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Conservation of organ pipes: protective treatments of lead exposed to acetic acid vapours

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Abstract

Indoor atmospheric corrosion of lead pipes is a severe problem for European historical organs. The action of the organic acid vapours emitted by the wood structures is known to be one of the main causes accountable for lead corrosion.

In order to develop a conservation strategy, the protective efficiency of different surface treatments for lead exposed to organic acids has been evaluated. In the present paper, the results of electrochemical measurements and artificial weathering experiments are reported. Lead specimens were treated by different inhibiting solutions: (i) sodium decanoate, (ii) sodium undecanoate, (iii) thiourea, (iv) sulphuric acid and (v) phosphoric acid. Polarisation curves (PC) offered a preliminary screening of the protectiveness of the treatments in acetic acid solutions. The treated surfaces were then exposed to acetic acid atmospheres. The protectiveness of the surface treatments was checked by Optical Microscopy (OM), Stereo Microscopy (SM), X Ray Diffractometry (XRD), Scanning Electronic Microscopy (SEM) with EDS (Energy Dispersive Spectroscopy) analyses. Gravimetric measurements (mass variation and weight loss) were performed. On the basis of the results, a comparative evaluation of the protective properties of the treatments was performed.

Keywords: lead, organ pipe, corrosion, protective treatments, weathering tests, corrosion inhibitors.

1. Introduction

Historical pipe organs are an essential part of the European musical and cultural heritage. One major danger for this heritage is the indoor atmospheric corrosion of lead and lead-tin alloys of organ pipes. It is well known that wood emits organic vapours, including acetic acid, that are corrosive towards lead (Graedel 1994, Shreir et al.1994, Hallebeek 1994, Tetreault et al.1998). Many of the European historical organs suffer from an increasing corrosion attack on pipe metal (lead rich alloys) and the number of historical organs affected by corrosion seems to grow rapidly. The aggressiveness of this kind of corrosion is a major environmental threat against pipe organs.

When the organ pipes corrode through, there is no other way to solve the problem than replacing the historic pipes with modern ones and a part of the sounding cultural heritage is forever lost.

In order to identify all factors responsible for the decay of the instruments and so to develop a conservation strategy, a research project (COLLAPSE, Corrosion of Lead and Lead alloys of Organ Pipes in Europe; www.goart.gu.se/collapse) composed of both field studies and laboratory experiments has been set up. During field studies, samples from corroded pipes in reference historical instruments have been taken and analysed (Chiavari et al. 2004) and the concentration of organic compounds in the atmosphere of the organs has been measured by the Department of Environmental Inorganic Chemistry, Chalmers University of Technology, Göteborg (Sweden).

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Meanwhile, in the same laboratory, experiments for the evaluation of the influence of environmental factors on corrosion behaviour are in progress (Niklasson et al. 2004). Laboratory experiments within COLLAPSE also aim at identifying and testing a set of surface treatments for the protection of lead-rich pipes from corrosion. The first results obtained are reported in this paper.

Candidate surface treatments for the protection of pipes have been selected on the basis of a survey of the literature. Treatments for both corroded and uncorroded lead were surveyed, however, the first step of the work, reported in this paper, is dedicated to uncorroded lead.

Many organic compounds are reported to provide a high degree of corrosion inhibition for uncorroded lead and lead alloys: thiourea protects lead alloys in acetic acid media (Fawzy et al.1981), tosylhydrazine protects lead from acetic acid vapours by blocking anodic reaction sites (Sankarapapavinasam et al. 1989, Sankarapapavinasam et al. 1990), pyrazole derivatives (-CH_3, -OCH_3 and -Cl derivatives of 3(5) amino, 5(3) phenyl pyrazole) are effective as corrosion inhibitors for lead in HCl solutions (Badawy et al.1990). The most interesting data on the protection of lead are reported by Rocca *et al*. (Rocca and Steinmetz 2001, Rocca et al. 2004): the ability of sodium monocarboxylates to react with lead and to form lead monocarboxylates and so to inhibit the aqueous corrosion of lead has been demonstrated and, in particular, sodium decanoate has been proposed as a promising inhibitor treatment for lead object exposed to acetic acid atmospheres. Also inorganic compounds such as phosphates (Boffardi 1990) are known to be effective as corrosion inhibitors for lead in aqueous solution. The formation of a protective layer of lead phosphate is proposed as an explanation of the protective efficiency of phosphate-based inhibitors: this suggests conversion treatments with phosphoric acid as an interesting option for the protection of lead. Similarly, the well-known resistance of lead to sulphuric acid is due to the formation of a layer of lead sulphate and also conversion treatments based on sulphuric acid have been proposed for the protection of lead. The protectiveness of layers formed as a consequence of the reaction between lead and sulphuric acid is evaluated and discussed in many papers on lead acid battery grids (Ruetschi and Angstadt 1964, Winand 1978, Ijomah 1988) as well as in conservation literature (Lane 1979, Degrigny and Le Gall 1999).

