

# Surface analysis and depth profiling of corrosion products formed in lead pipes used to supply low alkalinity drinking water

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## Abstract

Modern analytical techniques have been applied to investigate the nature of lead pipe corrosion products formed in pH adjusted, orthophosphate-treated, low alkalinity water, under supply conditions. Depth profiling and surface analysis have been carried out on pipe samples obtained from the water distribution system in Glasgow, Scotland, UK. X-ray diffraction spectrometry identified basic lead carbonate, lead oxide and lead phosphate as the principle components. Scanning electron microscopy / energy-dispersive x-ray spectrometry revealed the crystalline structure within the corrosion product and also showed spatial correlations existed between calcium, iron, lead, oxygen and phosphorus. Elemental profiling, conducted by means of secondary ion mass spectrometry (SIMS) and secondary neutrals mass spectrometry (SNMS) indicated that the corrosion product was not uniform with depth. However, no clear stratification was apparent. Indeed, counts obtained for carbonate, phosphate and oxide were well-correlated within the depth range probed by SIMS. SNMS showed relationships existed between carbon, calcium, iron, and phosphorus within the bulk of the scale, as well as at the surface. SIMS imaging confirmed the relationship between calcium and lead and suggested there might also be an association between chlorine and phosphorus.

## Keywords

Plumbosolvency, lead, lead scale, lead pipe corrosion products, chemical analysis.

## INTRODUCTION

Lead enters drinking water mainly through dissolution of lead pipe corrosion products ("lead scale"). A phased reduction in maximum admissible concentration of lead in water is currently being implemented in the European Union. The current value of 50  $\mu\text{g Pb L}^{-1}$  will be reduced to 25  $\mu\text{g Pb L}^{-1}$  in April 2003, and then to 10  $\mu\text{g Pb L}^{-1}$  in 2013 (Commission of the European Union, 1995).

The UK water industry has made significant progress towards compliance with the new legislation. Implementation of appropriate water treatment regimes (pH adjustment and orthophosphate dosing) has reduced plumbosolvency. Lead communication pipes have been removed from many water distribution systems, although debate continues about whether such an undertaking is necessary (Hayes *et al.*, 1997). However, whether or not water suppliers choose to eliminate lead in supply networks, the reluctance of many consumers to undertake lead pipe replacement within their own properties means that health effects associated with lead in drinking water are likely to remain of concern for the foreseeable future.

An improved understanding of the nature of lead scale is important since it will allow water suppliers to optimise plumbosolvency control strategies and thus minimise lead concentrations in potable water. Early work (Sheiham and Jackson, 1981; Schock and Gardels, 1983) indicated scale to be composed mainly of lead carbonate ( $\text{PbCO}_3$ ) and / or basic lead carbonate ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ). Evidence from lead pipe test rig studies suggested that a pyromorphite-like species, probably hydroxypyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ) formed when orthophosphate was added to the water supply. Scanning electron microscopy (SEM) has been applied to scale samples obtained by running high alkalinity water through a test rig (Colling *et al.*, 1987). Results showed that the water used, and the addition of phosphate, affected the physical appearance of the corrosion product. Hexagonal, plate-like deposits were identified as basic lead carbonate whilst lead carbonate had a smoother, more uniform, appearance. The deposit formed in phosphate-treated water consisted of rounded particles. Although the mineral could not be precisely identified, elemental analysis (energy-dispersive x-ray spectrometry (EDX) revealed it to contain lead, phosphorus and some calcium.

More recent studies on the  $\text{Pb}^{2+}$ - $\text{CO}_3^{2-}$ - $\text{PO}_4^{3-}$  system, by Grimes *et al.* (1995), used powder x-ray diffraction spectroscopy and Raman spectroscopy to study the results of dispersing normal and basic lead carbonates in orthophosphate solution. Replacement of carbonate species by hydroxypyromorphite occurred over a period of 900 days. The same researchers exposed new lead pipes to water from the public supply that had been spiked with different concentrations of orthophosphate. A variety of analytical techniques were used to characterise the corrosion products formed. Complex, stratified materials were found. With no phosphate addition, a basal layer of tetragonal lead (II) oxide ( $\text{PbO}$ ) was mixed with normal lead carbonate and overlain with basic lead carbonate. In the presence of orthophosphate, the lead oxide was overlain by hydroxypyromorphite. Evidence was also reported for the isomorphous substitution of lead by calcium, to yield a mineral ( $\text{Pb}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{OH}$ ) with composition intermediate between hydroxypyromorphite and hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ).

