

SUPPORTING INFORMATION

Orthophosphate Interactions with Destabilized PbO₂ Scales

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18 Pages

6 Tables

7 Figures

Methods

2 Lead Service Line (LSL) Scale Descriptions

References

Table S1. Treatment change timeline and operation highlights for Utility A

		1992	1993	1994	1995	1996	1997	1998	1999	2000	2002	2003	2004	2005
Corrosion Control Studies				Submitted CC study to Region			Conditional OCCT designation to use pH adjustment. Utility to assess feasibility of alternative CCTs			Designated pH adjustment as OCCT, minimum pH of 7.7 to be maintained	Region changed the minimum pH at DS sample locations from 7.7 to 7.0			
Corrosion Control	pH/ Alkalinity			Annual system average pH 8.0				Average DS pH 7.8 with a range of 7.0-8.7 (seasonal variability, lows of 7.0-7.2 to >8.5)			pH 7.7-8.5, alkalinity 43-115 mg/L CaCO ₃	pH 7.7-8.4, 47-83 mg/L CaCO ₃	pH 7.6-8.5, alkalinity 52-90 mg/L CaCO ₃	pH 7.2-8.2, alkalinity 33-109 mg/L CaCO ₃
	Inhibitor												Orthophosphate June: Started partial system application August: Full system application, DS residual ND-3.23 mg PO ₄ /L 2005 Average 3.0 2006 Average: 2.6 2007 Average: 2.3 2008 Average: 2.3 2009 Average: 2.1	
Disinfection	Chlorine	EP Residual 1-2 mg/L	EP Residual increased to 2-4 mg/L		EP Residual maintained around 2-4 mg/L	EP Residual reduced to around 2-3 mg/L		EP Residual maintained around 2-3 mg/L						
	Chloramine									November: Chloramination begins	NH ₂ Cl DS residual 3.4-3.7 mg/L	NH ₂ Cl DS residual 3.5-3.8 mg/L	NH ₂ Cl DS residual 3.3-3.8 mg/L	
Other	Regulations	Lead ALE	Lead ALE and violated TCR	Violated turbidity requirements of the SWTR and lead ALE	Violated TCR						Lead ALE			

CC- Corrosion Control
 OCCT- Optimal Corrosion Control Treatment
 CCT- Corrosion Control Treatment
 DS-Distribution System

EP- Entry Point
 ND- Non-detect
 ALE- Action Level Exceedance
 TCR- Total Coliform Rule

SWTR- Surface Water Treatment Rule

Table S2. 90th Percentile Lead (mg/L) Results by Utility

Monitoring Period	1992	1993		1994		1997		2000	2001	2002	2003		2004		2005		2006		2007		2008	
		Jan-June	July-Dec	Jan-June	July-Dec	Jan-June	July-Dec				Jan-June	July-Dec	Jan-June	July-Dec	Jan-June	July-Dec	Jan-June	July-Dec	Jan-June	July-Dec	Jan-June	July-Dec
Utility A	0.039	0.012	0.028	0.014	0.012	0.006	0.008	0.012	0.035	0.075	0.04	0.063	0.059	0.054	0.015	0.015	0.01	0.012	0.01	0.011	0.007	0.008
Utility B	0.028					0.023*			0.012				0.014						0.013	0.026	0.012	0.006

90th Percentile Pb results recorded in mg/L

*Estimated from historical records

Blanks indicate no data available, **bold values** indicate a result above the 90th percentile lead action level of 0.015 mg/L.

