaning. This treatment is based on the ultrasonic vibration of a solution, which mechanically attacks the existing corrosion crust. Depending on the solution, there can be a solvent action as well. The strongly attached corrosion products, however, appear to remain on the surface after this type of treatment, and can provoke re-corrosion after a period of time. The authors consider it as not advisable to treat active corrosion crusts since all information in the crust will be lost.

1.4.2 Stabilization

Previous treatments were focused on cleaning the surface. When dealing with thick active corrosion layers, these cleaning protocols destroy the entire corrosion crust, losing nearly every detail of the corrosion crust present. In what follows an overview will be given on the various stabilization processes used for thick active corrosion layers.

In 1926, Rathgen [36] described a procedure for the conservation of various lead pieces. The corroded pieces were put into a beaker, in which they were surrounded with zinc granules, and treated with dilute nitric acid. Rathgen does not mention the evolution of H_2 -gas and bubble formation. The idea was to convert the lead corrosion products ($Pb^{2+} + 2e^- \longrightarrow Pb$, electron acceptor) into lead, and oxidize the zinc granules ($Zn - 2e^- \longrightarrow Zn^{2+}$, electron donor). The lack of control of this electrolytic reduction however is a strong disadvantage of the method, primarily because the object was not visible during treatment. Moreover diluted HNO_3 dissolves the corrosion products and attacks the bare metal quite seriously. Perhaps the effectiveness of this method is due to this solvent action, and not to the expected reduction process [30].

Other techniques relied on the use of an electric current intended to reduce the corrosion crust. These methods do not remove the corrosion products, but convert them into a metallic state. The treatment was first used to conserve other metal objects, particularly copper alloys, and was not generally favoured for lead [37, 38]. The first application of this treatment on lead objects was by Organ [39] in the early sixties. Actively corroded lead bullae were reduced separately using a current generator. For a period of three days, a current of 100 mA dm^{-2} was applied on the object in a solution of sodium hydroxide (10 % w/v). The counter electrodes, which close the electrical circuit, were made of platinized titanium. The object was held in position using porous foam pads (Figure 1.10). After the reduction in the alkaline electrolyte, the objects were successively bathed in 1 mM sulphuric acid until the pH of the acid remained unchanged for 30 minutes, and then similarly in distilled water. From that point of view, no hydroxide ions remained on the

object [39]. Afterwards the object was dried, brightened with a glass-bristle brush and impregnated with hot paraffin wax. It should be mentioned that the second step is rather destructive and should be avoided after applying a method which conserves the original design. This method has been used in many cases [40–42]. However it is well known that when the current is lost, the object will be attacked by the $NaOH$ solution, resulting in the corrosion of the surface [14]. In that regard other harmless solutions could be used (see below).

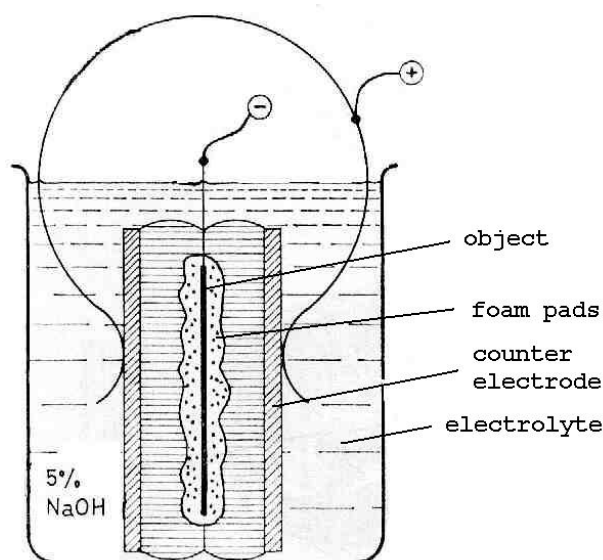


Figure 1.10: Setup of the electrolytic reduction proposed by Organ [39].

The treatment of corroded lead objects by electrochemical reduction was fully under investigation in the British Museum Research Laboratory in the mid sixties [43]. It was observed that by treating the objects as stated by Organ [39], the corrosion re-appears after a certain period of time. It is not mentioned whether the objects were stored in the same conditions. First of all, the potential use of a sulphuric acid solution was examined to replace the aggressive sodium hydroxide solution. The object functioned as the cathode in a 10% solution of sulphuric acid, while the anode was made out of lead, stainless steel or platinized titanium. The author does not mention whether any corrosion appeared on the

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counter electrodes [43]. The current density could be chosen as (a) a 'normal' reduction, which refers to the setup of reductions applied to other metals, requiring $2 - 5 \text{ A dm}^{-2}$; and (b) a 'consolidative' reduction, implying that the corrosion crust is conserved, requiring 100 mA dm^{-2} . Attention was needed to determine the end of the treatment by observing the presence of hydrogen bubbles. For this reason, it was not favourable to leave the treatment running during the night. When reduction was thought to be complete by visual inspection, and this could last for several weeks, an oxidative current was applied for 30 s ($2 - 5 \text{ A dm}^{-2}$) in the same solution and a lead dioxide layer was formed. The washing procedure was the same as described by Organ [39], with the exception of the washing in sulphuric acid since this was the original reduction solution. However, they still recommended the application of a further protective coating, for example paraffin wax or microcrystalline wax (Cosmolloid 80H). However, wax is dangerous to apply here since it is almost impossible to remove it from reduced corrosion layers. It must be noted that lead dioxide is a black product, and the formation of this type of a layer gave the object a very dark colour, which was unacceptable to some people [44]. It is clear that the use of different electrolytes and the application of various coatings provide plenty of procedures and surface finishes. The choice of a particular method was governed by the condition of the lead object and the results which were desired to achieve.

A few years later, Lane [44] described in more detail the application of consolidative reduction on corroded lead objects, including comments regarding the experimental setup. In particular the contact with the object, to supply the current, was experienced as a difficult issue. The use of platinized titanium and iron wires showed the occurrence of lead plating on the wire from the object. Also the use of lead strips provoked some plating in the form of long whiskers. Furthermore a counter electrode of lead was not advisable, as the lead goes into solution and is transferred towards the object. Different current densities were investigated ($30, 100, 200$ and 300 mA dm^{-2}) and experiments showed the higher the current, the lower the reduction time. At 300 mA dm^{-2} tiny bubbles of hydrogen appeared on the surface, but the results were good. Since the production of any bubble should be

prevented, a current density of $100 - 200 \text{ mA dm}^{-2}$ seems to be ideal. However, the end of the reduction could not be well defined. NaOH and H_2SO_4 solutions were used for the reductions described, and it could be observed that sulphuric acid gave the objects sometimes a darker colour after treatment. In the mean time many conservation professionals have described the reduction process applied to lead objects and the procedure has become a standard treatment [45–51].

An improved control of the electrolytic reduction became possible using a three electrode configuration and a potentiostat. This equipment makes it possible to maintain a constant potential, allowing the performance of a defined reaction (more information in section 2.1 about chronoamperometry). In the case of cerussite (PbCO_3) for example, -1.2 V vs. saturated calomel electrode (SCE) makes it possible to convert into metallic lead¹. The formation of hydrogen bubbles (reaction at the work electrode) does not occur at this potential, which makes the electrolytic reduction perfectly controllable. The first article about consolidative reduction of lead objects, using the above mentioned method is by Carradice and Campbell [7]. At a potential of -1.2 V vs. SCE, a collection of lead communion tokens was reduced for 30 to 40 minutes in $0.5 \text{ M H}_2\text{SO}_4$. Tokens with active encrustation (thick and powdery white corrosion layer) were reduced at a lower rate at -1.0 V vs. SCE for several hours. Before the reduction treatment, the tokens were degreased by soaking in dichloromethane (CH_2Cl_2) in an ultrasonic bath for 15 minutes, washed with distilled water and dried. After the reduction treatment, the tokens were washed twice in distilled water in an ultrasonic bath for 10 minutes. The evaluation of the process was very encouraging and according to the authors the application of a coating was not needed. As the reduction process transformed the lead carbonates back into lead particles which were disrupted in an ultrasonic bath, the process can be considered more as a cleaning process.

In 1999, Degriigny and Le Gall [14] studied the conservation of actively corroded lead

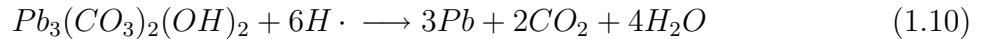
¹The saturated calomel electrode (SCE) has a potential 0.241 V positive of the standard hydrogen electrode (SHE).

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artefacts (more information concerning these artefacts is given in Section 3.1.1). They investigated the effect of various electrolytes ($NaOH$, Na_2CO_3 , H_2SO_4 and Na_2SO_4) upon the treatment result and concluded that Na_2SO_4 is a relatively inactive solution, implying that it is therefore a safe and efficient electrolyte. The potential used for the reduction was -0.9 V vs. SCE and the duration of the treatment lasted for about five days. For the first time, a reduction curve was analyzed by plotting the logarithm of the reduction current versus reduction time (Figure 1.11). The existence of four different regions was described. The first step (I) shows a small plateau and is due to the progressive polarization of the entire sample. A large decrease in the current indicates the progressive reduction over the total thickness (II). It is accompanied by a decrease in the solution pH from 7 to a value between 3.5 and 4 due to H^+ production at the anode which is not compensated by similar production of OH^- . The third step (III) is the reduction of thick lead carbonate patches. Then the current remained stable in step four (IV), which indicated the end of the reduction process.

A relatively new conservation approach involves a local reduction of small corrosion patches [36], where the object functions as the cathode and a graphite rod is connected as the anode. Cotton wool swabs damped with the electrolyte solution (5 % $NaOH$ or 5 % H_2SO_4) are held on the area to be treated with plastic tweezers. The applied current is 10 – 15 mA.

Another relatively recent method is the use of a hydrogen plasma to convert the corrosion crust into metallic lead [14, 52]. The reaction for hydrocerussite is shown below (Reaction 1.10).



The conversion of the corrosion products starts from the outer surface, and the converted lead obstructs the further reduction process. Therefore, the reduced layer has a maximum thickness of 0.1 to 0.2 mm, limiting this method for pieces covered with thin corrosion layers. The plasma treatment described in references [14, 52], lasted about one hour and

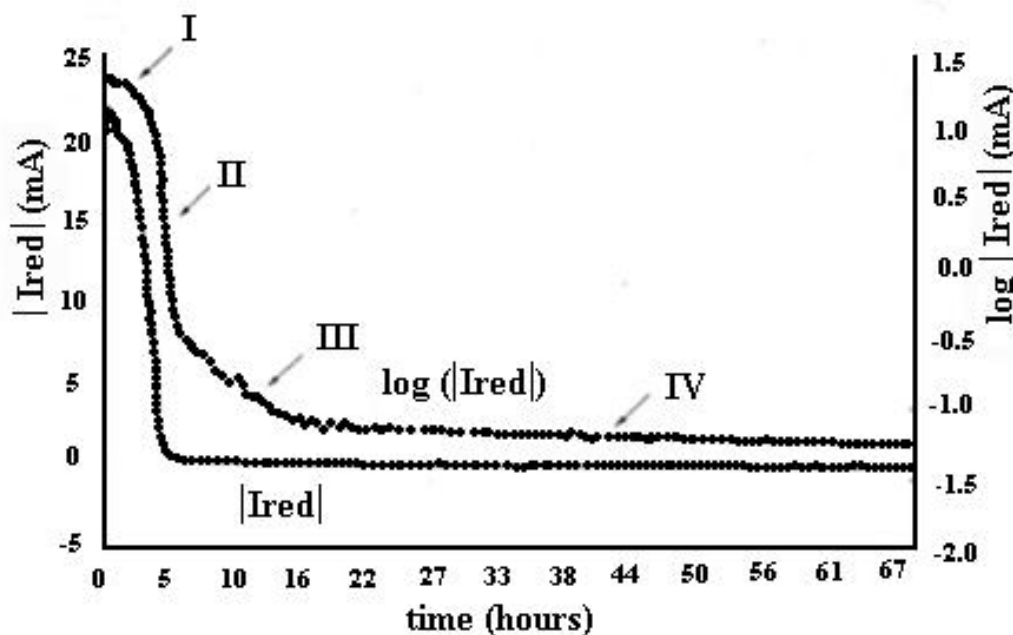


Figure 1.11: The lower curve represents the reduction curve of an actively corroded lead object from the museum CNAM. The interpretation was performed on the logarithm of this reduction curve (upper curve), where four regions could be observed (I-IV) (from [14]).

afterwards a new oxygen plasma was created. The object formed a protective layer of litharge ($\alpha - PbO$) on the surface. It was advisable to apply another organic coating (paraffin wax) afterwards.

Most of the publications quoted above make no comment on the stability of the artefact(s) after treatment. In most cases, however, the treatments are not successful in stopping the corrosion progression. Therefore, further research is essential concerning the protection of the artefact after treatment.

Another important issue which is rarely mentioned in conservation studies concerns the toxicity of lead. Conservation professionals working with lead artefacts should be aware of

these risks and protect themselves properly. This implies wearing a dust mask and gloves and working under a fume hood.

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Chapter 2

Experimental methods

In this chapter, the principles of the experimental techniques used in this work will be discussed. They include the electrochemical techniques chronoamperometry and impedance spectroscopy (EIS), mass gain and mass loss measurements, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), neutron tomography (NT) and synchrotron radiation X-ray diffraction (SR-XRD). The last part of this chapter describes the basic principles of contact angle and conductivity measurements.

2.1 Chronoamperometry (CA)

Chronoamperometry is an electrochemical technique which involves monitoring the current-time curve, when the working electrode is held at a constant potential [1]. The electric charge transferred during the reaction can be estimated by integrating the area under the current-time curve. The technique is related to coulometry at constant potential [1]. Faraday's law states [1, 2]:

$$Q = nFM \tag{2.1}$$

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where Q is the charge in coulomb resulting from the reaction of the species, n the number of electrons transferred per molecule; F the Faraday's constant ($= 96487 \text{ C mol}^{-1}$) and M the numbers of moles of corrosion product reacting. If uniform corrosion is assumed, the layer thickness of a certain corrosion product can be calculated by [2]:

$$\text{layer thickness} = \frac{QM_m}{nF\rho A} \quad (2.2)$$

with M_m the molar mass of the corrosion product, ρ the density of the corrosion product and A the surface of metal which is covered with this corrosion product.

Within the conservation field, chronoamperometry is used for the reduction of corrosion products [3] (electrolytic reduction) and to evaluate the amount of corrosion products on the surface of objects [2]. In this work, the technique was used as a treatment method, aiming the reduction of lead corrosion products.

2.2 Electrochemical Impedance Spectroscopy (EIS)

2.2.1 Fundamental principles

Electrochemical impedance spectroscopy (EIS) is an electrochemical method which applies an alternating current (AC) signal to a system, and measures the impedance as a function of the frequency of the AC wave [4, 5]. Generally, an AC voltage is applied as described by [5]:

$$E(t) = E_0 \sin(\omega t) \quad (2.3)$$

where E_0 is the maximum amplitude, ω the angular frequency of the sine wave and t time. The angular frequency is defined as follows:

$$\omega = 2\pi f \quad (2.4)$$

Using EIS, the applied voltage amplitude is small in order to obtain a linear current-time

response [4, 5]. The resulting AC current, under this condition, is given by:

$$I(t) = I_0 \sin(\omega t + \phi) \quad (2.5)$$

where I_0 is the maximum current and ϕ the phase shift.

The transfer function between the current and voltage, under these conditions, is the impedance (Z):

$$E = IZ \quad (2.6)$$

The impedance consists of two contributions [4]: (1) resistive contribution, which implies no phase shift between the current and the voltage, in comparison to (2) capacitive and reactive contributions. Time dependent problems are mathematically solved using complex notation by incorporating the complex number j where

$$j^2 = -1 \quad (2.7)$$

The $E(t)$ and $I(t)$ signals are then [4]:

$$E(t) = E_0 e^{j\omega t} \quad (2.8)$$

$$I(t) = I_0 e^{(j\omega t - \theta)} \quad (2.9)$$

The most common graphical representation is the Nyquist plot in which the real part of the measured impedance (i.e. that in phase with the impressed cell voltage) is plotted against the imaginary part (i.e. 90° out of phase of the impressed cell voltage) [4, 5].

2.2.2 Interpretation [5]

The analysis of EIS data is done by fitting to an equivalent electronic circuit built up by resistors, capacitors or inductors. The electronic circuit, which impedance behaves similar to the electrochemical system, must be chosen carefully in order to attach a physical meaning to its constituting components.

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The most common circuit elements used are given in Table 2.1 and will be discussed in more detail for the next two situations.

Table 2.1: Circuit elements used in models. CPE stands for constant phase element and replaces a capacitor for better fit quality (see below).

Equivalent element	Impedance
R	R
C	$\frac{1}{j\omega C}$
Q (CPE)	$\frac{1}{(j\omega C)^\alpha}$

Corroding metal

A Randles circuit can be used to represent a corroding metal. The Randles circuit is given in Figure 2.1a and contains a resistor (R_p) and a capacitor (C_{dl}) in parallel, in series with another resistor (R_s).

The R_s represents the solution resistance between the metal substrate and the reference electrode. The polarization resistance (R_p) originates from the potential perturbation applied to the system. The polarization induces an electrochemical reaction at the surface of the electrode. The capacitance (C_{dl}) then represents the electric double layer which exists between an electrode and the surrounding electrolyte.

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE) as defined in Table 2.1. Several theories have been proposed to account for the non-ideal behaviour, but none of them has been universally accepted. The impact of such a CPE on a Nyquist plot is the occurrence of a depressed half-circle as shown in Figure 2.1b.

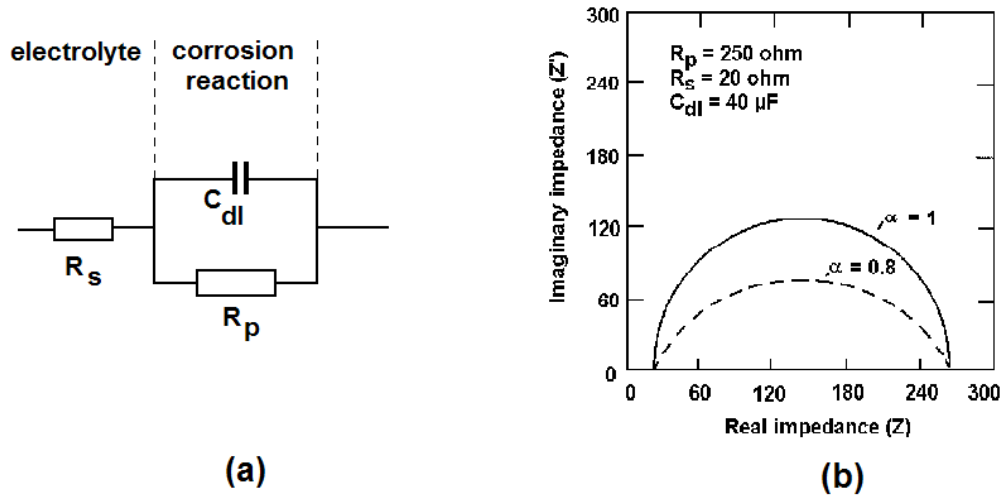


Figure 2.1: Electronic configuration of the Randles circuit (a) and its corresponding Nyquist plot (b) (from [5]). It is indicated on the circuit which elements are representative for the corrosion reaction and the electrolyte.

Coated metal

A circuit representing a coated metal is presented in Figure 2.2a. The R_s , C_{dl} and R_p have the same interpretation as mentioned for the corroding metal. The coating capacitance C_c and the coating resistance R_c respectively originate from the capacitor which is formed between the two conducting plates separated by the dielectric (coating) and the resistance through the pores in the coating. The resulting Nyquist plot shows two half-circles (Figure 2.2b).

This work makes use of EIS to monitor the coating resistance of the growing lead decanoate layer (Chapter 7 and 9). EIS was also used for the optimization of the coating process, to obtain a most rigid coating (Chapter 8).

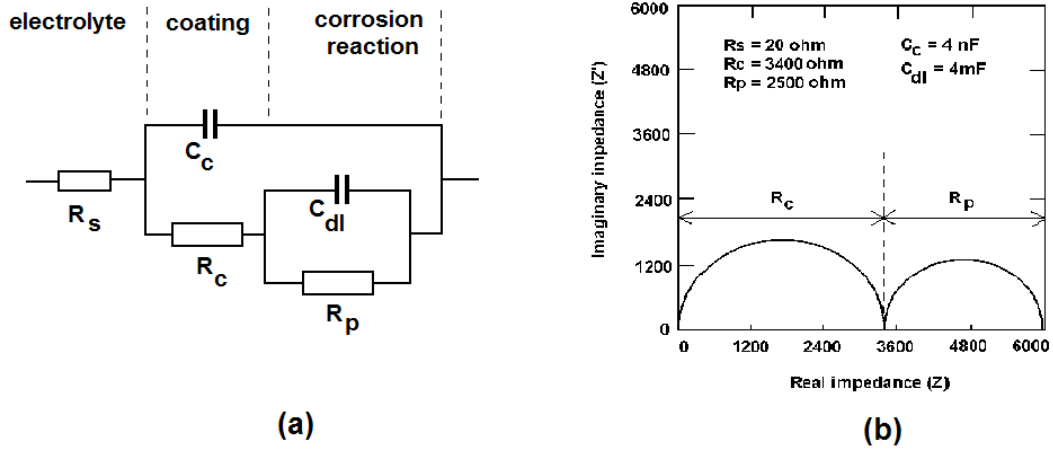


Figure 2.2: Equivalent circuit representing a coated metal (a) and the corresponding Nyquist plot (b) (from [5]).

2.3 X-ray photoelectron spectroscopy (XPS) [6]

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique, which is based upon the photoelectric effect. Each atom has core electrons with well-defined binding (or ionization) energies that are characteristic of the atom and the electron shell in question. When an X-ray beam impinges on the sample surface, the energy of the X-ray photon (undergoing photoelectric effect) is absorbed completely by a core electron of an atom. If the photon energy, $h\nu$, is large enough, the core electron will be ejected from the atom and escapes from the surface. The emitted electron with the kinetic energy of E_k is referred to as the photoelectron. The detection of these photoelectron requires a vacuum chamber. The binding energy of the core electron is given by the Einstein relationship:

$$E_b = h\nu - E_k - \phi \quad (2.10)$$

Where $h\nu$ is the X-ray photon energy; E_k is the kinetic energy of the considered photoelectron, which can be measured by the energy analyzer; and ϕ is the work function, which is the measure of the energy needed for the electron to leave the surface of the solid sample.

Since the work function ϕ can be compensated artificially by the XPS instrument, the binding energy can be expressed directly by the difference between the incident photon energy and the kinetic energy of the photoelectron, as follows:

$$E_b = h\nu - E_k \quad (2.11)$$

According to Equation 2.11, and considering that the incident photon energy is known, the measurement of the binding energy is equivalent to the determination of the kinetic energy of the emitted photoelectron. The core electron of an element has a unique binding energy, which is like a *fingerprint*. Furthermore, the binding energy of core electrons is very sensitive to the chemical environment of the element. The same atom, bonded to different chemical species, leads to a change in binding energy of its core electrons. The variation of binding energy results in the shift of the corresponding XPS peaks, ranging from 0.1 eV to 10 eV.

In this work, XPS was used for the analysis of the corrosion layer of lead artefacts, before and after electrolytic reduction, in order to evaluate the chemical changes of the surface. (Chapter 4).

2.4 Scanning Electron Microscopy (SEM) [7]

Scanning electron microscopy is a technique that uses an electron beam to image the surface of a sample. The electron beam is mostly produced by tungsten filament thermionic emission, although field emission gun sources are increasingly being used for higher resolution. The generated electrons are accelerated to energies between 1 keV and 30 keV. Two or three condenser lenses then demagnify the electron beam further till a beam of 2-10 nm hits the sample. The fine beam of electrons is then scanned across the specimen, while the detector counts the number of low energy secondary electrons, or other radiation, given off from each point of the surface. Digital scanning allows the resulting image to be displayed on a monitor.

SEM was used in this work to study the surface appearance of lead artefacts, prior to and after electrolytic reduction (Chapter 4). In addition, the technique was used to visualize the surface appearance of lead samples coated with a lead decanoate layer (Chapter 7).

2.5 Mass gain and mass loss measurements [8]

The corrosion rate is often determined using mass gain and mass loss measurements. In both techniques, the metal under study is weighed before exposure to a corrosive environment. During incubation, the metal corrodes and gets covered by corrosion products.

The mass gain, function of incubation time (t), is then calculated according to following formula:

$$mass\ gain\ (t) = \frac{\text{measured mass (t)} - \text{initial mass}}{\text{surface area}} \quad (2.12)$$

The determination of the corrosion rate requires the knowledge of the amounts of corrosion products thus formed.

On the other hand, the corrosion products can also be removed chemically by a stripping agent (e.g. a strong $NaOH$ solution). The mass loss is calculated as follows:

$$mass\ loss\ (t) = \frac{\text{initial mass} - \text{measured mass (t)}}{\text{surface area}} \quad (2.13)$$

This method mostly requires a correction for the effect of the stripping agent on the metal and for possible recorrosion during drying.

In this work, lead samples were exposed to an artificial corrosive vapour. Mass gain measurements were used to determine the corrosion rate. This technique was used instead of mass loss measurements, because we wanted to perform qualitative analysis on the corrosion products (Chapter 5).

2.6 Neutron Tomography (NT)

2.6.1 Neutron interaction with matter [9]

In contrast to X-rays, which interact dominantly with the electron shells of atoms, neutrons interact with the nuclei. The interaction probability is high for elements with low Z number (= number of protons) such as hydrogen, oxygen, etc. In contrast to this, comparatively lower interaction probability is observed for metals. Therefore, neutron tomography is considered as complementary to X-ray tomography.

2.6.2 Neutron tomography [10]

Tomography is a method which provides cross-sectional images of an object from transmission data. The non-destructive analysis of an object by neutron radiography implies taking 2D parallel projections, which is mostly achieved by rotating the object in small angular steps over 180°. The transmitted neutrons are captured on a scintillator screen, which produces X-rays, that are focussed on a CCD device. The neutron tomography setup is shown in Figure 2.3.

Backprojection algorithms allow the reconstruction of the constituting slices. Finally, all slices are collected in an image stack, representing the 3D volume data of the neutron attenuation properties of the object. The latter can be visualized using 3D rendering software.

In this work, neutron tomography was used to visualize potential changes on a corroded lead artefact treated by electrolytic reduction (Chapter 4).

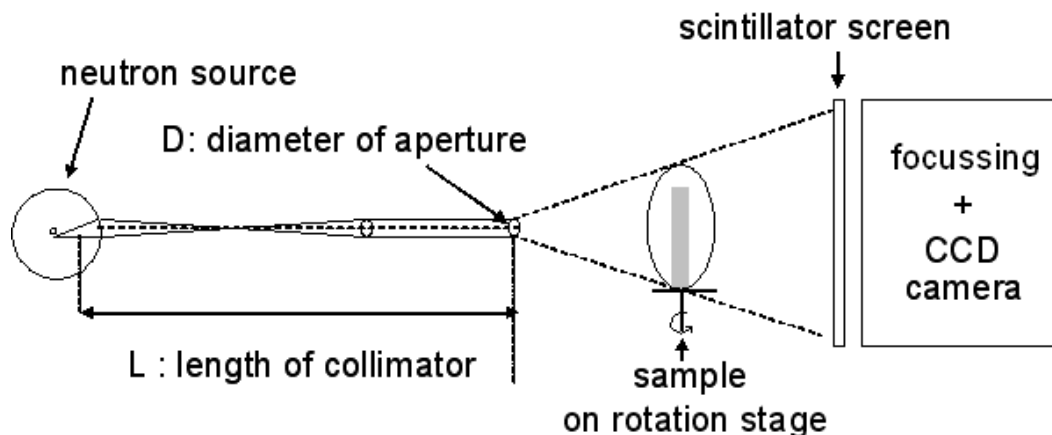


Figure 2.3: Setup for neutron tomographical experiments. The collimator is a device for improvement of a parallel beam. The L/D value characterizes the beam divergence and also affects the geometrical sharpness of the projected image (after [11]).

2.7 Synchrotron Radiation X-Ray Diffraction [12]

2.7.1 Synchrotron Radiation (SR)

In this work, X-rays produced by a synchrotron source have been used for chemical analysis. The principle of a synchrotron is based on the acceleration of charged particles, which consequently emit electromagnetic radiation. At synchrotron facilities, bunches of electrons (or positrons) are stored in a near-circular ring (storage ring). The electrons/positrons are guided through the ring by steering, focusing and bending magnets and the energy loss is compensated by the input of energy from radiofrequency cavities. As each 'bunch' of charged particles is accelerated inwards, an instantaneous jet of 'white' electromagnetic radiation is emitted along the forward tangent in the form of a fan emanating from each bending magnet. Next to bending magnets, current third generation synchrotron sources mainly rely on improved sources, such as wigglers and undulators, which are inserted in the so-called straight sections of the storage rings to achieve higher performance. A schematic presentation of a synchrotron storage ring is shown in Figure 2.4).

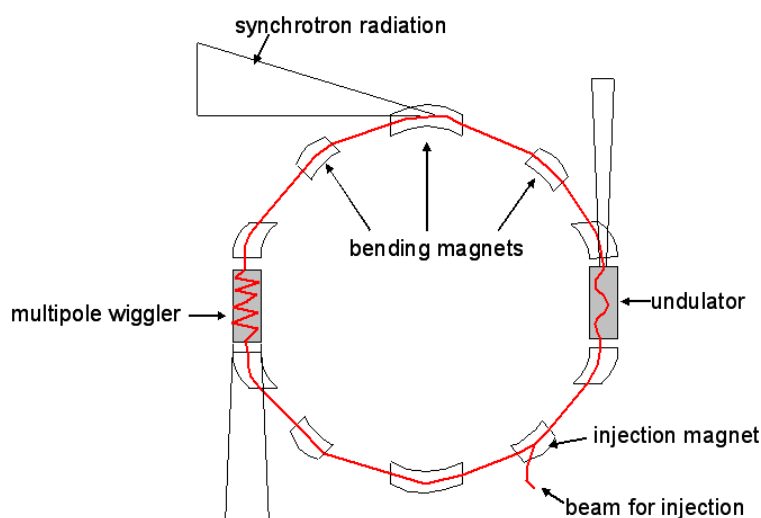


Figure 2.4: Schematic and simplified illustration of a synchrotron storage ring. The charged particles are kept into an almost circular orbit by bending magnets. The bending magnets, wigglers and undulators produce synchrotron radiation with specific characteristics (after [13]).

The synchrotron radiation covers a broad and continuous range of energies from infrared to hard X-rays at high intensities. The high intensities allow the production of intense monoenergetic/tunable beams through the use of monochromators. Other important characteristics of synchrotron radiation are its pulsed time structure (due to the several bunches of electrons in the ring), its high degree of natural collimation and its polarized character.

2.7.2 X-Ray Powder Diffraction (XRD)

Principles ([14])

X-ray diffraction is a frequently applied technique which is based on the irradiation of crystalline materials by a mono or polychromatic X-ray beam to produce back and forward reflections as a result of the periodicity and symmetry of the crystal. The reflections basically are produced by interference effects; constructive interference occurs when the path length differences, between the waves reflected from the various lattice planes, are

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integer multiples of the wavelength. The interference pattern is specific to the crystal structure being analysed, making the identification of crystalline substances possible.

The Bragg equation relates the wavelength of the incoming beam to the distance between parallel lattice planes:

$$2 d \sin\theta = n \lambda \quad (2.14)$$

where n is the order of a reflection, λ the wavelength, d the distance between parallel lattice planes and θ the so-called Bragg angle between the incident beam and a lattice plane. The identification of a given compound relies on the combination of the peak positions and the intensity, either calculated or compared with reference diffraction patterns.

Surface powder diffraction and the Hart-Parrisch geometry

Powder diffraction makes use of a microcrystalline powder sample ([14]). The sample, ideally, contains every crystalline orientation (e.g. by grinding), resulting in smooth diffraction cones. A schematic presentation of powder diffraction is shown in Figure 2.5.

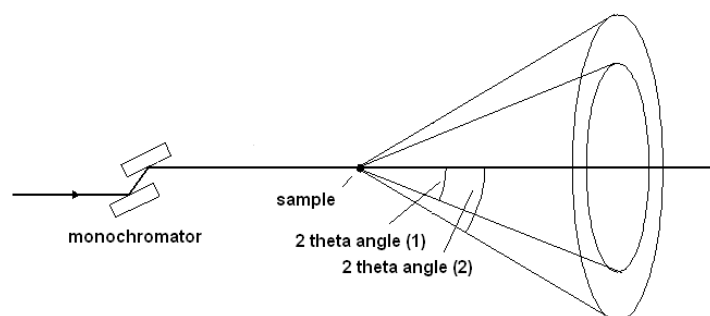


Figure 2.5: Illustration of the forward reflections of powder diffraction. The powder, in this case, contains two crystalline phases in any orientation, resulting in two smooth diffraction cones (after [14]).

Surface powder diffraction has the same principles of powder diffraction. The surface is

irradiated and produces diffraction cones. However, only the upper part of the diffraction cones can be observed due to absorption of the other part in the bulk material (see Figure 2.6). Parrish and Hart [15] designed a special geometry for synchrotron X-ray powder diffractometry, which is shown in Figure 2.6.

In this work, synchrotron radiation based (monochromatic) X-ray diffraction was used for the qualitative analysis of corrosion products (Chapters 4 and 5). The technique was also used for the in-situ monitoring of a growing lead decanoate coating (Chapter 7).

