

STUDIES OF CHEMICAL CLEANING ON HISTORICAL LEAD

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Abstract

This study has been focused on the evaluation and comparison of the chemical treatments applied (aqueous solutions of CH₃COOH (1 %), CH₃COONH₄ (5/25 %), EDTA (3/5 %), HCl (5/10 %) and ion exchange resin) or possible applicable (H₂SO₄, Na₃PO₄·12H₂O or KNaC₄H₄O₆·4H₂O) to the heritage of lead stored in museums. The evaluation of the different solutions used for chemical treatment on lead samples is based on lead surface changes (colour, morphology, chemical composition) observation and on the impact of the chemical treatments (mass loss and cleaning efficiency). Examination of the lead samples before and after different chemical treatments showed that each of used solutions induced any chemical and/ or physical changes.

Keywords: Lead, chemical cleaning, chemical treatment, pickling, passivity

1. INTRODUCTION

Lead has been highly employed from ancient times to the present day (various artefacts of everyday life, statues, coins, organ pipes, stained glass) [1-5]. Due to its high corrosion resistance, many of these artefacts are stored in museums and archives [1-12]. The major risk to historical lead is acetic acid which concentration could be up to 20 times higher in museum environment than outdoors [4]. In the presence of acetic acid lead corrodes while voluminous corrosion products (mainly cerussite, hydrocerussite or plumbonacryte) without protective properties are formed [1-12]. Due high humidity acetic acid should be at least partly released from corrosion products and further lead corrosion process occurs [1,3,4,7]. Cleaning of corroded lead artefacts may be necessary either to stop the active corrosion and to restore its legibility and aesthetic appearance [4]. The chemical treatment of corroded lead prevents poisoning by inhalation of toxic lead corrosion products (compared to mechanical cleaning) and does not required any specific equipment and the skills of the conservator (compared to electrochemical cleaning) [4]. In the past the "Caley method" (aqueous solution of HCl (1:10)) or aqueous solution of H₂SO₄, CH₃COOH or CH₃COONH₄ to remove corrosion products from lead surface were employed. Now is frequently used chelating agent EDTA (aqueous solution 3-10 % w/w) [3,4,6]. In order to find the best way to remove corrosion product from historical lead surface due to chemical treatment was this research done.

2. EXPERIMENTAL PART

2.1. Samples

Lead samples (Pb 99.9 %) in dimensions 10 x 50 x 1 mm were used in this work. The evaluation of the different solutions used for chemical cleaning was carried out on lead samples with a pure lead surface and on lead samples with artificially prepared corrosion products (corroded lead samples). The pure lead surface was obtained with grinding of the surface with abrasive wadding (3M Scotch-Brite CF-MF), subsequent rinsing with ethanol and then air drying. The corroded surface was obtained by immersing the non-treated lead samples into HNO₃ (65 % w/w) for 20 minutes, subsequent fast replace (without rinsing by distilled water or another solution) of lead samples into (NH₄)₂CO₃ solution (5 g of (NH₄)₂CO₃/100 ml of distilled water) and immersing in this for 24 hours, subsequent rinsing by distilled water and ethanol and air drying. The surface composition of corroded lead samples was analysed by X-ray diffraction (XRD) with a X'Pert PRO diffractometer and

HighScore Plus software (Malvern Panalytical Ltd.). They presented 27 wt% of lead, 71 wt% of cerussite (PbCO_3) and 2 wt% of hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$).

2.2. Chemical cleaning

As evaluated solutions for chemical cleaning were used aqueous solutions of acetic acid (CH_3COOH) 1 % w/w, ammonium acetate ($\text{CH}_3\text{COONH}_4$) 5 and 25 % w/w, chelating agent EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$) 3 and 10 % w/w, hydrochloric acid (HCl) 5 and 10 % w/w, sulfuric acid (H_2SO_4) 10 % w/w, sodium phosphate dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) 15 % w/w, Rochelle salt (15 g $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ + 5 g NaOH /100 ml of distilled water) and ion exchange resin PMB 102-2 (Waterfilter s.r.o.) (50 g PMB 102-2/100 ml of distilled water). The solutions of acetic acid and sodium phosphate dodecahydrate were used boiling. The ion exchange resin and both of ammonium acetate solutions were used at 60 °C (± 5 °C). The others were used at room temperature.