Different options are described in the literature for the treatment of corroded lead objects, the choice of the treatment method being related to the state of conservation as well as to the need of preserving surface details such as inscriptions or engravings that give important historical and artistic information. In the latter case, consolidative reduction is a well established method (Organ 1963, Carradice and Campbell 1994, Degrigny and Le Gall 1999). A more simple option, i.e. the application of an overlay coating, is likely to be the best one for organ pipes, since in this case it is not necessary to retrieve surface details but only to consolidate and protect from further corrosion. Most of the protection treatments developed for lead antiquities consist of an overlay coating of wax or lacquer applied on the object after stabilisation/consolidation of the corrosion products (Organ 1953, Organ 1963, Lane 1979, Nosek 1985, Watson 1985, Green 1989).

The selection of candidate surface protection treatments for lead was made on the basis of the (i) environmental impact, user-friendliness and dimensional requirements of the process for treating the surface; (ii) reversibility/irreversibility and aesthetical impact of the treatment.

In the present paper, the results of a comparative evaluation of the protectiveness of candidate surface applied on uncorroded lead are reported.

2. Experimental

Among the protective methods for lead, a set of candidate surface treatments to be applied on sample pipes has been identified and tested on lead coupons produced so as to mimic the recrystallised microstructure with equiaxed grains, which is typical of lead-based pipes.

In particular, the selected treatments were based on the following compounds: (i) linear sodium monocarboxylates ($CH_3(CH_2)_{n-2}COONa$), (ii) thiourea ($SC(NH_2)_2$), (iii) sulphuric acid (H_2SO_4) and (iv) phosphoric acid (H_3PO_4). All these treatments could be performed simply by immersion of the material to be treated into an aqueous solution at room temperature.

The protectiveness of sodium monocarboxylates was reported to increase with the number of carbon atoms (n) in the range between 7 to 11 (Rocca 2001), therefore sodium decanoate (n=10, henceforward C10) and undecanoate (n=11, henceforward C11) were selected for the comparative testing campaign. On the contrary, other organic corrosion inhibitors such as tosylhydrazine and pyrazole derivatives were not considered for this study because of their toxicity and because they were not conveniently available on the market.

In the first step of the experimental evaluation of the protectiveness of candidate treatments, commercially available 99.95 pure lead coupons (3x3cm) were polished by SiC abrasive paper up to 1000 grit, degreased and inhibited by immersion in the different aqueous solutions (with a total volume of 100 mL per coupon and a concentration in the range 0.5-0.05 M). The pH of the solutions has been measured at the end of the treatment.

In order to define the treatment conditions (concentration of the treatment solution and time of immersion of the sample), different measurements, such as mass variation of the samples, concentration of dissolved Pb in the treatment solution (measured by Atomic Absorption Spectroscopy) and characterisation of the conversion products on treated samples (XRD, SEM), were performed at increasing immersion time. The immersion time has been selected in the range of constant mass gain and constant Pb concentration in the treatment solution, considering these conditions as indicative of the formation of a stable layer on the surface.

Once the optimised treatment conditions were defined, a preliminary screening of the protective efficiency of the treatments in acetic acid solutions was performed by polarization current (PC) measurements, at short times. Cathodic and anodic polarization curves (1mV/s) were recorded by using a Solartron Potentiostat/Galvanostat model 1280B, after 1h immersion of the lead electrodes in 0.01M acetic acid solution neutralised with NaOH.

2.1 Accelerated corrosion tests

In order to investigate the corrosion behaviour of the treated samples exposed to a very aggressive acetic acid atmosphere, an accelerated corrosion test was set up, according to the procedure suggested by the Department of Environmental Inorganic Chemistry of Chalmers University of Technology (Niklasson, Johansson, and Svensson 2003). The corrosion tests were performed by exposing the coupons, hanging from a coupon rack in a desiccator, to acetic acid in gas phase (about 7 ppm), as illustrated in Figure 1. During the exposure, the temperature (T=22°C) was controlled by a thermostatic chamber. The maximum exposure time was 168h. Lead coupons were weighed before and after exposure.

Figure 1 Accelerated corrosion test equipment.

Before and after exposure, the surfaces of metal samples were also observed by Stereo Microscopy (SM), Scanning Electronic Microscopy (SEM) with Energy Dispersive (EDS) microprobe. Corrosion products on square samples were analysed by X Ray Diffractometry (XRD).