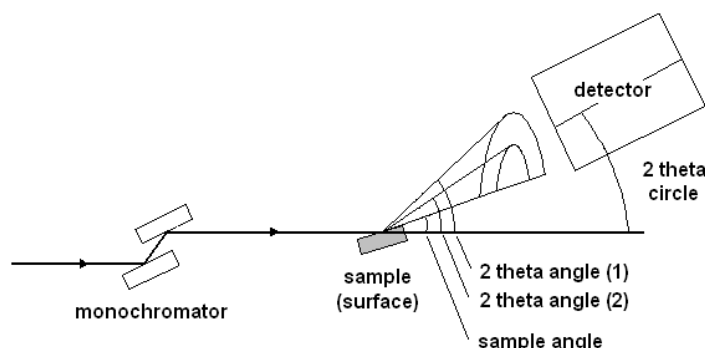


Figure 2.6: Schematic diagram of the Hart-Parrish geometry used for synchrotron powder diffraction. The sample is mounted under an incident angle so that the surface is irradiated. The detector is attached to a diffractometer for accurate positioning.

2.8 Contact angle measurements

2.8.1 Introduction

The magnitude of solid/liquid contact angles is determined by interfacial tensions, temperature and by surface roughness [16, 17]. Contact angle measurements with water as a test liquid provide information about the varying hydrophobicity of surfaces upon treatment, if/when other parameters such as surface roughness remain constant. Obviously, temperature is the easiest parameter to stabilize while surface roughness, usually, is a property

which is more difficult to modify. The surface tension of the liquid is readily decreased by the addition of surfactants, and, to some extent, increased by addition of electrolytes. In the next subsection, some theoretical aspects of surface tension will be considered.

2.8.2 Surface tension: principles

Surface tension is a consequence of intermolecular attraction, the so-called Van der Waals forces [18]. In bulk liquids, each molecule is symmetrically surrounded. Any intermolecular attraction forces are cancelling. ($\sum_i F_i = 0$). However, at the liquid/vapour interface, a molecule is pulled inwards, i.e. towards the bulk liquid, due to a resultant force caused by the molecule's asymmetrical surrounding (Figure 2.7). This force is essentially short-range, because it occurs within the radius of intermolecular attraction. The force, furthermore, is counteracted by the liquids' resistance to compression. Similar effects are essentially absent in the vapour phase, because of its much lower density.

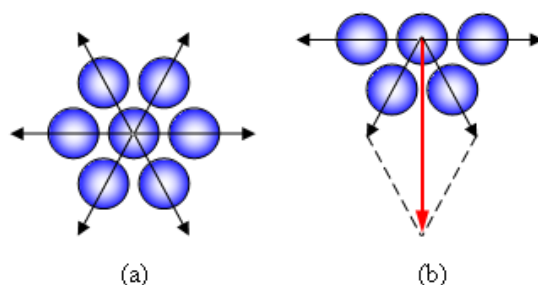


Figure 2.7: Cohesion forces working on molecules in a liquid phase; a) in the bulk of the liquid and b) at the vapour-liquid interface (after [18]).

The inward force implies the existence of a specific liquid/vapour interfacial free energy, since work is to be done upon moving a bulk molecule towards the interface [16]. This work, in conditions of constant liquid temperature and volume, is nothing else but the (specific) interfacial free energy, in agreement with the well known formulation from thermodynamics:

$$\gamma_i = \left(\frac{\partial F}{\partial A_i} \right)_{T,V} \quad (2.15)$$

Hence, the change of free energy of a multi-phase system, under conditions of constant temperature and volume and in the absence of chemical reactions becomes

$$(dF)_{T,V} = \sum_i \gamma_i dA_i + dU_{pot} \quad (2.16)$$

where

γ_i = interfacial free energy (Equation 2.15)

A_i = the surface area of the i^{th} type

U_p = potential energy in the gravitational field

The profile of sessile liquid drops appears to be governed by the requirement of minimal free energy (Figure 2.8), including gravitational potential energy and interfacial contributions, and under the constraint of a constant liquid volume (Equation 2.17) [17, 19]. The drop profile $y(x)$ is the one that minimizes the free energy, and can be calculated by applying the formalisms of variational calculus.

$$W = \int_0^R [\pi \rho g x y^2 - 2\pi \gamma_{LV} x y' (1 + \frac{1}{y'^2})^{\frac{1}{2}} + 2\pi x (\gamma_{SL} - \gamma_{SV}) + 2\pi P_v x y] dx \quad (2.17)$$

R : the droplet's radius in the ground plane

P_v : the pressure in the vapour phase

g : the gravitational constant

ρ : the apparent density of the fluid (ρ_l), i.e. the density of the fluid minus the vapour density (ρ_v)

y' : the first derivative of $y(x)$

Here, the conservation of the liquid volume has to be taken into account. This is done by

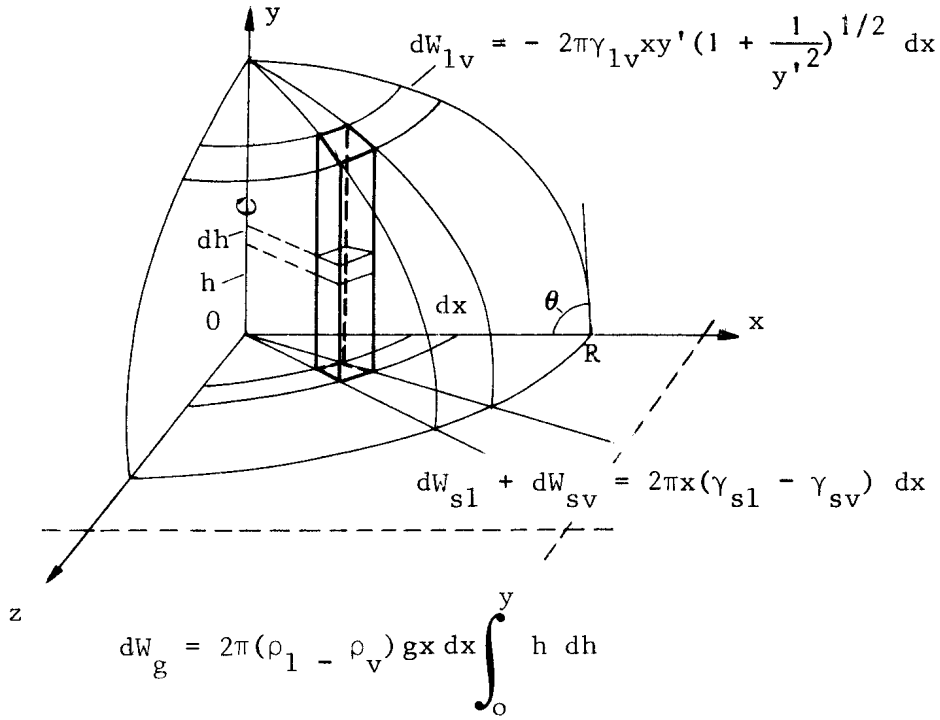


Figure 2.8: Physical model for the calculation of the profile of sessile liquid drops on a horizontal plane. The solid surface, i.e. the solid/vapour + solid/liquid interface is constant (from [17]).

multiplying the liquid volume by a Lagrange multiplier λ , and, by adding this quantity as an additional term in the integrand (Equation 2.18).

$$\bar{F}(x, y, y', \lambda) = \pi\rho gxy^2 - 2\pi\gamma_{LV}xy' \left(1 + \frac{1}{y'^2}\right)^{1/2} + 2\pi x(\gamma_{SL} - \gamma_{SV}) + 2\pi(P_v - \lambda)xy \quad (2.18)$$

In order to obtain the extremal profile $y(x)$ that minimizes the system's free energy, the following Euler equation has to be solved:

$$\rho gxy + (P_v - \lambda)x + \gamma_{LV} \frac{d}{dx} \left[\frac{x}{(1 + \frac{1}{y'^2})^{1/2}} \right] = 0 \quad (2.19)$$

The integration can only be done numerically. An additional problem, in this context, is the fact that the Lagrange multiplier λ occurs as an unknown system parameter. The numerical integration, initiated with an arbitrary λ , therefore, has to be iterated until the function $y(x)$ meets specific requirements, e.g. the correct drop volume, drop height and drop radius in the ground plane.

Coming back to equation 2.15, it is seen that interfacial tension, which is normally formulated in terms of free energy per unit of interfacial surface area, can also be thought as a force per unit length of a real or imaginary rim/cut of the interface. The direction of that force, in any case, is perpendicular to the cut/rim and tangent to the interface. Therefore, surface tension, commonly measured in joules per square meter ($J\Delta m^{-2}$) is also expressed in units of $N.m^{-1}$ [16, 20].

Interfacial tensions can be represented as vectors acting at the rim of solid-liquid (γ_{SL}), solid-vapor (γ_{SV}), and liquid-vapor (γ_{LV}) interfaces (Figure 2.9).

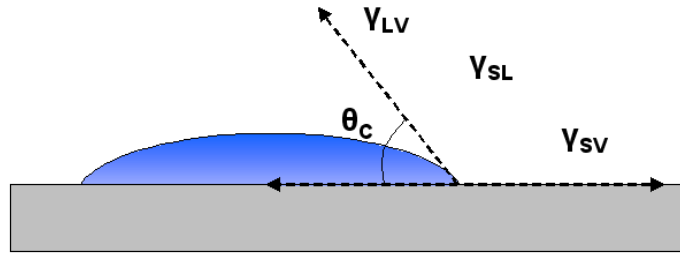


Figure 2.9: Vector presentation of the forces implicated in the horizontal equilibration and the contact angle magnitude, where γ_{SV} is solid/vapour interfacial tension; γ_{SL} is liquid/solid interfacial tension; γ_{LV} = surface tension of the liquid and θ is the contact angle (after [16]).

As it is seen from Figure 2.9, Young's equation (Equation 2.20) describes how interfacial

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tensions determine the magnitude of the contact angle. This is confirmed by the aforementioned thermodynamic analysis, more specifically as an occurring boundary condition in the extremation. Apparent deviations from that relationship [17], on closer scrutiny, appear due to non-uniformity (physical and/or chemical) of the solid surface.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2.20)$$

which equation is commonly known as Young's law.

The geometry of sessile liquid drops of known γ_{LV} and θ , in thermodynamic equilibrium, provides information about the difference $\gamma_{SV} - \gamma_{SL}$.

Interfacial free energies of the γ_{SL} type strongly depend on the chemical nature of the solid: metals and crystalline materials inherently are highly energetic, and, therefore, tend to lower that energy by adsorption. These materials are hydrophilic. Conversely, low energy solids such as hydrocarbons and polymers, for similar reasons, are less prone to adhesion and/or adsorption and hydrophobic [16].

On the other hand, γ_{LV} strongly depends on the presence of dissolved surfactants which tend to accumulate at the liquid/vapour interface, and, possibly, also at the solid/liquid interface. The phenomenon is known as interfacial adsorption [16].

Surfactants, acting as dielectrics, shield the polar water molecules at the liquid/vapour and/or solid/liquid interface, thereby drastically decreasing the effects of London-Van der Waals forces. Surfactant concentrations in the order of a few ppm already bring down the surface tension of pure water from $\sim 72 \text{ mNm}^{-1}$ to about $\sim 20 \text{ mNm}^{-1}$. On increasing the surfactant concentration, the surface tension sometimes decreases to a minimum value and thereafter becomes constant (Figure 2.10) at a concentration known as the *critical micelle concentration* or cmc [16].

Similar processes, presumably, also occur at the solid/liquid interface. The global effect is readily understood on grounds of Young's law:

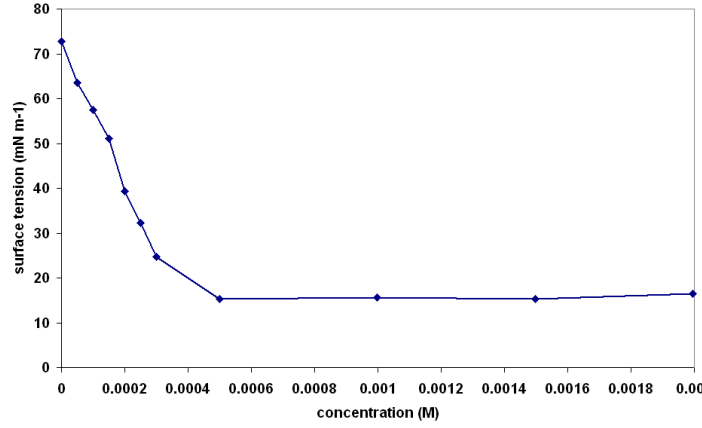


Figure 2.10: Typical curve presenting the effect of surfactants on the surface tension. This curve was obtained by increasing the concentration of the surfactant sodium decanoate.

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.21)$$

Indeed, addition of surfactants commonly results in decreasing γ_{LV} , while γ_{SL} and γ_{SV} remain unaffected, so that the contact angle θ is reduced to lower values. Their concentration, which is inherently low and non-uniform in most applications, may be further affected (i.e. decreased) by adsorption, e.g. at the wall of receptacles wherein dilution takes place. It is important, therefore, to adopt working concentrations well above cmc, whenever a stable and well-known surface tension is required [16].

2.8.3 Determination of surface coverage

Substrate/liquid contact angles θ^* on composite surfaces, under certain restrictions, respond to the relation [16]:

$$\cos\theta^* = \epsilon\cos\theta_1 + (1 - \epsilon)\cos\theta_2 \quad (2.22)$$

hence

$$\epsilon = \frac{\cos\theta^* - \cos\theta_2}{\cos\theta_1 - \cos\theta_2} \quad (2.23)$$

where θ_1 and θ_2 are the contact angles on the constituting (pure) surfaces and ϵ is the fractional surface coverage with θ^* , θ_1 and θ_2 known by experiment.

However, Equations 2.22 and 2.23 only hold if/when the surface coverage is uniform on an almost molecular scale. Sessile drops of a test liquid, in such circumstances show axial symmetry and a unique contact angle, at least when the contact angle is sufficiently large.

In this work, contact angle measurements were performed in order to determine the fractional surface coverage of substrates, upon coating with lead decanoate (Chapter 9).

2.9 Conductivity measurements [20]

Conductivity is the ability of a solution to pass electric current. The current, carried by ions, increases with the ions concentration and with increasing ion mobility.

The conductivity is measured by applying a small voltage (U) to two platinum electrodes of the conductivity sensor. The resulting current (I) is measured. In order to reduce the polarisation of the electrodes, the conductivity meter uses an alternating voltage at a dedicated frequency. By using Ohm's law ($U = RI$), the resistance of the solution (R) can be calculated.

From that, the conductance (G) is determined using the formula:

$$G = \frac{1}{R} = \frac{I}{U} \quad (2.24)$$

The conductivity κ ($S\text{cm}^{-1}$) of a solution is calculated on the basis of the conductance G (S) and the cell constant K (cm^{-1}):

$$\kappa = GK \quad (2.25)$$

The cell constant (K) is based on the cell geometry and in theory can be calculated from the dimensions of the electrodes (plates or rings) using the following formula:

$$K = \frac{l}{A} \quad (2.26)$$

with l the distance between the electrodes (cm) and A the area of the electrodes (cm^2).

In practice, it is difficult to measure the real area of the electrodes precisely. Therefore, standard solutions of known conductivity are used to calibrate the cell.

This work used conductivity measurements for the optimization of the $Pb(C_{10})_2$ coating process discussed in Chapter 8, but also for the determination of the critical micelle concentration (Chapter 9).

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Part II

Study of the electrolytic reduction of actively corroded lead objects

Chapter 3

A fundamental study of the electrochemical reduction treatment applied to actively corroded lead artefacts *

This chapter aims at an understanding of the mechanism of the ongoing reduction in the corrosion layer, and how it affects the profile of the corresponding reduction curve. Degriigny and Le Gall have already tried to explain this (Subsection 1.4.2, [1, 2]). By plotting the logarithm of the reduction current versus reduction time, they observed four different regions in the profile (Figure 1.11). They formulated the following hypothesis: The first region (I) is marked by an increase in the reduction current, due to the progressive polarization of the entire sample. This is followed by a large decrease (second region), indicating the progressive reduction over the total thickness of the corrosion layer (II). The third region (III) shows a smaller decrease in reduction current from thick corrosion

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patches. During the last step (IV), the current remains stable indicating the end of the reduction process.

Basically, the present study is a continuation of the work of Degriigny and Le Gall. Our experiments involved studying cross sections of (half)-reduced artefacts by optical microscopy, in order to understand the ongoing reduction in the corrosion layers. In this context, half-reduced artefacts are treated by electrochemical reduction without reaching the end of the treatment. In addition, the changes in the corrosion layer were visualized by optical microscopy during reduction in real time. The experiments allowed specification of a mechanism of the proceeding reduction process.

3.1 Experimental

3.1.1 Corroded lead artefacts

Lead artefacts were kindly provided by the Musée des Arts et Métiers (CNAM) in France and consisted of components in a model of a *Jacquard* weaving loom, whose function was to keep tension on the twinning threads (Figure 3.1). Generally, the *Jacquard* loom, invented by Joseph Marie Jacquard in 1801, utilizes a hole punched pasteboard to make up the design in the textile [3]. The model entered the museum in 1874 and was stored in a display case. The model itself, and the display cabinet consist partly of wood, thereby creating conditions to promote active corrosion [1]. In contrast to the wooden part, the lead weights have seriously degraded as shown in Figure 3.5 (see below). Analysis of the metal core showed some inclusions of copper and antimony [2].

3.1.2 Reduction equipment

The reduction of the corroded artefacts was performed with a potentiostat (PGSTAT20, Eco Chem, The Netherlands), coupled to a computer running the Autolab software (version 4.9, Eco Chem). The reference electrode was a saturated $Hg/HgSO_4$ electrode (XR210,



Figure 3.1: Model of the weaving loom by *Jacquard*. The corroded lead weights are still hanging on their original thread and are indicated with an arrow.

Radiometer Analytical, Denmark) with a potential of 0.658 V versus the standard hydrogen electrode ($T = 295\text{ K}$). All the data presented in this chapter have been referred to this reference. A cylindrical platinum electrode was used as a counter electrode. The working electrodes were the lead tensioning weights, and more specifically the remaining lead core. The applied reduction potential was -1.3 V [1]. The electrolyte, used in both experiments, was 0.1 M Na_2SO_4 (Carlo Erba, 99.95%). Sodium sulphate solutions, according to Degriigny and Le Gall [1], are not corrosive and appear efficient for the treatment of corroded lead artefacts.

Two experiments were performed. The first one involved studying the cross sections of half reduced artefacts by optical microscopy. Therefore, lead weights were divided into several sections by removing small areas of the corrosion crust with a file at equal distances of 1 cm. The grooves produced were coated by a varnish layer (Epoxy jaune, Du Pont, Belgium) in order to prevent the electrolyte rising to another section as a result of capillary forces. The core metal was electrically connected by a crocodile clip, thereby penetrating the corrosion crust. The upper part of the lead artefact was never in contact with the electrolyte (Figure 3.2).

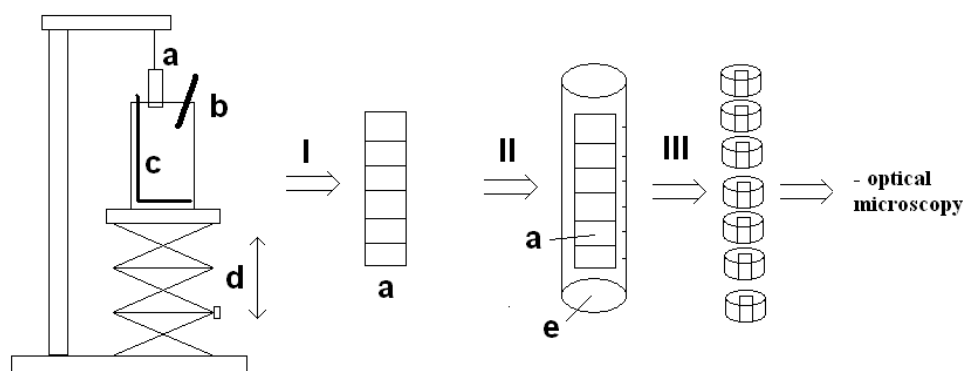


Figure 3.2: Schematic overview of the first experiment with a: sectioned artefact/working electrode, b: reference electrode, c: platinum counter electrode, d: labjack and e: epoxy resin.

The reduction of the corroded lead artefacts was stopped at specific times, covering the different regions of the reduction curve. The electrolytic reduction started by immersing only the lowest part of the artefact (up to the first groove) into the solution. At specific times, the beaker was positioned higher with a labjack to immerse/reduce the next section of the artefact in the electrolyte. The time intervals were carefully chosen to yield (half) reduced sections, each characteristic of another region in the profile. The potential on every segment in the solution remained -1.3 V . By repeating this procedure in several steps, the lowest section was exposed to the longest reduction time at the end of the experiment, while

A fundamental study of the electrochemical reduction treatment

the upper part of the artefact was subjected to the shortest reduction time. The sectioning, as such, has two advantages: (1) each sectioned artefact yields information of several (half) reduced states in its different sections, thereby avoiding the need of more irreplaceable artefacts and (2) the time of the overall experiment is considerably shorter than the time that would be spent for performing multiple reduction experiments on separate artefacts.

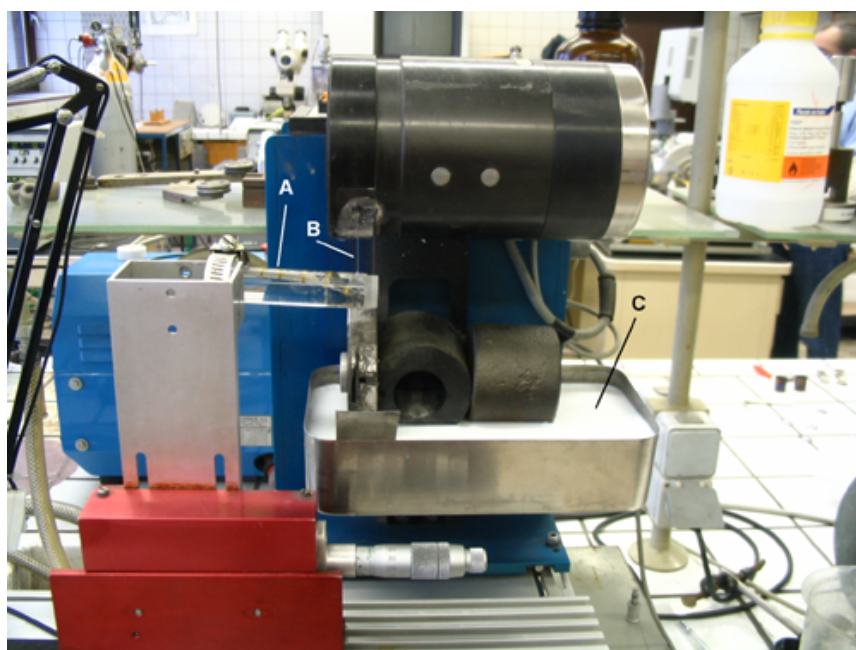


Figure 3.3: Diamond thread saw cutting the embedded lead artefacts with a: embedded lead artefact, b: diamond thread and c: lubricant.

Evaporation of the solvent was prevented by sealing the cell with parafilm®. Evaporation would not only affect the reduction curve by decreasing the surface area of the working electrode, but also the concentration of the electrolyte. After the reduction treatment (Figure 3.2), the artefacts were rinsed with tap water and dried for one hour, in a container with forced cold air flow (step I). The lead weights were then embedded in epoxy resin (step II) (Epofix kit, Struers, France) and cut transversely using a diamond thread saw (step III) (Figure 3.3). The disks obtained this way were polished on a cloth with diamond spray and a lubricating liquid (MD Mol, DP-spray 3 μm and DP-Lubricant Red, Struers).

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The second experiment aimed at examining the reduction mechanism in more detail. The complete setup is shown in Figure 3.4.

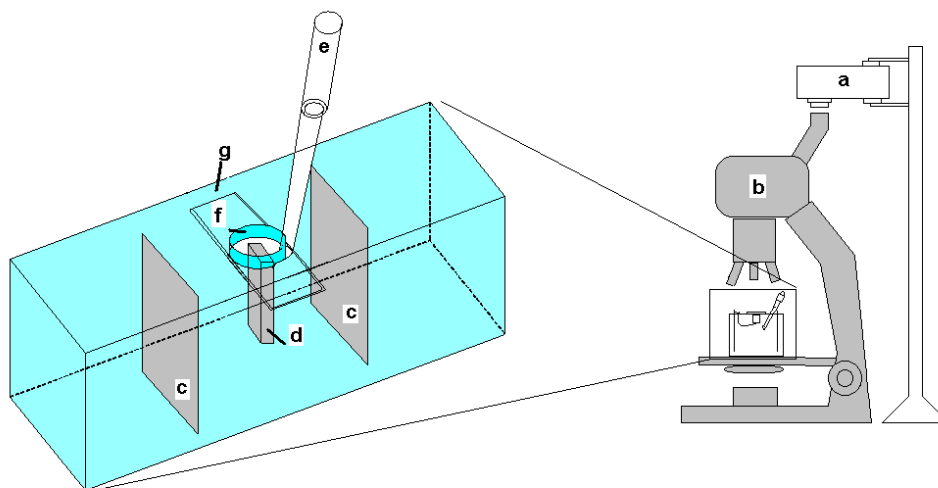


Figure 3.4: Schematic overview (without electrical connections) of the experiment to observe the changes in the corrosion layer in real time with a: camera, b: microscope, c: platinum counter electrodes, d: artefact/working electrode, e: reference electrode, f: plastic ring, g: glass plate.

The detailed study was performed by taking in-situ optical micrographs of a cross section during reduction. In this experiment the artefacts are studied during reduction, and do not require to be dried, nor embedded and cut as in the previous experiment. Moreover, the experiment gives continuous time-related information.

The procedure involved cutting an artefact so that the cross section of the corrosion crust became visible. Gently grinding (1200 grit SiC paper, Struers) and polishing (same procedure as described in the previous paragraph) flattens the cross section, after which it is possible to fix onto a glass window making use of glue (Bison Kombi). The glass window contains a plastic ring on the upper side, which prevents the working electrode from drying during treatment. An electrical contact is made with the core metal on the lower side of the coupon. The connection was insulated from the electrolyte with varnish (Epoxy jaune).

The element is placed in a cell filled with electrolyte (0.1 M Na_2SO_4). In addition, a platinum counter electrode is placed on both sides of the coupon and a reference electrode is placed near the working electrode. It is important that oxygen bubbles, formed on the counter electrodes, do not migrate towards the working electrode. Therefore, the counter electrodes may not be shielded by the glass plate. The entire setup was positioned under an optical microscope, so that the cross section is visible through the system. The optical system of the microscope allows recording of the focused image every five minutes using a digital camera and appropriate software (Canon Powershot A75).

3.2 Results

A photograph of a typical coupon obtained from CNAM is shown in Figure 3.5 (left). The surface is covered by white corrosion products. Some regions are attacked more severely than others and, as a result, the original shape of the coupon has been deformed (pitting corrosion). A cross section of the embedded artefact, shown in Figure 3.5 (right), gives information about the internal structure of the corrosion layer and shows that the deformations are clearly part of corroded areas. Those patches appear to be very porous and consist of corrosion products and remaining metal veins. The veins are easily visible using optical microscopy, especially from the light reflections of the metal. Other corrosion products still follow the contours of the bare metal closely and seem to be very compact (uniform corrosion). In conclusion, two different kinds of corrosion are observed: a thin compact corrosion layer (20 μm) and thick porous patches (< 200 μm). These are indicated respectively in Figure 3.5 with a and b.

The reduction curve of a three-sectioned artefact is shown in Figure 3.6. The abrupt jumps in the reduction current at 23000 s and 79000 s correspond to the repositioning of the beaker to allow the reduction of another section.

The reduction curve consists of three parts, indicated with the numbers 1-3 (Figure 3.6) and will be referred to as sectional reduction curves. The first of these (1) contains information

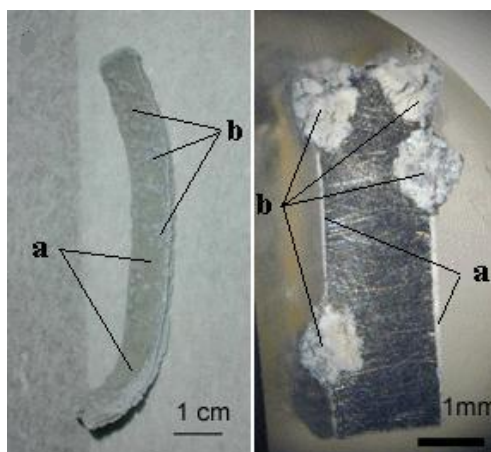


Figure 3.5: Photographs of (left) an entire lead coupon obtained from CNAM and its cross section (right). Two different kinds of corrosion, uniform and pitting corrosion, are respectively indicated with the letters a and b

about the first section, which was reduced for 180000 s in total. The second part (2) contains information on the two sections in solution, and was reduced for 157000 s (180000-23000 s). The last part (3), was reduced for 100000 s, resulting in a sectional reduction curve which also contains contributions from the previous sections. For this reason, the sectional reduction curve of each new segment reaches higher currents, e.g. ~ 10 mA for the first segment towards ~ 15 mA for the second one.

Figure 3.7 shows the extraction of six sectional reduction curves, obtained from three separate experiments. The third sectional reduction curve of Figure 3.6 is also present as the 100000 s reduced section. The last part of each sectional reduction curve, marked by two vertical lines, was estimated. This actually is the time period when other sections were enabled to reduce by repositioning the beaker. In the case of the sectional reduction curves 1 and 2 in Figure 3.6, the estimated parts equals respectively 157000 s (time to reduce the second and last segment) and 100000 s (the reduction time of the last/third segment). The last segment has no estimated part since no other segments were reduced afterwards. The estimated parts were based on the characteristic profile of a reduced lead weight (Figure

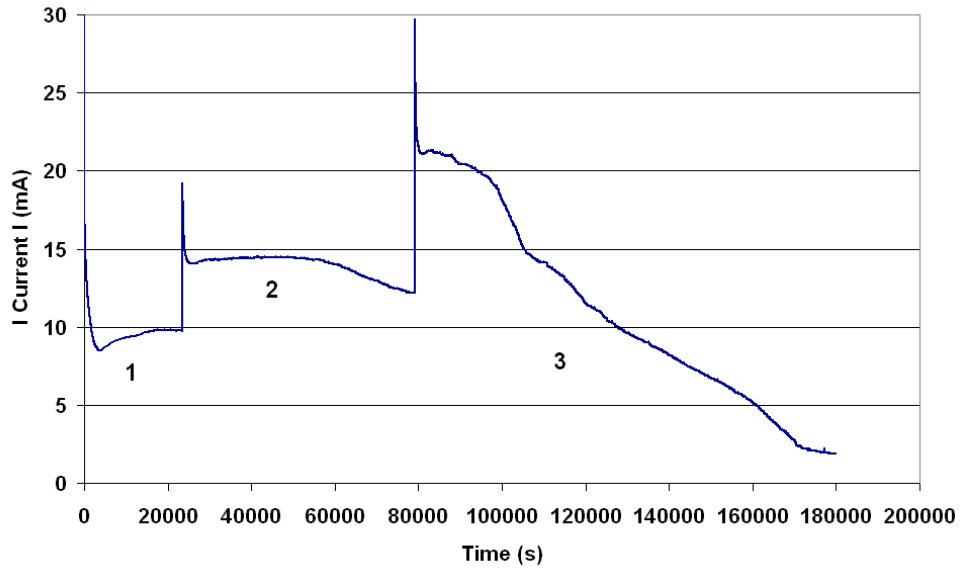


Figure 3.6: Reduction curve as recorded from a sectioned artefact. The abrupt changes in current indicate the reduction of another section. The reduction curve is built up by three sectional reduction curves, indicated by 1, 2 and 3.

1.11). The sectional reduction curve of 300000 s (Figure 3.7) marks an estimated segment of about 150000 s, but as it is seen from the general profile in Figure 1.11, this is justified since the current almost remains stable. Smaller estimations had to be made when the current was changing, e.g. for reduction times <100000 s. The sectional reduction curve of the 100000 s reduced section was the last reduced section of that particular experiment (see Figure 3.6), and therefore lacks an estimated part.