Table S3. Treatment change timeline and operation highlights for Utility B

		Spring 1997	September 2000	February 2001	June 2001	May 2002	January 2004	2005	2006	2007	2008
Corrosion Control	pH	Plant effluent pH 7.5, using lime				Switched to NaOH		Target pH of 8.0	Target pH of 8.0-8.4	Target pH of 7.7	Target pH of 7.7
	Inhibitor	Started orthophosphate feed at 3.5 mg PO ₄ /L		Reduced dosage to 3.5-2.5 mg PO ₄ /L	Reduced dosage to 2.5-2.0 mg PO ₄ /L			Maintained dose at 2.0 mg PO ₄ /L	Maintained 2.0 mg PO ₄ /L	Maintained 2.0 mg PO ₄ /L	Maintained 2.0 mg PO ₄ /L
Disinfection	Chlorine	Gaseous Cl ₂ dosage range 3-7 mg/L in plant with plant effluent target of 1.5-3.0 mg/L					Switch from gaseous Cl ₂ to NaOCl	Average total chlorine distribution system residual 0.76 mg/L (range: 0.00-2.33 mg/L)			
									Chloramine October: chloramination begins (4:1 ratio, 2.0-3.0 mg/L plant effluent residual)	Plant effluent total chlorine residual average 2.21 mg/L (range: 1.03-3.64 mg/L). DS average 1.9 mg/L (range: 0.07-3.8 mg/L)	Plant effluent total chlorine residual average 2.35 mg/L (range: 1.12-3.20 mg/L). DS average 1.87 mg/L (range: 0.00-3.5 mg/L)
							UV Started UV disinfection (late 2004)	UV disinfection unit was placed into full service in March			
Other	Coagulant	Alum primary coagulant, dosage range 35-70 mg/L	Switch to PACL, typical dosage 35-50 mg/L (neat)				Start enhanced coagulation, using high dosage PACL (80-120 mg/L)				
	Fluoride	Fluoride at 1.0 mg/L using NaF	Switch to H ₂ SiF ₆ , fluoride ion dosage 1.0 mg/L					Offline for 189 days	Offline all year	Offline until June 18th	Offline since February, will not come back online. Source water has natural background concentration of fluoride (average: 0.10 mg/L, range: 0.06-0.13 mg/L)

DS- Distribution System

PACL- Polyaluminum Chloride

Table S4. Existing phases in the solid solution series between hydroxypyromorphite and hydroxyapatite

PDF card #	Formula	Ca (mol)	d ₂₁₁ (Å)
00-024-0586	Pb ₅ (PO ₄) ₃ OH	0	2.9740
00-008-0259	Pb ₅ (PO ₄) ₃ OH	0	2.9650
04-011-0857	Pb ₅ (PO ₄) ₃ OH	0	2.9615
04-010-3163	Ca _{0.805} Pb _{4.195} (PO ₄) ₃ OH	0.805	2.9290
00-040-1495	Ca ₂ Pb ₈ (PO ₄) ₆ (OH) ₂	1	2.9300
04-010-3162	Ca _{2.74} Pb _{2.26} (PO ₄) ₃ OH	2.74	2.8742
01-079-0685	Ca _{2.79} Pb _{2.21} (PO ₄) ₃ OH	2.79	2.8742
00-040-1496	Ca _{5.5} Pb _{4.5} (PO ₄) ₆ (OH) ₂	2.75	2.8740
04-010-3161	Ca _{3.915} Pb _{1.085} (PO ₄) ₃ OH	3.915	2.8364
01-079-0684	Ca _{3.93} Pb _{1.07} (PO ₄) ₃ OH	3.93	2.8364
00-040-1497	Ca ₈ Pb ₂ (PO ₄) ₆ (OH) ₂	4	2.8370
00-047-1758	Ca _{8.78} Pb _{1.22} (PO ₄ ,CO ₃) ₆ (OH,F,Cl) _{2.56}	4.39	2.8000
00-009-0432	Ca ₅ (PO ₄) ₃ OH	5	2.8140
01-074-0565	Ca ₁₀ (PO ₄) ₆ (OH) ₂	5	2.8147

Table S5. Detected mineral phases by powder X-Ray Diffraction for each pipe scale layer sampled

Sample	Layer	Approximate Thickness (μm)	Plattnerite Pb(IV)	Scrutinyite Pb(IV)	Litharge Pb(II)	Massicot Pb(II)	Hydrocerussite Pb(II)	Plumbonacrite Pb(II)	Ca-Pb phosphates Pb(II)	Pb	Qtz	Amph
A_prePO4	L1	30-50	++++		+		++					
	L2	125	++		++++		++			D		
A_postPO4	L1	0-100	++++		++	++	+					++
	L2	25	++++				+					
	L3	25	++++	++++			+++		+++			
	L4a	150-170	+		++++		++		+			
	L4b				++++		+			D		
B_area1	L1	400-500	+								D	++++
	L2	40	++++						++			
	L3	40	+++						+++			
	L4	20	+++		++++				+++	D		
B_area2	L1	10-30	+++		++	++	++	++++		D		
	L2	30	++++			++	++	++	+			
	L3	20	+++		++++	+	+	+	+	D		

++++ Major +++ Moderate ++ Minor + Trace **D** Detected **Pb** Metallic lead **Qtz** Quartz **Amph** Amorphous Component