At the end of each test, after the characterisation of the oxidation products on the metal surface, the corrosion rates were determined by gravimetric measurements. The samples were pickled by an aqueous solution of ammonium acetate (250g/L), according to the ASTM standard procedure for weight loss measurements of lead and lead alloy (G1-03).

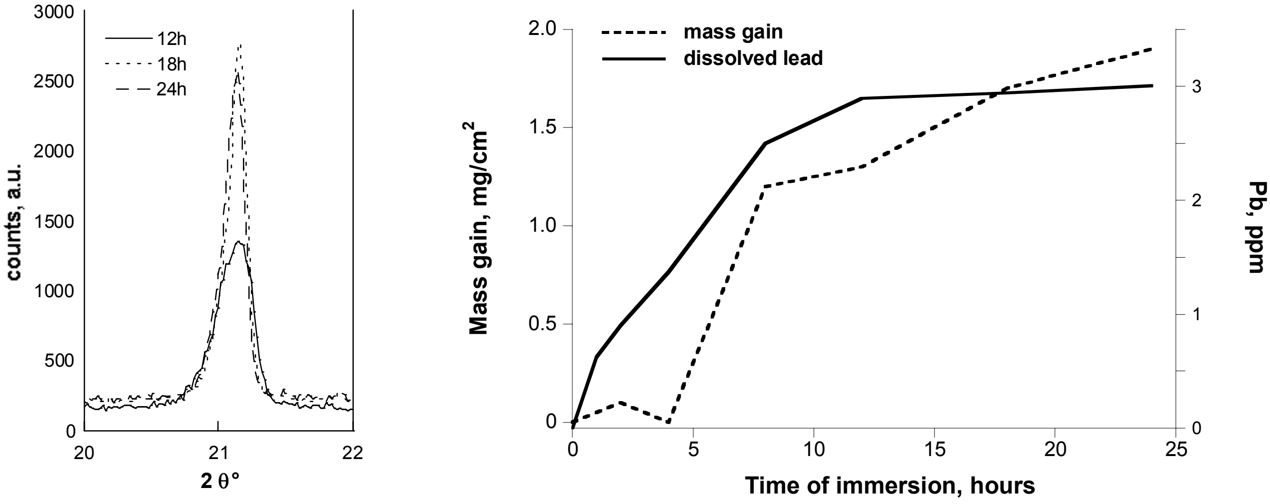


Figure 2

(a) (b)

Figure 2. Set-up of treatment conditions for lead sulphatising (immersion in H_2SO_4 0.05 M): (a) XRD pattern of the surface of suphatised lead: intensity of peak (101) of lead sulphate $PbSO_4$ at different immersion times; (b) mass gain of the lead coupon and concentration of lead dissolved in the treatment solution as a function of immersion time.