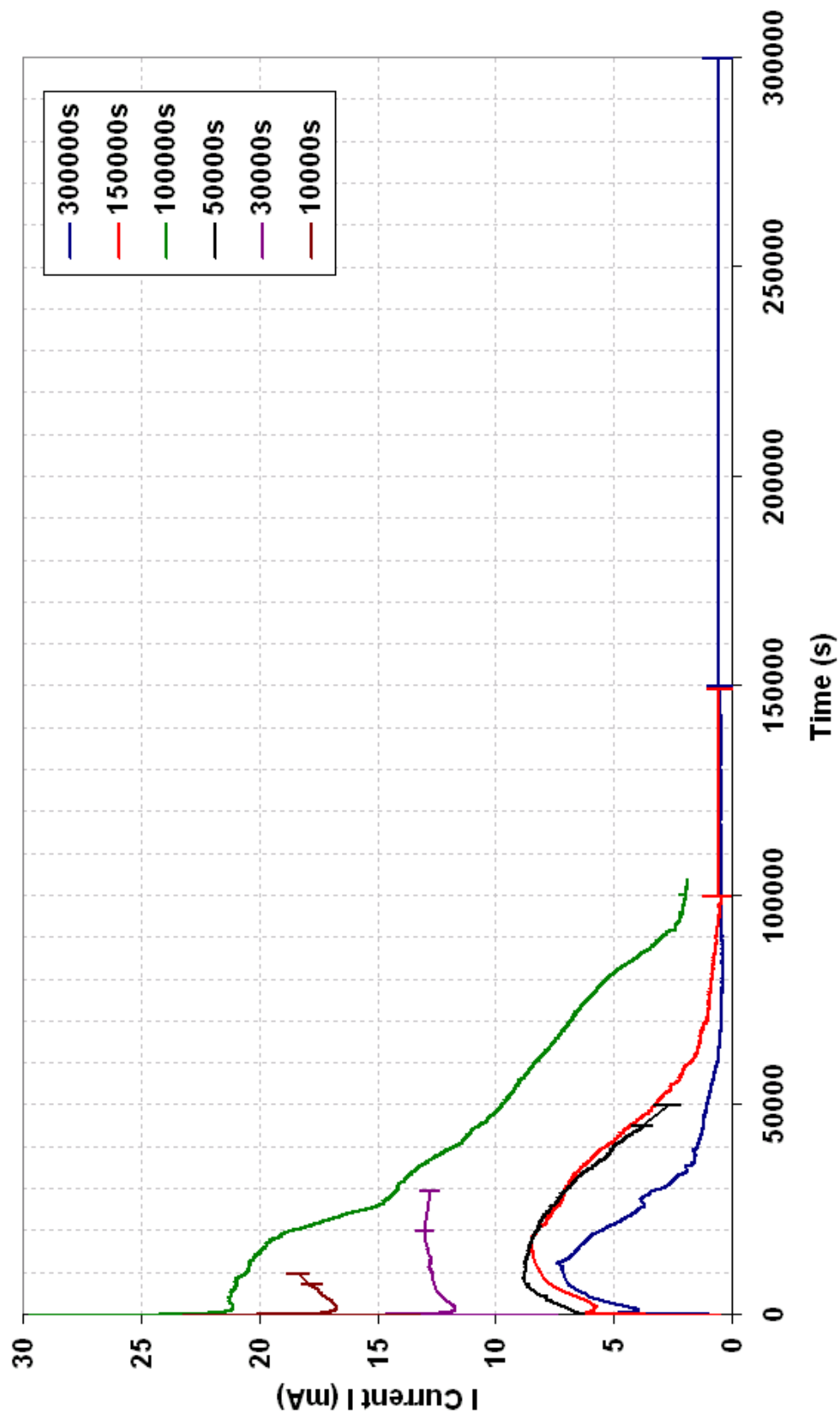


Figure 3.7 : Superposition of sectional reduction curves representing several half- reduced sections.

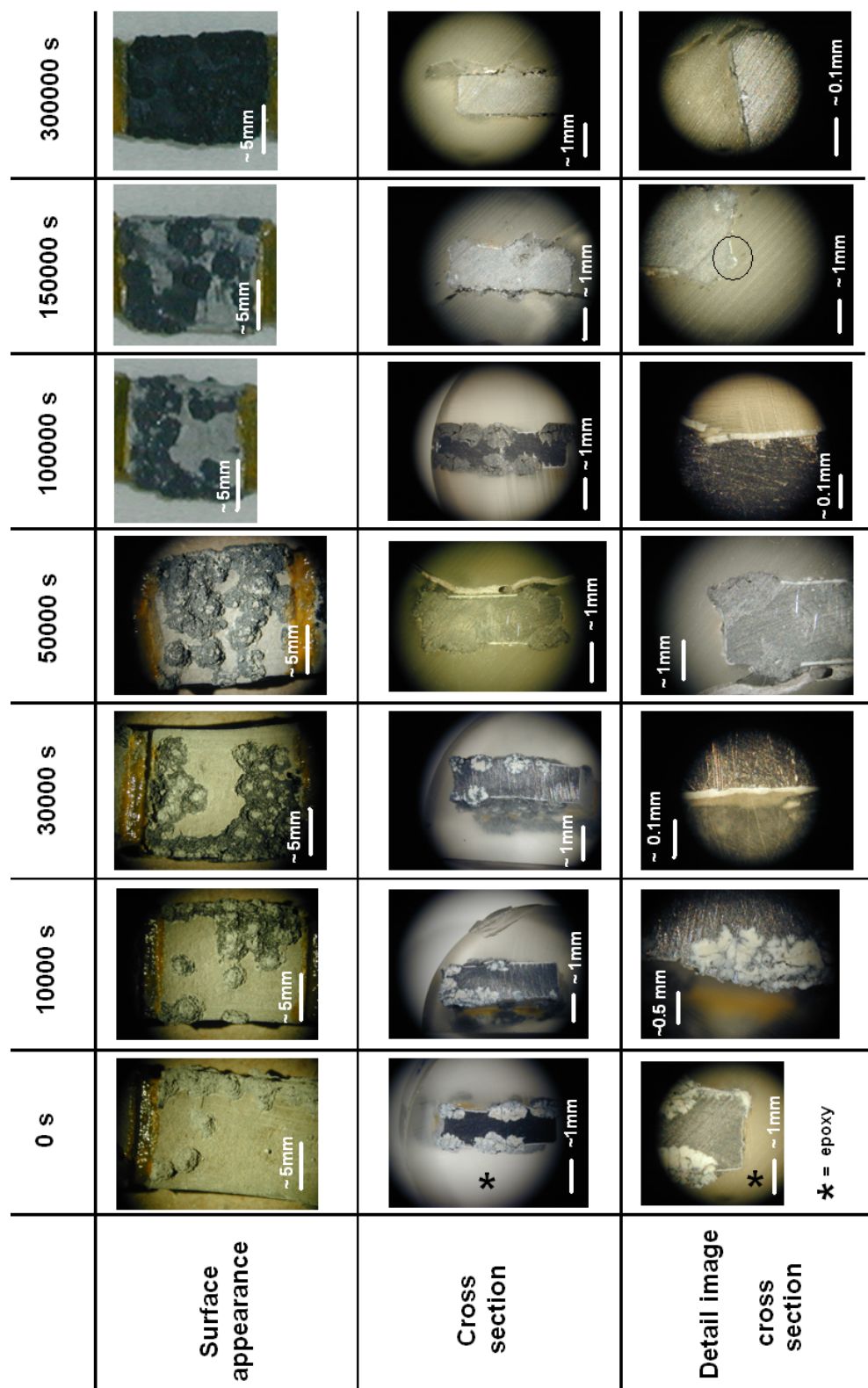


Figure 3.8: Surface appearances and (detailed) cross sections of the (half) reduced sections, which sectional reduction curves are presented in Figure 3.7. The circle in the detailed cross section after 150000s of reduction, shows that the process progresses from the metal towards the solution.

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The sectional reduction curves in Figure 3.7 represent a number of half reduced states, covering the general profile of a reduction curve. The surface appearances and (detailed) cross sections of the corresponding half reduced sections are shown in Figure 3.8¹. The column of 0 s shows the non-reduced state of a section. The deformations on the surface of a non-reduced section correspond to the porous corrosion structures. The groove is also visible from the insulating yellow varnish. The second and last rows of Figure 3.7 show the cross sections at different magnifications.

One can see that the porous corrosion structures are initially reduced over time. The surface appearance becomes a darker grey, until the entire porous structures have been reduced (0-100000 s). This is better visualized in the cross sections, which clearly show the reduced/non reduced parts. The cross section of the 30000 s section nicely shows the newly reduced metallic regions. After 100000 s of reduction, the porous patches appear totally reduced. This also affects the profile of the reduction curve, since a stable current is reached (Figure 3.7). However, the uniform corrosion structures, as seen in the detailed image at 100000 s, have not yet changed. A longer reduction time results in the conversion of those structures too: the surface appearance of the uniform corrosion discolours and a detailed image after 150000 s even shows that the reduction occurs from the inner crust outwards towards the solution (indicated by the circle). Finally, after 300000 s of reduction, all corrosion products present on the artefact have been fully reduced.

In the second experiment, the changes in the corrosion layer were visualized by optical microscopy during the reduction process in real time. Figure 3.9 (left) shows an optical image of the cross section before the reduction started.

¹This figure is magnified in the appendices.

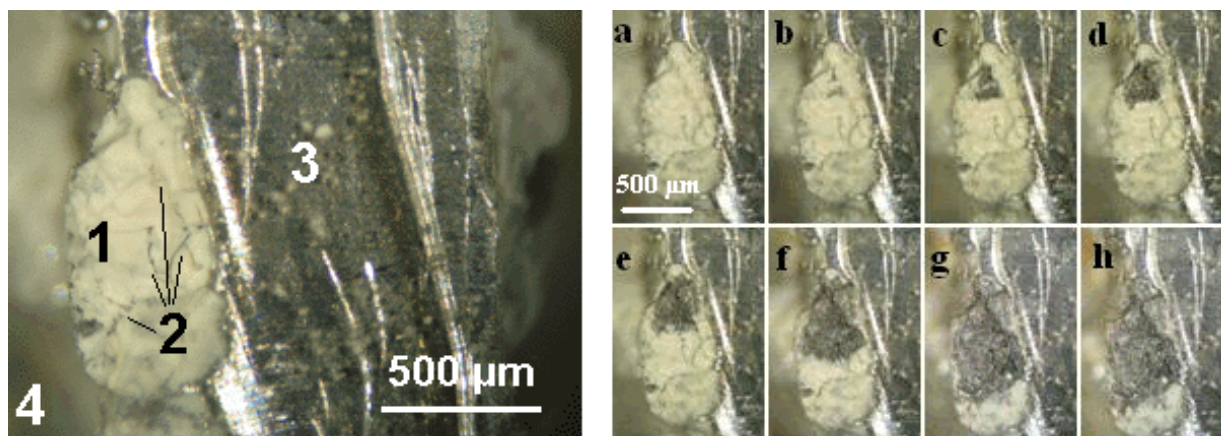


Figure 3.9: (left) Detailed image of the first image with (1) the porous corrosion patch, (2) some metal veins, (3) the metal core and (4) the electrolyte (4). (right) Time-elapsing optical images (a-h) of the reduction process in the porous corrosion layer.

The image shows a porous corrosion patch (1), some remaining metal veins, indicated by the lines (2), the metal core (3) and the electrolyte (4). A sequence of optical images is shown in Figure 3.9 (right). The first image (a) is the same as the one shown on the left hand side. In the second image (b), some reduced lead is visible in the proximity of a lead vein. The local reduction is even clearer in the next image (c). The reduction of the entire patch proceeds from the initially reduced lead.

3.3 Discussion

Both experiments show that the reduction starts with the conversion of the corrosion products at their interface with the lead metal. In the case of the porous patches, the metal phase consists of lead veins, and in the case of the uniform corrosion, it consists of the remaining metal core. However, the reduction of the two corrosion structures takes place one after the other as observed in the first experiment. A possible explanation for this behaviour lies in the differing porosity of each structure. The porous structures allow ions to be transported through easily, which results in an initial and kinetically favoured

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reduction. The dense structures, on the other hand, are more difficult to reduce. First, the layer has to be saturated with electrolyte to ensure ion transport, and this is slow because of the dense characteristics. Once established, the reduction of these structures is slow, again because of reduced ion transport throughout the layer.

The present study shows that the profile of the reduction curve must be interpreted in a slightly different way as described by Degriigny and Le Gall [1].

Degriigny and Le Gall stated that the first region (I) is marked by an increase in the reduction current, due to the progressive polarization of the entire sample (Figure 1.11). This is confirmed; from the start of the reduction towards the maximum reduction current implies the progressive penetration of the electrolyte into both corrosion structures, reaching maximum efficiency in conversion.

The second and third region, according to Degriigny and Le Gall, was due to the decreasing amount of corrosion products which are converted, and the progressive reduction of the total thickness. This study shows that the decrease indeed is due to the conversion of porous patches.

The last step, however, according to our findings, is associated with the reduction of the thin uniform corrosion layer, without immediately indicating the end of the treatment as claimed by Degriigny and Le Gall. The end of the treatment, however, is well determined by visual inspection. The last step, i.e. the reduction of the thin corrosion layer, starts from the metal towards the electrolyte. Therefore, the treatment is finished when the entire surface has turned from white to dark grey.

3.4 Conclusions

Corroded lead coupons of the *Centre National des Arts et Métiers* (CNAM) were used to study the electrochemical reduction process at constant potential. The coupons show two

types of corrosion: a thick porous crust ($< 200\text{ }\mu\text{m}$) and a thin compact layer ($20\text{ }\mu\text{m}$).

Electrolytic reduction of the coupons was performed in a $0.1\text{ M Na}_2\text{SO}_4$ solution at -1.3 V vs Hg/HgSO_4 . First, the porous corrosion crust is reduced. The reduction starts at metallic veins still present in this layer, and progresses further in all directions. The reduction of the porous crust corresponds to almost the entire peak of the reduction curve. This process is followed by the reduction of the compact layer, which starts from the bare metal progressing towards the solution. This process corresponds to the stable current.

One of the most important conclusions of this chapter for conservators is that the mechanism allows the determination of the end of the reduction treatment by visual inspection of the surface appearance.

3.5 References

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Chapter 4

Insights into the chemical and morphological changes after electrolytic reduction *

This chapter focuses on the evaluation of the chemical and morphological changes of corroded lead artefacts when using electrolytic reduction as a stabilization method. Synchrotron radiation X-ray diffraction (SR-XRD) and X-ray photoelectron spectroscopy (XPS) were used to study the chemical changes of the corrosion layer and on the top nanometre of the surface, respectively. Neutron tomography (NT) and scanning electron microscopy (SEM) were used to visualize potential morphological changes at the millimetre and micrometre scale, respectively. The results of this study show that the electrolytic reduction

*This material formed the basis for a publication: B. Schotte, A. Adriaens, F. Dhooghe, D. Depla, M. Dierick, M. Dowsett, E. Lehmann, and P. Vontobel. Chemical and morphological changes of historical lead objects as a result of the use of electrolytic reduction as a stabilization treatment. *Analytical Chemistry*, 78:8319-8323, 2006. This work has also been presented in part at the Kick-off meeting of the ICOM-CC Metal Working Group, 13 march 2005 (Ghent, Belgium), at the 7th Indoor Air Quality Meeting, 15-17 november 2006 (Braunschweig, Germany), at the Eastern Analytical Symposium, 12-15 november 2006 (New Jersey, US) and at Conservation Strategies for Saving Indoor Metallic Collections (CSSIM), 25 february - 2 march 2007, (Cairo, Egypt).

is a reliable way to stabilize and conserve actively corroded lead artefacts. The corrosion products actually are converted into metallic lead, while the morphological changes due to the treatment are limited.

4.1 Experimental

Also for this study, we used corroded lead artefacts obtained from the *Centre National des Arts et Métiers* (CNAM) as described in Subsection 3.1.1.

NT, SEM, XPS and SR-XRD measurements were performed on two samples before and after the reduction treatment. Prior to these analyses, the samples were lightly brushed to remove weakly adhering corrosion particles from the surface. An insulated (Epofix kit, Struers, France) crocodile clip was fixed to one end of the object, so that the electrical connection would not disfigure it (Figure 4.1).

The reduction itself was performed with the same equipment as discussed in Subsection 3.1.2. A difference, however, in this experiment was that the working electrode was fixed during the reduction. After the reduction, the object was rinsed and dried quickly using blowing air. If the object was to dry slowly, a superficial layer of lead oxides would be formed [1]. In addition, for the neutron tomography analyses, it is advisable that the sample is positioned in exactly the same manner before and after treatment so that images may be compared. Therefore the sample was mounted on a holder (Figure 4.1). The holder was designed so that a lid could protect the lead weight during transport to and from the NT facility.

SR-XRD data were acquired at the synchrotron radiation station XMaS (Station BM28, European Synchrotron Radiation Facility, Grenoble) [2] using the Hart-Parrish geometry (Subsection 2.7.2). On this station, a beam with a wavelength of $1.5498 \text{ \AA}$ and with dimensions of 1 mm at $200 \text{ }\mu\text{m}$ was used. These dimensions were selected to give a good intensity without saturating the detector. A 2D Mar CCD165 detector (Mar USA Inc.)

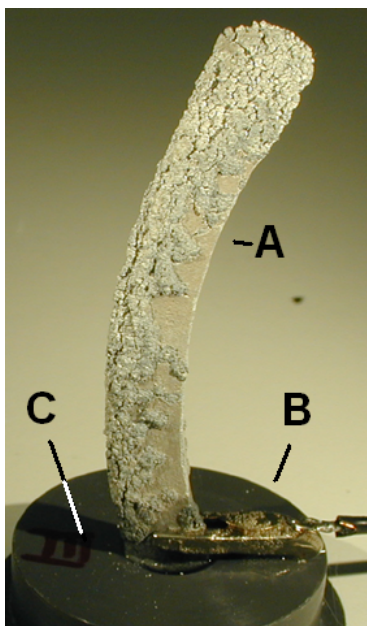


Figure 4.1: Photograph of a corroded sample (A), connected electrically using a crocodile clip (B) and mounted on a rigid holder (C), prepared for the Neutron Tomography analysis.

was used to record the diffraction patterns [3]. The angle of the camera to the beam was 35° for acquisition of the signals between 15° and 75° 2θ . Under these conditions, the diffraction centre is outside the field of view of the camera, and the camera plane intersects the diffraction cones at an angle, so as to produce elliptical 'rings'. Powder diffraction, as described in Subsection 5.1.4, was not used here because the setup actually was built for spectro-electrochemical experiments. The images were analysed using a new software program, EsaProject (© 2006 Mark Dowsett, EVA Surface Analysis), which was developed to process such images. Samples of the corrosion products were taken of the uniform and pitting corrosion (Subsection 3.1.1) covering the entire thicknesses of the treated and untreated corrosion layers. The preparation of the samples included grinding the material to a fine powder and fixing it between Kapton® tape.

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The XPS measurements were recorded with a Perkin-Elmer Phi ESCA 5500 system equipped with a monochromated 450 W Al K source. Experiments were recorded with 220 W source power and an angular acceptance of 7° . The analyser axis was inclined at an angle of 45° with the specimen surface (see Section 2.3). Wide scan spectra were measured over a binding energy range of 0-1400 eV and a pass energy of 187.85 eV. The C 1s, O 1s and Pb 4f core levels were recorded with a step of 0.05 eV and a pass energy of 11.75 eV. The C 1s core level taken at 285 eV for adventitious carbon is used as binding energy reference. The sample volume and depth under these conditions is respectively in the range of nm^2 and nm .

NT experiments were performed using thermal neutrons at the thermal beam line 32 of the spallation neutron source SINQ, known as the NEUTRA facility [4]. The neutrons have a polychromatic Maxwellian energy spectrum with the most probable energy at about 25 meV. The neutron flux at the sample position was $9.410^6 \text{ n cm}^{-2}\text{s}^{-1}$. The collimation ratio L/D (see Subsection 2.6.2 and Figure 2.3) describing beam divergence was 350, inducing a geometrical unsharpness of about 0.15 mm. Radiographies were recorded with a Peltier cooled (-45°C) slow scan CCD featuring a 1024×1024 pixel chip (camera type DV 434, Andor Technology). The neutron flux was converted into light with a Li-6 doped ZnS screen having a thickness of 46 μm for run 1 (prior to reduction) and 300 μm for run 2 (after reduction). The field of view captured by the 50 mm Pentax F 1.2 normal lens was $97 \times 97 \text{ mm}$, representing a nominal pixel size of $95 \times 95 \mu\text{m}^2$. Exposure time was 30 s (run 1) and 8 s (run 2). A total of 240 projections were taken whilst rotating the object through 180 degrees. The projections were reconstructed to 3D-images by the program OCTOPUS [5] and compared to each other using the software VGStudio Max 1 [6]. This software package enables the analysis, processing and visualization of volumetric data.

SEM analyses were performed on a Quanta 200F (FEI) at 12.5 kV acceleration voltage.

4.2 Results and discussion

4.2.1 Characterization of potential chemical changes

The SR-XRD data of the pitting and uniform corrosion products show that they are similar in chemical composition. A typical spectrum is shown in Figure 4.2a which shows the characteristic peaks of lead (Pb), hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) and plumbonacrite ($6PbCO_3 \cdot 3Pb(OH)_2 \cdot PbO$). After reduction, all spectra only have the characteristic peaks of metallic lead (Figure 4.2b).

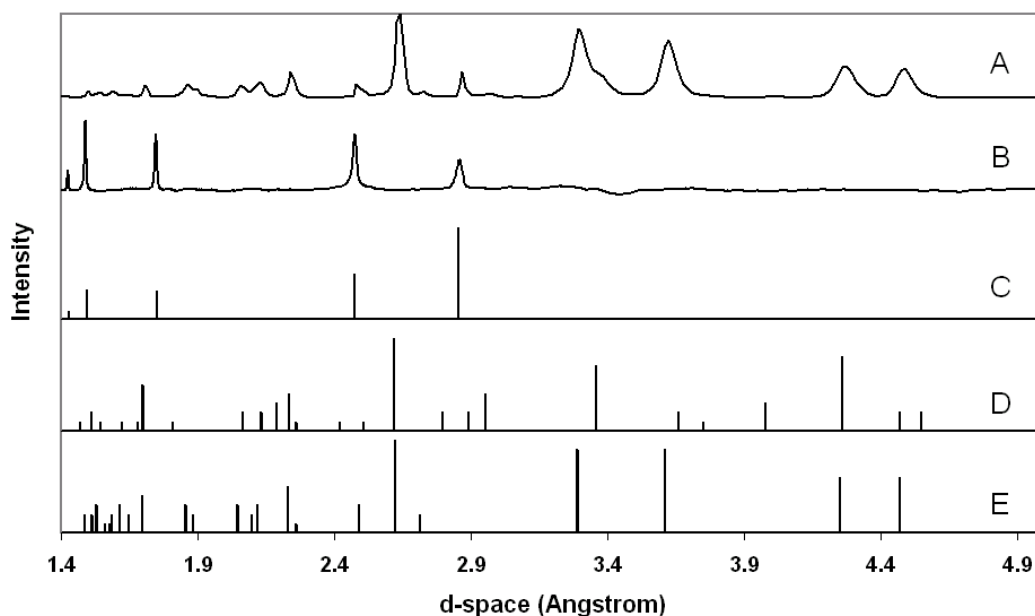


Figure 4.2: SR-XRD patterns of corrosion product (a), reduced pitting corrosion area (b), reference spectrum of lead (c), plumbonacrite (d) and hydrocerussite (e). Reference spectra were from the American Society for Testing Materials database (2003)

XPS results did not reveal any significant changes for the Pb 4f peak before and after reduction. The spectra obtained (not shown) can be fitted using two Gaussian peaks indicating the contribution of two different chemical states of lead. The contribution at

low binding energy can be attributed to metallic lead ($136.6(\pm 0.15)$ eV) [7] while the contribution at higher energy ($137.9(\pm 0.15)$ eV) corresponds to an oxidized form of lead [8]. Also the C 1s spectrum (not shown) does not change significantly before and after reduction. The deconvolution of the O 1s spectra yields 3 peaks. However, one can clearly notice a difference before and after reduction (Figure 4.3). Indeed, the spectra after reduction show a larger contribution at high binding energy and a lower contribution at low binding energy. The high energy contribution cannot be attributed to $PbCO_3$, as no changes were noticed in the C 1s. Moreover $PbSO_4$ or $Pb(NO_3)_2$ can be ruled out since both compounds have a high binding energy for Pb 4f_{7/2} [9, 10]. Therefore we attribute the high energy contribution to $Pb(OH)_2$, which corresponds to the value reported by Nowak et al. [10]. The binding energy for the low binding energy contribution ($529.2(\pm 0.10)$ eV) indicates the presence of a lead oxide (e.g. PbO , PbO_2 , Pb_3O_4), while the contribution at 531.1 eV probably originates from a lead carbonate [11].

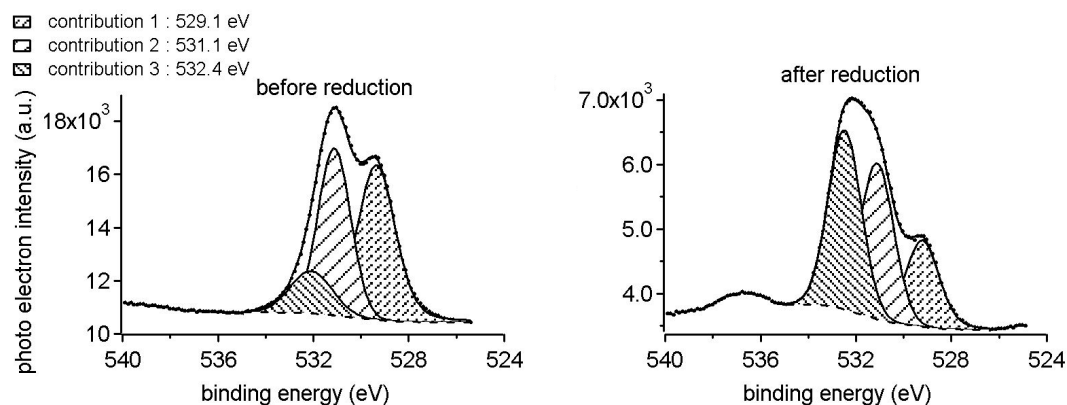


Figure 4.3: XPS spectra of O1s before and after reduction. The dashed areas are the fitting results for the overall spectra. The individual contributions at 529.1 eV, 531.1 eV and 532.4 eV are respectively from a lead oxide, a lead carbonate and lead hydroxide.

4.2.2 Characterization of potential morphological changes

Potential morphological changes were examined using neutron tomography and scanning electron microscopy. Neutron transmission, in general, is strongly dependent on the element. In this case, contrary to X-rays where heavier elements cause stronger attenuation, there is no simple relationship between attenuation and the atom number. Hydrogen in particular is a strong neutron scatterer. Lead metal, on the other hand, shows weak absorption and is almost transparent to neutrons. For this particular sample, the hydrogen present in the secondary minerals from the corrosion crust such as hydrocerussite and plumbonacrite will be detected. It should be noticed, after the reduction treatment, not only the core but also the corrosion crust mainly consists of lead metal, which implies that the visualization is more difficult. X-ray tomography cannot be used since the thickness of the bare metal on its thinnest side is 2 mm, causing X-rays to be totally absorbed.

The reconstructed neutron tomography images of the surface shell before and after reduction are compared to each other in Figure 4.4 (a). It is clear that the overall bent structure of the sample is similar. The fine structure seems to be well preserved, as can be seen for example from the various deformations on the surface finish which match very well. Figure 4.4 (b) displays the cross sections of the same samples. The red coloured area seen in the sample before reduction represents a higher attenuation coefficient, indicating the presence of corrosion products. The sample after the reduction treatment lacks these corrosion products, resulting in the same coloration as the rest of the sample. In Figure 4.1, it is clear that the entire sample was covered with white corrosion products, and this is not seen in the tomography images before treatment in Figure 4.4. This can be explained considering the high attenuation at the surface, which is blurred across the air-sample interface (because of the small beam divergence) so that it appears to be artificially low. The voxel size of the reconstruction is $95\text{ }\mu\text{m}^3$, meaning that the geometrical blurring occurs across 2 voxels. Other blurring effects (e.g. motion/parallax unsharpness) probably increase this number of voxels. These surface voxels are rendered in VGStudio Max and grouped with a low absorption colour, creating a sharp absorption edge on the surface. It was also possible

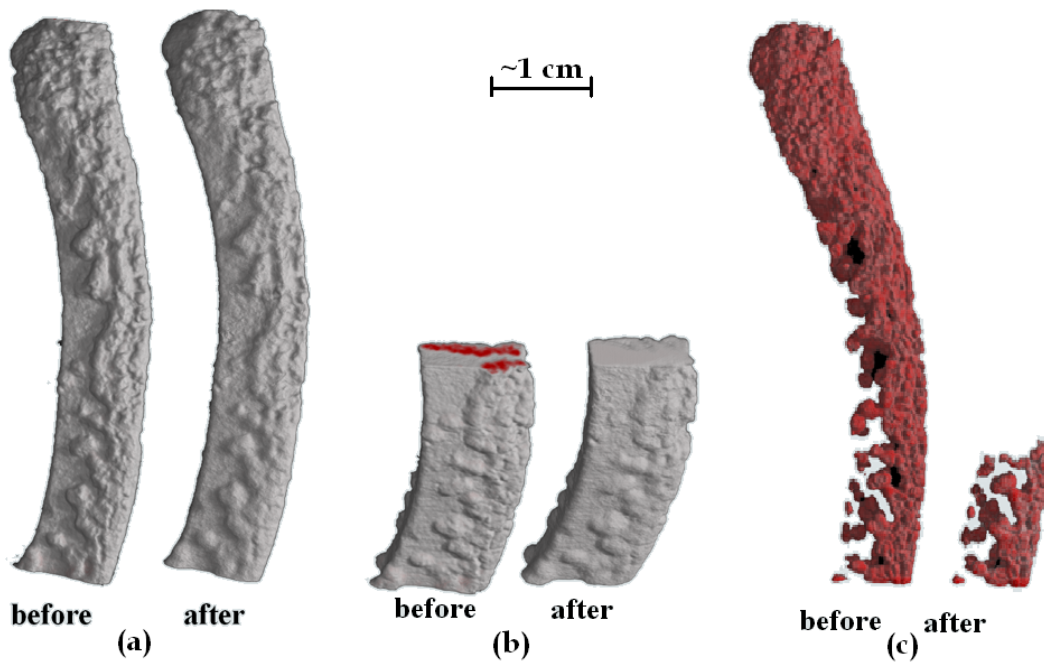


Figure 4.4: (a) reconstructed tomography images, (b) reconstructed images showing the cross section. The red areas indicate the presence of corrosion products and (c) the visualization of the corrosion products.

to visualise the corrosion products alone as shown in Figure 4.4 (c).

Scanning electron microscopy images were taken on the two kinds of corrosion before and after reduction. The comparison between pitting corrosion is shown in Figure 4.5 (top) on exactly the same position of the sample. The original structure has been deformed and has lost a lot of surface detail. Above, the structure seems to be flattened. The scale of the image is $200\text{ }\mu\text{m}$, implying that these deformations could be seen by the naked eye. The images on the uniform corrosion layer are presented in Figure 4.5 (bottom). The granular structure before has been transformed into a surface covered with diffuse lamellar aggregates.

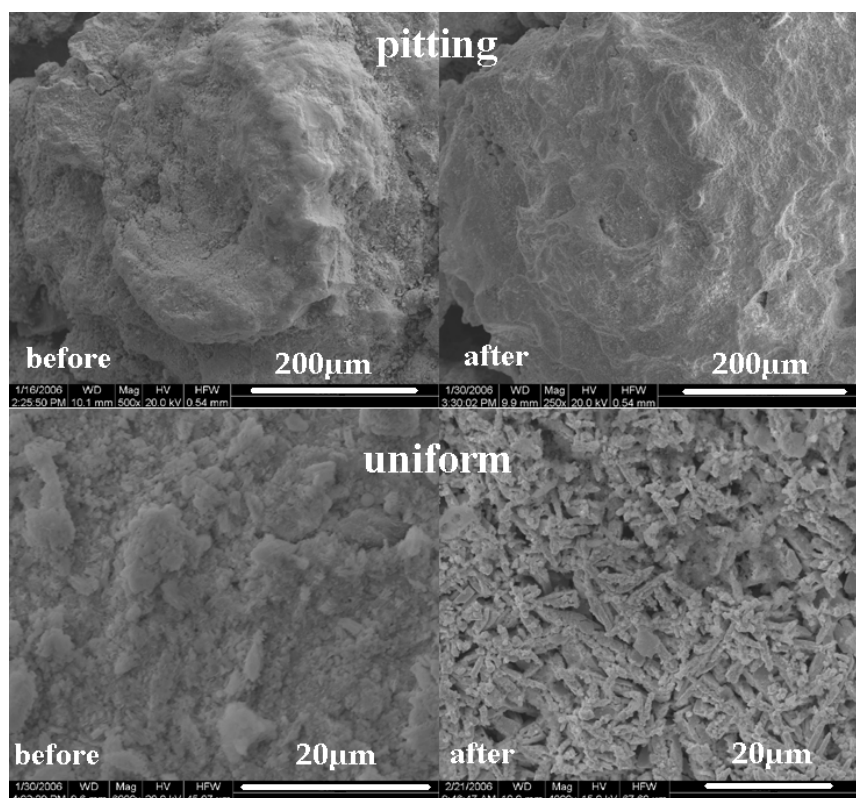


Figure 4.5: Scanning electron images before and after reduction of the pitting corrosion (top) and the uniform corrosion (bottom).

4.3 Conclusions

SR-XRD data prove that the electrolytic reduction treatment converts corrosion products originally present on the artefact into metallic lead. It should be noted that the samples represented the entire thickness of the corrosion layers (uniform and pitting corrosion). The conversion to metallic lead results in a surface colour, changing from white to a dark grey.

The XPS measurements, on the other hand, reveal that after the reduction procedure, the surface re-oxidizes, forming $Pb(OH)_2$. The results of the SR-XRD and the XPS data are apparently in disagreement. However, both data were acquired with different sampling depth/volumetric ranges. The SR-XRD samples were taken from the entire corrosion

crust ($>200\text{ }\mu\text{m}$), whereas the XPS measures the top layer ($\sim\text{nm}$). Moreover, the XPS measurements, in comparison to these of SR-XRD, have been performed in vacuum, which might affect the surface characteristics.

Neutron tomography is shown to be a powerful technique for the study of morphological changes of actively corroded lead artefacts. This is due to the very different attenuation coefficients of lead and its corrosion products. The technique is a suitable non-destructive technique for the visualization of the corrosion state of an object. It should be noticed that the entire sample, visualized in the 3D maps, have a resolution of $\sim 1\text{ mm}$.

Results show that the fine structure of the object remains well conserved. The resulting changes on a microscopic level are seen by a decrease in volume of the pitting corrosion structures. The uniform corrosion structures obtain a more porous and lamellar surface appearance.

The results of this study imply that electrolytic reduction is a reliable technique for the stabilization and conservation of actively corroded lead artefacts. The corrosion products actually are converted into metallic lead, while the morphological changes due to the treatment are limited.

4.4 References

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Chapter 5

Electrolytic reduction of artificially corroded lead and lead alloys *

Lead objects are often alloyed with other elements such as tin, antimony and bismuth [1]. The presence of alloying elements can affect the reduction treatment of corroded lead alloys [2]. In this work, a systematic study was performed to evaluate the reduction treatment on common corroded lead alloys.