Few studies have investigated the nature of lead pipe corrosion products formed under supply conditions. Peters *et al.* (1999) analysed samples from the City of Glasgow by Fourier transform infra-red spectrometry (FTIR), ion chromatography and flame atomic absorption spectrometry. Glasgow is supplied with water from Loch Katrine, a freshwater lake ~ 50 km north west of the city. The supply had been pH-adjusted since 1978 (typical alkalinity  $10 \text{ mg HCO}_3^- \text{ L}^{-1}$ ) and dosed with orthophosphate since 1989 (initial dose  $1.0 \text{ mg P L}^{-1}$ , subsequently reduced to  $0.6 \text{ mg P L}^{-1}$ ). Corrosion products obtained from pipes exhumed prior to phosphate dosing were composed of normal and/or basic lead carbonate, whilst those collected in the late 1990's contained up to 30 % (w/w) of an apatite-like species, most probably hydroxypyromorphite, in addition to carbonates. Calcium was detected in some of the samples.

Subsequent analysis of corrosion products collected from lead pipes removed from the Glasgow distribution system has involved the application of ion chromatography and Fourier transform infra-red spectrometry. Inductively coupled plasma atomic emission spectrometry and thermogravimetry have also been used to gain information on heavy metals and organic matter, respectively. In addition, a number of surface analysis techniques, which can be applied directly to corrosion products *in situ* (i.e. without removal from the pipe surface) have been investigated. X-ray diffraction spectrometry (XRDS), SEM/EDX, secondary ion mass spectrometry (SIMS) and secondary neutrals mass spectrometry (SNMS) have been used.

This contribution will focus on the results of surface analysis and depth profiling of selected lead water pipes collected from the Glasgow water distribution system.

## METHODS

Lead communication pipes were exhumed in the City of Glasgow, Scotland, UK as part of West of Scotland Water's pipe replacement programme. The pipes were returned to the laboratory where they were cut into ~ 15 cm segments and then sectioned lengthways. The scale was either (a) scraped from the interior surfaces using a plastic spatula (EDX) or (b) studied *in situ* (XRFS, SEM/EDX and SIMS/SNMS). For SIMS and SNMS, a small section was cut from the pipe (~ 1 cm<sup>2</sup>) suitable for insertion into the ion source of the mass spectrometer.

The XRDS measurements were carried out using a Philips PW 1820 goniometer with PW 1830 generator (Philips, Eindhoven, The Netherlands). The radiation used was Cu K<sub>α</sub> with  $\theta/2\theta$  geometry. SEM measurements were made with an environmental scanning electron microscope, model FEI-Philips XL30-ESEM-FEG (from FEI Company, Eindhoven, The Netherlands).

SIMS and SNMS analysis were undertaken by MATS UK (Warrington, Cheshire) using a quadrupole instrument. Negative ion SIMS was performed using ion bombardment (Ar<sup>+</sup> primary ions, 80 nA beam current). SNMS was performed by post-sputtering electron impact ionisation of neutral species in the plume generated by a (2 μA) Ar<sup>+</sup> primary ion beam.

## RESULTS and DISCUSSION

### XRDS

Both the external and the internal surfaces of the same pipe were analysed. Examination of the external surface indicated the presence of lead carbonate, quartz (SiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>). Residual contamination may be responsible for the presence of common soil minerals. Results of analysis of two separate areas of the internal surface revealed the presence of basic lead carbonate, lead oxide, and lead phosphate (Pb<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>). Lead carbonate was also observed when Glasgow pipes were analysed by FTIR (Peters *et al.* 1999) and the detection of PbO is concordant with the work of Grimes *et al.* (1995). However, lead carbonate has not previously been reported as a component of lead scale. No evidence was found for the presence of the expected phosphate species, hydroxypyromorphite.