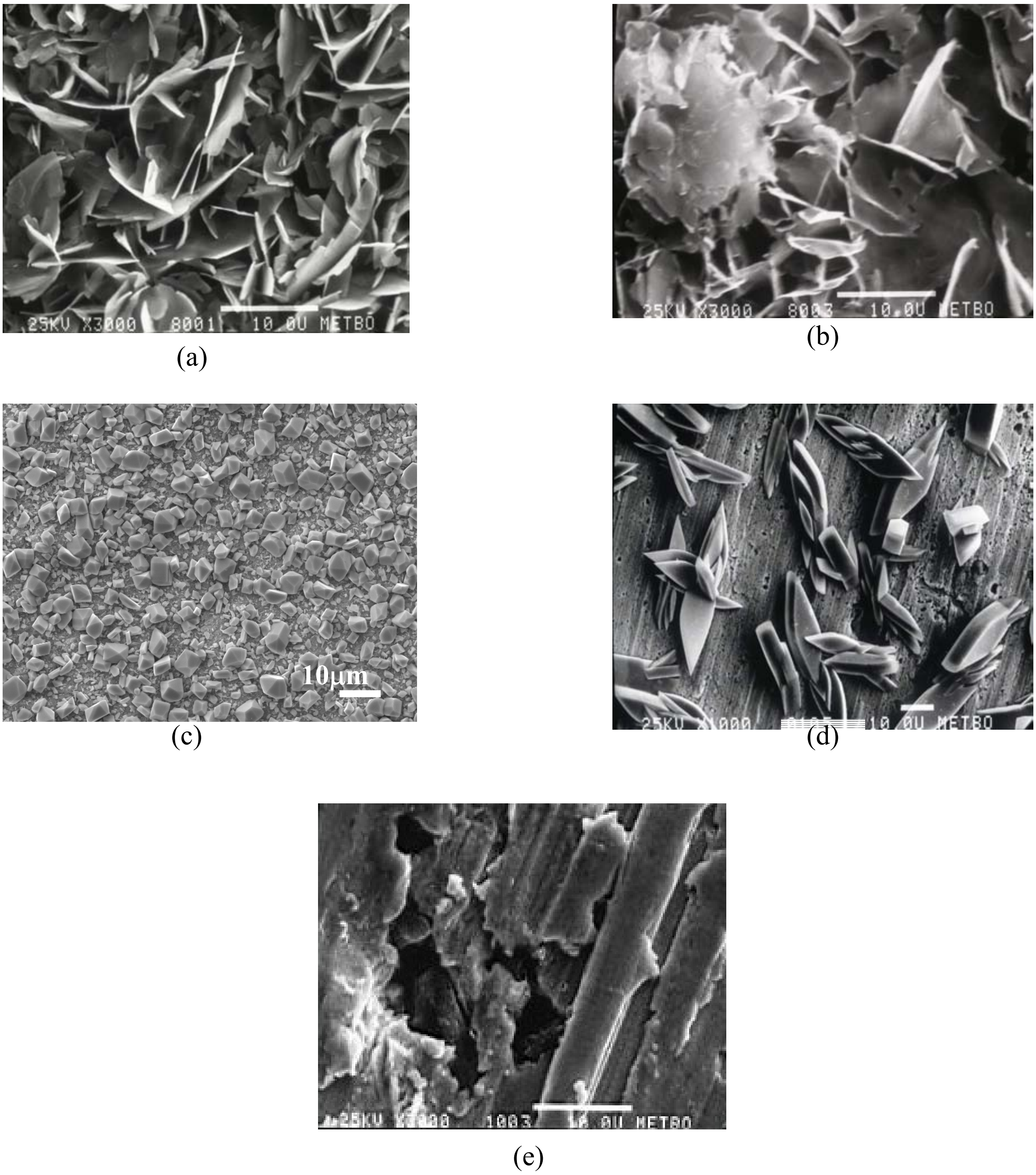
3. Results and Discussion

The lowest concentration in the testing range (0.05 M) produced a detectable layer of conversion products at different immersion times for each treatment; Figure 2 shows an example of the procedure for the definition of immersion time in the case of sulphatising. The intensity of peaks of lead sulphate ($PbSO_4$) increased with increasing immersion time from 12 to 18 h and then remained almost constant. Also mass variation and concentration of lead dissolved in the treatment solution remain constant from 18 to 24 h of immersion, probably indicating a complete coverage of the surface by a stable layer of conversion products.

Table 1 lists all the optimised treatment conditions. At the end of the treatment a very low amount of lead was measured in the sulphatising solution, whereas the highest amount of dissolved lead was determined in the phosphatising solution as indicated in table 1. It is worth noting that the treatments based on C10 and C11, applied in the conditions suggested by Rocca et al. (Rocca and Steinmetz 2001), were not aggressive towards lead, as demonstrated by the measurements of lead dissolved in the inhibiting solution (Table 1). Lead coupons have been immersed in the thiourea inhibiting solution for a short time (1 h) according to the indications reported in the literature (Fawzy et al.1981).

The morphology of the treated surfaces before exposure is shown in the SEM images of Figure 3 and the phase composition of conversion products is summarised in Table 2. Samples treated with C11 and C10 were covered by a continuous layer of flake-shaped crystals (Figures 3 a-b). XRD analyses showed that lead was converted into lead monocarboxylate, in agreement with data reported by Rocca et al. (Rocca and Steinmetz 2001).

Figure 3 Morphology of the treated surfaces before the exposures: (a) C10; (b) C11; (c) sulphatised (d) phosphatised; (e) thiourea.



(a) (b) (c) (d) (e)