Table S6. ICP-MS results from Utility A LSL Scale Layers

Utility A LSLs					
	Layer	Al (wt %)	Ca (wt %)	Fe (wt %)	P (wt %)
Pre-phosphate 1 (n=1)	L1	1.3	0.19	0.6	<0.1
Pre-phosphate 2 (n=1)	L1	0.84	0.15	0.24	<0.1
Pre-phosphate 3 (n=1)	L1	3.6	0.41	2.4	<0.1
A_postPO4 (n=1)	L1	2.3	0.86	2.3	0.75
Post-phosphate (n=8)	L1	0.6-3.2	0.9-4.25	0.6-5.1	0.9-5.9
Pre-phosphate 2 (n=1)	L2	0.46	0.1	0.14	<0.1
A_postPO4 (n=1)	L2	0.63	0.88	0.34	1.1
Post-phosphate (n=9)	L2	0.08-1.9	0.6-4.8	0.1-1.1	0.8-5
A_postPO4 (n=1)	L3	0.1	0.5	0.01	0.58
Post-phosphate (n=9)	L3	0.03-0.4	0.2-1.7	0.01-0.08	0.3-3.6

"<" indicates result was less than the detection limit

Figure S1: Application of Vegard's Law using the phases identified in Table S4

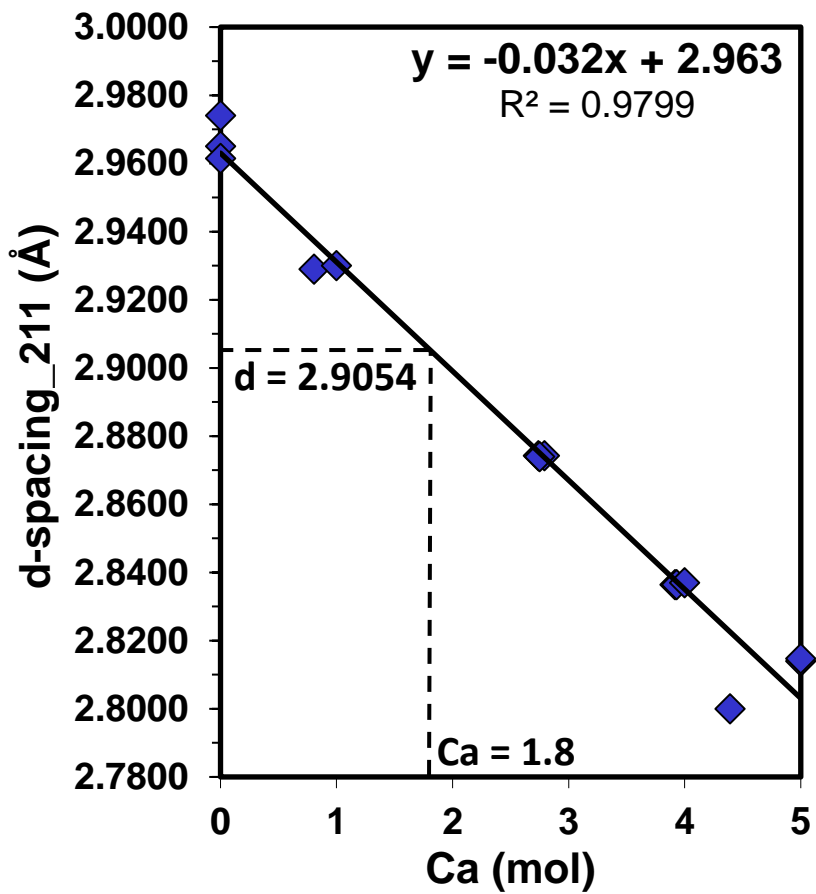


Figure S2. Close-up photographs of Utility A pipes: A) A_prePO4 B) A_postPO4. Scale bar in mm.