### SEM / EDX

Results of elemental analysis of both pipe exterior and corrosion product scraped from the pipe interior are presented in Table 1. The high levels of carbon and oxygen present on both surfaces may be correlated with carbonate, oxide and possible hydrated species. Silicon and aluminium on the exterior are probably due to residual soil contamination. The presence of small amounts of phosphorus in the interior is consistent with the suggestion that the scale may be composed mainly of lead carbonate or oxide species but with a minor phosphate component. The presence of calcium is consistent with findings of other workers (Colling *et al.*, 1987; Grimes *et al.* 1995).

SEM images of the interior of a section of pipe are shown in Figures 1 and 2. When the elemental composition of the surface was mapped, it was found that the dark area to the right of Figure 1 was associated with high concentrations of oxygen, phosphorus and lead, and with moderate levels of calcium and iron. The lighter area to the left was predominantly lead. It would thus appear that the dark area is corrosion product and the light region mainly base metal. Figure 2 shows the detailed structure of the lead scale. Both plate-like structures (possible basic lead carbonate) and nodular features (which could represent pyromorphite) are evident.

**Table 1:** Quantitative elemental analysis of pipe exterior and internal corrosion product

Element	Pipe exterior		Corrosion product	
	Percentage by mass	Mole percent	Percentage by mass	Mole percent
C	23.39	33.00	30.77	58.13
O	53.19	56.34	24.36	34.55
Al	6.87	4.32	0.03	0.02
Si	8.27	4.99	0.31	0.25
P	0.40	0.22	2.25	1.65
K	0.35	0.15	ND	
Ca	0.24	0.10	0.95	0.54
Fe	1.30	0.39	0.45	0.18
Cu	ND		0.78	0.28
Pb	5.99	0.49	40.08	4.39

ND : not detected

### GLOSSY PHOTOS (to be inserted)

**Figure 1:** SEM of the interior surface of a pipe from the Glasgow supply (the darker material is the lead scale

**Figure 2:** SEM showing detailed structure of lead scale formed under supply conditions.

### SIMS and SNMS

Profiling was carried out on two pipes (obtained from different geographic areas of Glasgow) to investigate variations in chemical composition through the depth of the scale product. Both negative ion SIMS and SNMS were used. In SIMS, the scale is “cratered” slowly due to the low ion beam current used. Detailed information on composition close to the surface is obtained. The higher ion beam intensity used in SNMS means the sample is sputtered much more rapidly, allowing the material to be probed to greater depth. A disadvantage of SIMS is that ion yields vary markedly across the periodic table, depending on the ionisation potential (for positive SIMS) or electronegativity (for negative SIMS) of the analyte element. This effect is reduced, though not eliminated, in SNMS.

Figure 3 shows the SIMS depth profile for pipe A. Note that in this, and subsequent, figures “time” is related to “depth”. Unfortunately, precise depth calibration is not possible because of the complex

nature of the sample and the lack of suitable standard materials. Total carbon and phosphorus counts decreased slightly with depth. In contrast, the  $\text{CO}_3^-$ ,  $\text{PO}_3^-$  and  $\text{PbO}_2^-$  ions increased. The difference between total and inorganic C, and between total and inorganic P, may be due to the presence of organic species at the surface of the pipe deposit. Chlorine was also detected, although the high apparent concentration may be an artefact caused by the relative ease of formation of the  $\text{Cl}^-$  ion. The SIMS profile for pipe B is shown in figure 4.