In this part of the study, we worked with artificially corroded samples. A preliminary study on pure lead (99.95%) was performed to determine favourable conditions to promote corrosion attack within several weeks. The corrosive environment/vapour phase was created by an equilibration of a liquid phase containing one organic compound. The organics, which are commonly observed in display cabinets, include formic acid, acetic acid, propionic acid and acetaldehyde [3]. Lead samples were then exposed to the artificially created corrosive vapour phase. The corrosion rate was followed by determining the mass gain of the samples as a function of time.

*This work has been presented in part at Metal 2004, 4-8 october 2004 (Canberra, Australia), at the COST G8 working group meeting on degradation processes, corrosion and weathering, 13-14 february 2004 (Bronnbach, Germany) and at Art '05, 15-19 may 2005 (Lecce, Italy).

Chapter 5

The corrosion layer, if present, was characterized using X-ray diffraction. Finally, the electrolytic reduction of these samples was evaluated.

Lead alloys, including lead-tin, lead-antimony and lead-bismuth were then corroded under similar conditions. Also here, X-ray diffraction was applied to study the corrosion layer, followed by the evaluation of the electrolytic reduction on the corroded alloys.

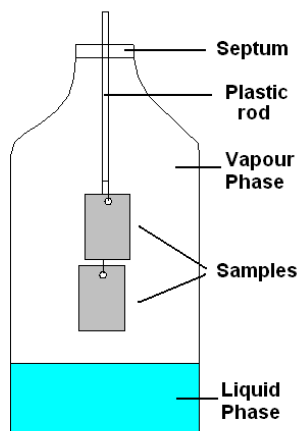
5.1 Experimental

5.1.1 Materials and sample preparation

The test samples were cut from a larger sheet of lead, resulting in individual pieces having dimensions of $2 \times 20 \times 10$ mm (Goodfellow Inc., UK, purity 99.95 %). A hole was drilled in the middle at one end of the sample so that it could be suspended using a nylon thread. The plates were polished using 1200 grit SiC paper, rinsed with ethanol and smoothed using a soft tissue.

The binary alloys were prepared at the 'Kunstacademie' in Antwerp (Belgium). Lead, tin, antimony and bismuth were purchased at Goodfellow and had a purity of 99.95%. The preparation procedure for the binary alloys involved weighing the individual constituents (95% lead/5% minor constituent) and melting in an oven until a homogeneous melt was reached. Before casting into ingots of $10 \times 10 \times 50$ mm, the melt was intensively stirred with a steel rod. After casting, the melt was allowed to solidify without active cooling. Samples with a dimension of $2 \times 20 \times 10$ mm were cut with a fret-saw out of those ingots and prepared the same way as the lead samples.

5.1.2 Creation of the corrosive environment



The samples were placed in vapour phases, controlled by an equilibrium with an aqueous solution (inset). The environments were created in a sealed bottle (with septum) of 0.2 L volume, containing 20 mL of an aggressive solution. Through the septum, a small plastic rod was positioned to which the samples were fixed with nylon thread (see setup). Each solution contained one organic over a concentration range of 30 to 0.3 mmol L⁻¹. The liquid concentrations were based on a study, which made use of acetic acid environments, created by an equilibrium with an aqueous solution

[4]. The highest concentration of acetic acid in the liquid phase should create vapour phases that contain acetic acid in the order of 1 mg m⁻³. On this basis, similar liquid concentrations were used for the other organics. The different organics were formic acid ($CHOOH$, 95%), acetic acid (CH_3COOH , 99%), propionic acid (CH_3CH_2COOH , 99.5%) and acetaldehyde (CH_3CHO , 95%). All organics were purchased from Sigma Aldrich (Belgium). In total, twelve stock solutions were prepared as shown in Table 5.1. The highest concentration level is referred to as the solutions A. These solutions were diluted 10 times and 100 times and are referred to as respectively solutions B and C. Higher concentrations in the liquid phase give rise to higher concentrations in the vapour phase [3, 5]. The determination of the effective vapour concentrations, however, was not the subject of this study.

Table 5.1: Concentrations of the organics in the stock solutions (mmol.L⁻¹).

	$CHOOH$	CH_3COOH	CH_3CH_2COOH	CH_3CHO
Solutions A	27.8	28.2	28.1	32.7
Solutions B	2.78	2.82	2.81	3.27
Solutions C	0.278	0.0282	0.281	0.327

5.1.3 Mass gain analyses

The samples under study were characterized by mass measurements as discussed in Section 2.5 (Mettler AE240, precision of 0.1 mg), performed at the beginning and after exposure of 2, 4, 7 and 9 weeks to the vapour phases. Prior to the measurements, the samples were dried by blowing cold air.

After a total of nine weeks, the samples were cut into two pieces (each $2 \times 10 \times 10$ mm). One part was used for the qualitative analysis of the corroded surface using SR-XRD and later on for the study of the reduction process.

5.1.4 XRD analyses

SR-XRD data were collected at beam line 9.6 of the Synchrotron Radiation Source (SRS) at Daresbury (UK) [6]. The corrosion products were scraped off one side of the sample and ground in a mortar. Scotch tape was used since it does not give rise to interfering diffraction patterns compared to other tapes. The tape was glued to a metal washer and powder was put into the well thus generated. Another piece of tape was fixed on the other side of the washer to prevent spreading of lead dust. It is important to mount only a small amount of powder on the tape to obtain clear X-ray diffraction patterns for two reasons: (1) strongly absorbs X-rays, resulting in diffraction rings of weak intensity and (2) results in a lot of backscattering towards the surrounding equipment, which in turn backscatters radiation towards the detector, thereby increasing the background signal. The sample was mounted on a goniometer head for proper sample position. An intense monochromatic beam with photons of relatively high energy was used (14.25 keV, $\lambda = 0.87\text{\AA}$). The XRD patterns were collected using a Quantum-4 CCD detector. An optical microscope was used to position the beam on the samples. The analysis of the data was performed with the ESRF software FIT2D [7].

5.1.5 Electrolytic reduction

The samples were connected to a conductive wire, and the connection was insulated with a varnish (Epoxy jaune, Du Pont, Belgium). The samples were reduced in a 0.1 M Na_2SO_4 solution at a potential of -1.3 V according to the procedure elaborated in Chapter 2. The reference electrode used was a $Hg/HgSO_4$ -electrode (XR210, Radiometer Analytical), which has a potential of 0.658 V versus the standard hydrogen electrode ($T = 295$ K). The counter electrode consisted of two platinum cylinders of diameters 10 mm and 35 mm respectively. The smallest cylinder was placed concentrically inside the largest one. In order to treat more samples simultaneously, four samples (working electrodes) were reduced at the same time by connecting them together. The samples and the reference electrode were positioned between the two counter electrodes. The reduction was stopped when the current reached a stable value, which was reached after four days. The samples were immediately dried with blowing air to avoid any re-corrosion.

5.2 Results: Corrosion tests on lead

5.2.1 Mass gain measurements

Figure 5.1a-d shows the relative mass gain as a function of different concentrations for formic acid, acetic acid, propionic acid and acetaldehyde respectively. The results show that higher concentrations of the organic in the solution result in a faster attack of the metal. This clearly demonstrates that higher concentrations in the liquid phase result in higher concentrations in the vapour phase. When corroded with formic acid and formaldehyde, the corrosion develops strongly between two and four weeks (Figure 5.1a and d). In the cases of acetic and propionic acid, the mass gain is considerable after two weeks (Figure 5.1b and c). The corrosion development even increases after 4 weeks. The mass gain of the lead substrates exposed to the highest concentrations (solutions A) still increases after 7 weeks. The corrosion development almost stabilizes on the substrates after seven weeks

of exposure to solutions B and C tend. The only exception are the plates exposed to propionic acid, which corrosion development appears to be decreasing. This is probably due to condensed droplets which fell off, thereby removing part of the corrosion products (Figure 5.1c).

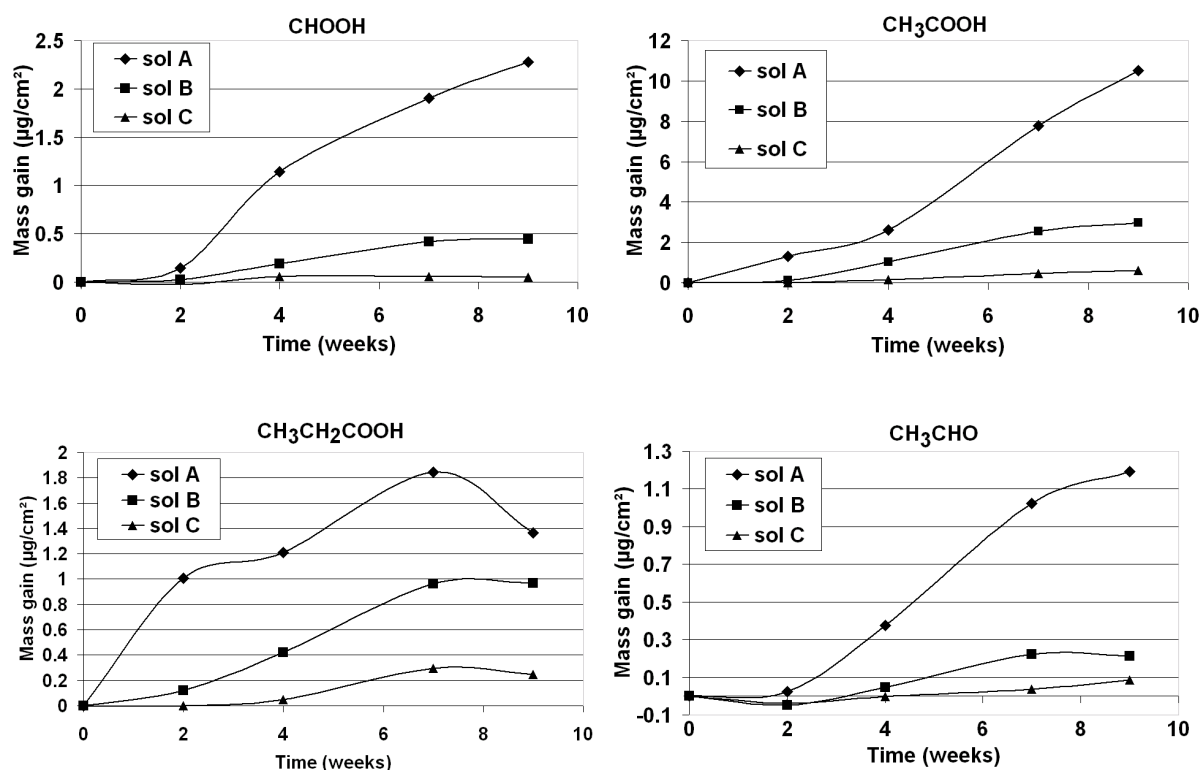


Figure 5.1: Relative mass gain versus time for different concentrations of the organics. Solutions A, B and C respectively represent concentrations in the liquid phase of $\sim 30 \text{ mmol L}^{-1}$, $\sim 3 \text{ mmol L}^{-1}$ and $\sim 0.3 \text{ mmol L}^{-1}$ as defined in Table 5.1.

5.2.2 SR-XRD measurements

Table 5.2 shows the corrosion products which have been identified on the lead samples after nine weeks of corrosion. At the lowest concentration level (solutions C), all substrates are covered with hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and plumbonacrite ($6\text{PbCO}_3 \cdot 3\text{Pb}(\text{OH})_2 \cdot \text{PbO}$).

This is most probably due to the dominating effect of the humidity, and to a minor influence of the present organic. Litharge ($\alpha - PbO$) was observed in all cases except when corroded with formic acid. This was also observed by Niklasson et al. [8]. Lead formate ($Pb(CHOO)_2$) or lead formate hydroxide ($Pb(CHOO)(OH)$) are generally observed corrosion products when the organic is formic acid. Litharge and plumbonacrite are observed when lead is corroded with acetic acid. Lead acetate oxide hydrate ($Pb(CH_3COO)_2 \cdot 2PbO \cdot H_2O$) is only observed at the highest concentration of acetic acid. The combination of litharge, hydrocerussite and plumbonacrite is observed when corroded with propionic acid and acetaldehyde. It should be noted that plumbonacrite is observed on almost all the samples. This means that this product is easily formed in any of the conditions studied.

Table 5.2: Corrosion products observed on the corroded lead for different concentrations of the organics in the liquid phase as defined in Table 5.1.

	<i>CHOOH</i>	<i>CH₃COOH</i>	<i>CH₃CH₂COOH</i>	<i>CH₃CHO</i>
Solutions A	Lead formate	Litharge	Litharge	Litharge
	Lead formate hydroxide	Lead acetate oxide hydrate	Hydrocerussite	Hydrocerussite
		Plumbonacrite	Plumbonacrite	Plumbonacrite
Solutions B	Lead formate hydroxide	Litharge	Litharge	Litharge
	Plumbonacrite	Plumbonacrite	Plumbonacrite	Hydrocerussite
			Hydrocerussite	Plumbonacrite
Solutions C	Hydrocerussite	Hydrocerussite	Litharge	Litharge
	Plumbonacrite	Plumbonacrite	Plumbonacrite	Hydrocerussite
		Litharge	Hydrocerussite	Plumbonacrite

5.2.3 Reduction treatment of the corroded lead samples

After nine weeks of exposure, under the conditions mentioned in Table 5.1, all samples were electrolytically reduced. Photographic images taken before and after the reduction are shown in Figures 5.2a and b (three first rows). They show that most of the corrosion products are reduced, as the colour of the surface has completely turned to dark grey.

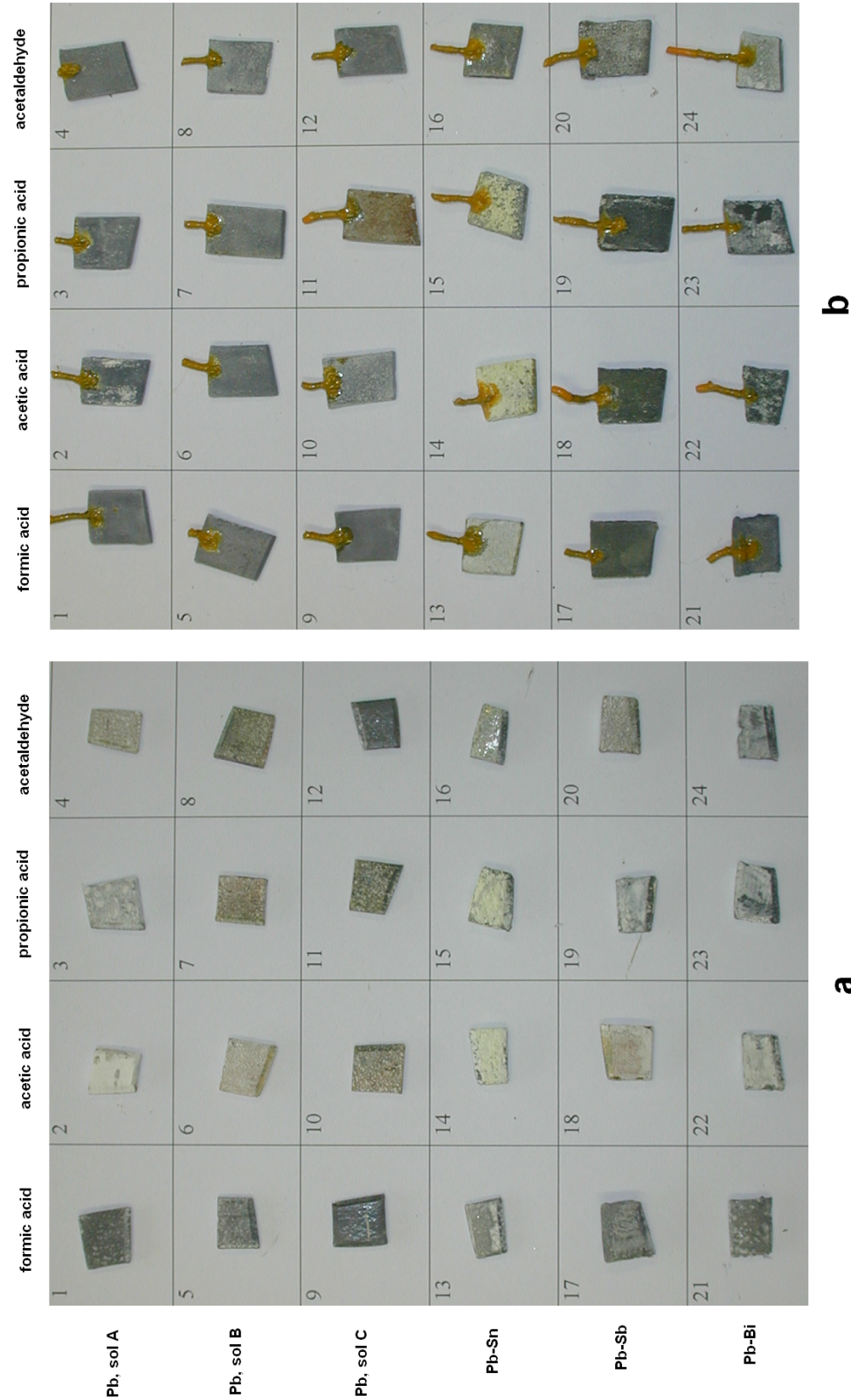


Figure 5.2: Surface appearance before (a) and after (b) reduction treatment. The first three rows contain the pure lead samples, corroded with the three solutions. The last three rows are the lead alloys corroded with solution A.

Only the sample which was corroded with acetic acid at the highest concentration (28.2 mM) and the one corroded with the 0.0281 mM solution of propionic acid show remaining corrosion products. This is somewhat unexpected: the other substrates corroded with acetic and propionic acid are covered with the same corrosion products and showed a successful reduction. There is, consequently, a strong argument that the reduction time was either too short or that the corrosion products were not 'electrochemically' attached to the surface.

From the results of this section, one can conclude that:

1. The higher the concentration of the organic, the more the samples were attacked by corrosion
2. The highest concentration of organic resulted in typical corrosion products of that specific organic
3. The electrolytic reduction applied under the mentioned conditions converts the corrosion products very well

5.3 Results: corrosion tests on lead alloys: Pb-Sn, Pb-Bi and Pb-Sb

Following the preliminary investigation on pure lead, it was decided to use the highest concentration to attack the alloyed samples. After exposure, the samples were characterized by XRD and optical microscopy. This was followed by the evaluation of the electrolytic reduction treatment on those corroded alloys.

5.3.1 SR-XRD measurements

Table 5.3 summarizes the corrosion products observed on the different alloys. It must be noted here that only lead corrosion products were observed, implying that corrosion products of the minor constituents were not present or were too low in concentration to

detect. Results show that lead formate is generally observed when samples are corroded with formic acid. Lead formate hydroxide is also formed on all substrates except for the the $Pb - Sn$ alloy. In the case of the $Pb - Sb$ alloy, hydrocerussite is observed as well. Lead acetate oxide hydrate and plumbonacrite are observed in almost all cases when the organic is acetic acid. The $Pb - Sn$ alloy has only one corrosion product, namely hydrocerussite. The combination of litharge, hydrocerussite and plumbonacrite is commonly observed when corroded with the organics propionic acid and acetaldehyde. Plumbonacrite was not observed on the $Pb - Sb$ alloy, which was only covered with hydrocerussite.

Table 5.3: Corrosion products observed on the corroded lead and lead alloys for the different organics

	$CHOOH$	CH_3COOH	CH_3CH_2COOH	CH_3CHO
Pb	Lead formate	Litharge	Litharge	Litharge
	Lead formate hydroxide	Lead acetate oxide hydrate	Hydrocerussite	Hydrocerussite
		Plumbonacrite	Plumbonacrite	Plumbonacrite
Pb/Sn	Lead formate	Hydrocerussite	Litharge	Plumbonacrite
			Plumbonacrite	Hydrocerussite
			Hydrocerussite	
Pb/Bi	Lead formate	Hydrocerussite	Litharge	Litharge
	Lead formate hydroxide	Plumbonacrite	Plumbonacrite	Hydrocerussite
		Lead acetate oxide hydrate	Hydrocerussite	Plumbonacrite
Pb/Sb	Lead formate	Hydrocerussite	Hydrocerussite	Litharge
	Lead formate hydroxide	Plumbonacrite		Hydrocerussite
	Hydrocerussite	Lead acetate oxide hydrate		Plumbonacrite

5.3.2 Reduction of the corroded samples

Photographic images before and after reduction are shown in Figures 5.2a and b (last three rows). For the $Pb - Sn$ alloy, a thick and good attached corrosion layer covered the surface when corroded with the three organic acids, and some little patches when corroded with acetaldehyde. After reduction, the surface appeared still to be covered by a layer

of corrosion products, implying a dysfunctional reduction treatment. For the $Pb - Sb$ alloy corroded with the three organic acids, the corrosion products were converted and the surface finish after treatment was dark grey. In the case of acetaldehyde, some patches of white corrosion products were still observed after the reduction treatment. For the $Pb - Bi$ alloys, the reduction treatment seems not to work, as the surface after treatment was still covered with white corrosion products in all cases. The dark grey surface of the right part on sample 23 is a result of the corrosion products which were very poorly attached to the surface, essentially forming a separate layer, which has partially fallen off.

5.4 Discussion

All substrates studied (Pb , $Pb - Sn$, $Pb - Bi$ and $Pb - Sb$) were apparently corroded uniformly under the studied conditions. No corrosion products of the alloying elements, however, were detected by with X-ray diffraction. This is somewhat unexpected. In the specific case of a $Pb - Sn$ alloys (80/20 m%), Degriigny [2] reported complex corrosion layers, consisting of both lead and tin corrosion products. For $Pb - Sn$ alloys, the corrosion layers are less complex with decreasing tin content [9].

The reduction treatment, as applied to corroded pure lead objects, shows that the reduction of uniform corrosion starts at the interface between the metal and the corrosion layer (Chapter 3). For the $Pb - Bi$ and the $Pb - Sn$ alloy, the reduction treatment seems not to work. Since the alloys are conducting, electrons certainly can reach the interface of the metal/corrosion layer.

Three hypotheses could explain why the treatment does not work: (1) the electron transfer between the metal and the corrosion layer is inhibited, (2) if corrosion products were reduced only at the interface, the reduced structure (at the interface) inhibited the electron transfer or (3) the corrosion layer is so dense that water absorption (and electrolytic conduction) is not possible. In any case, the occurrence of the alloying elements certainly has its impact on the treatment.

5.5 Conclusions

The corrosive action of different concentrations of formic acid, acetic acid, propionic acid and acetaldehyde was studied on pure lead samples (99.95 m%). Mass measurements as a function of time showed that the highest concentration of the organic resulted in the highest values for mass gain. The same experiments were performed on the binary alloys $Pb - Sn$, $Pb - Bi$ and $Pb - Sb$ (95 m% Pb).

X-ray diffraction data showed that the corrosion products were dependent on the organic, especially at the higher concentrations, but did not differ much at lower concentrations. It should be noted that corrosion products of the alloying elements Sn , Bi and Sb were not observed.

The reduction treatment (0.1 M Na_2SO_4 , -1.3 V) gave good results for corroded lead and the $Pb - Sb$ alloy, in that sense that the surface finish obtains a dark grey appearance. For the $Pb - Sn$ and the $Pb - Bi$ alloys, the presence of the binary constituent inhibits the reduction process and the corrosion products are not converted. For these reasons, the composition of the alloy is very important, and has to be known before an artefact is treated by electrolytic reduction.

5.6 References

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Part III

Lead soaps

Chapter 6

Lead carboxylate coatings: General introduction

6.1 Lead carboxylates

The second part of this work deals with the application of a lead carboxylate coating by immersing lead samples in a solution of corresponding sodium salts, thereby aiming at the protection of this type of sample. The idea of using this kind of coating comes from earlier studies by Rocca et al. [1, 2].

In their first article [1], Rocca et al. studied the ability of linear sodium monocarboxylates with a general formula $CH_3(CH_2)_{n-2}COONa$ ($n = 7 - 11$, briefly NaC_n) to inhibit the aqueous corrosion of lead. The aqueous environment was simulated by a ASTM solution (ASTM D1384-87), containing $148 \text{ mg L}^{-1} Na_2SO_4$, $138 \text{ mg L}^{-1} NaHCO_3$ and $165 \text{ mg L}^{-1} NaCl$. Linear sodium carboxylates were added, in different concentrations, to the ASTM solution by neutralization of the corresponding carboxylic acid with sodium hydroxide to pH 8.

In Figure 6.1, the effect of immersion time on the polarization resistance (R_p) for several sodium carboxylates ($n = 7-11$) is presented. The plot clearly shows that inhibition ef-

iciencies of these compounds increase with the length of the carbon chains. Additional Tafel experiments confirmed the same trend [1].

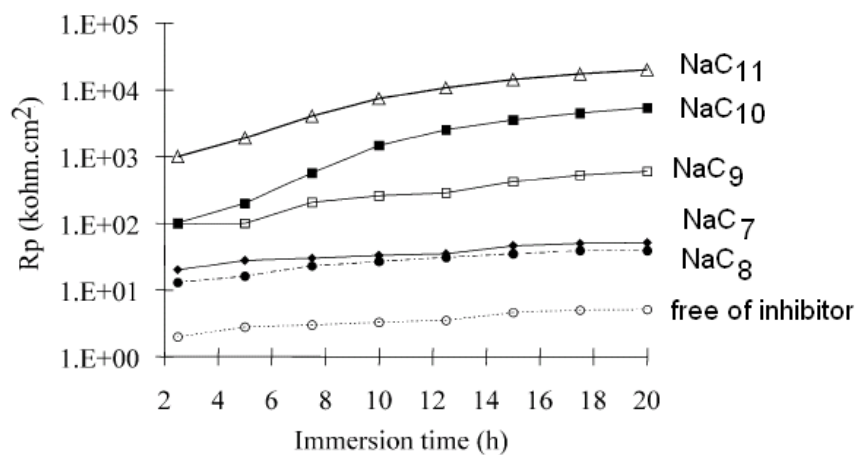


Figure 6.1: Effect of immersion time and carbon chain length of NaC_n ($n=7-11$) in a ASTM solution containing 0.01 M NaC_n on the polarization resistance (from [1]).

Figure 6.2 shows scanning electron micrographs of lead sheet surfaces after a treatment of 24 hours by using (a) an ASTM solution containing 0.01 M NaC_7 or (b) an ASTM solution containing 0.01 M NaC_{11} .

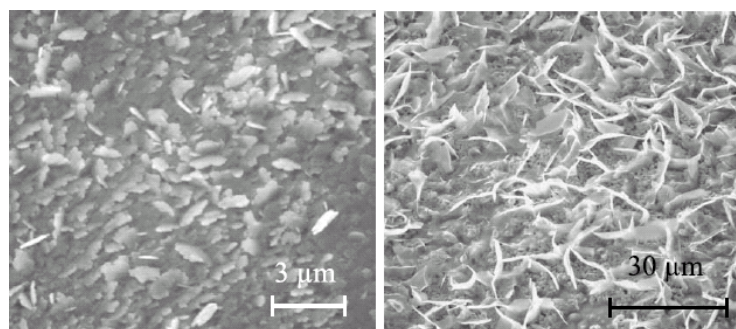


Figure 6.2: Scanning electron micrographs of lead sheets immersed for 24 hours in (a) a ASTM solution containing 0.01 M NaC_7 and (b) a ASTM solution containing 0.01 M NaC_{11} (from [1]).

Both surfaces are covered with a layer of more or less tangled crystals which are flake shaped. The lead heptanoate layer seems to have a lower crystal density, in comparison with the lead undecanoate layer. It is clear that both surface layers, shown in Fig.1.2, have a high specific surface area [1].

The crystallographic structure of the lead soap $Pb(C_7)_2$, identified by Lacouture et al. [3], is presented in Figure 6.3. It is characterized by a lamellar structure of units containing a central metallic plane from which the aliphatic chains project perpendicularly. The lead atoms are located on a zigzag chain in these plains, coordinated to six oxygen anions in a very distorted polyhedron. Rocca et al. claimed that other lead carboxylates (other n) should have similar structures [1].

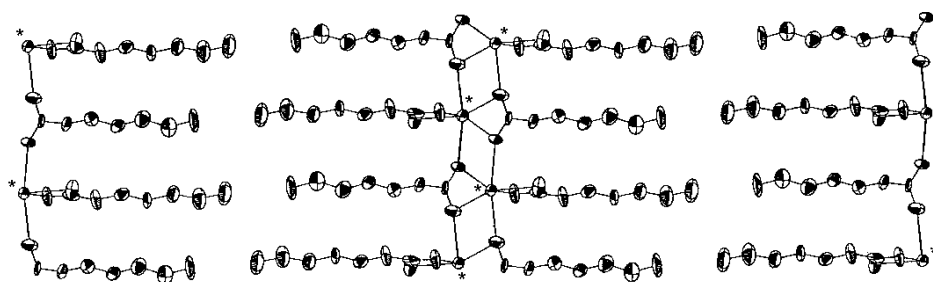


Figure 6.3: Projection along the crystal plane [100] of the structure of $Pb(C_7)_2$. The lead atoms are marked with * (from [3]).

The deposition of a lead carboxylate ($n=10$) was confirmed by the XRD pattern of a coated surface, exhibiting the same characteristic diffraction peaks as a synthesised powder (Figure 6.4) [2].

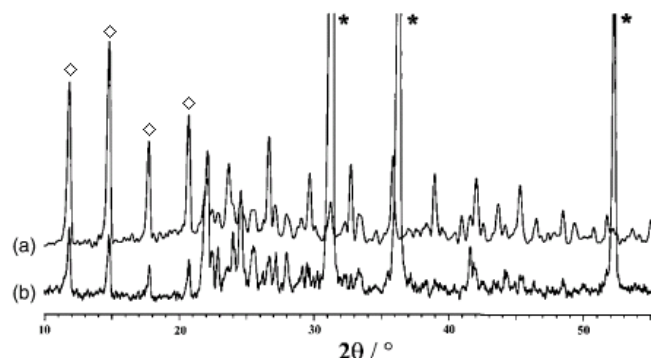


Figure 6.4: XRD patterns of (a) $Pb(C_{10})_2$ powder, and (b) a coating formed on lead after a 24h treatment 0.05 M NaC_{10} (* peaks of lead substrate; ◇: main characteristic peaks of the layered structure of $Pb(C_{10})_2$) (from [2]).

Additional information was obtained by measuring the contact angle of a droplet of water on a surface treated for 24 hours in ASTM containing 0.01 M NaC_{10} [1]. The inhibited surface was remarkably hydrophobic properties; the contact angle of a 50 μ L water drop was about 120°, whereas a similar drop on a corroded sample has a contact angle of about 20°. The authors mention that this clearly demonstrates the presence of metallic soaps in the passive layer, and these are responsible for the hydrophobic character of the surface.

6.2 Lead decanoate

The second article by Rocca et al. [2] focused on the inhibition efficiency of sodium decanoate (NaC_{10}). Lead decanoate was chosen as opposed to other soaps because it represents a good compromise between the cost, a long carbon chain and a good solubility in water [2]. The inhibitive properties were tested as a function of the NaC_{10} concentration in aqueous solutions (ASTM D1384-87). Again, the solutions were prepared by neutralizing the corresponding acid to pH 8. The polarization resistance was studied as a function of time for several concentrations ranging from 0 to 0.05 M (which is almost at maximum solubility of this compound). The results are presented in Figure 6.5.

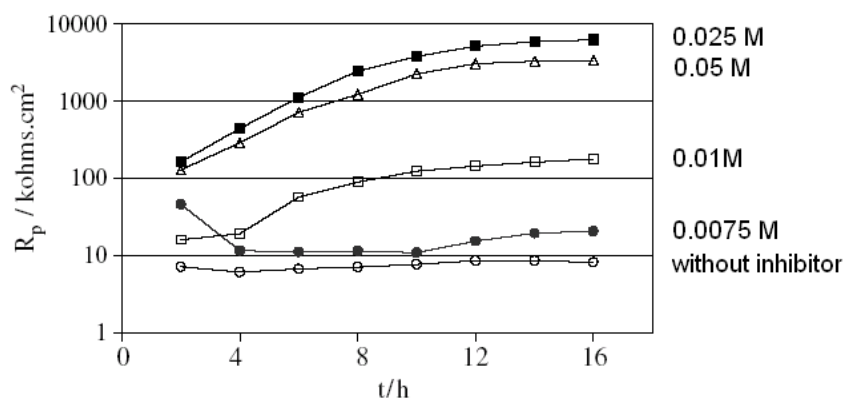


Figure 6.5: Effect of immersion time and NaC_{10} concentration in the ASTM solution on the polarization resistance of lead (from [2]).

For concentrations higher than 0.01 M, the R_p values increase drastically about 2-3 orders of magnitude after 16 hours of application. Additional Tafel experiments, performed on surfaces after 24 hours of immersion in ASTM and inhibitor, showed that almost no breakdown potential shows up when exceeding critical concentrations of 0.01 M (Figure 6.6) [2].

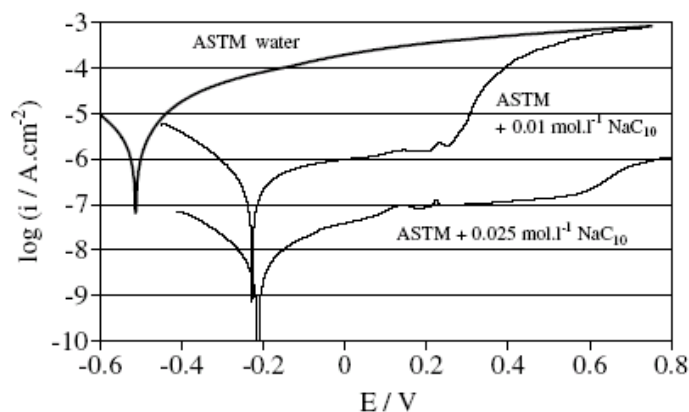


Figure 6.6: Potentiodynamic curves of lead in ASTM solution containing 0.01 M or 0.025 M of NaC_{10} after 24 hours of immersion (from [2]).