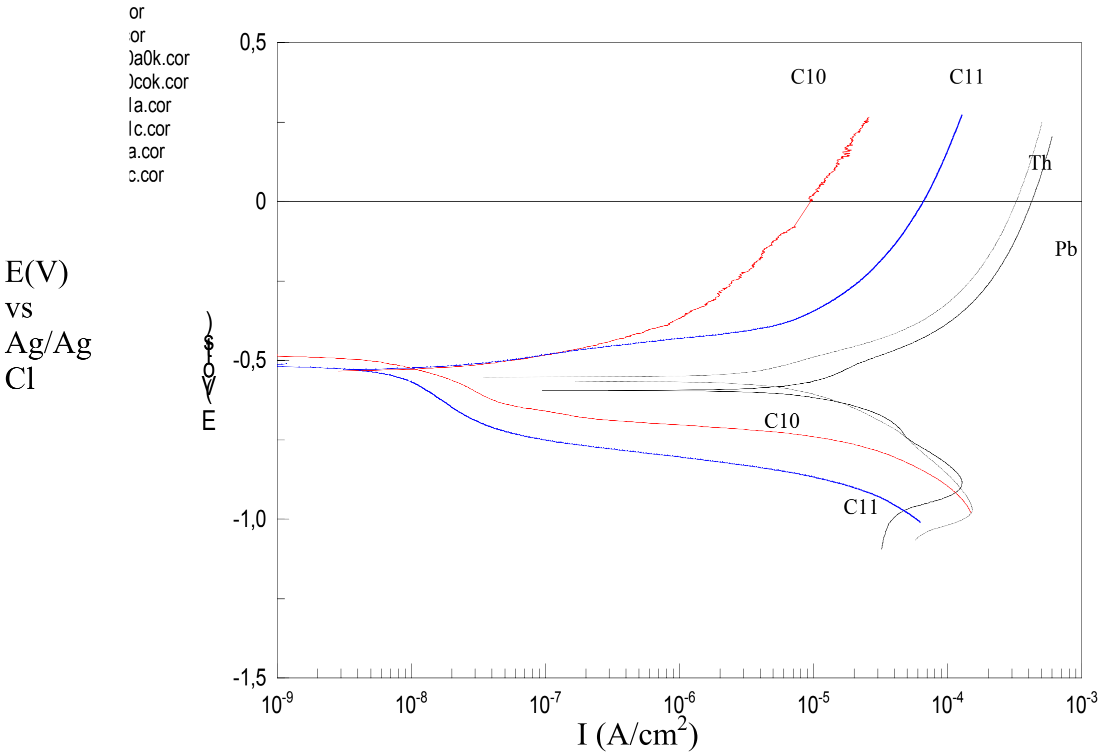
Sulphatising formed a continuous layer of fine-sized crystals (Figure 3c) of lead sulphate ($PbSO_4$), whereas phosphatising produced a discontinuous layer of lead hydrogen phosphate ($PbHPO_4$), consisting of isolated clusters and uncovered areas (Figure 3d) even after 30 h of immersion. After the immersion in the thiourea inhibiting solution, polishing marks were still visible on the surface (Figure 3e) and XRD spectra revealed the presence of an amorphous phase.

C10 and C11 treated surfaces showed a very high hydrophobicity, as reported in (Rocca and Steinmetz 2001, Rocca et al.2004), while the other treated surfaces were not hydrophobic, as demonstrated by the shape of a water drop in contact with the inhibited surfaces. It is also worth pointing out that C11 is less water soluble than C10, and therefore it tends to produce a less homogeneous layer of conversion products.

3.1 Electrochemical measurements

The anodic and cathodic polarisation curves are presented in Figure 4, where unprotected lead electrodes are compared with the treated ones. The PC plots show that, in the case of C10, the anodic current density decreased by two orders of magnitude compared to the blank electrode.

Figure 4 Anodic and catodhic polarisation curves of samples treated with organic inhibitors: thiourea (Th) or sodium monocarboxylates (C10, C11) compared with untreated lead (Pb) in neutralised acetic acid solution.