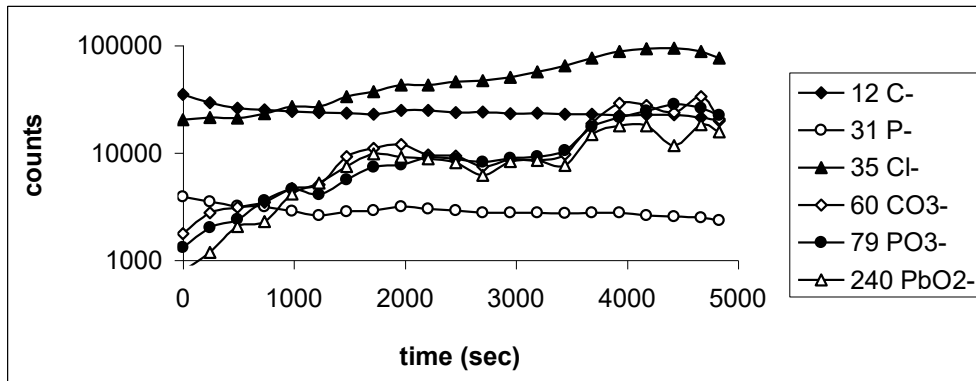


Figure 3: Negative ion SIMS depth profile of Pipe A

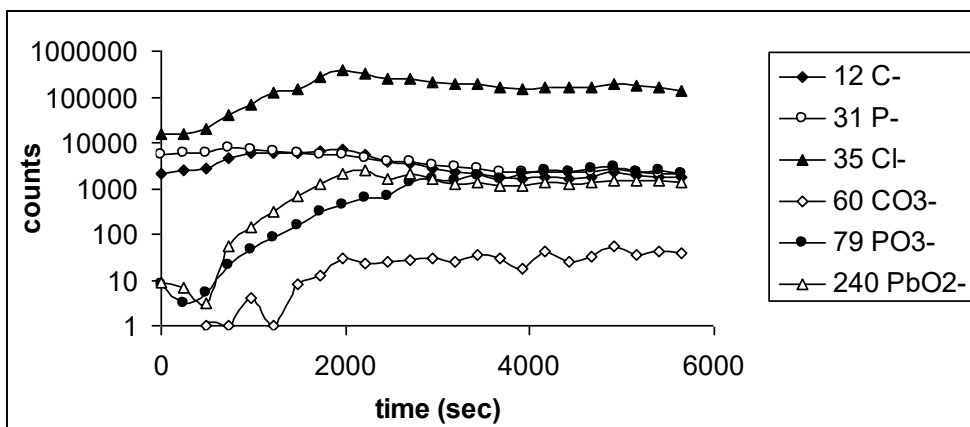


Figure 4: Negative ion SIMS depth profile of Pipe B

Lower counts for carbon were present (both total C and  $\text{CO}_3^-$ ) than in pipe A. However, broadly similar trends were apparent. The similarity in profiles obtained for the oxyanions,  $\text{CO}_3^-$ ,  $\text{PO}_3^-$  and  $\text{PbO}_2^-$  may indicate a direct relationship between the concentrations of carbonate, phosphate and lead oxide in the scale samples, within the depth range investigated, rather than clear stratification as reported by Grimes *et al.* (1995).

SNMS results for pipes A and B are shown in Figures 5 and 6, respectively. The count for the lead ion was higher than that obtained by the SIMS technique, more accurately reflecting the true concentration of this element relative to the other analytes present in the sample. Carbon, phosphorus, calcium and iron followed similar trends with depth. They each gave approximately the same response up to 1000 sec and then decreased. A small enhancement in concentrations of these four elements at the surface was also apparent. The increase in lead concentration, and decrease in other elements, from 1000-2000 sec profiling time may indicate that the  $\text{Ar}^+$  ion beam has ablated all the way through the scale and into base metal. Scanning the mass range identified the presence of minor elemental components in the sample, namely aluminium, magnesium, potassium, sodium

and tin. The counts obtained for potassium, sodium and tin were consistent throughout the depth range, while the counts for magnesium and aluminium decreased with depth.