Additional information about the pitting sensitivity was obtained by recording Tafel plots

after 24 hours of treatment in corrosive solutions containing respectively 0.01 and 0.05 mol L⁻¹ $CH_3COOH + CH_3COONa$ at pH 7 (Figure 6.7).

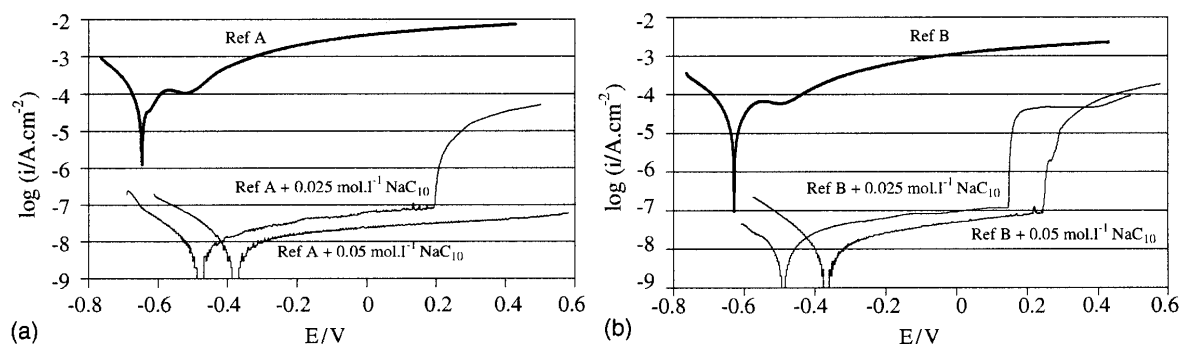


Figure 6.7: Potentiodynamic curves of lead in corrosive solution containing 0.01 (A) and 0.05 M (B) concentrations ($CH_3COOH + CH_3COONa$) at pH 7 after 24 hours of immersion (from [2]).

One can note that the addition of 0.025 M of NaC_{10} is sufficient to decrease drastically the corrosion current density of lead from 0.1 mA cm⁻² down to 10 μA cm⁻². Nevertheless, this concentration is too low to limit the pitting corrosion as shown by the presence of breakdown at 0.2 V. In case of applying 0.05 M NaC_{10} , the breakdown potential disappears in reference water A, whereas it slightly increases in more corrosive reference water B.

In the same article, the authors mention the application of a $Pb(C_{10})_2$ coating on a number of lead artifacts, obtained by immersion in ASTM solution containing 0.05 M NaC_{10} at pH 8. They evaluated the treatment as successful, not only considering the aspect of corrosion protection, but also from an esthetical point of view.

In addition, climatic chamber tests (100% relative humidity and concentrations of 10⁻³ mol L⁻¹ acetic acid added to the water to create the humidity) were performed on lead sheets coated by a treatment of 24 hours in different NaC_{10} solutions. The best results concerning corrosion resistance were obtained with 0.025 and 0.05 M NaC_{10} .

6.3 Overview of new work

The work by Rocca et al. [1, 2] was focussed on inhibition studies of lead using linear sodium carboxylates. The inhibition effects were tested in aqueous/corrosive solutions with its pH either 7 or 8.

This work elaborates the topic further by studying the application of the lead decanoate layer with the goal of protecting lead objects. Another research group also reported the promising protective performance of this kind of coatings [4]. One should note, that the application does not require an aqueous/corrosive solution. Therefore, a 0.05 M $CH_3(CH_2)_8COOH$ (HC_{10}) was prepared (in deionized water) by neutralizing with $NaOH$ to pH 7, similar to the protocol of Rocca. Using this solution, the layer growth was intensively studied as a function of time using SR-XRD, mass gain analysis and electrochemical impedance measurements (Chapter 7).

Our experiments, however, showed that solutions characterized by their pH gave rise to irreproducible results. Decanoate layers, applied in these solutions, showed that measured coating resistances varied over a broad range. Investigation showed that the pH is inappropriate for evaluating the solution quality. Therefore, we established a new protocol on the basis of conductivity (Chapter 8). The solution, prepared by this new protocol, guarantees the production of dense and effective coatings.

Using this new solution, we investigated the layer growth using EIS and contact angle measurements. In addition, we studied the effects of stirring and of the layer thickness of the liquid phase as a function of mass gain. Finally, the protection of the coating was evaluated by exposing treated samples to corrosive environments (Chapter 9).

6.4 References

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- [2] E. Rocca, C. Rapin, and F. Mirambet. Inhibition treatment of the corrosion of lead artefacts in atmospheric conditions and by acetic acid vapour: use of sodium decanoate. *Corrosion Science*, 46:653–665, 2004.
- [3] F. Lacouture, M. François, C. Didierjean, J.-P. Rivera, E. Rocca, and J. Steinmetz. Anhydrous lead(II) heptanoate. *Acta Crystallographica*, C57:530–531, 2001.
- [4] C. Chiavari, C. Martini, G. Poli, and D. Prandstraller. Conservation of organ pipes: protective treatments of lead exposed to acetic acid vapours. In *Proceedings of Metal 2004*, pages 281–293, Canberra, 2004. National Museum of Australia Canberra ACT.

Chapter 7

Real time monitoring of spectroelectrochemical growth of a lead decanoate coating in an electrochemical/environmental cell (*eCell*) *

This chapter presents a study of the growth of a lead decanoate coating ($CH_3(CH_2)_8COO)_2Pb$ deposited on lead substrates. This work was carried out in an electrochemical/environmental cell (*eCell*) which is configurable for electrochemistry, gaseous/vapour exposure and other types of experiment.

Using a combination of synchrotron X-ray diffraction (SR-XRD) and electrochemical impedance

*A brief outline appeared in ESRF Highlights 2006 and more complete accounts will appear in Metal 07 and elsewhere. This work has also been presented in part at '8° Vlaams Jongerencongres Sectie Jong KVLV', 7 april 2006 (Leuven, Belgium), at Synchrotron Radiation in Art and Archaeology (SR2A), 26-29 september 2006 (Berlin, Germany), at Conservation Science 2007, 9-11 may 2007 (Milan, Italy) and will be presented at Metal 07, 17-21 september 2007, (Amsterdam, The Netherlands).

spectroscopy (EIS) we demonstrate the monitoring of the growth of the coating in real-time. Additional experiments involved the recording of mass gain to estimate the average thickness of the layer and the study of the surface finish using scanning electron microscopy (SEM).

7.1 Experimental

7.1.1 Simultaneous X-ray diffraction and electrochemical experiments: *eCell*

For these combined experiments, a special electrochemical cell which enabled us to investigate rough and heterogeneous metal surfaces in-situ during an electrochemical reaction [1]. In the past, other cells have been designed by other groups to investigate surfaces which were more ideal in some way [2–6]. The newly designed cell was named *eCell*. The 'e' in *eCell* has a dual meaning: (1) environmental, meaning that a specific environment is created inside and (2) electrochemical, as *eCell* is also designed to perform electrochemical experiments. *eCell* has been developed and optimized in several steps. A description of this development from design MkI towards design MkII can be found in the PhD work of K. Leyssens [7].

The entire system consists of three main modules: the hardware, a custom interface and potentiostat, and specific software [8]. In the next subsections, all components of *eCell* are described as it has been used for the experiments studied in this chapter. In what follows, a detailed description of the *eCell* is given.

Hardware: eCell MkII [8]

A schematic cross sectional representation of *eCell* (MkII) is shown in Figure 7.1. The body of the cell basically is a cylinder, made of PCTFE for good chemical resistance and reasonable mechanical stability. The working electrode is made from a lead disc (99.95%,

Goodfellow Inc., 10 mm diameter), fixed with conducting glue to a cylindrical brass piece, and encapsulated with epoxy resin (Epofix, Struers) (Figure 7.2a).

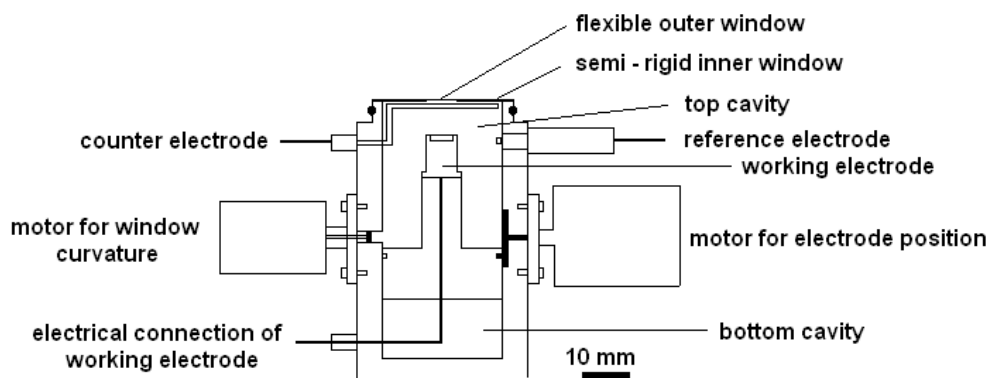


Figure 7.1: Schematic drawing of the cross sectional view of the MkII cell.

A hole was tapped in the brass piece to screw into the cell with a brass stud. This stud not only fixes the working electrode, but also ensures an electrical connection towards the outer side of the cell.

The reference electrode and the counter electrode, (see Figure 7.1), extend to the top cavity of the cell, where the electrochemical processes take place. The reference electrode is a $Ag/AgCl$ reference electrode and is shown schematically in Figure 7.2b. A silver wire of 1 mm diameter (99.95%, Alpha Chemicals Ltd, UK), electrochemically coated with a silver chloride layer is in contact with a 3 M KCl solution. The reference has a potential of 210 mV with respect to the standard hydrogen electrode [9].

The counter electrode is a platinum ring through which the working electrode can be moved by a motor (see Figures 7.1 and 7.3). The proper positioning of the working electrode is necessary to combine electrochemical experiments and surface analysing techniques. Electrochemistry can only be performed on working electrodes sufficiently covered with electrolyte to ensure transport to and from the electrode. Surface analysis, as done with *eCell*, requires a minimal thickness of an electrolyte layer above the investigated surface,

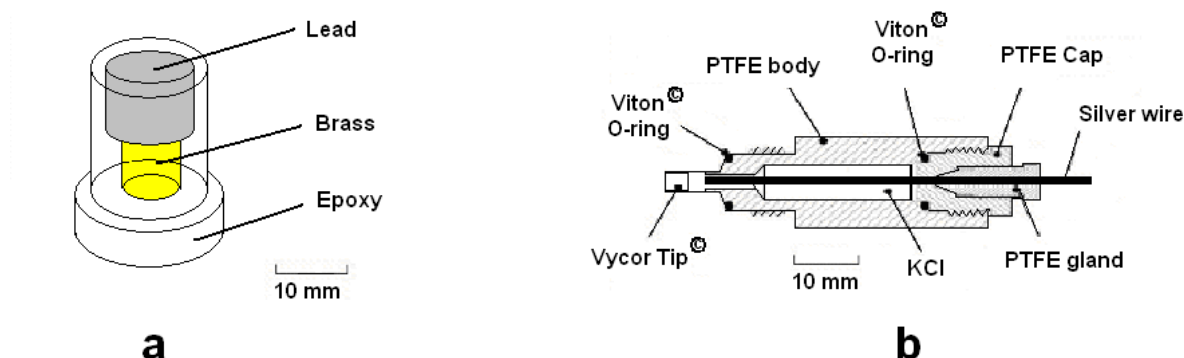


Figure 7.2: Schematic of the working (a) and the reference electrode (b) used in the MkII cell (from [1]).

to ensure diffracted X-rays reaching the detector. The thickness of this layer, which is $125\text{ }\mu\text{m}$, is controlled by an inner polyethelene window. Another motor controls the profile of the $8\text{ }\mu\text{m}$ thick Kapton®X-ray window, which encloses the cell. The body of the cell is attached to a bracket for easy attachment to the sample stage. A schematic representation and photograph of *eCell* (MkII) is shown in Figure 7.3.

Custom interface and potentiostat (from [7])

The potentiostat and interface use a multifunction analogue card (ExacqTM 2120) in a PCMCIA to PCI conversion crate (MagmaTM CB 232) so that the system can be controlled from a laptop PC. The Exacq card controls a custom potentiostat designed specifically for this application and capable of communicating with the interface at a distance of 9 m. The system is complemented by a webcam which allows video or stills of the *eCell* operation to be observed and captured [8]. The potentiostat, however, at this moment is not configured to perform impedance measurements. Therefore, only the interface was used to position the working electrode.

Software

Dedicated software by Professor Mark Dowsett and Gareth Jones (University of Warwick, UK) enables a proper control of the cell [8]. Experimental parameters can be set up in

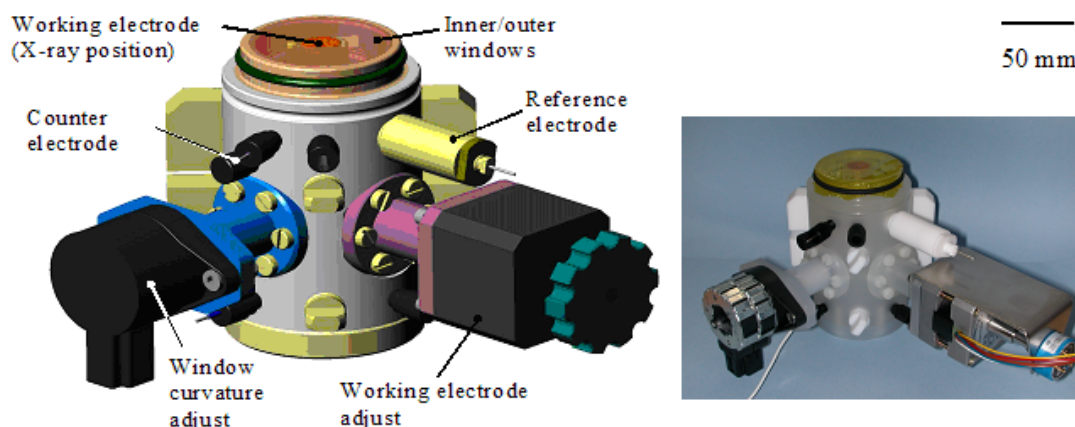


Figure 7.3: The *eCell* Mk II with automatic working electrode positioning, window deformation and full computer control. Left: schematic presentation; right: an image of the cell (from [8]).

a user friendly GUI. This includes motor control to adjust electrode position and window curvature, webcam and potentiostat control. The positioning of the working electrode can be programmed as shown in Figure 7.4, and the system can issue a trigger pulse to the XRD acquisition software as soon as the electrode is in position. The position of the working electrode, webcam view and electrochemical data can be displayed during the experiments.

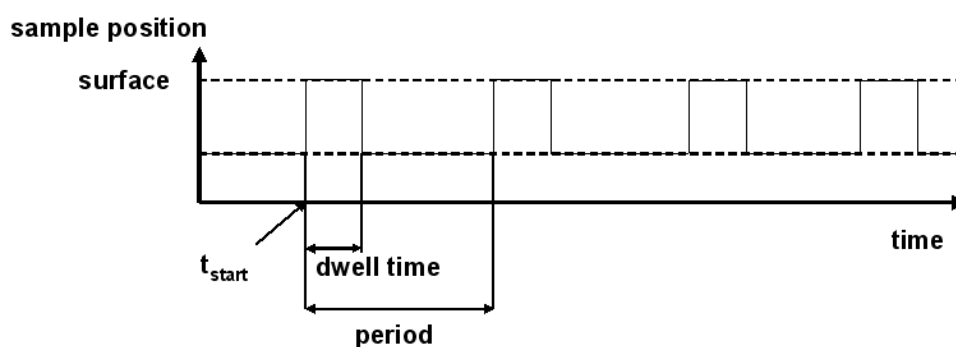


Figure 7.4: Start, dwell time and period of an experiment (from [7]).

7.1.2 Measurement conditions and setup at beamline BM28

The experiments were carried out at BM28 (XMaS), the UK Collaborating Research Group Beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble [10]. At BM28, a beam having a wavelength of 1.5498 Å (8 keV) with dimensions of $1\text{ mm} \times 200\text{ }\mu\text{m}$ was used, which had a footprint on the sample of $6\text{ mm} \times 1\text{ mm}$. A two dimensional detector, a Mar CCD 165 camera (Mar USA Inc.) was used to record the diffraction patterns. X-rays were incident at 10° to the sample surface (we show elsewhere [1] that this results in a good compromise of surface specificity and short path length in the fluid). The two dimensional detector provides more detailed information about any preferred orientation by recording out of plane scattering of the crystals on the surface as opposed to a one dimensional detector. This allows us to improve the statistics in the case preferred crystal orientations are present when comparing time related data. On the other hand, the range of 2θ is smaller using a 2 dimensional detector. Moreover, the data processing is more complicated and requires specific software (see below). The cell was mounted in the ring of an 11-axis Huber goniometer. The angle of the camera to the beam was 35° and positioned at 130 mm in order to acquire the signals between 2θ values $\sim 10^\circ$ and 65° . In some of our experiments, we used other camera angles of 0° and 45° to extend the range of 2θ . Under any of these conditions, the diffraction centre is outside the field of view of the camera, and the camera plane intersects the diffraction cones at an angle to produce elliptical 'rings'. A schematic illustration of the setup, according to the Hart-Parrish geometry, is shown in Figure 2.6.

The images were processed using new XRD evaluation software, called esaProject (EVA Surface Analysis, UK), which was developed for this purpose. The program re-maps the images into a 2Θ - γ space (or, alternatively, a d - γ space), where 2Θ is the total scattering angle, γ is the out of plane scattering angle (and d in this case is the lattice spacing divided by the order of diffraction). In this map, the elliptical XRD powder rings are straight bars and all or part of the image is easy to integrate to form a spectrum. The program allows spectrum processing, including background correction, smoothing, calibration, normaliza-

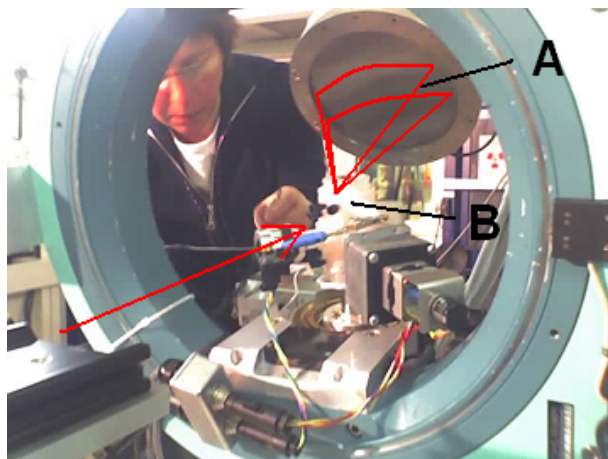


Figure 7.5: Professor Adriaens installing the cell at the beamline, with A the detector and B the cell. In red, the path of the incoming beam is visualized, together with diffracted radiation reaching the detector (from [8]).

tion and integration. The latest version of the software can process an entire set of spectra in one batch, and displays intensities of all selected peaks.

EIS data were obtained with an Autolab PGSTAT20 (Eco Chemie BV) placed inside the hutch and controlled using the manufacturer's software FRA. A frequency range of 0.1 Hz to 1000 Hz was used. Data were taken in parallel with the SR-XRD measurements.

Sample preparation and solutions

The surface preparation consisted of abrasive polishing using 1200 grit SiC paper. This was followed by polishing with hard tissue in order to remove the SiC particles which had penetrated the soft lead surface, a phenomenon which is clearly visible in secondary electron images (Figure 7.6). The surface was then rinsed with propan-2-ol and wiped with a soft lint-free tissue. Because the lead is so soft, the latter process provides a final burnish to the surface.

The cell was filled with ~ 35 mL of 0.05 M sodium decanoate solution. The latter was

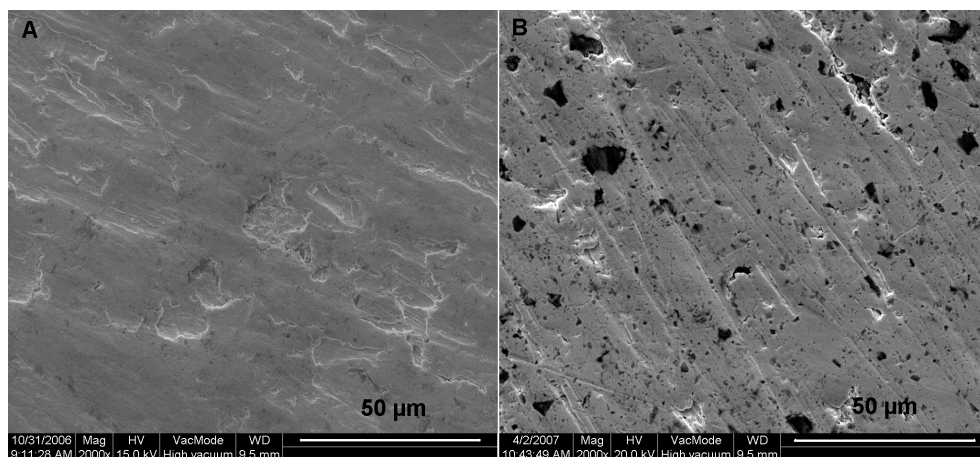


Figure 7.6: Final surface finish with (a) and without (b) polishing with hard tissue. The black spots in (b) are SiC particles from the grinding paper.

prepared by neutralizing decanoic acid (98%, Fluka) with $NaOH$ (98%, VEL) to pH 7, similar to the protocol proposed by Rocca et al. [11] (without using the ASTM solution).

7.1.3 Additional Laboratory experiments

Open circuit potential measurements

Open circuit potential (OCP) measurements were performed with an Autolab PGSTAT20 potentiostat (Eco Chemie BV, The Netherlands), controlled by GPES software. The reference electrode was a saturated $Hg/HgSO_4$ electrode (XR210, Radiometer Analytical, Denmark) with a potential of 0.658 V versus the standard hydrogen electrode ($T = 295$ K).

Mass gain analyses and SEM imaging

Mass gain analyses were performed on lead plates (Goodfellow, 99.95%, $20 \times 20 \times 1$ mm) to obtain information on the coating thickness. A hole was drilled at one side of the plate, allowing it to be suspended in the solution using a nylon thread. The plates were coated as a function of time using the solution as described above and dried by blowing cold air

onto them. After determining the mass gain, the same plates were used for scanning electron microscopy imaging.

7.2 Results

7.2.1 SR-XRD measurements

Figure 7.7 shows a selected set of the SR-XRD image sequence which was acquired while the lead electrode was immersed into the NaC_{10} solution. The upper row shows the data as collected by the CCD camera, whilst the bottom row shows the reprojected data using the esaProject software. Prior to explaining the sequence, we will focus on the details of the last image.

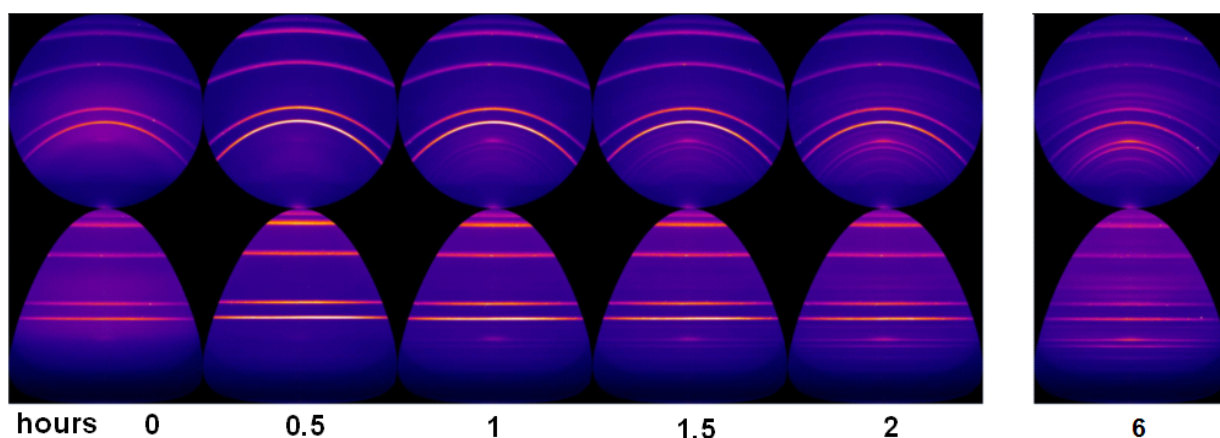


Figure 7.7: Raw images as taken by the camera (first row), and processed to integrate with esaProject (second row).

A detailed image from a 6 hours coated substrate is shown in Figure 7.8. The lines of the egg shaped image, as a result of diffraction, correspond to the 2θ values given in the y axis. Integration of all lines across the entire image results in the spectrum is given on the right hand side. The arrows indicate the diffraction lines/peaks of lead. The other lines, which are much less intense, are due to the coating. The diffraction pattern is similar to that

observed by Rocca et al. [12] (see Figure 6.4). The main diffraction peaks of the coating are indeed observed in the 2θ range between 10° and 25° . The inset shows a magnified segment on the image. It is observed that the 'lead lines' contain spots, due to a non-uniform distribution of orientation of lead crystallites in the metal. On the other hand, the lines of the coating lack any spots, implying that very small lead decanoate crystallites are formed in any given orientation. Back to Figure 7.7, it can be seen that the appearance of characteristic bands of $Pb(C_{10})_2$ is clearly visible after 2 hours and is very significant after 5 hours. At the same time the intensity of the lead rings decreases, confirming that a layer is formed on the surface.

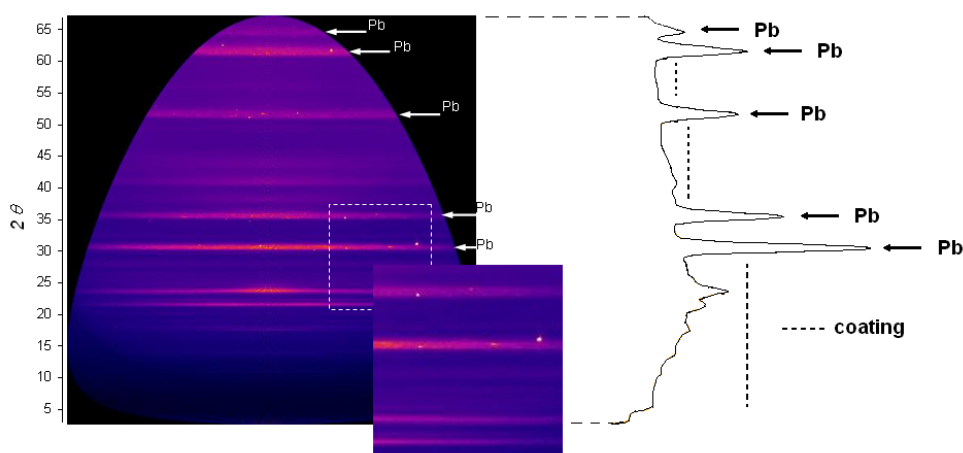


Figure 7.8: Reprojected X-ray diffractograms of the $Pb(C_{10})_2$ coating after 6 hours of growth.

On the right hand side, the integrated spectrum is given. The arrows indicate the diffracted lead bands/peaks; all other bands/peaks (regions indicated with the dashed line) originate from the lead decanoate coating (after [8]).

The data sequence was processed by plotting the X-ray peak areas as a function of time (Figure 7.9). Figure 7.9 shows the (normalized) intensities of various diffraction peaks versus time, obtained from the sequence of images from Figure 7.7. These peaks were selected from the spectra since the profiles were different.

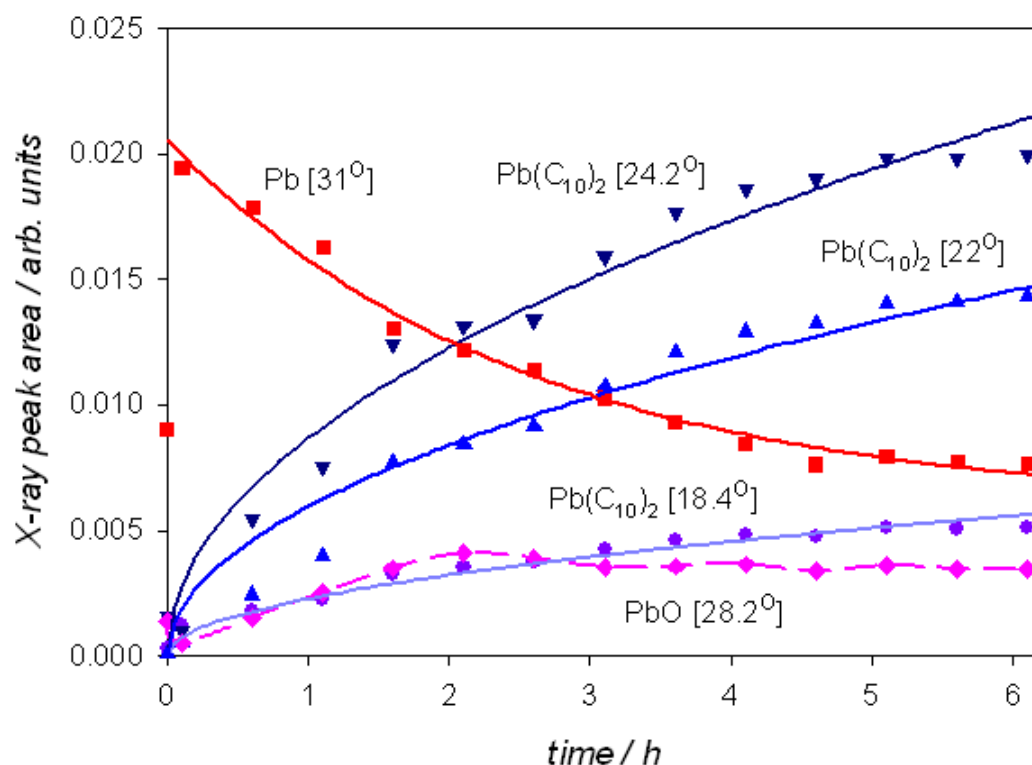


Figure 7.9: Time dependence of peak areas extracted from a sequence of images shown in Figure 7.7 (from [8]).

The intensity curve from the most intense lead peak ($2\theta=31^\circ$) can be approximated well by the function:

$$A_{Pb} = A_0 - ae^{-bt} \quad (7.1)$$

where A_0 (initial intensity), a and b are fitting parameters and t is time. The behaviour predicted by Equation 7.1 is the result of the growing layer on the surface; the (normalised) beam intensity reaching the substrate and the diffracted X-rays are attenuated by the layer.

Some intensities of the coating at $2\theta=24.4$, 22 and 28.2° show an increasing trend which can be fitted well by the function:

$$A_{Pb(C_{10})_2} = A\sqrt{t} \quad (7.2)$$

The intensity of the $2\theta=24.4^\circ$ series is in any case higher than the other two profiles, due to more intense diffraction of that specific lattice plane (and vice versa). The profiles approach constant values after ~ 6 hours, due to effects of self-absorption. Mathematical procedures, based on density, mass absorption coefficient and thickness of the layer as a function of time, enable to correct for these effects. However, the unknown thickness, function of time, as well as the unknown density of lead decanoate forbid the application of such corrections.

One peak of the spectrum at $2\theta=28.2^\circ$ shows a totally different behaviour. The intensity increases during the first three hours, and approaches a constant value afterwards. This peak is most probably provoked by litharge ($\alpha - PbO$, strongest intensity at $2\theta=28.2^\circ$), initially formed together with the lead decanoate.

7.2.2 Electrochemical impedance data

Prior to the discussion of the EIS data, some considerations and the applied model will be discussed. The reader is referred to Chapter 2 for some of the figures. The electronic circuit, characterizing a coated metal (Figure 2.2a), results in the formation of two halfcircles in the Nyquist plot: a halfcircle due to the coating, another due to the metal (Figure 2.2b).

If the coating resistance of the system is very high compared to the polarization resistance, the electronic circuit can be simplified to a Randles circuit (Figure 2.1a) with specific resistance and capacitance due to the coating (R_c and C_c). The resulted Nyquist plot is only one half circle (Figure 2.1b). It should be noticed that Figures 2.1 and 2.2b represent data from a static system. Imagine now the application of a coating on a 1 cm^2 lead substrate with negligible polarization resistance, which coating resistance increases 1 ohm every minute. If it was possible to measure every minute all frequencies simultaneously, a

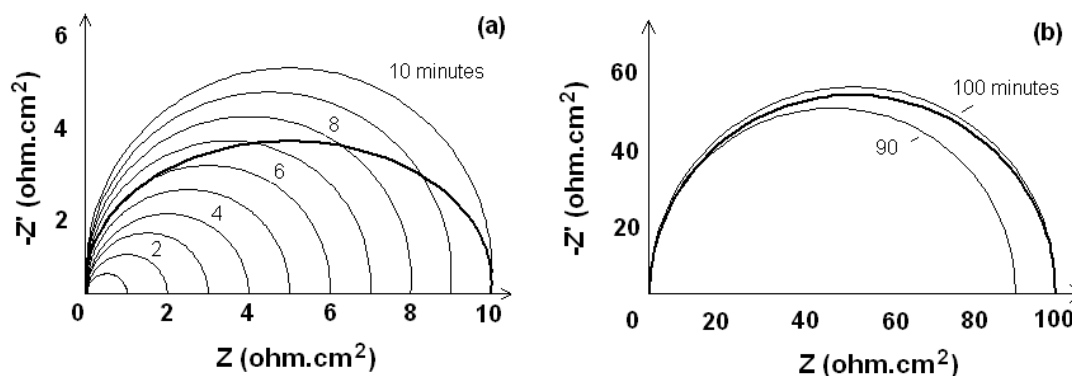


Figure 7.10: (a) The bold line is the measured Nyquist plot at the start of a coating application with a growth of $1 \Omega \text{ minute}^{-1}$, constituted of different half circles of progressively increasing radius. (b) The same system measured after 90 minutes, indicating that the relative error decreases as a function of time.

series of half circles would give the exact time related information on the coating (indicated as 2-10 minutes in Figure 7.10a). In practice, due to the finite measurement time, one sees points which are members of different half circles of progressively increasing radius, due to the changing values of R_c and C_c during measurement.