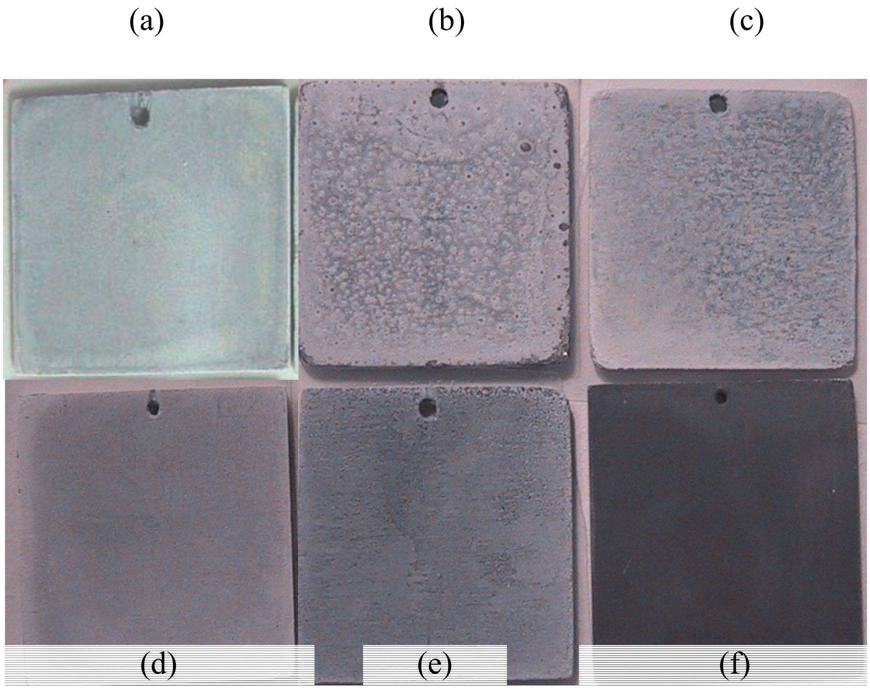


Treatments with C10 and C11 effectively reduced both the anodic and the cathodic polarization current values, whereas thiourea revealed a much weaker inhibiting action, showing a trend very similar to that of unprotected lead. As concerns sulphatised and phosphatised samples, the polarisation curves showed current values comparable to those of unprotected lead and, in the case of phosphates even lightly enhanced current densities were recorded.

The preliminary screening of the protective performance through electrochemical data showed that the most promising inhibitors for lead are C10 and C11.

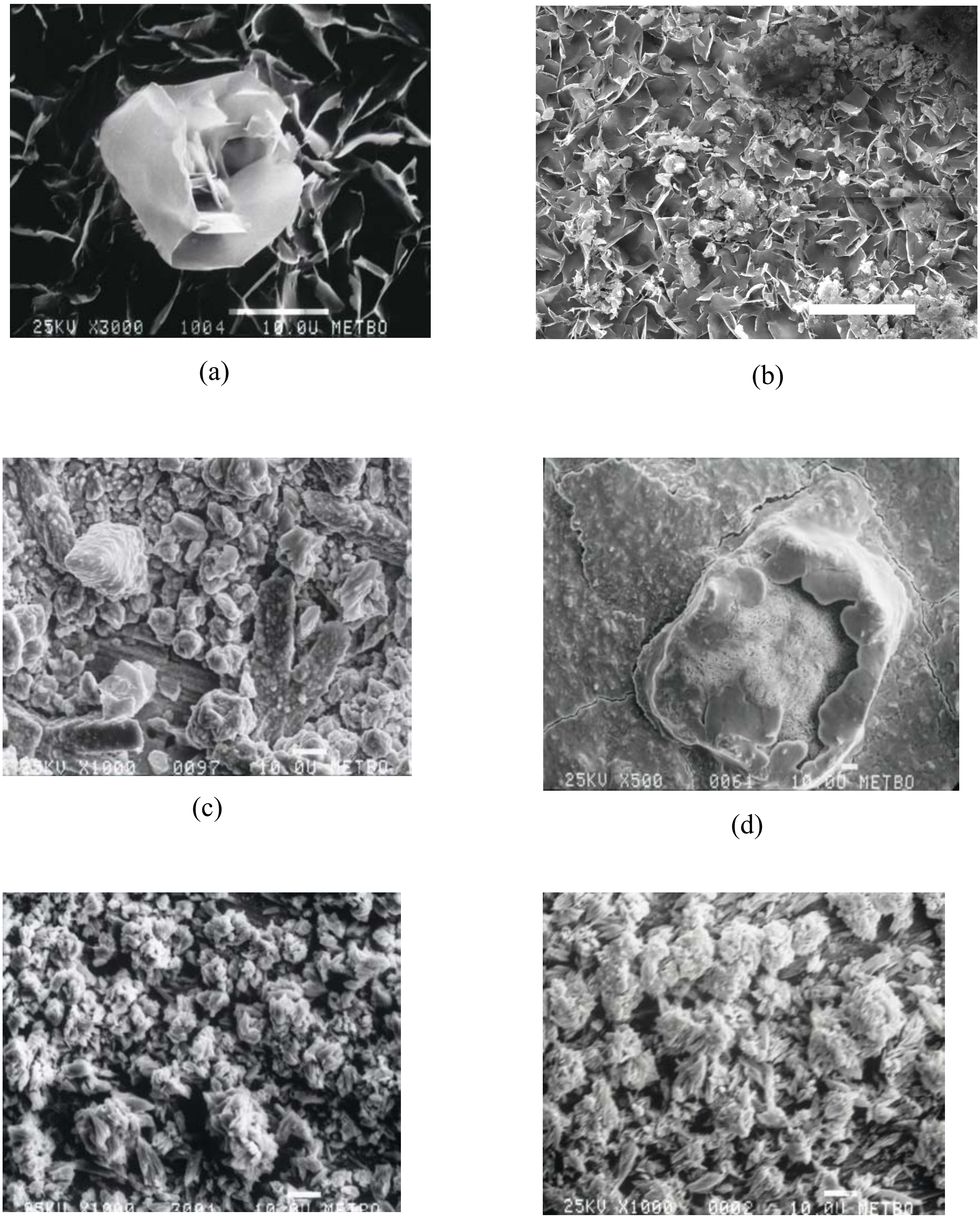
3.2 Accelerated corrosion tests

Figure 5 **Treated (a: thiourea; b: sulphatised; d: phosphatised; e: C10) and untreated (c) lead coupons after exposure; untreated and unexposed lead (f) is also shown for comparison.**