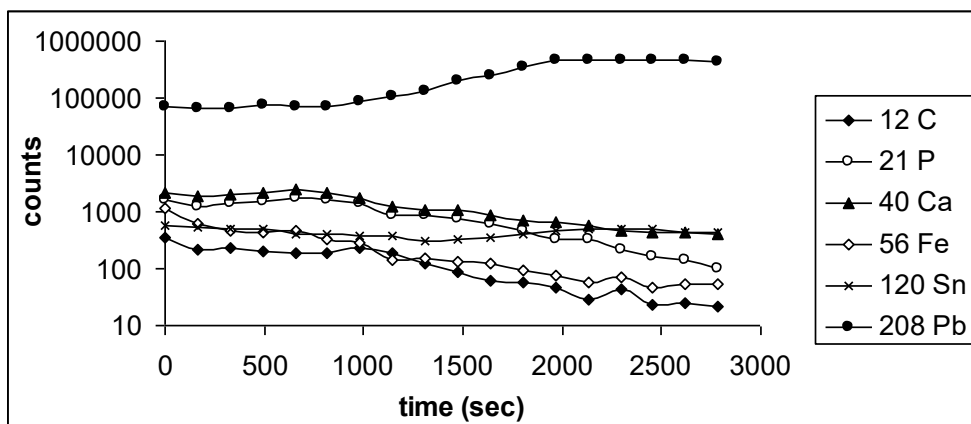


Figure 5: SNMS depth profile of Pipe A

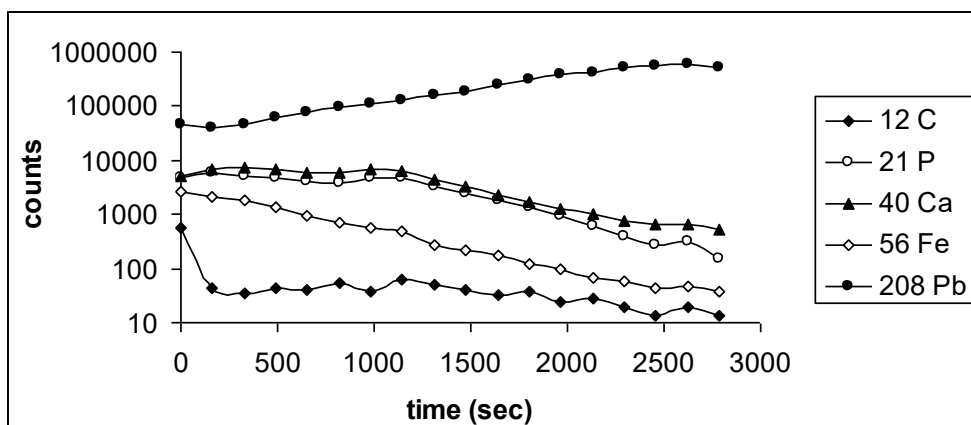


Figure 6: SNMS depth profile of Pipe B

SNMS of pipe B again revealed high lead levels and similar trends in the counts obtained for calcium and phosphorus. The iron concentration decreased with depth. Carbon content was lower than in pipe A, as previously shown by SIMS. Trace amounts of common water cations were again detected, but no tin.

It was also possible to obtain elemental maps of areas of the interior pipe surface by SIMS. Spatial correlations were observed between concentrations of phosphorus and chlorine (by negative ion SIMS) and between calcium and lead (by positive ion SIMS) (Peters, 1999).

## CONCLUSIONS

Four analytical techniques have been used to investigate the nature of lead pipe corrosion products which had formed in pH adjusted, orthophosphate-treated, low alkalinity water, under real supply conditions. XRDS identified basic lead carbonate, lead oxide and lead phosphate as the principle components. SEM/EDX revealed a crystalline structure within the corrosion product and also showed spatial correlations existed between calcium, iron, lead, oxygen and phosphorus. Elemental profiling indicated that the corrosion product was not uniform with depth, but clear

stratification was not apparent. Indeed, counts obtained for carbonate, phosphate and oxide were well-correlated within the depth range probed by SIMS. SNMS showed relationships between carbon, calcium, iron, and phosphorus existed within the bulk of the scale, as well as at the surface. SIMS imaging confirmed the relationship between calcium and lead and suggested there might also be an association between chlorine and phosphorus.

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