The measurement of this dynamic system, scanning from high to low frequency, therefore appears as an almost depressed (we will use the word 'stretched') half circle which is the bold line in Figure 7.10a. Since the measurement of the low frequencies takes considerably more time, the stretching is more expressed at the low frequency end.

The measured (stretched) half circle of the same system after 90 minutes is given in the bold line in Figure 7.10b. Longer application times give rise to more accurate fittings for R_c and C_c due to the smaller relative changes in the entire coating. For the same reason, the stretching of the half-circles will decrease for longer application times.

The EIS data measured simultaneously with the XRD experiment at intervals of 1 hour, starting 10 min after the growth commenced, are shown in the Nyquist plot of Figure

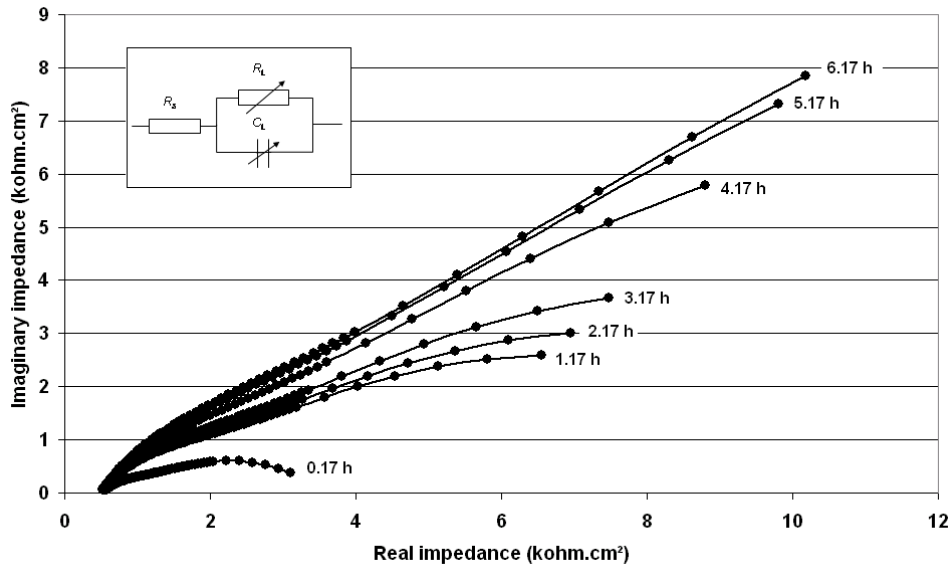


Figure 7.11: Nyquist plots of the EIS data measured simultaneously with the SR-XRD sequence. Inset shows effective model with variable impedances.

7.11. The data were recorded with frequency scanned from high to low, so time runs from left to right across the plot. Keeping in mind the previously discussed model, one can estimate, by fitting the stretched halfcircles by depressed ones, that the layer resistance is $\sim 25 \text{ k}\Omega \text{ cm}^2$ after more than 6 hours (diameter of the 6.17h fitted half-circle in Figure 7.11), which is rather low for a protective coating [13]. Our simple model, however, does not allow to explain these data. The polarization resistance most probably does not meet the requirement of being negligible compared to the coating resistance. However, we will show later on in this work, that the application of coatings of which the polarization resistance can be neglected, that the model is very appropriate.

7.2.3 Additional ex-situ analyses

The open circuit potential was measured during the layer growth to indicate possible passivation processes. The recorded curve is shown in Figure 7.12. The potential increases

about 500 mV to reach an almost stable potential after five hours; the main change occurring the first three hours. This, most probably, is a result of the formation of lead oxide on the surface. Indeed, during the first two-three hours, a lead oxide layer is formed (Figure 7.9). This is enforced by the observation of the similar behaviour on copper samples: the open circuit potential is only affected by the superficial cuprite (Cu_2O) layer, and not by the (artificially created) corrosion products on top [14].

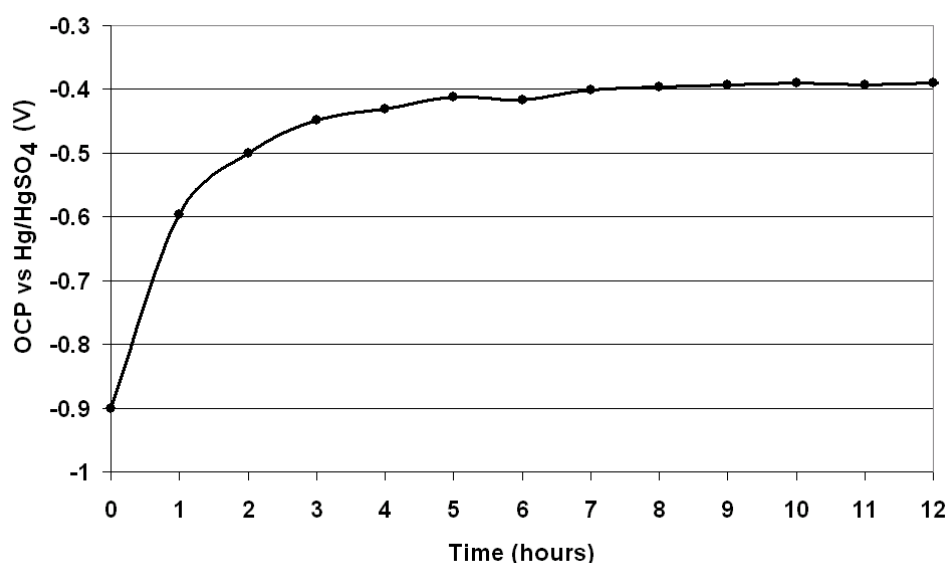


Figure 7.12: The open circuit potential during growth shows the passivation of the surface.

The surface morphology from the start towards coated surfaces after 1, 4 and 6 hours of immersion was studied using scanning electron microscopy (secondary electron images) and is presented in Figure 7.13. The bare metal shows some discontinuity due to the surface preparation (0 hours). The surface appearance after 1 hour shows the presence of regions covered by flake-shaped crystals, but also bare areas (not shown). A detail of a crystal rich region after one hour is shown. After 4 hours, the density of the flake-shaped crystals has increased and covers almost the entire surface. The further growth of the crystals results in a dense flake-shaped surface appearance.

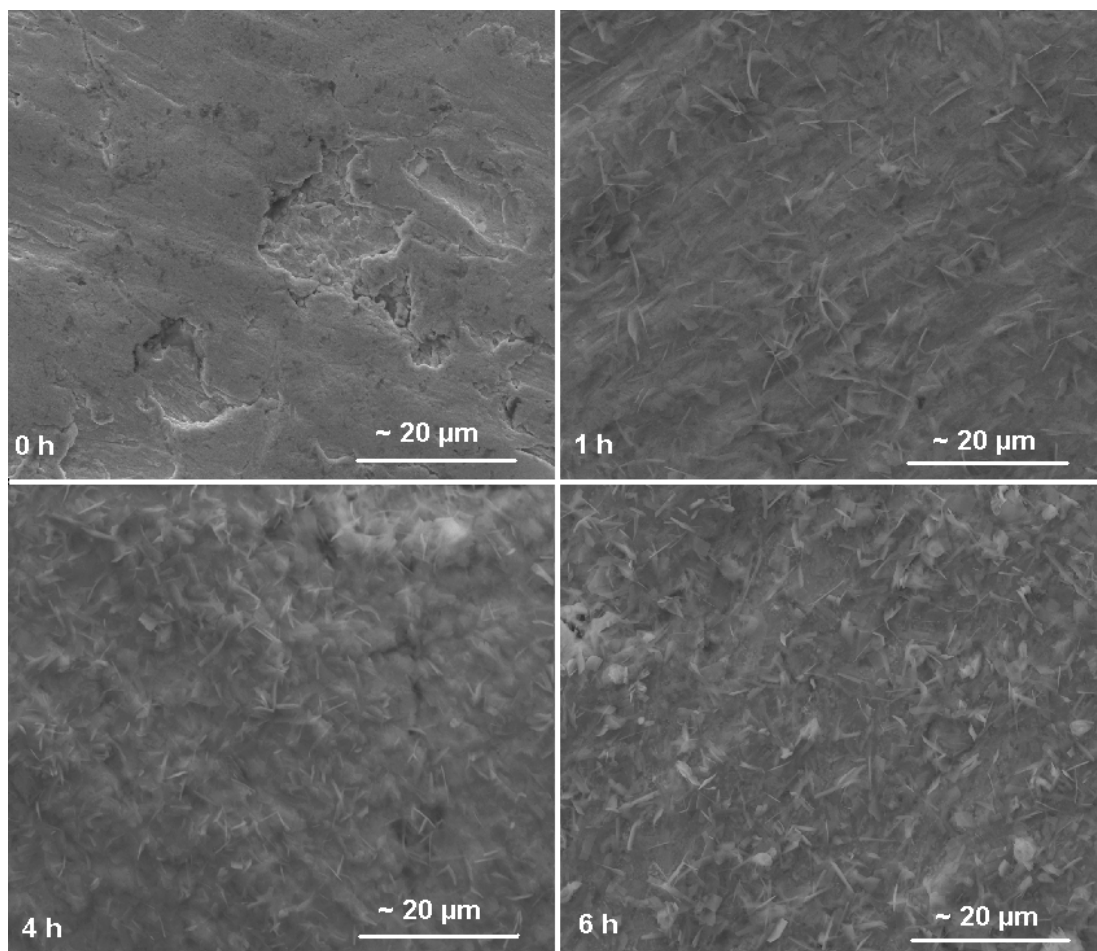


Figure 7.13: Secondary electron images of the $Pb(C_{10})_2$ layer applied at respectively 0, 1, 4 and 6 hours.

Figure 7.14 shows the mass gain and thickness data, fitted by Professor Mark Dowsett. We decided to calculate the thickness on a basis of the density of lead heptanoate, since the density of lead decanoate was not found in the literature. The thickness will probably be underestimated (more heavy lead atoms will be present for a given volume of lead heptanoate). Moreover, the thickness data have to be considered carefully since it presumes a uniform layer, which is not the case as was shown in the SEM data (e.g. Figure 7.13). The data imply an initially higher growth rate, followed by a constant deposition rate. The profile, as such, is well fitted by a combination of parabolic and linear function:

$$m = 0.625t + 0.091\sqrt{t} \quad (7.3)$$

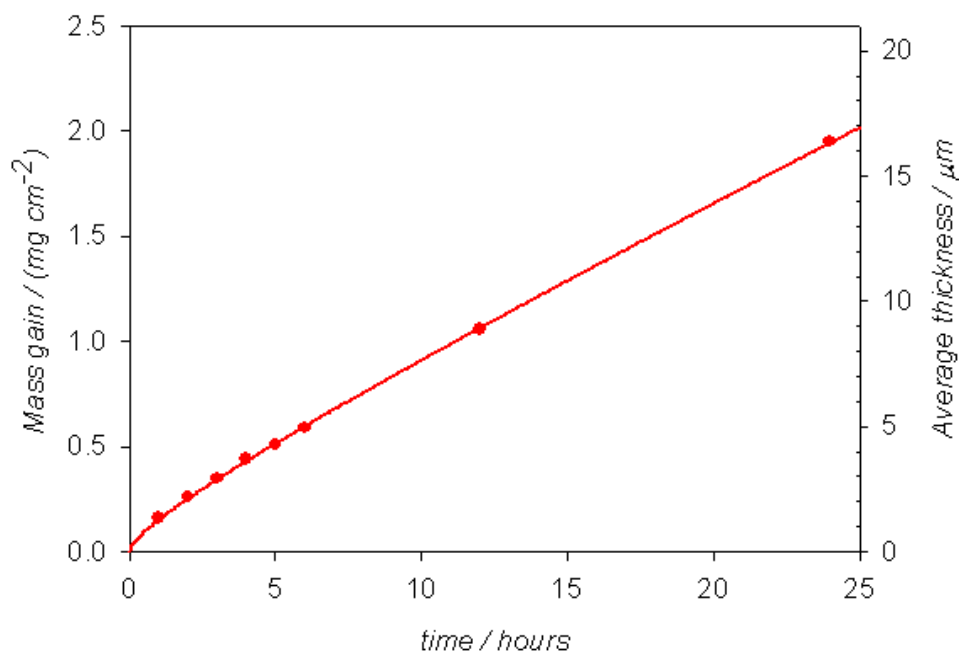


Figure 7.14: Mass gain and thickness data (points) and parabolic+linear fit (solid line) of growing lead decanoate layer (from [8]).

7.3 Discussion and conclusions

The interpretation of all data to a coherent theory was mainly achieved by fruitful discussions with Professor Mark Dowsett. All experiments reflect the possible occurrence of two growth contributions; (1) a 2 D crystallite spread across the surface followed by (2) 1 D vertical growth. The mass gain data already suggested a parabolic and linear growth contribution, which in this context, respectively reflect the 2 D areal and 1 D vertical growth. Starting from a naked surface, the 2 D growth dominates the deposition. However, once the surface is almost entirely covered, this growth contribution decreases. In contrary, the 1 D growth shows linear behaviour. Secondary electron images show that

the lead substrate is gradually covered with flake-shaped crystals, representing the 2 D growth contribution. The SR-XRD intensities of the lead decanoate peaks show as well a parabolic contribution (both growth contributions are measured). The coating resistance, mainly determined by the vertical growth, shows an almost linear tendency after more than 3 hours. This linearity is not apparent during the first hours because the metal is not sufficiently covered.

A number of questions subsist about the growth at the molecular scale: lead and a decanoate species have to interact before lead decanoate can be formed. Some possible growth mechanisms are summarized:

- (1) lead species migrate through the coating to form lead decanoate at the coating/solution interface.
- (2) lead species migrate through the solution to form lead decanoate at the coating/solution interface.
- (3) lead decanoate species migrate through the coating to form lead decanoate at the metal/coating interface.

Laboratory experiments showed that the solution, prepared using the protocol similar to that of Rocca et al.[11, 12], could not be prepared in a reproducible manner. It was observed that the pH was an inappropriate parameter to evaluate the solution quality. This clearly shows the need for a protocol, describing the preparation of solutions that produce dense and effective coatings. The latter is elaborated further in Chapter 8.

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Chapter 8

Optimization of the lead decanoate coating process *

This chapter presents the optimization of the $Pb(C_{10})_2$ coating process. The impact of the pH and conductivity of the decanoate solution upon treatment, the coating resistance and the mass gain were investigated. Based on these results, a protocol is proposed for preparing decanoate solutions that produce dense and effective coatings.

8.1 Experimental

8.1.1 pH and conductivity of partially/totally neutralized decanoic acid solutions

Previous experiments showed that the pH is unresponsive to variations in concentration over a critical range. The pH also appeared inappropriate for any characterization of the quality of decanoate solutions. Therefore, we examined the use of conductivity as an alternative. The pH and conductivity were studied with solutions containing 4.3068 g of decanoic acid and different amounts of $NaOH$, so as to obtain 500 mL volumes of

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partially/totally neutralized decanoic acid. Some of the partially neutralized solutions are turbid, and are referred to as suspensions. In addition, a 0.05 M sodium decanoate solution was prepared by dissolving the salt (Fluka, 98%). pH values were measured with a pH electrode (Metrohm, Unitrode, Belgium), to an accuracy of 0.01 units. Conductivities were measured with a Radiometer CDC 641T, in combination with a CDM 210 controller.

8.1.2 Resistance of the lead decanoate coating treated by partially/totally neutralized decanoic acid solutions

The resistance of the lead decanoate coatings can be evaluated by electrochemical impedance measurements. The effects of partially/totally neutralized decanoate solutions on the coating process were investigated by treating lead electrodes with partially/totally neutralized decanoic acid solutions. The reader is referred to Subsection 8.1.1 for the preparation of these solutions. A six hour treatment time was accepted, in order to limit the effects of growth during measurement (see Subsection 7.2.2). Impedance data were acquired using an Autolab PGSTAT20 potentiostat with FRA software (Ecochemie B.V., The Netherlands). A signal amplitude of 0.01 V was adopted in the frequency range from 1 kHz to 100 mHz.

8.1.3 Mass gain as a result of decanoate layer growth in partially/totally neutralized decanoic acid solutions

The mass gain was studied as a function of the degree of neutralization of decanoic acid in order to investigate the deposition rate. Lead plates with dimensions of $20 \times 20 \times 1$ mm (Goodfellow, UK, purity 99.95 %) were polished using a hard tissue and subsequently rinsed with propan-2-ol. The mass gain was determined after 6 hours treatments (Mettler AE240, US, precision of 0.1 mg) with a series of decanoic acid solutions neutralized close to pH 7 as described above (see Subsection 8.1.1).

8.2 Results

8.2.1 pH and conductivity of partially/totally neutralized decanoic acid solutions

Figure 8.1a and b show the pH and conductivity of suspensions/solutions that contain 25 mmol decanoic acid, as a function of the added mmol $NaOH$.

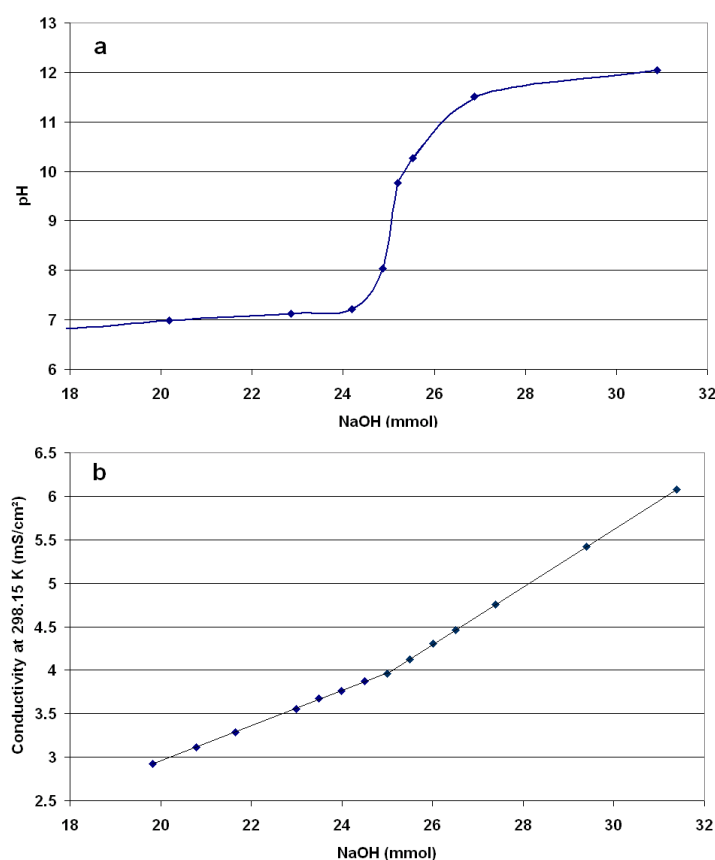


Figure 8.1: (a) pH and (b) conductivity of decanoic acid as a function of the degree of neutralization.

A pH jump (Figure 8.1a and b) occurs between 24 and 26 mmol $NaOH$, as expected. The curve, before the pH jump, typifies a buffered system, with its pH almost constant at 7.

This is rather unexpected as the pK_a of decanoic acid is 4.83 [1]. However, the solubility of decanoic acid is extremely low, which explains the pH values and the turbidity before the equivalence/stoichiometric point.

The equivalence point is well observed in the conductivity curve (25 mmol). The conductivity rises linearly before the equivalence point (Figure 8.1b) due to increasing sodium and decanoate concentrations. At the pH jump, hydroxide ions (with much higher mobility) come into solution, in addition to sodium ions, producing the sudden increase of the slope.

The conductivity of 0.05 M neutralized decanoic acid measures 3.96 mS cm^{-2} at 298.15 K. It should be noticed that this value differs from the one measured when using NaC_{10} solutions prepared from the pure salt. The conductivity of 3.44 mS cm^{-2} , measured in that case, is probably due to a lower impurity content.

8.2.2 Resistance of the lead decanoate coating obtained by partially/totally neutralized decanoate solutions

EIS data of decanoate coatings were measured as a function of the degree of neutralization of decanoic acid upon treatment (Figure 8.2). The Nyquist plots show depressed half-circles, that fit the equivalent circuit shown in the inset.

The resistance R_c and capacitance C_c values, obtained by fitting, are characteristic for coatings of this type (Subsection 7.2.2). The resistance values were extracted from fitted impedance data (see Figure 8.2). The resistance, function of the added $NaOH$, reaches a maximum just before the equivalence point (Figure 8.3) to drop dramatically during/beyond the pH jump (Figure 8.1a). The maximum resistance reaches about $2.9 \text{ M}\Omega \text{ cm}^2$ at 24.2 mmol added $NaOH$, i.e. with almost perfectly neutralized decanoic acid. Tests with decanoate solutions prepared from pure NaC_{10} produce similar results. Data figuring inside the rectangle in Figure 8.3 remain irreproducible, and therefore, are considered non-representative.

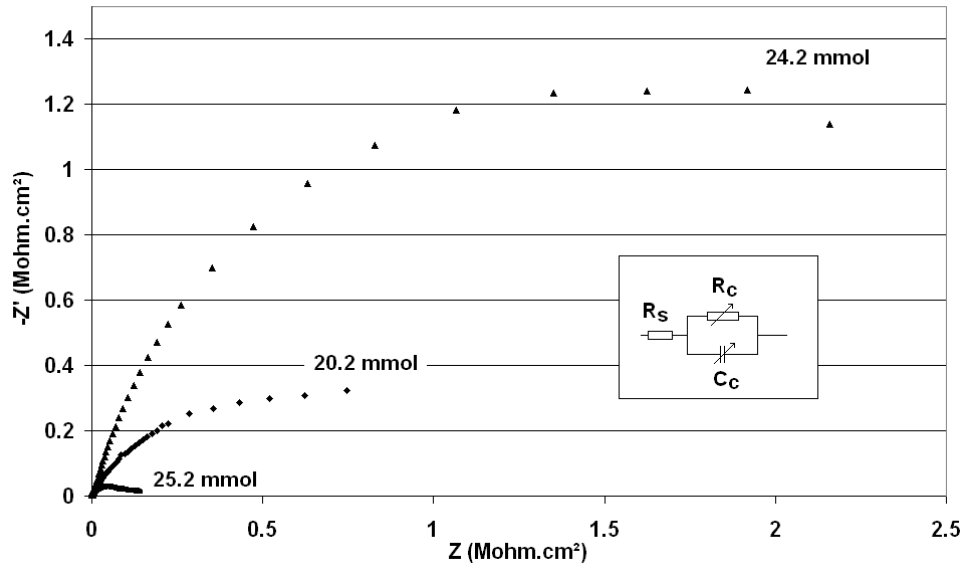


Figure 8.2: EIS Nyquist plots after six hours of exposure of lead substrates to decanoic acid solutions of different degrees of neutralization. Inset: equivalent circuit that fits the data. R_s : resistance of the solution, R_c , C_c : coating resistance and capacitance.

Figure 8.3, apparently, confirms a previous study on sodium heptanoate treated copper [2], which study also mentions the use of heptanoic acid at various degrees of neutralization. The lower resistances observed before the equivalence point may be attributed to the formation of relatively large $Pb(C_{10})_2$ crystals, resulting in a rather porous deposit. The increase in decanoate ion concentration (Figure 8.1b), upon approaching the equivalence point, enhances the process of nucleation and gives rise to the formation of a tighter non-porous protective layer.

The drop in resistance at and beyond the equivalence point, similarly to the copper heptanoate case, must most probably be attributed to corrosion [2]. Specifically dealing with lead, more evidence is found in literature: PbO and soluble lead hydroxides are formed in alkaline media [3, 4]. This is also consistent with the potential/pH diagram of lead undecanoate ($Pb(C_{11})_2$) [5], which leads to expect the formation of lead oxide (PbO) and of water soluble biphumbite ($HPbO_2^-$), beyond the pH of 10 and 11.5 respectively.

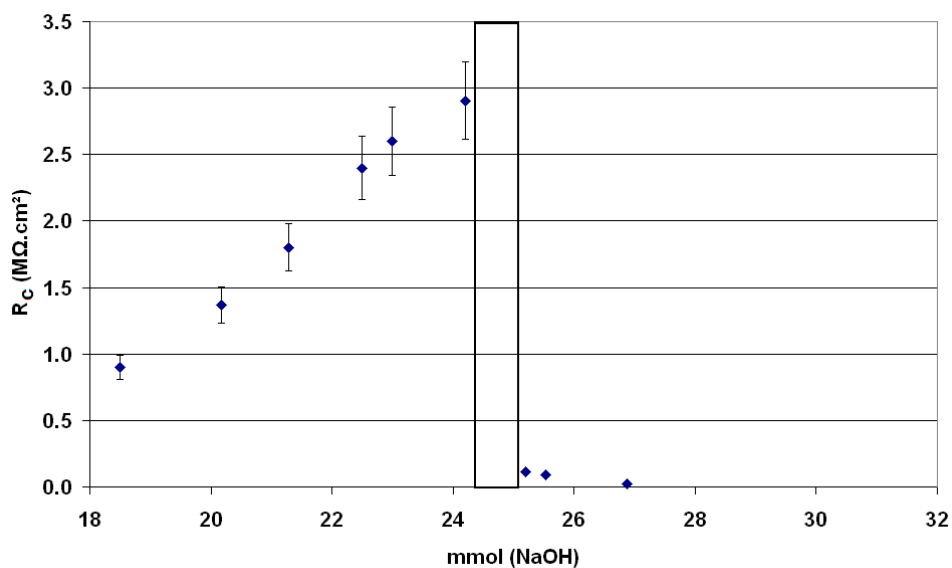


Figure 8.3: Resistance of the decanoate coatings as a function of the partial neutralization of decanoic acid upon treatment, after six hours of exposure. 10% error bars were used in the graph to indicate the standard deviation on the datapoints.

8.2.3 Mass gain analyses

Figure 8.4 shows the mass gain of decanoate treated substrates as a function of the pH of decanoic acid suspensions/solutions upon treatment. The mass gain with time is initially parabolic, meanwhile the colour changes from light to dark grey. A white appearance is observed beyond the equivalence point.

Similar to the varying resistance (Figure 8.3) the lower mass gain before the equivalence point, is likely to be due to decreasing crystal size. The dashed line in the curve corresponds to the pH jump (see Figure 8.1a), with values that were considered non-representative. The additional drop beyond the equivalence point is considered to be an effect of corrosion (ut supra).

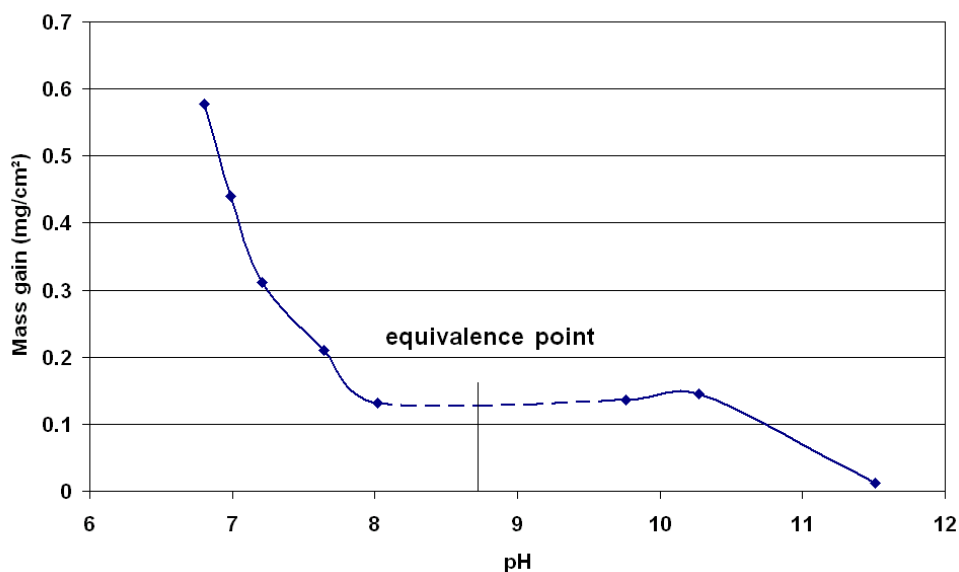


Figure 8.4: Mass gain after 6 hours of exposure to partially/totally neutralized decanoic acid, as a function of pH.

8.3 Discussion and conclusions

The quality of lead decanoate coatings was evaluated by measuring the resistance of the deposited layers (Figure 8.3): the resistance reaches its highest values if/when almost neutralized decanoate solutions are applied. From Figure 8.1a, it is seen that a pH of about 7 (as proposed by Rocca) is not the only requirement for the deposition of a dense and effective coating (Figure 8.3).

Decanoic acid is preferred as a starting product, rather than the corresponding salt, for economic reasons. However, the neutralisation of decanoic acid appears time consuming and delicate. The protocol outlined below describes the preparation of almost neutralized decanoate solutions, for the production of high quality coatings.

The increasing decanoate concentration, approaching the equivalence point, enhances the process of nucleation. Higher decanoate concentrations decrease the size of $Pb(C_{10})_2$ crystals, thereby improving the tightness and effectiveness of the coatings.

Decanoate coating and its dependency on the neutralization of decanoic acid, used for the present purposes, shows a marked similarity to Cu-heptanoate coating [2]: the resistance drop of coatings deposited at pH values beyond the equivalence point (Figure 8.3), is probably due to the formation of lead oxide [3] and of water soluble lead hydroxides [4].

Below, a protocol is described to prepare solutions that produce dense and effective coatings. A first step of the protocol (A) involves the determination of the equivalence point of decanoic acid neutralized with $NaOH$. This step is based on conductivity measurements, which can be affected by impurities in the product(s) used. Prior to preparing the solutions, the equivalence point needs to be determined for the specific materials. Once this is known, the protocol only involves the preparation of the solution (B).

8.4 Protocol to prepare solutions that produce dense and effective coatings

A. Preparatory steps

1. Dissolve 5 ± 0.05 g $NaOH$ in deionised water and adjust the volume in a 500 mL flask so as to obtain a 0.25 M solution;
2. Determine the exact concentration of the $NaOH$ solution by a standard procedure (e.g. titration with oxalic acid);
3. Prepare 7 suspensions, each containing 4.3068 g decanoic acid, in 500 mL volumetric flasks. Add respectively 70, 80, 90, 100, 110, 120 and 130 mL of the 0.25 M $NaOH$ solution. Add deionized water to adjust the volume to 500 mL;
4. Stir all suspensions until slightly turbid/homogeneous solutions are obtained (takes approximately 8 hours);
5. Determine the conductivity (at constant temperature) as a function of moles $NaOH$.

B. Solution

1. Determine the desired volume of decanoate solution;
2. Determine the volume of 0.25 M $NaOH$ needed to prepare the desired solution; an excess (100 mL) has to be prepared to determine the exact molar concentration;
3. Determine the exact molar concentration of the $NaOH$ solution;
4. Calculate the exact volume of the prepared $NaOH$ solution needed to neutralize the decanoate solution to a conductivity value 0.25 mS cm^{-2} below the value that marks the equivalence point (from the plot made in A5); take into account that this amount of sodium hydroxide corresponds to 500 mL decanoic solution;
5. Prepare the desired decanoate solution;
6. Check the pH (should be below 7.5) and conductivity (as determined from conductivity curve) of the decanoate solution.

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Chapter 9

Growth and real time corrosion resistance monitoring of lead decanoate coatings *

This chapter begins with a study of the surface coverage, assessed on the basis of solid/liquid contact angle measurements. The latter was performed on lead substrates, coated for regular time intervals. Next, a description is given of the monitoring of the growth of the coating by EIS, making use of solutions prepared according to the proposed protocol. In addition, the effects of stirring and layer thickness of the liquid phase were studied.

Finally, lead decanoate layers were exposed to high levels of acetic acid vapour (6.6% by weight in air) and high relative humidity (75%) to promote attack within the time span of a single synchrotron beam-time allocation (typically 3-4 days). These experiments were carried out in order to evaluate the protection offered by the coating, and to give more insight in the way of breakdown.

*This work has been presented in part at '8° Vlaams Jongerencongres Sectie Jong KVLV', 7 april 2006 (Leuven, Belgium) and at Conservation Strategies for Saving Indoor Metallic Collections (CSSIM), 25 february - 2 march 2007, (Cairo, Egypt)

9.1 Experimental

9.1.1 Assessment of surface coverage

The surface coverage was determined by measuring the contact angle of sessile droplets positioned on decanoate treated surfaces. Contact angle determinations were based on a thermodynamic/mathematical model [1, 2] for calculating the profile of such sessile drops. The method uses readily accessible parameters such as the height and base radius of the drop (Figure 9.1, left hand side), the drop volume, the density of the liquid and surface tension for a mathematical reconstruction of the drop profile, including a calculation of the solid/liquid contact angle. A Zeiss projection microscope (Figure 9.1) and a calliper were used to measure the height and the ground plane radii of 50 μL sessile droplets, to an accuracy of 0.001 mm. The measurements were performed on lead electrodes made out of a lead disc, 10 mm in diameter (Goodfellow, purity 99.95 %). The lead coupons were fixed on top of a brass rod by means of conducting glue and encapsulated in epoxy resin (Struers, France, Epofix kit). The electrodes were ground on a 1200 grit SiC paper, to obtain a fresh surface. Further smoothing was achieved by the use of a soft abrasive-free tissue. The lead surface, finally, was degreased with propan-2-ol. The electrodes were then treated for different time intervals between 0 and 180 minutes with a 0.05 M NaC_{10} solution, prepared according to our protocol.