Lead samples with pure lead surface were treated by immersion into different solutions for chemical cleaning for 1 hour (without interruption), subsequent rinsing by distilled water and ethanol and air drying. The corroded lead samples were treated by cyclically interrupted immersion into different solutions for chemical cleaning (interval pickling), after each interruption the samples were rinsed by distilled water and ethanol and air dried. The pickling intervals (in minutes): 1-1-1-1-1-1-2-2-2-3-5-5-5-10-10-10. Overall the corroded lead sample was immersed into the solution for chemical cleaning for 1 hour also.

2.3. Characterization techniques

The samples were characterized before and after full treatment by different techniques such as gravimetry, colorimetry, optical microscopy (OM), scanning electron microscopy (SEM) and infrared (IR) spectroscopy.

All samples were weighted to determine the mass loss during treatment. Mass loss is calculated with equation (1). Lead samples with corroded surface were weighted after each cycle of sample immersion (number of cycles: 16), lead samples with pure lead surface were weighted after 1 hour of sample immersion (number of cycles: 1).

$$\Delta m = m_{\text{treated lead}} - m_{\text{original lead}} \quad (1)$$

where: Δm - the mass loss of the sample during treatment (g);

$m_{\text{treated lead}}$ - the mass of the sample after each cycle of sample immersion (g);

$m_{\text{original lead}}$ - the mass of the sample before treatment (g).

Konica Minolta spectrophotometer CM-700d measured the chromatic properties of the samples. Results were expressed using the CIE-L*a*b* colorspace with Specular Component Included (SCI). Three spectra were acquired from each side of the sample and averaged.

The chemical composition of the surface was analyzed by FT-IR spectrometer Nicolet NEXUS with Omnic Spectra software.

Samples surface was observed by optical microscope Olympus PME 3 and surface morphology was observed by SEM Tescan VEGA 3.

3. RESULTS AND DISCUSSION

3.1. Gravimetry

Chemical cleaning should be designed to remove all corrosion products without mass loss of base metal. However, according to **Figure 1** all used chemical treatments produced mass loss of lead samples. The most aggressive treatment with high loss of material were $\text{CH}_3\text{COONH}_4$ (25 %) and HCl (5 %) solutions. On the contrary small mass loss during full treatment procedure reported both H_2SO_4 solutions. CH_3COOH ,

KNaC₄H₄O₆·4H₂O and EDTA (10 %) solutions removed corrosion products during 1 - 2 treatment cycle and after this produced a small mass loss of base lead. The nonlinear mass loss produced mainly by both CH₃COONH₄ and Na₃PO₄·12H₂O, H₂SO₄ (20 %), CH₃COOH and ion exchange resin should be due to active lead surface cleaning left and new PbO surface layer after cleaning fast formed.

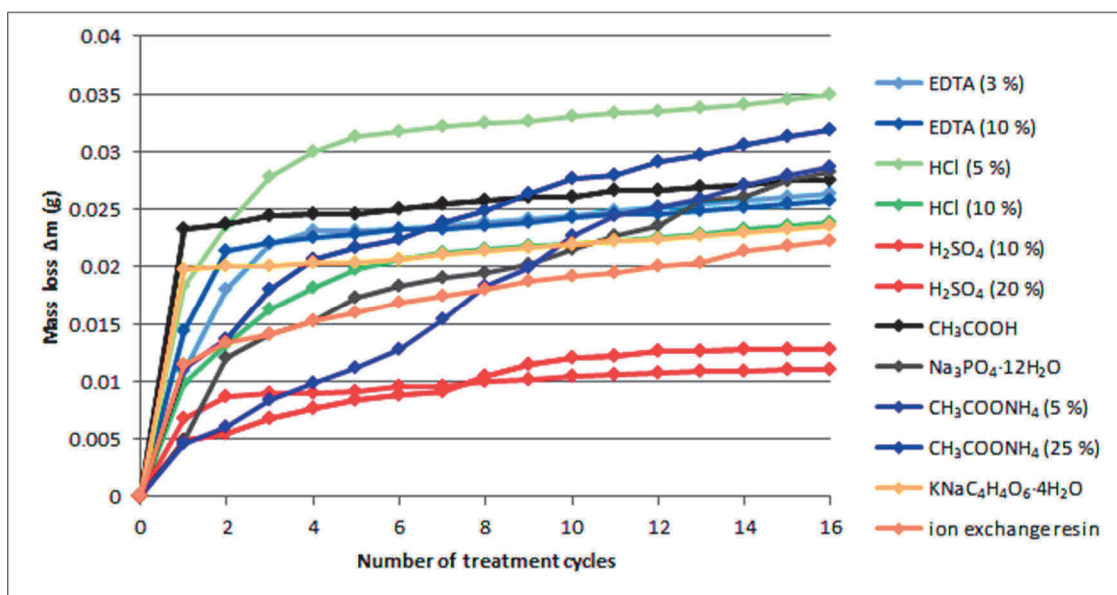


Figure 1 The mass loss of lead samples with corroded surface as a function of the number of treatment cycles