After exposure all treated surfaces showed the presence of corrosion products (Figure 5). In all cases the amount of corrosion products increased with increasing exposure time. Nevertheless, the morphology and the nature of the corrosion products change from treatment to treatment (Figure 6, Table 2). Actually, only scattered crystals of corrosion products grew on the unchanged surface of C11 and C10 treated samples: the layer of flake-shaped crystals of lead monocarboxylates was still clearly visible after exposure (Figures 6 a,b).

Figure 6 **Morphology of the treated surfaces after the exposures: (a) C10; (b) C11; (c) phosphates; (d) sulphates; (e) thiourea; (f) unprotected lead.**



(a) (b)

(c) (d)

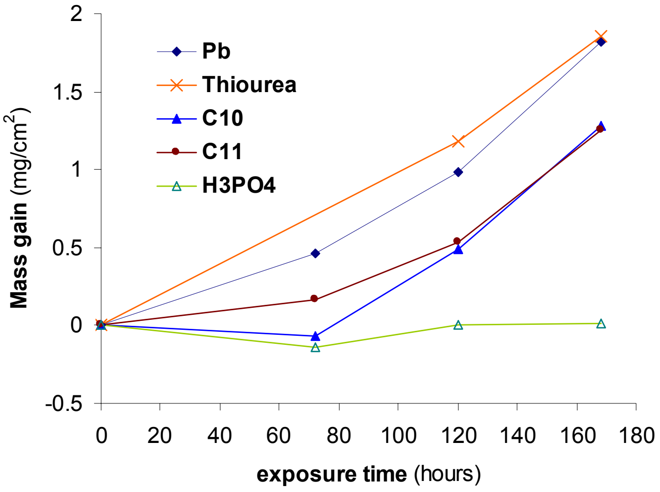
(e) (f)

Phosphatised samples developed a fine grained and adherent layer of corrosion products that fills in the gaps between the needles of lead phosphate (Figure 6c). On the contrary, the oxidation layer grown on samples treated with sulphates was brittle and non-adherent (Figure 6d). The exposed surface treated with thiourea revealed a morphology similar to that of unprotected lead.

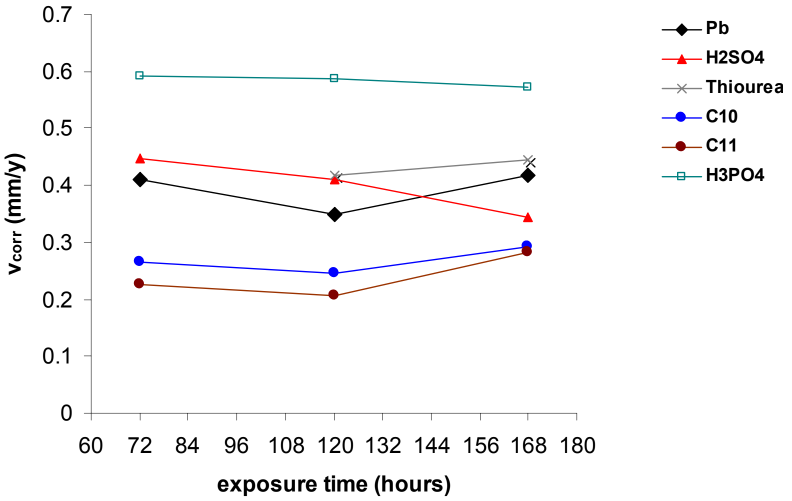
The phase composition of the oxidation layers determined by XRD is summarised in Table 2. The results point out the protective behaviour of the C10 and C11 treatments: after 168h of exposure to a very aggressive atmosphere, only traces of lead oxides and carbonates were detected. In addition, the peaks of lead and lead carboxylates were still well detectable as before exposure, revealing few alterations of the original protected surface. On the contrary, both on unprotected lead and on the other treated samples a thick oxidation layer formed, mainly consisting of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and in some cases plumbonacrite ($Pb_{10}(CO_3)_6(OH)_6O$), which are final products resulting from active corrosion processes involving acetic acid (Niklasson et al. 2004). In the case of sulphatised samples, the layer of $PbSO_4$ was still visible after the exposure, probably because the corrosion layer spalls off, whereas in the case of phosphatised samples the height of the peaks of $PbHPO_4$ strongly decreased. Besides crystalline compounds, the presence of an amorphous phase was revealed, in most cases, by a rising of the background line at low angle.