The selection of an appropriate test liquid for the contact angle measurements appears rather delicate. Water serving as a test liquid could be affected by a release of $\text{Pb}(\text{C}_{10})_2$, thereby changing its interfacial tensions (γ_{LV} , γ_{SL}) and the magnitude of the contact angle (θ). The latter, indeed, are interrelated on a basis of Young's law (Equation 2.20).

The presumed effects of $\text{Pb}(\text{C}_{10})_2$ desorption were studied, therefore, prior to the contact angle measurements, using a Wilhelmy set-up for measurements of surface tension. The traction force exerted on a decanoate coated lead platelet (coating time: 15 minutes, $20 \times 20 \times 0.1$ mm, Goodfellow, 99.95%, 0.05 M NaC_{10} prepared by our protocol) was recorded.

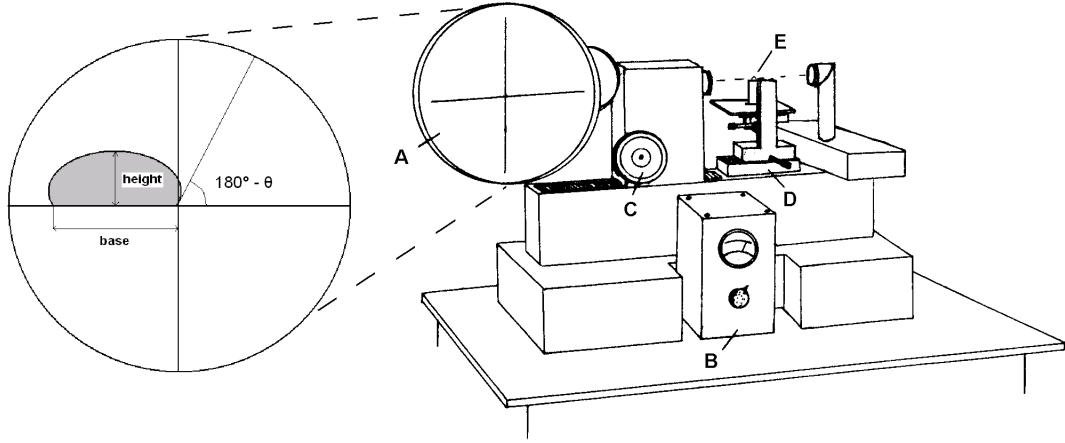


Figure 9.1: Projection microscope used for verifying the validity of equation (1), and for determining the geometrical parameters of sessile drops. A: screen; B: light intensity control; C: focussing; E: sample; D: tri-axial support (from [2]).

The platelet was suspended from an electro-balance to ensure reproducible positioning and to avoid any effects of buoyancy. The traction force, $F_{platelet}$, in such circumstances, is given by:

$$F_{platelet} = p \cdot \gamma_{LV} \cdot \cos\theta \quad (9.1)$$

where γ_{LV} is the surface tension and p stands for the platelet perimeter. Any release of $Pb(C_{10})_2$ was expected to affect the traction force on the balance, thereby providing information of the desorption rate.

The desorption, presumably, could be encountered by using droplets with a sodium decanoate concentration well above the critical micelle concentration (cmc). The surface tension, in these circumstances, would be almost constant and independent of the effects of desorption (Subsection 2.8.2). However, the cmc for sodium decanoate was unknown. With that objective, a set of solutions was prepared that contained concentrations up to 20 mM sodium decanoate (Fluka, 98%). The surface tension and conductivity of these were determined after four days of stabilization, in order to extract the cmc. Surface

tension measurements were determined in a similar way to the desorption effects (the Wilhelmy method [3]), i.e. by measuring the traction force, in this case exerted on a platinum platelet. The wetting of the platinum platelet was perfect in any of these measurements, i.e. $\theta=0^\circ$. Conductivities were measured using a type CDC 641T sensor (Radiometer, Denmark), with a CDM 210 controller from the same manufacturer.

9.1.2 Monitoring of coating resistance during growth

EIS data were obtained with an Autolab PGSTAT20 (Eco Chemie BV) controlled by the manufacturer's software FRA. The range of 0.1 Hz to 1000 Hz was adopted as working frequencies.

9.1.3 Impact of diffusion on the coating process

The impact of diffusion was studied on a basis of mass gain measurements. A Mettler AE240 balance (precision of 0.1 mg) was used to determine the layer thickness of the decanoate solution that gives rise to the most efficient deposition. For this experiment, lead plates with dimensions of $20 \times 20 \times 1$ mm (Goodfellow Inc., 99.95 %) were immersed in 0.05 M decanoate solution prepared by our protocol. A small hole was drilled in a corner to fix the plate with a nylon thread upon treatment (see later).

The setup consisted of parallel PVC plates, each 4 by 15 cm, immersed in the decanoate solution. The separation of each pair of plates was adjusted to yield surrounding liquid layers of 4.5 mm, 8.5 mm, 12.5 mm and 50 mm thickness, on each side of an immersed lead plate. Mass gain was determined with a Mettler AE240 (US, precision of 0.1 mg) electro-balance.

9.1.4 Monitoring of coating protection

The coating protection was monitored by X-ray diffraction using *eCell* at beamline BM28 at the ESRF. The reader is referred to Section 7.1 for the experimental setup. Effects of exposure to acetic acid vapour were evaluated in two experiments: (1) with uncoated lead electrodes, as a reference, and (2) with 6 h treated lead electrodes. The bottom of the cell was filled with a saturated *NaCl* solution (~ 10 mL) to create/maintain 75% relative humidity [4]. A 2.5 μ L droplet of acetic acid (Merck, >96%) was positioned on the inside of the inner polyethylene window to create a 6.3% (%m/m) acetic acid vapour¹. First, the electrodes were placed in the diffraction position to obtain an XRD pattern of the initial uncorroded substrate. Then, the electrodes were moved deeper into the cell, to be exposed to the corrosive atmosphere. These experiments were carried out with time intervals of 30 minutes. A second set of experiments was carried out under the same conditions, except a shorter interval time of 10 minutes.

9.2 Results

9.2.1 Assessment of surface coverage

Initial contact angle measurements using deionized water showed some interference from decanoate desorption: the latter, lowering the substrate's superficial coverage and the liquid's surface tension, actually decreased the contact angle. The effect was visualised and confirmed by monitoring the traction force on a decanoate treated lead platelet (coating time 15 min) by means of the Wilhelmy method (Figure 9.2), with pure water serving as a test liquid. The lower side of the platelet was slightly submerged, which causes the initial traction to be negative. The decrease of the contact angle actually dominates the increase of traction, any lowering of surface tension due to released decanoate having an opposite effect.

¹This concentration is more than 10^5 times higher than observed in indoor environments [5].

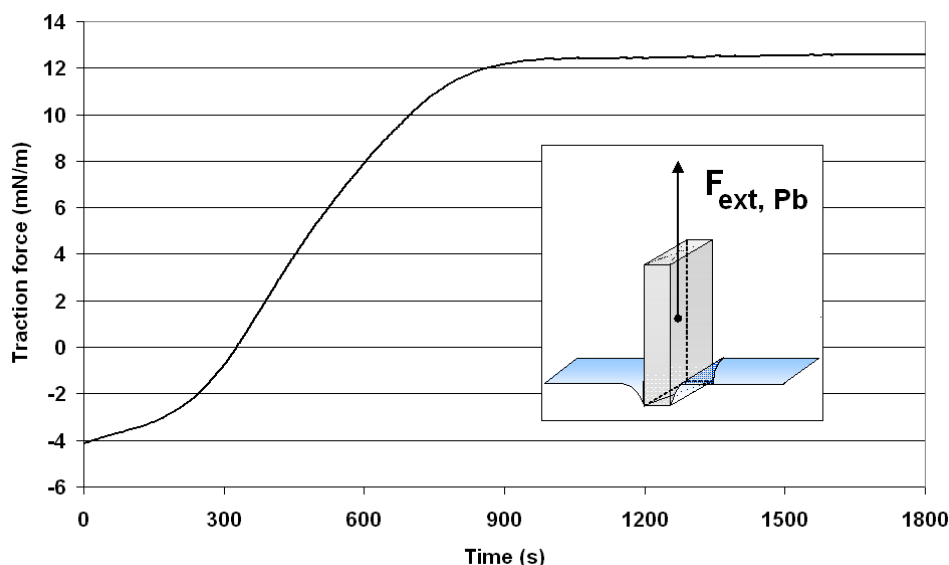


Figure 9.2: Traction force on a decanoate treated lead platelet as a function of time, pure water serving as a test liquid. Inset: initial configuration with $\theta = 113.9^\circ$, progressively decreasing.

A decanoate solution with concentration well above cmc initially was presumed most appropriate as a test liquid for contact angle measurements, countering decanoate desorption and its effects. Surface tension and conductivity were measured as a function of the NaC_{10} concentration in order to determine the cmc (Figure 9.3). The relationship appears characteristic of many surfactants [6]. The bent actually marks a saturation of interfacial adsorption, in this case at about 3.6 mM. The conductivity curve (squares) shows a distinct discontinuity already at 1.5 mM, indicating a limitation of the free decanoate ion concentration in the bulk while interfacial adsorption still is in the process of saturation.

Anyhow, from Figure 9.3, it is evident that a real cmc, in the case of decanoate, does not occur, even when saturation of interfacial adsorption clearly shows up at the aforementioned concentration. Droplets of higher concentration, serving as test liquid in contact angle measurements, inherently show a low surface tension and enhanced spreading. The latter seriously deteriorates the symmetry of sessile drops of any such solutions on decanoate

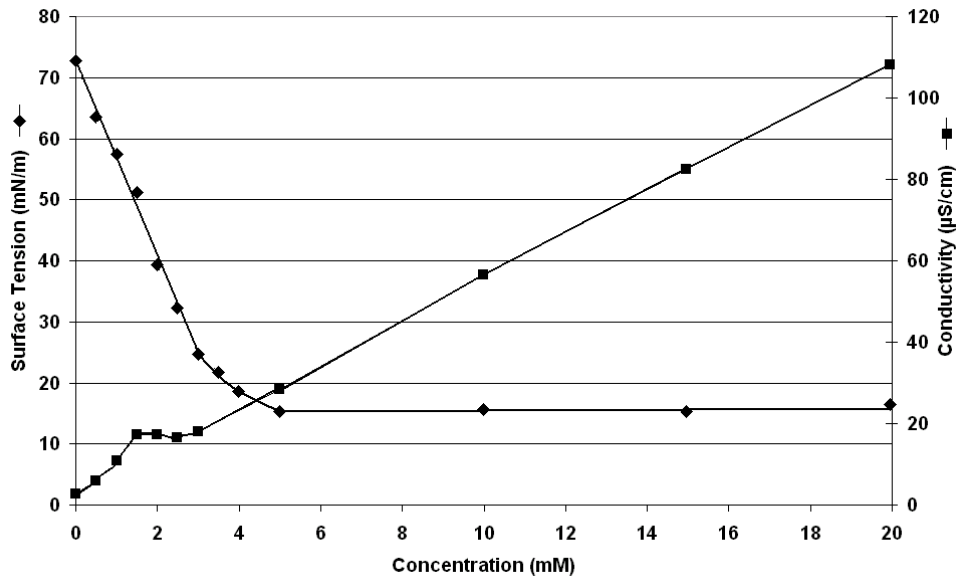


Figure 9.3: Surface tension and conductivity as a function of added NaC_{10} .

treated surfaces. This is the reason, actually, why the use of concentrated decanoate solutions as test liquids was abandoned in contact angle measurements.

Furthermore, from Figure 9.2, it is clear that decanoate desorption and its complicating effects remain negligible during the first tens of seconds. This actually allows to determine contact angles to a sufficient degree of accuracy, with pure water serving as the test liquid. Consecutive tests prove the error to remain below 1 degree, during the first five minutes.

The fractional surface coverage ($0 \leq \epsilon \leq 1$), function of treatment time, could therefore be assessed on a basis of contact angle measurements using droplets of deionized water. The fractional surface coverage was calculated on a basis of the Equations 2.22 and 2.23 (Figure 9.4).

The initial contact angle of 88.8° (on bare lead) is found to increase to about 113.9° after one hour, the most rapid increase taking place during the first 15 minutes. A similar profile is obtained for the fractional surface coverage. Starting with bare lead substrates, the coverage reaches 91% after 15 minutes and about 100 % after 1 hour.

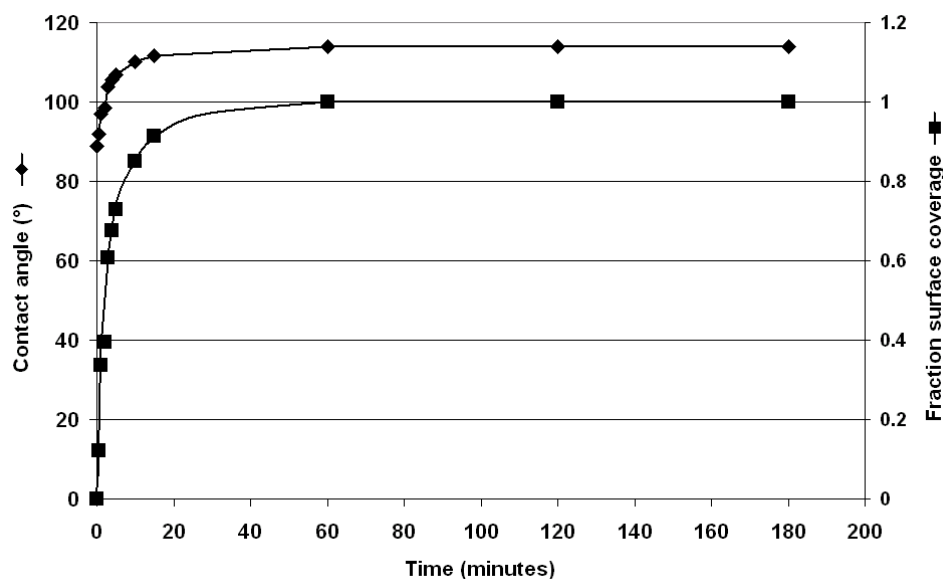


Figure 9.4: Contact angle and fractional surface coverage as a function of treatment time.

9.2.2 Monitoring of coating resistance

The application of coatings was followed by electrochemical impedance measurements, the outcomes of which are compared with data obtained in the in-situ experiment discussed in Section 7.2.2.

Figure 9.5 shows EIS data, which can be interpreted using the model described in Subsection 7.2.2. However, it is impossible to interpret the first plot (see inset), since the surface changes fast (possible formation of a native oxide layer). It must be noted that in the beginning, starting from a pure metal surface, only low impedances are measured. It is therefore suspected that the impedances of the pure metal, probably in the order of $k\Omega$, are not in the order of $M\Omega$. The stretched halfcircles can be fitted to obtain information about the constant phase element (Table 2.1). The α -values of the CPE as a function of time are given in Table 9.1. The increasing values indicate that the degree of depression decreases, which is a strong argument to validate the suggested model. Layer resistances, applied in solutions prepared by our protocol (Section 8.3), are much higher $\sim 2.6 M\Omega \text{ cm}^2$

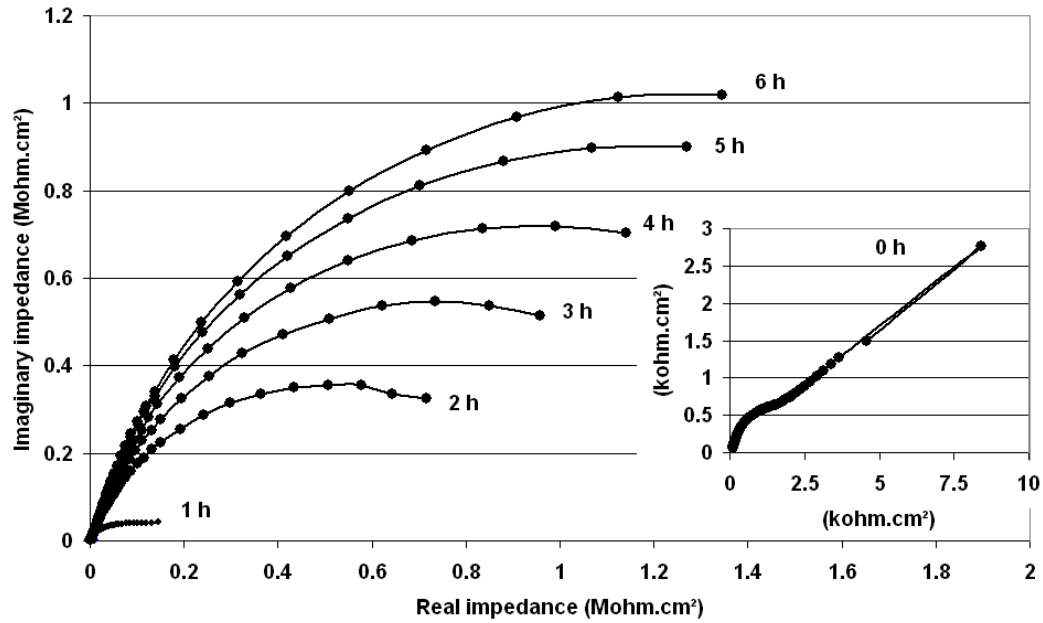


Figure 9.5: Nyquist plots of EIS data measured ex-situ applied in sodium decanoate solutions characterized by pH.

after 6 hours (diameter of the 6h fitted half-circle), indicating much improved coverage of the lead. The values for the coating resistance from the fitted depressed half circles have an almost linear tendency after more than two hours (Figure 9.6).

Table 9.1: α values of the CPE as a function of application time (solution prepared by our protocol (Section 8.3)).

time (hours)	1	2	3	4	5	6
α -value	0.59	0.77	0.80	0.83	0.85	0.86

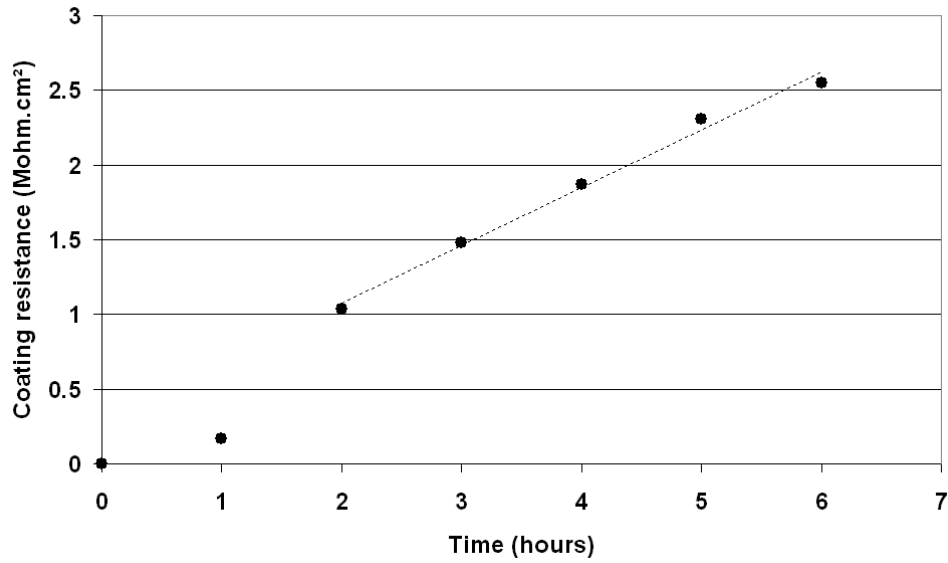


Figure 9.6: Coating resistances obtained from fitting the obtained data.

9.2.3 Impact of diffusion on coating process

Figure 9.7 relates mass gain to the thickness (4.5 mm, 8.5 mm, 12.5 mm and 50 mm) of the liquid layer in contact with the plates, upon treatment. At the lowest layer thickness, the mass gain is dominated by parabolic behaviour, but then becomes increasingly linear.

The constant deposition rates at 12.5 mm and 50 mm layer thickness imply a uniform transport density $J(x, C)$ and concentration gradient $\partial C / \partial x$ at various distances (x) to the solid/liquid interface, as required by the continuity principle and Fick's law:

$$J(x, C) = -D \frac{\partial C}{\partial x} \quad (9.2)$$

where D represents the diffusion coefficient of the decanoate ion. The curves indicate a limitation of transport at any fluid layer thickness of less than 10 mm. Lower gain rates at 4.5 mm and 8.5 mm layer thickness mark occurring depletion and limiting effects of transport parallel to the surface.

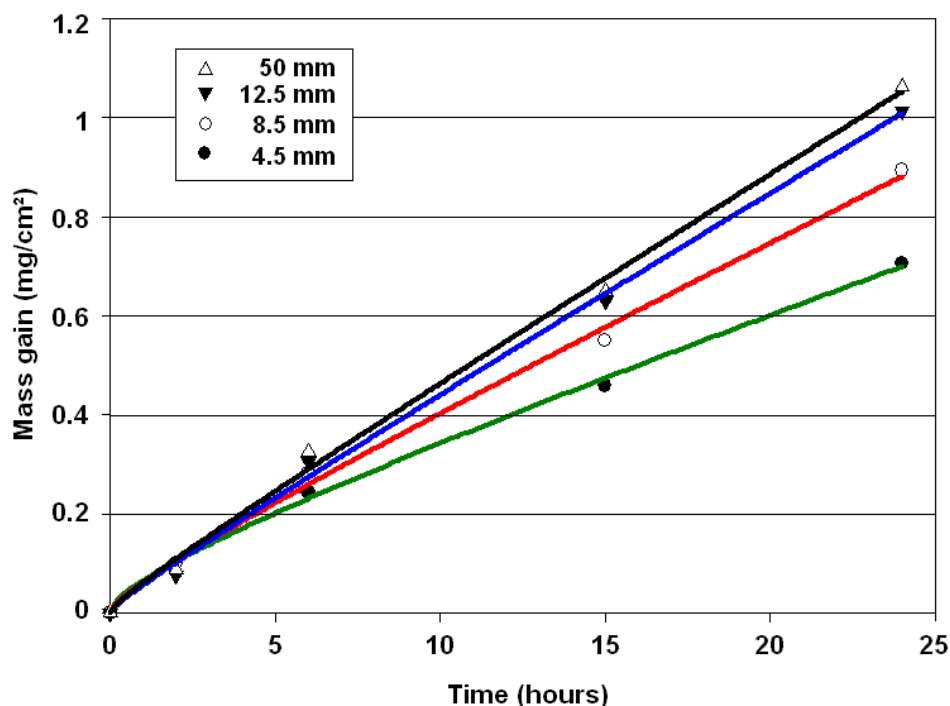


Figure 9.7: Mass gain as a function of time for varying thickness of the decanoate solution layer that surrounds the lead substrate.

These results have some implementations concerning the measurements performed using *eCell*. The thickness of the electrolyte layer on top, using *eCell*, measures 3-4 mm, implying that some depletion effects could occur (Figure 9.7). However, the situation is more complicated since the electrode is moved for positioning between X-ray analysis and electrochemical measurements. This certainly affects the transport characteristics and the growth rate of the coating.

9.2.4 Study of in-situ corrosion

Untreated lead

In Figure 9.8, a set of raw X-ray images monitoring the progressive corrosion of lead is shown. During the first hours (0h00 till 1h30), the visible bands constitute the diffraction

pattern of lead. After two hours, some diffraction spots already show induced corrosion. The spots are well-defined since corrosion crystals grow in preferred orientations. The detected corrosion product was identified as lead acetate ($Pb(CH_3COO)_2$).

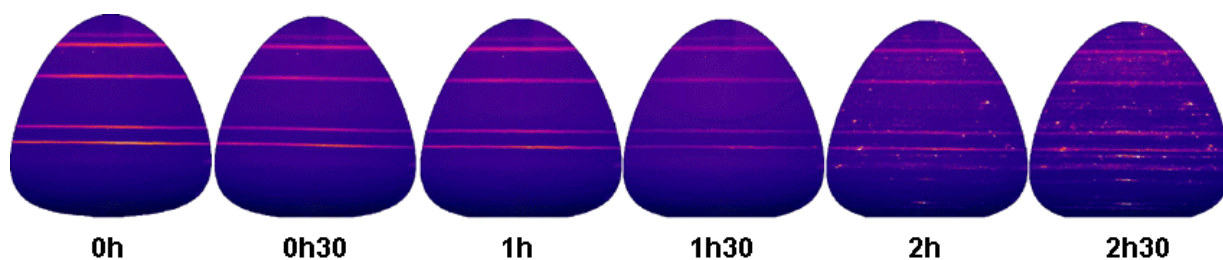


Figure 9.8: Raw X-ray data of the corrosion experiment on uncoated lead. The image, after two hours, displays diffraction spots that indicate the formation of corrosion products.

The intensities of some of the main peaks of lead and lead acetate from both experiments are presented as a function of time (Figure 9.9a and b).

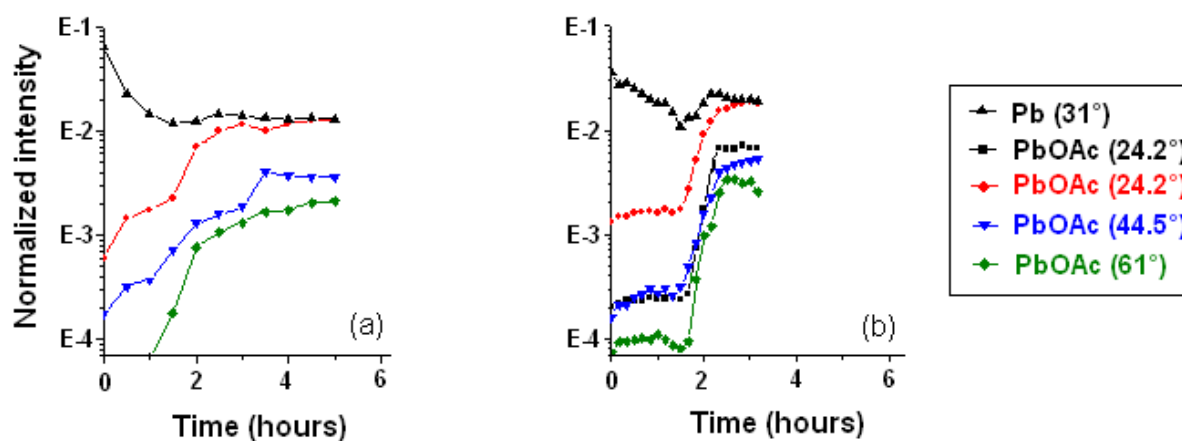


Figure 9.9: Real-time SR-XRD data for 6.3% acetic acid exposure at 75% RH (from [7]).

The first experiment (a) shows progressive attack of the metal. The intensities of the lead acetate peaks, despite the preferred crystalline phases, are in agreement with each other. They show a progressive corrosion of the metal, starting immediately after exposure. After some time, the intensities become almost stable, meaning that no further corrosion products are formed. The second experiment (b) shows a totally different corrosion behaviour. The corrosion seems to start abruptly after two hours. After some time, the intensities stabilize, indicating that no further corrosion develops on the surface.

Treated lead

A set of raw data dealing with in-situ corrosion of coated electrodes is presented in Figure 9.10. The image sequence should be interpreted the same way as in case of the bare lead substrate, the only difference being that more bands are visible from the start on, due to the presence of the coating. After 7 hours, XRD images feature clear diffraction spots, indicating the formation of lead acetate.

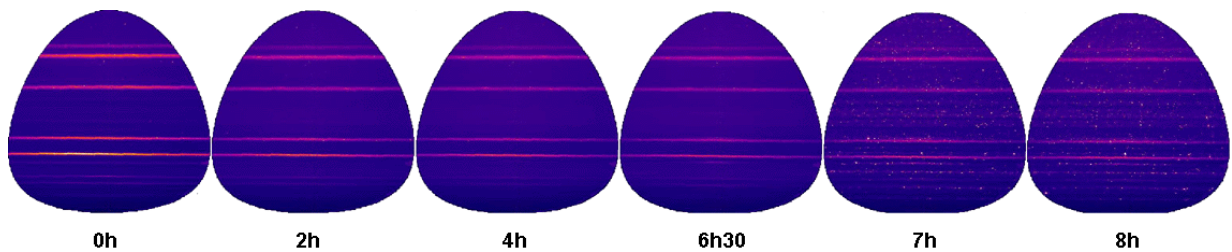
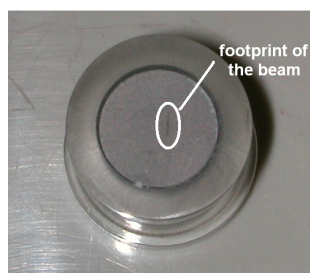


Figure 9.10: Raw X-ray data resulting from the corrosion experiment performed on a decanoate coated lead surface. At the beginning of the experiment, only characteristic diffraction peaks of lead are observed. After seven hours, the image features well-defined diffraction spots, indicating corrosion.



X-ray diffraction is assumed to be non-destructive. However, it was observed that the coated sample, after exposure, shows a clear footprint of the beam. At this point, it remains unclear how the beam affects the surface. This will be elaborated further, in future.

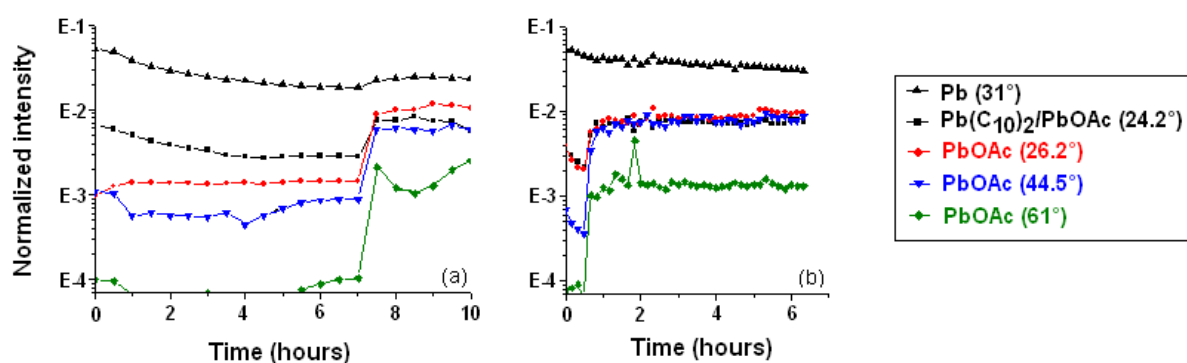


Figure 9.11: Real-time SR-XRD data for 6.3% acetic acid for exposure to 75% RH (from [7]).

The results of real time exposure to acetic acid vapour is summarized in Figure 9.11a and b, where peak areas of key peaks of lead, lead decanoate and lead acetate are shown. In the first experiment (a), the breakdown of the coating takes place, very abruptly, after 7 hours of exposure. Thereafter, the surface remains quite stable. The images imply that the net corroded areas are too small to produce strong diffraction rings, but introduce spots due to local preferential orientations. The second experiment is very similar, except that the breakdown occurs already after 40 minutes. Afterwards, a relatively stable situation is maintained.

9.3 Discussion and conclusions

Solid/liquid contact angle measurements, using water as the test liquid, allow the determination of the fractional surface coverage of Pb substrates coated with $Pb(C_{10})_2$, as a function of treatment time in an accurate way. The perturbing effects of decanoate desorption hereby remain negligible, provided the measurements are done within a reasonably short time.

Starting with bare lead substrates, the initial contact angle of 88.8° is found to increase to about 113.9° after one hour, the most rapid changes taking place within the first 15 minutes (Figure 9.4). The surface coverage proceeds at a similar rate, reaching 91% after 15 minutes and about 100% after 1 hour.

The coating resistance, as discussed in Figure 9.5, at this point, can be compared with the results obtained in Figure 7.11. The variation of coating resistance clearly shows the effects of dissimilar preparation of the solutions used for the application. A solution prepared according to our protocol, guarantees a dense coating and optimal deposition.

The layer thickness of the decanoate solution in contact with the substrate, clearly affects the growth rate (Fig. 9). The highest deposition rate is obtained in conditions of uniform decanoate transport towards the surface. Decanoate transport in such conditions is diffusion limited, with the decanoate concentration linearly decreasing towards the substrate. Any layer thickness below 15 mm, for a 24 hours treatment, markedly decreases the mass gain rate because of depletion and limiting effects of transport parallel to the surface.

From the data gathered from in-situ monitoring of the corrosion of lead, it is difficult to formulate a decisive conclusion: it appears that after corrosion attack, the surface remains almost stable. It is suspected that a superficial lead acetate layer drastically decreases the corrosion rate, thereby protecting the underlying metal. However, long term exposure to similar environments leads to active corrosion, which results in total disintegration of the metal [8].

Data dealing with in-situ corrosion of coated substrates appear more reliable. A sudden formation of corrosion products, most probably, indicates effective protection of the metal substrate until breakdown of the protective layer. This suggests that the coating forms a physical barrier between the environment and the metal. The stable region after the breakdown does not exclude that the present decanoate ions inhibit further corrosion. From that point of view, the protection should not only be physical, but also chemical.

Overall, the in-situ experiments show that *eCell* is a valuable instrument for the monitoring of corrosion development. It should be noted, however, that the concentrations of acetic acid, as used in the cell, are unrealistically high in comparison with indoor environments (even in closed display cabinets). A better approach would be to simulate exposure in well controlled environments over a long period of time and to schedule measurement sessions periodically to monitor the occurring changes. The experiments, in this way, would be more realistic and would provide information of long time exposure.

9.4 References

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Summary and conclusions

The corrosion of lead objects primarily depends on the surroundings, e.g. on environmental conditions. When buried in soil or exposed to the atmosphere, a stable corrosion layer (mainly composed of lead carbonates) is formed, which, in general, protects the metal against further corrosion. However, lead artefacts can keep on corroding actively when stored in humid and organic acid atmospheres. Such circumstances often are created in wooden display cases, used in museums for storage or exhibition of art and archaeological objects.

Organic acids condense on the surface and dissolve the protective corrosion layer. The remaining core metal is then exposed to similar aggressive conditions, resulting in active corrosion. The corrosion products, which are more voluminous than the metal, push away the superficial and protective corrosion layer. If/when the process is not stabilized by any treatment, the entire object can turn into dust.