Table 1 Corrosion rates (ng/year) of lead samples immersed in different solutions for chemical cleaning measured on samples with corroded surface during corrosion products removal (0-1 treatment cycles) and after corrosion products removal (14-15 treatment cycles) or on samples with pure lead surface during full treatment

chemical cleaning solution	lead samples with corroded surface		samples with pure lead surface
	0-1 treatment cycles	14-15 treatment cycles	full treatment
EDTA (3 %)	20.55	0.38	0.02
EDTA (10 %)	27.21	0.57	0.02
HCl (5 %)	34.82	0.95	0.04
HCl (10 %)	18.65	0.57	0.03
H ₂ SO ₄ (10 %)	12.94	0.02	0.00
H ₂ SO ₄ (20 %)	9.13	0.02	0.00
CH ₃ COOH	44.14	0.76	0.03
Na ₃ PO ₄ ·12H ₂ O	9.32	2.66	0.01
CH ₃ COONH ₄ (5 %)	8.56	1.90	0.03
CH ₃ COONH ₄ (25 %)	21.31	1.33	0.02
KNaC ₄ H ₄ O ₆ ·4H ₂ O	37.48	0.95	0.02
Ion exchange resin	21.88	1.14	0.01

According to corrosion rates reported in **Table 1** both HCl, CH₃COOH and CH₃COONH₄ (5 %) solutions were very aggressive and both H₂SO₄, Na₃PO₄·12H₂O solutions and ion exchange resin non-aggressive to samples

with pure lead surface. In the presence of corrosion products on lead sample surface both H_2SO_4 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{CH}_3\text{COONH}_4$ (5 %) solutions were non-aggressive. After corrosion products removal both EDTA, HCl (10 %) and both H_2SO_4 solutions were non-aggressive for base lead (**Table 1** and **Figure 1**).

3.2. Surface characterization

According to mass loss data all used chemical treatments look effectively. Nevertheless, optical microscopy of corroded samples after full chemical treatment reported both H_2SO_4 and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ solutions and ion exchange resin as non-efficient chemical cleaning agents due to corrosion products on lead samples after treatment presence (**Figure 2**). In the case of ion exchange resin the new texture on the treated sample surface (there are pure lead surface pits (the place with resin and sample contact) between corrosion products (the place without resin and sample contact)) occurred. The brown tarnishing on sample surface after 24 hours after treatment of the sample in $\text{CH}_3\text{COONH}_4$ (25 %) solution occurred (**Figure 2**).

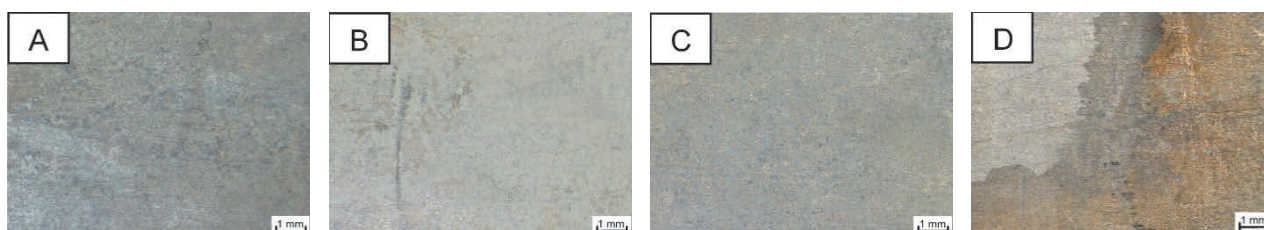


Figure 2 The optical microscopy of artificially corroded lead samples after chemical treatment in H_2SO_4 (10 %) solution (A), $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ solution (B), ion exchange resin (C) and $\text{CH}_3\text{COONH}_4$ (25 %) solution (D)

Chemical cleaning have to leaving original colour of base material. Nevertheless used chemical treatments caused a significant gloss change on treated samples (except samples treated with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and both H_2SO_4 solutions and ion exchange resin, which did not remove the corrosion products). The sample with pure lead surface had higher gloss value. The variation of luminosity and chromatic variation on treated samples and sample with pure lead surface was low (except samples treated with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and both H_2SO_4 solutions and ion exchange resin) because the chemical cleaning agents removed all corrosion products on the sample exposing pure lead surface.