Gravimetric measurements were also performed in order to have further information on the inhibiting performance of the tested treatments. In the graph of Figure 7a dry mass gain values are reported as a function of exposure time for treated samples exposed to acetic acid. Treatments with C10 and C11 induced a lower mass gain compared to the case of pure lead, which indicates the formation of a lower amount of insoluble corrosion products on the protected surface. In the case of thiourea, the mass gain was slightly higher than in the case of unprotected lead. The lowest mass gain was found in the case of phosphatised samples, showing low and constant values during all the exposure period. The results on sulphatised samples are not included in Figure 7a because the brittleness of the corrosion layer induced a random mass decrease and the values were not reproducible.

Figure 7 Gravimetric measurements: (a) mass gain vs exposure time; (b) corrosion rate (v_{corr}) vs exposure time.



(a)



(b)

Table1 - Treatment conditions and data measured at the end of treatments.

	Concentration of treatment solution, mol/L	Immersion time, h	Mass gain, mg/cm^2	Concentration of dissolved lead, ppm	pH
C10	0.05	24	0.38	n.d.	8.7
C11	0.05	24	0.33	n.d.	7.3
Thiourea	0.05	1	0.03	1	6.6
H_2SO_4	0.05	24	0.40	3	1.3
H_3PO_4	0.05	30	0.07	30	1.9

n.d.: non detectable.

Table 2 - XRD analysis of products on the surface of lead coupons, before and after exposure.

Treatments	Pb	PbO	Hy	Pl	PbC10/C11	$PbSO_4$	$PbHPO_4$
Pb	++	--	--	--			
Pb, *168h ageing*	+/-	+	+	++			
C11	+	+/-	--	--	+		
C11, *168h ageing*	+	+/-	+/-	--	+		
C10	+	--	--	--	+		
C10, *168h ageing*	+	+/-	+/-	--	+		
Thiourea	+	--	+/-	--			
Thiourea,*168h ageing*	--	++	++	--			
Sulphate	+/-	--	--	--		+	
Sulphate, *168h ageing*	+/-	--	++	--		+	
Phosphate	+	--	--	--			++
Phosphate,*168h ageing*	+/-	--	++	++			+/-

-- (non detectable) ; +/- (traces) ; +(well detectable) ; ++ (abundant).
Hy (hydrocerussite, $Pb_3(CO_3)_2(OH)_2$); Pl (plumbonacrite, $Pb_{10}(CO_3)_6(OH)_6O$); PbC10/C11 (lead monocarboxylates)

The results of weight loss measurements, carried out by pickling the corroded samples in order to evaluate the corrosion rate, are shown in Figure 7b, where the values of the corrosion rate as a function of the exposure time are reported. The results of the weight loss measurements confirmed in most cases the trend of dry mass gain data. The corrosion rate of the C10 and C11 inhibited samples is lower by two orders of magnitude than that of all other samples. Thiourea and sulphatised samples corrode at the same rate of unprotected lead, confirming the low protectiveness of the two treatments. In the case of phosphates, the small mass gain and the very high corrosion rate suggest the formation of very soluble oxidation products and therefore a very unstable and unprotective patina that does not hinder the dissolution of lead. On the contrary, in the case of C10 and C11, the low mass gain and the low corrosion rates suggest a quite good insulation of the metal surface from the aggressive environment.

4. Conclusions

On the basis of the comparative evaluation of the candidate treatments, we can exclude treatments with sulphuric acid, phosphoric acid and thiourea as protective methods against corrosion of lead-rich organ pipes in acetic acid atmosphere.

The results of the comparison among the different tested treatments indicate that the protectiveness of the treatments with sodium undecanoate (C11) and sodium decanoate (C10) is (i) comparable and (ii) the highest among all the inhibitors tested on lead. Comparing the two monocarboxylate-based treatments, it can be said that, in the testing conditions, C11 is as protective as C10 but the lower solubility of C11 in water makes the production of an homogeneous layer more difficult. Consequently, the most promising candidate to be applied on uncorroded lead-rich pipes is C10.

It is also worth remembering that the reversibility of the treatment with C10 and C11, i.e. the possibility to remove lead carboxylates by a solvent like ethanol, is a feature of main importance in the case of organ pipes, where conservation measures have hitherto been mainly irreversible.

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