A possible treatment is the electrolytic reduction at constant potential. The object, during such treatment, acts as the working electrode in an electrochemical cell and the corrosion products are reduced. The objects, however, have to be dried once the reduction has finished. This is a critical step since recorrosion occurs on the surface, appearing as a visible yellow/red surface layer as a result of the formation of lead oxides.

In order to protect lead objects and to avoid the drying step in the case of reduced objects, a coating could be applied. Next to corrosion protection, the coatings applied to (often unique) lead artefacts may meet additional demands. The color, the reversibility and even

the treatment cost need to be considered.

This work is composed of two main parts. The first part handles a fundamental study concerning the electrolytic reduction process. A study on the application and characterization of a lead soap coating applicable to lead artefacts is described in the second part.

Electrolytic reduction of actively corroded lead objects

The electrolytic reduction was studied on actively corroded lead artefacts obtained from the Centre National des Arts et Métiers (CNAM - Paris). These samples were covered with a uniform corrosion layer, including active corroded patches. In a first series of experiments, investigating the cross sections of half-reduced samples, it was observed that the reduction starts on the metal/corrosion interface of the patches. The interface is present as metallic veins across these. The process then continues with the reduction of the uniform corrosion layer away from the interface. The consecutive reduction can be a result of a different porosity of both structures: The porous structure allows easy ion transport, resulting in initial reduction. The dense structures, on the contrary, are more difficult to reduce. First, the layer has to be soaked with electrolyte to ensure ion transport. In addition of this mechanism, it was possible to link the reduction curve to the ongoing reduction inside the corrosion layer.

In the next series of experiments, the morphological, superficial and chemical changes were studied as a result of the treatment. The morphological changes were studied using neutron tomography. Lead metal (high Z), in comparison with hydrogen, carbon and oxygen (low Z), almost does not absorb neutrons. Therefore, this method was very effective in differentiating metal and corrosion structures. Computer techniques allowed visualizing the corrosion structures, thereby showing the actual state of the object. Also the metal underneath could be visualized and studied for present details. The corrosion structures before and after reduction were studied using scanning electron microscopy (SEM). The volume of the patches with active corrosion had decreased and was clear at a $\sim 200\text{ }\mu\text{m}$ scale. The surface appearance of the uniform corrosion structures is granular, but, after

reduction, the surface is covered by lamellar structures ($\sim 20\ \mu\text{m}$). The increase in specific area could explain the recorrosion when drying the object. The chemical constitution of the corrosion structures was studied on powder samples, taken before and after reduction. All corrosion structures were composed of hydrocerussite ($2\text{PbCO}_3.\text{Pb}(\text{OH})_2$) and plumbonacrite ($6\text{PbCO}_3.2\text{Pb}(\text{OH})_2.\text{PbO}$). After reduction, only the presence of lead was observed, proving that the reduction occurred for 100%. The surface was studied in more detail using X-ray photoelectron spectroscopy. More lead hydroxide ($\text{Pb}(\text{OH})_2$) and less lead oxide (PbO) were observed on the surface after reduction. However, it should be noticed that the volumetric/depth ranges and the measurement conditions of XPS are totally different opposed to SR-XRD.

The effectiveness of the reduction treatment was studied on artificially corroded lead alloys. The binary alloys $\text{Pb} - \text{Sn}$, $\text{Pb} - \text{Bi}$ and $\text{Pb} - \text{Sb}$ (95 w% Pb) were exposed to vapours of formic acid, acetic acid, propionic acid and acetaldehyde to promote corrosion attack in several weeks. X-ray diffraction data of the observed corrosion products showed that the corrosion products were dependent on the organic substance. It should be noted that corrosion products of the alloying elements Sn , Bi and Sb were not observed. Electrolytic reduction, applied on these corroded alloys appeared effective for the $\text{Pb} - \text{Sb}$ alloy, in the sense that the surface finish obtains a dark grey appearance. For the $\text{Pb} - \text{Sn}$ and the $\text{Pb} - \text{Bi}$ alloys, the presence of the binary constituent inhibits the reduction process and the corrosion products are not converted. As a conclusion, the composition of the alloy is important, and has to be known before an artefact is treated by electrolytic reduction.

Study of a lead soap coating ($\text{CH}_3(\text{CH}_2)_8\text{COO})_2\text{Pb}$ (briefly $\text{Pb}(\text{C}_{10})_2$)

The coating was initially applied in 0.05 M of $\text{CH}_3(\text{CH}_2)_8\text{COONa}$ (NaC_{10}), prepared by the neutralisation of decanoic acid $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ (HC_{10}) to pH 7. The growth of the coating was studied in-situ using a spectro-electrochemical cell (*eCell*). This cell allows the in-situ monitoring of processes with electrochemical and spectroscopic techniques. For the monitoring of the coating growth, synchrotron based X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS) was used.

The deposition of the lead decanoate layer is observed by the increasing intensities of its characteristic diffraction peaks. Another series of diffraction peaks, corresponding to lead oxide, increased during the first two hours of the measurement, to slightly decrease afterwards. This shows that during the first two hours, the surface is covered simultaneously by lead oxide. The coating resistance and capacitance, obtained by EIS, are variable during measurements due to the finite time to perform an EIS measurement. However, fitting showed that the coating resistance changes linear with time after more than 3 hours. During the first hours, the coverage of the metal surface is incomplete, implying lower coating resistances. The linear tendency after three hours could be associated with vertical layer growth, which mainly determines the coating resistance.

The growth rate and thickness were determined on a basis of mass gain measurements. A sum of a hyperbolic and a linear function fits the data. These contributions could respectively represent 2D (surface coverage) and 1D layer growth (vertical).

SEM images agree with the proposed growth mechanism; islands of flakes cover the surface the first hour. After two/three hours, the islands fuse into a uniform flake covered surface layer. Longer application times have little effect on the surface appearance.

Laboratory experiments showed that the solution, used in the previous experiments, could not be prepared in a reproducible manner. Therefore, a strict protocol for the preparation of solutions that produce dense coatings was established. Decanoic acid is preferred as a starting product, rather than the corresponding salt, for economical reasons. The achievement of the protocol implied the evaluation of the coatings resistance as a function of the decanoic acid neutralization. The tightness and resistance reach their highest values upon treatment with almost neutralized decanoate solutions. The application of coatings using this solution enhances the process of nucleation and decreases the size of $Pb(C_{10})_2$ crystals, thereby improving the tightness and rigidity of the coating. The protocol was based on conductivity measurements.

The surface coverage was assessed on a basis of contact angle measurements of sessile

droplets on substrates, treated by solutions prepared according to our protocol. The selection of a test liquid for the contact angle measurements turned out to be more complicated than expected; the release of $Pb(C_{10})_2$ when using water droplets may affect the contact angle. The effect, however, remains negligible during the first tens of seconds, which allowed the use of water. The surface was covered for about 91% after 15 minutes and about 100% after 1 hour. The use of NaC_{10} as a test liquid, with concentrations well above the critical micelle concentration, could avoid these effects. However, the use of these liquids were abandoned due to spreading and non-uniformity of these droplets.

The layer thickness of the decanoate solution in contact with the substrate, clearly affects the growth rate. The highest deposition rate is obtained in conditions of uniform transport towards the surface. A 24 hours treatment demands a layer about 15 mm thick. Decanoate transport in such conditions is diffusion limited, with the concentration linearly decreasing towards the substrate. Any layer thickness below 15 mm, for a 24 hours treatment, markedly decreases the mass gain rate because of depletion and limiting effects of sidewise transport.

The protection of the coating was evaluated by monitoring the behaviour in corrosive acetic acid vapours using *eCell* and compared to similar exposure of uncoated (bare) lead substrates. The corrosion processes on bare lead metal could proceed either progressively or abruptly. The layer, however, seems to give a reasonable protection since breakdown is observed after some exposure time. The time before breakdown is observed is very variable and the breakdown itself occurs in an abrupt manner. In each case, the coverage of corrosion products, detected by the XRD, is less extensive after a shorter time than for the bare metal, thereby indicating possible inhibitive properties of the layer.

In summary, this PhD work aims at a better understanding of the electrolytic reduction process applied on lead artefacts exhibiting active corrosion. In addition, the potential of applying a lead decanoate coating as a protective layer was studied and optimized. The growth process of such a layer was studied in detail, leading to a better understanding of

the coating process. Preliminary tests revealed that the protection mechanism is associated with the application of the lead soap layer.

Suggestions for the future

Electrolytic reduction

The reason why the electrolytic reduction is not effective for some corroded lead alloys is not clear. It would be interesting to know why a small amount of alloying element inhibits the electrolytic reduction of the corrosion layer. In this work, no crystalline corrosion products were observed containing the alloying element. Other techniques could prove the occurrence of these corrosion products, and study the effects of their occurrence.

Corrosion testing of the coating

We studied the corrosion breakdown of the coating for a short time at unrealistic high concentrations of acetic acid. However, it is of major importance that, before application as protective coating on authentic museum objects, the long-term corrosion resistance is known. The experimental setup using *eCell* could be modified in order to create a better controlled environment (e.g. relative humidity, organics,...).

The growth of the coating

At this stage, it is not clear how the coating is growing in terms of crystal growth. There are strong arguments that a combination of one dimensional and two dimensional growth occur at the same time. The mechanism of growth at molecular scale is not clear. Some hypothesis could be supposed:

- Initially, lead dissolves from the substrate and reacts with C_{10}^- ions in the electrolyte. These adducts adsorb at the surface and form a crystalline layer. The continuous deposition finally results in the observed flake-shaped surface appearance.
- C_{10}^- ions migrate to the surface and react with Pb to form lead decanoate. The layer continues growing by the migration of Pb^{2+} ions through the layer to react with decanoate ions. Another possibility is the migration of decanoate ions through the

layer to react on the interface of the lead and lead decanoate layer. However, it should be surprising that the larger decanoate ions would migrate through the layer.

Samenvatting en besluiten

Loden voorwerpen corroderen vrij traag in atmosferische omstandigheden. De vorming van een passiverende laag, hoofdzakelijk bestaande uit loodcarbonaten, ligt aan de basis hiervan. Hoge relatieve vochtigheid in aanwezigheid van organische zuren (vb. azijnzuur) resulteert in een versnelde corrosie, dikwijls gerefereerd in de literatuur als actieve corrosie.

Deze corrosieve omstandigheden worden soms gecreëerd in uitstalkasten, lokalen van musea of kerken. Het hout van de kasten degradeert met vrijstelling van organische stoffen zoals azijnzuur. In weinig geventileerde ruimtes worden hierdoor lokaal hoge concentraties bereikt. Waterdamp en organische zuren kunnen condenseren op de bestaande (beschermende) corrosielaag van loden voorwerpen, en lossen deze lokaal op. Hierdoor wordt de resterende metaalkern blootgesteld aan dezelfde zure omstandigheden, resulterend in versnelde corrosie. De corrosieproducten worden gevormd aan de grenslaag van het metaal en de oorspronkelijke corrosielaag. Daar deze corrosiestructuren veel volumineuzer zijn dan de metaalmatrix, wordt de oorspronkelijke laag weggeduwd en brokkelt deze af. Het niet doorbreken van deze cyclus zou leiden tot een volledige desintegratie van het object. Een typisch voorbeeld is de corrosie van loden orgelpijpen: Het houten framework waarin de loden pijpen zijn bevestigd in combinatie met de moeilijk te controleren relatieve vochtigheid in kerken zijn omstandigheden waar actieve corrosie plaatsvindt.

Een mogelijke behandeling bestaat in elektrolytische reductie bij constante potentiaal. Het object fungeert als werkelektrode in een elektrochemische cel, waarbij de corrosieproducten bij constante potentiaal worden gereduceerd. De methode wordt reeds aangewend sinds

eind jaren '60, hoewel er tot op heden weinig fundamenteel onderzoek naar werd verricht. Een probleem van deze behandeling is dat de gereduceerde corrosiestructuren doordrenkt zijn van het elektrolyt en dienen gedroogd. Deze stap is vrij delicaat daar vernieuwde corrosie optreedt tijdens het droogproces. Deze corrosie is zichtbaar als een roodgele schijn op het oppervlak, afkomstig van loodoxides.

Een manier om actieve corrosie te verhinderen, al dan niet van gereduceerde voorwerpen, zou een grote vooruitgang betekenen. In dit verband zou een beschermende coating zeer efficiënt kunnen zijn. De vereisten voor een coating aangelegd op authentieke voorwerpen, zijn uiteraard meer dan enkel verhinderen van corrosie. Denk hierbij aan een esthetisch aanvaardbare kleur, de reversibiliteit en kostprijs.

Dit werk is opgebouwd uit twee grote delen: Enerzijds werd fundamenteel onderzoek verricht betreffende het elektrolytisch reductieproces met als doel meer inzicht te verkrijgen in deze behandelingsmethode. Anderzijds werd een nieuwe coating bestudeerd om loden voorwerpen te beschermen op basis van de loodzeep $(CH_3(CH_2)_8COO)_2Pb$.

Elektrolytische reductie

De reductie werd bestudeerd op actief gecorrodeerde stalen ter beschikking gesteld door het Centre National des Arts et Métiers (CNAM - Parijs). Deze stalen vertoonden niet enkel een uniforme corrosielaag, maar ook actief gecorrodeerde structuren. In een eerste reeks experimenten, uitgevoerd op de dwarsdoorsneden van half-gereduceerde stalen, werd aangetoond dat het reductieproces start met de actief gecorrodeerde corrosiestructuren vanaf de metaal/corrosie grenslaag. Deze grenslaag is aanwezig onder de vorm van loden aders die doorheen de actieve corrosiestructuren lopen. In een volgende stap wordt de uniforme corrosielaag omgezet naar metallisch lood. Deze reductie start ook hier van de grens tussen corrosielaag en metaal. Het feit dat de poreuze structuren eerst worden gereduceerd heeft wellicht te maken met de fysische eigenschappen (porositeit, gemakkelijk ionentransport) in vergelijking met de oorspronkelijke laag. Deze laag dient immers eerst doordrenkt te worden met elektrolyt vooraleer een reductie kan starten. Het profiel van de

reductiecurves werd gelinkt aan de veranderingen in de corrosiestructuren.

In een volgende reeks van experimenten werden de morfologische, oppervlakte en chemische veranderingen bestudeerd voor en na de behandeling. De morfologische veranderingen werden bestudeerd met neutronen tomografie, een uiterst geschikte techniek voor deze stalen; de resterende loodkern (hoge Z) absorbeert nagenoeg geen neutronen, doch de lage Z elementen waterstof, koolstof en zuurstof in de corrosielaag wel. Uit de gereconstitueerde beelden kon worden afgeleid dat de morfologie behouden bleef ~ 1 mm, en dat indien er zich veranderingen voordeden, deze zich op een veel kleinere schaal manifesteerden. Met behulp van computertechnieken werd het mogelijk om enkel de corrosiestructuren zichtbaar te maken. Dit kan bijvoorbeeld van belang zijn wanneer men wil nagaan in welke mate een loden object gecorrodeerd is. Anderzijds kan de resterende metaalkern worden gevisualiseerd, waarbij kan nagegaan worden welke details nog onder de corrosielaag aanwezig zijn. Het oppervlak voor en na reductie werd bestudeerd met behulp van raster elektronen microscopie (SEM). Uit de secundaire elektronenbeelden kon worden afgeleid dat een groot verschil bestond afhankelijk van het type corrosiestructuur. De poreuze, actief gecorrodeerde structuren waren na reductie in volume verminderd. Dit was duidelijk zichtbaar op een vergroting van $200\text{ }\mu\text{m}$, wat met het blote oog net waarneembaar is. De uniforme corrosiestructuren bestaan voor reductie hoofdzakelijk uit granulaire structuren ($20\text{ }\mu\text{m}$). Na reductie was een duidelijke oppervlaktevergroting waar te nemen. Het oppervlak was bezaaid met lamellaire structuren. Deze oppervlaktevergroting zou verklaren waarom het loodoppervlak na reductie zo snel terug corrodeert. De chemische samenstelling van de verschillende corrosiestructuren werd bestudeerd op poederstalen genomen voor en na reductie. Hieruit bleek dat alle corrosiestructuren bestonden uit dezelfde twee producten, namelijk hydrocerussiet ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) en plumbonacriet ($6\text{PbCO}_3 \cdot 2\text{Pb}(\text{OH})_2 \cdot \text{PbO}$). Na reductie werd met SR-XRD enkel de aanwezigheid van metallisch lood vastgesteld. Het oppervlak voor en na reductie werd in meer detail bestudeerd met behulp van X-straal foto-elektron spectroscopie (XPS). Hier werd duidelijk dat, relatief gezien, na reductie meer $\text{Pb}(\text{OH})_2$ en minder lood oxides aanwezig waren op het oppervlak.

De doeltreffendheid van de reductiebehandeling werd bestudeerd met artificieel gecorrodeerde loodlegeringen. De legeringen, bestaande uit 95% lood en 5% van ofwel *Sn*, *Bi* of *Sb*, werden gecorrodeerd in een dampfase van mierenzuur, azijnzuur, propionzuur of acetaldehyde. De gevormde producten werden geanalyseerd met behulp van X-straal diffractie. De corrosieproducten bleken afhankelijk te zijn van de soort agressor. Een opmerkelijk feit was dat geen corrosieproducten werden teruggevonden die één van de minderheidscomponent (*Sn*, *Bi* of *Sb*) bevatten. De elektrolytische reductie was zeer doeltreffend voor de *Pb* – *Sb* legering; het oppervlak na behandeling kreeg een esthetisch aanvaardbare donkergrijze kleur. Voor de *Pb* – *Sn* en de *Pb* – *Bi* legeringen was de behandeling niet doeltreffend; de corrosieproducten werden niet omgezet. Hieruit kan worden besloten dat de samenstelling van de legering zeer belangrijk is, en dient gekend te zijn vooraleer een object wordt onderworpen aan een elektrolytische reductie.

Studie van de loodzeep coating ($CH_3(CH_2)_8COO)_2Pb$ (afgekort $Pb(C_{10})_2$)

Het aanleggen van de coating gebeurde in een 0.05 M oplossing $CH_3(CH_2)_8COONa$ (NaC_{10}), verkregen door de neutralisatie van het overeenkomstige decaanzuur $CH_3(CH_2)_8COOH$ (HC_{10}) tot pH 7.

Er werd in detail gefocust op het groeiproces van de $Pb(C_{10})_2$ laag. Een eerste experiment bestond erin de groeisnelheid te bepalen. Hiervoor werden massawinst metingen uitgevoerd op loden plaatjes die gedurende verschillende aanlegtijden werden behandeld. Hieruit bleek dat de groei superlineair was, m.a.w. dat het eerste uur een zeer snelle groei kende, maar daarna tot een lineair verloop overging. De curve kon goed gefit worden met de som van een lineaire en een hyperbolische functie. De hyperbolische bijdrage kan geassocieerd worden met een tweedimensionale groei van de laag (horizontaal op het oppervlak), de lineaire bijdrage met een ééndimensionale groei (verticaal).

Een spectro-elektrochemische cel werd aangewend om de groei van de coating grondiger te bestuderen. De cel maakt het mogelijk om simultaan spectroscopische en elektrochemische technieken te uit te voeren. Gezien de kristalliniteit van het $Pb(C_{10})_2$ werd geopteerd om X-straal diffractie (XRD) aan te wenden in combinatie met elektrochemische

impedantiemetingen (EIS). Hieruit bleek dat de intensiteit van de karakteristieke diffractiepieken van het gevormde $Pb(C_{10})_2$ parabolisch stegen in functie van de tijd, daar waar de karakteristieke pieken van het onderliggende loodsubstraat quasi parabolisch daalden. Het parabolisch verloop van deze curven zou terug een aanwijzing zijn dat 2D groei bijdraagt tot de vorming van de coating. Een andere reeks diffractiepieken, afkomstig van loodoxide, vertoonde een lineair verband gedurende de eerste twee uren, om vervolgens licht te dalen. Dit betekent dat de eerste twee uur naast de loodzeep ook loodoxide wordt gevormd. De weerstand en de capaciteit van de gevormde laag zijn variabel gedurende de EIS meting als een gevolg van de meettijd. Dit in acht nemend kon worden afgeleid dat na meer dan drie uur een quasi lineair verband werd vastgesteld tussen de coating weerstand en de aanlegtijd. Dit kan geassocieerd worden met de veronderstelde lineaire verticale groei, dat de coating weerstand bepaalt.

Het oppervlak werd bestudeerd met behulp van SEM na verschillende aanlegtijden. Na een uur worden eilanden, bestaande uit schilfers, waargenomen op het oppervlak. Na twee à drie uur groeien deze eilanden dicht tot een uniform uitzicht van schilfers. Dit proces visualiseert de eerder veronderstelde 2D groei. Langere aanlegtijden hebben echter weinig invloed op het uitzicht van het oppervlak.

Tijdens het onderzoek werd duidelijk dat de oplossingen, bereid met evaluatie van pH, niet reproduceerbaar konden worden aangemaakt. Het voorgestelde protocol voor de aanmaak van meest beschermende coatings is in dit licht een belangrijke bijdrage. Decaanzuur is hierbij een goed uitgangspunt, gezien de relatief lage kostprijs in vergelijking met het corresponderende natriumzout. Daarom werd een vergelijkend onderzoek verricht naar de bescherming van coatings aangelegd in verschillend geneutraliseerde decaanzuur oplossingen. De meest beschermende coatings bekomen met bijna perfect geneutraliseerde oplossingen. De hoge concentratie aan decanoaat ionen vergroot daarbij de kans op nucleatie van lood decanoaat, en resulteert in een dense en beschermende kristallaag op het oppervlak. Het uiteindelijke protocol is gebaseerd op geleidbaarheidsmetingen.

De procentuele bedekkingsgraad werd bestudeerd met behulp van contacthoekmetingen van druppels gepositioneerd op gecoate oppervlakken. De keuze van een geschikte testvloeistof voor de druppels was niet evident. Het vrijkomen van lood decanoaat vanuit geadsorbeerde staat bij het gebruik van water druppels kan de grootte van de contacthoek beïnvloeden. De studie van deze effecten leerde dat desorptie van decanoaat verwaarloosbaar was indien de meting snel werd uitgevoerd (binnen een halve minuut). Op die manier werd verkregen dat de bedekkingsgraad nagenoeg 100% is na één uur behandeltijd. De gemeten contacthoek voor lood bedroeg 88.8° en 113.9° voor een nagenoeg 100% bedekt oppervlak. De desorptie effecten zouden echter kunnen worden vermeden door een testvloeistof te gebruiken die onafhankelijk is van voornoemde effecten. NaC_{10} oplossingen, met een concentratie boven de kritische micel concentratie (cmc), zouden de grootte van de contacthoek niet veranderen bij desorptie. Deze testvloeistof kon echter niet gebruikt worden wegens spreiding en non-uniformiteit van de druppels op het substraat.

De laagdikte van de decanoaat oplossing in contact met het substraat beïnvloedt de groeisnelheid. Een behandelingstijd van 24 uur vereist een laagdikte van 15 mm. Onder deze omstandigheden is het transport van de decanoate ionen diffusie gelimiteerd. De concentratie in de oplossing gedurende de behandeling verhoogt lineair in de richting van het substraat. De laagdikte voor een behandeling van 24 uur minder dan 15 mm, vermindert de afzetting door effecten van zijdelings transport.

Dezelfde spectro-elektrochemische cel werd aangewend om de in-situ corrosie van naakte en gecoate (6h, geoptimaliseerde oplossing) loodsubstraten te volgen met SR-XRD. In het celvolume werd hiervoor een corrosieve omgeving van azijnzuurdampen gecreëerd.

Beide metingen met het naakte substraat waren verschillend: in de ene meting werd abrupte corrosie ontwikkeling vastgesteld, terwijl de andere meting eerder een progressief verloop kende.

Bij de gecoate stalen was de breakdown zeer abrupt, wat betekent dat de coating een initiële bescherming biedt aan het loodsubstraat. In ieder geval, de corrosie, vastgesteld met XRD, is minder uitgesproken na een korte tijd dan voor het naakte substraat. Dit

geeft een indicatie naar de mogelijks inhibitieve eigenschappen van de laag.

Als algemeen besluit kan gesteld dat deze doctoraatsthesis een bijdrage heeft geleverd in het beter begrijpen van het elektrolytisch reductieproces toegepast op actief gecorrodeerde loden voorwerpen. Daarnaast werd ook de mogelijkheid onderzocht om loodzepen aan te wenden als beschermende laag. De optimale condities om de hoogste coating weerstand te bekomen werden bepaald. Het groeiproces is ook in detail bestudeerd en leidde tot een aantal nieuwe inzichten. Een aantal preliminaire testen toonde aan dat de coating bescherming biedt.

Suggesties voor de toekomst

Elektrolytische reductie

Het is nog stil onduidelijk waarom de elektrolytische reductie voor bepaalde gecorrodeerde loodlegeringen niet werkt. De reden hiervoor is nog steeds niet gevonden. Het niet voorkomen van kristallijne corrosieproducten van de legeringscomponent doet vermoeden dat de corrosieproducten van de legeringscomponent wellicht aanwezig zijn als niet-kristallijne materie. Andere technieken zouden het bestaan van deze corrosieproducten kunnen aantonen om zo de effecten ervan te bestuderen.

Testen van de coating

In dit werk werd de breakdown van de coating bestudeerd op korte termijn en met on-realistisch hoge aijnzuur concentraties. Het is echter van groot belang dat de corrosie bestendigheid op lange termijn gekend is alvorens deze te gaan aanbrengen op authentieke museumvoorwerpen. De experimenten op lange termijn zouden kunnen uitgevoerd worden met *eCell*, mits een betere controle van de relatieve vochtigheid en de concentratie van de organische zuren.

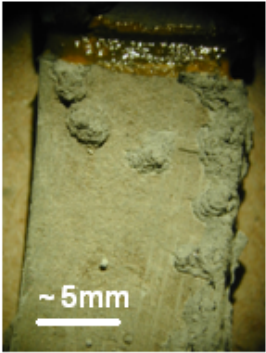
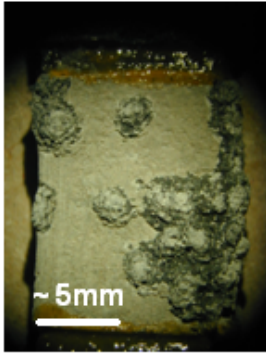
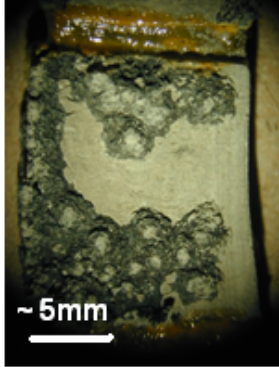
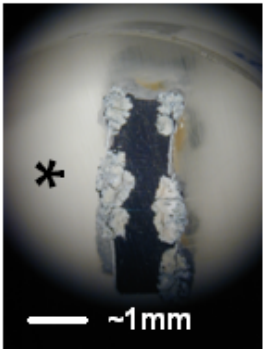
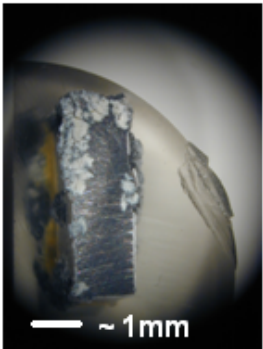
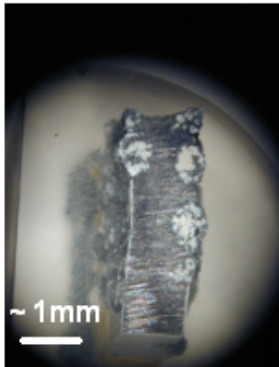
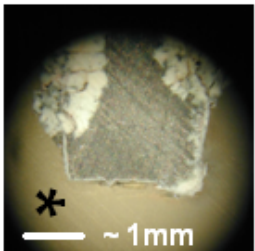
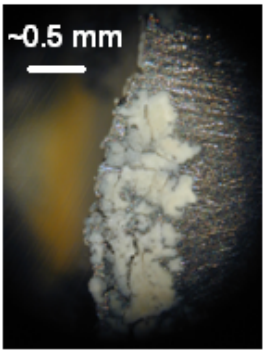
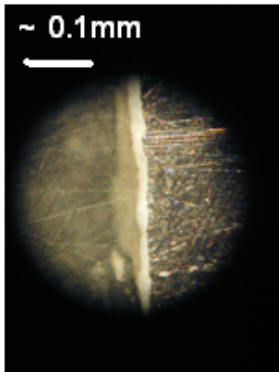
Groei van de coating

Op dit punt is het nog onduidelijk hoe de coating groeit. Er zijn sterke aanwijzingen dat het een combinatie betreft van één en tweedimensionale groei. Het mechanisme op moleculaire schaal is nog niet gekend. Enkele hypothesen kunnen worden onderzocht:

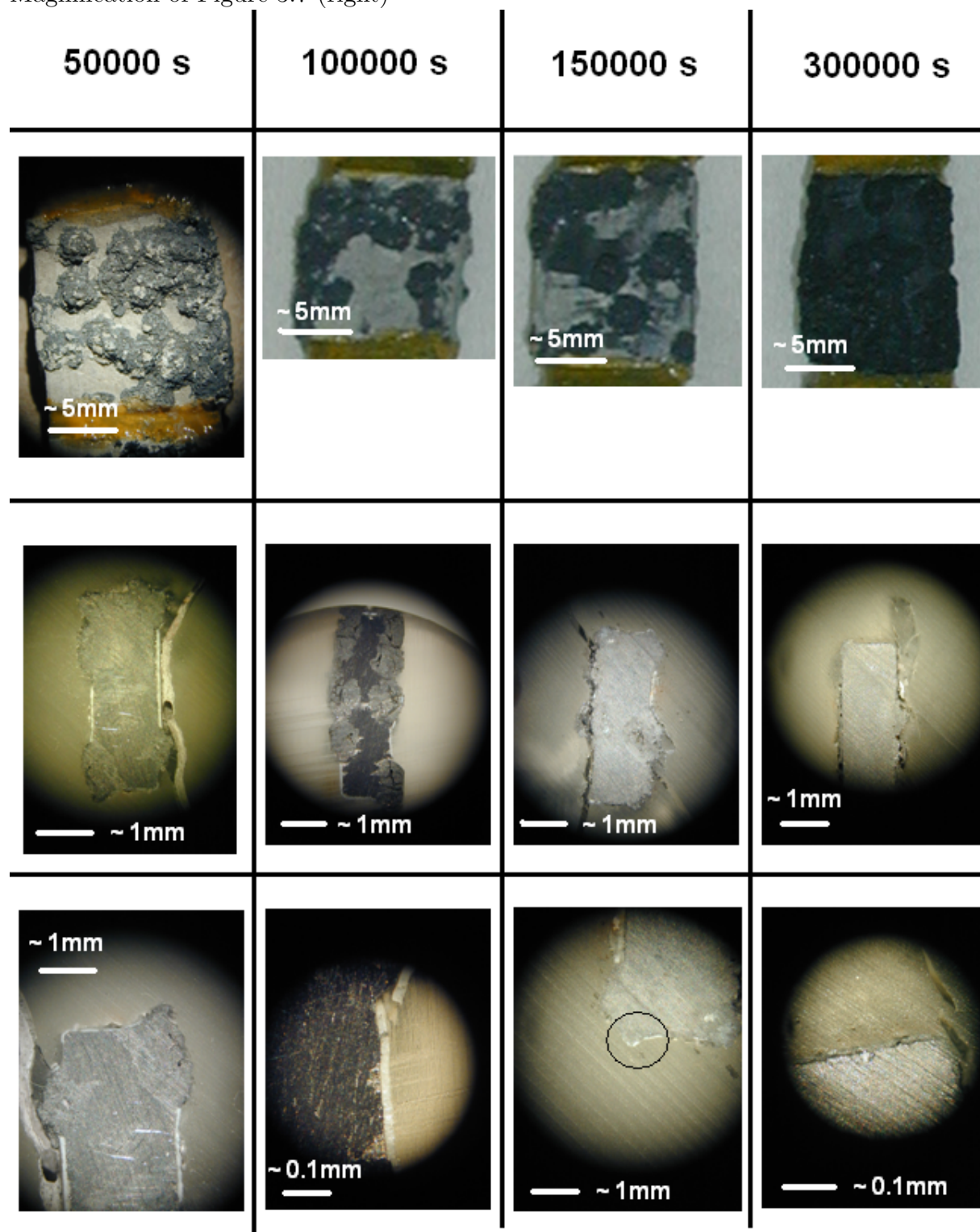
- Na onderdompeling van het substraat lost het lood aan de interface op en reageert met C_{10}^- ionen in het elektrolyt. Deze adducten adsorberen aan het oppervlak en vormen een kristallijne laag. De verdere depositie resulteert in een oppervlak bedekt met schilfers.
- C_{10}^- ionen migreren en reageren met Pb tot lood decanaat. De laag groeit verder door de migratie van Pb^{2+} ionen doorheen de laag om te reageren met decanoaat ionen. Een andere mogelijkheid is de migratie van decanoaat ionen doorheen de laag, om te reageren met lood aan de metaal/coating interface. Deze tweede mogelijkheid is echter weinig waarschijnlijk daar de grotere decanoaat ionen dienen te migreren door de reeds gevormde laag.

Appendices

Magnification of Figure 3.7 (left)

	0 s	10000 s	30000 s
Surface appearance	 ~ 5mm	 ~ 5mm	 ~ 5mm
Cross section	 * ~ 1mm	 ~ 1mm	 ~ 1mm
Detail image cross section	 * ~ 1mm * = epoxy	 ~ 0.5 mm	 ~ 0.1mm

Magnification of Figure 3.7 (right)



Magnification of detailed cross section after 150000 s. One can notice that the reduction of the uniform corroded layer proceeds from the interface of the metal and the corrosion layer towards the solution.