The SEM observation confirms for the corroded samples treated with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ solution and ion exchange resin the artificial corrosion products presence. On samples treated in H_2SO_4 solutions the formation of new globular crystals was by SEM observed (**Figure 3**). Chemical treatment of corroded samples in CH_3COOH solution artificially corrosion products removed and new lamellar corrosion products formed (**Figure 3**). Further chemical treatment agents (both EDTA, both HCl, both $\text{CH}_3\text{COONH}_4$ and $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) induced very heterogeneous surface on samples where original surface scratches were deepened and lots of pits were produced (**Figure 3**).

FT-IR analyse spectra for the corroded samples treated with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and CH_3COOH solution and ion exchange resin did not reveal any significant changes with referent corroded lead sample spectrum. The spectra indicate the presence of lead oxide and lead carbonates. On the contrary spectra for corroded samples treated with another chemical treatment agents (both HCl, both $\text{CH}_3\text{COONH}_4$ and $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) were similar to spectrum for referent sample with pure lead surface. These spectra indicate the presence of lead oxide due to the fast passivation of lead in atmospheric conditions. FT-IR spectroscopy for corroded samples treated with both H_2SO_4 solutions confirmed corrosion products chemical composition changing observed by SEM. The spectra indicate the presence of lead sulphate. The spectra obtained for corroded samples treated with EDTA solutions indicate the significant decrease in the intensity of lead oxide peaks and the presence of amine groups in the spectra were also observed. The spectra indicate remains of EDTA adsorbed on lead sample surface.

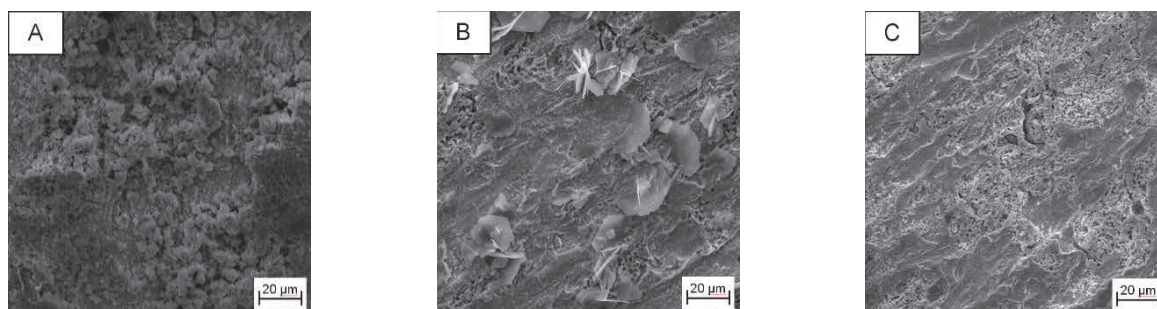


Figure 3 The SEM observation of artificially corroded lead samples after chemical treatment in H₂SO₄ (10 %) solution (A), CH₃COOH solution (B) and EDTA (3 %) solution (C)

4. CONCLUSION

Examination of the lead samples after chemical treatment in different solutions showed that all used chemical treatments induced chemical and/or physical changes. Mainly the gloss lost and the surface roughness increase. The chemical treatment with H₂SO₄ solution induced the formation of a PbSO₄ layer which acted as a corrosion barrier. Therefore, the PbSO₄ layer caused non-recuperation of the original lead appearance. The Na₃PO₄·12H₂O solution and ion exchange resin did not remove the artificial corrosion product from lead surface. The chemical treatment with EDTA, HCl, CH₃COOH, CH₃COONH₄ and KNaC₄H₄O₆·4H₂O removed the artificial corrosion products on lead samples. The CH₃COONH₄ solutions were high aggressive to base lead during the chemical treatment. Moreover, highest concentration of CH₃COONH₄ solution brown tarnishing on lead surface induced. The chemical treatment with CH₃COOH solution left an extremely active lead surface and due to the CO₂ presence in atmosphere new corrosion products based on lead carbonates are formed. The chelating agent EDTA remains of EDTA adsorbed on lead sample surface leaved. Depending on this study HCl and KNaC₄H₄O₆·4H₂O appear as the most appropriate chemical treatment agents for lead carbonates removing.

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