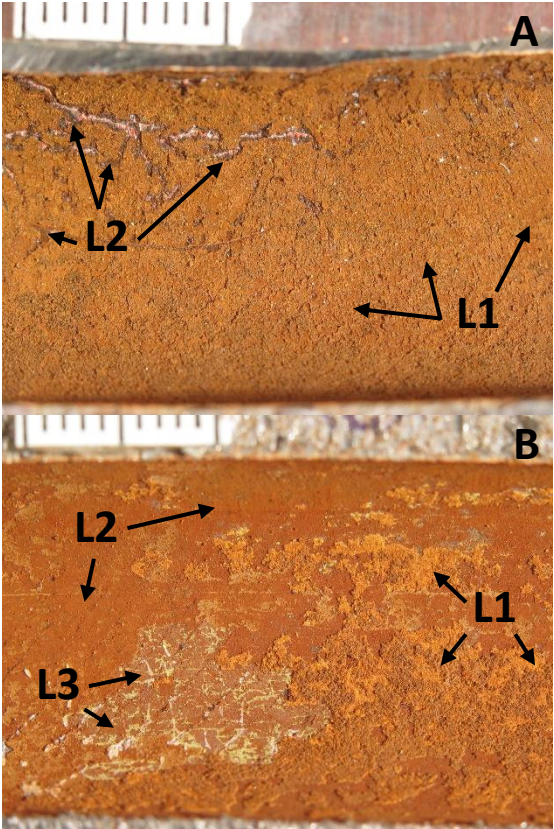


Figure S3. Utility A PXRD patterns for layers sampled from pipe A_postPO4. Numbered phases indicate the location of diffraction lines for the individual compounds identified

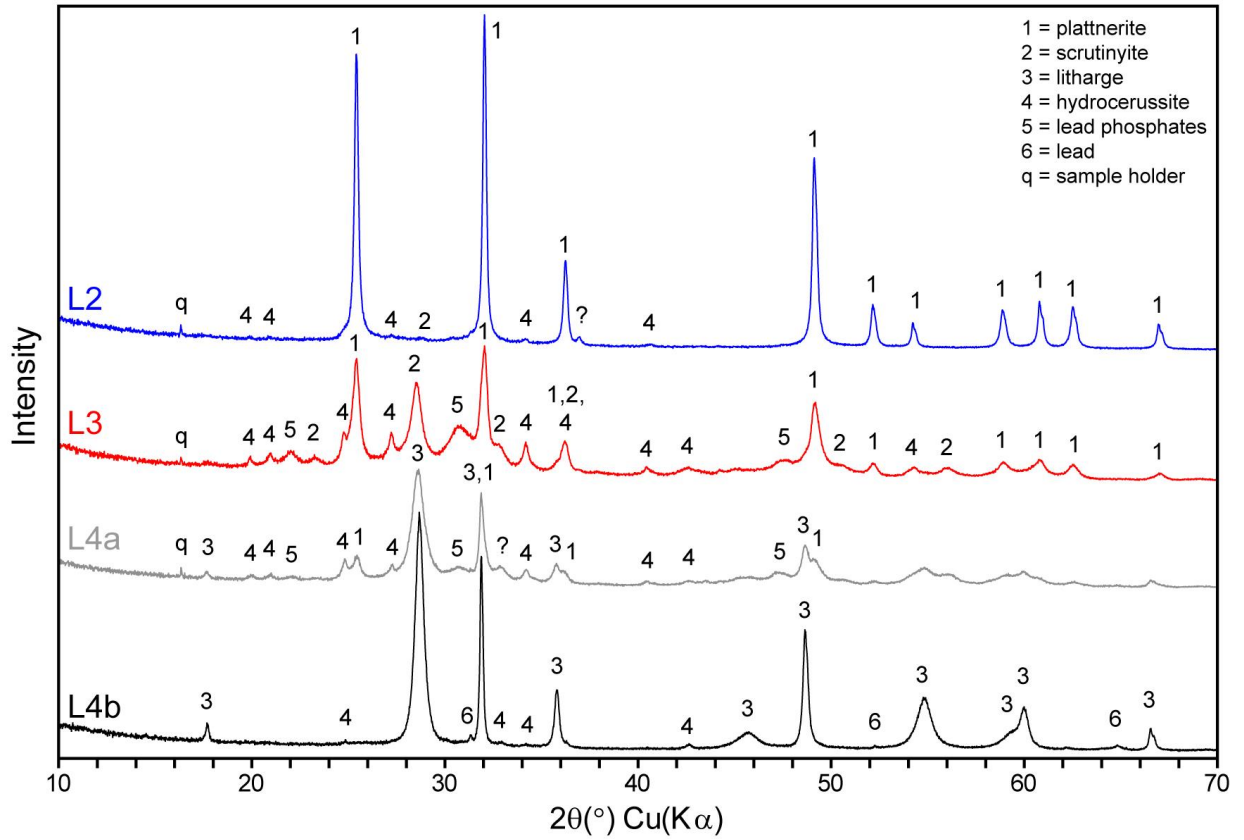


Figure S4. Macrophotography of the received LSL from Utility B. A) Close-up image of the transition from area 1 to area 2, scale bar in mm. B) Close-up image of the various scale layers sampled from area 1, scale bar = 100 μ m. C) Close-up image of the scale in area 2, scale bar in mm. D) Close-up image showing scale layers L1 and L2 from area 2, scale bar = 100 μ m.

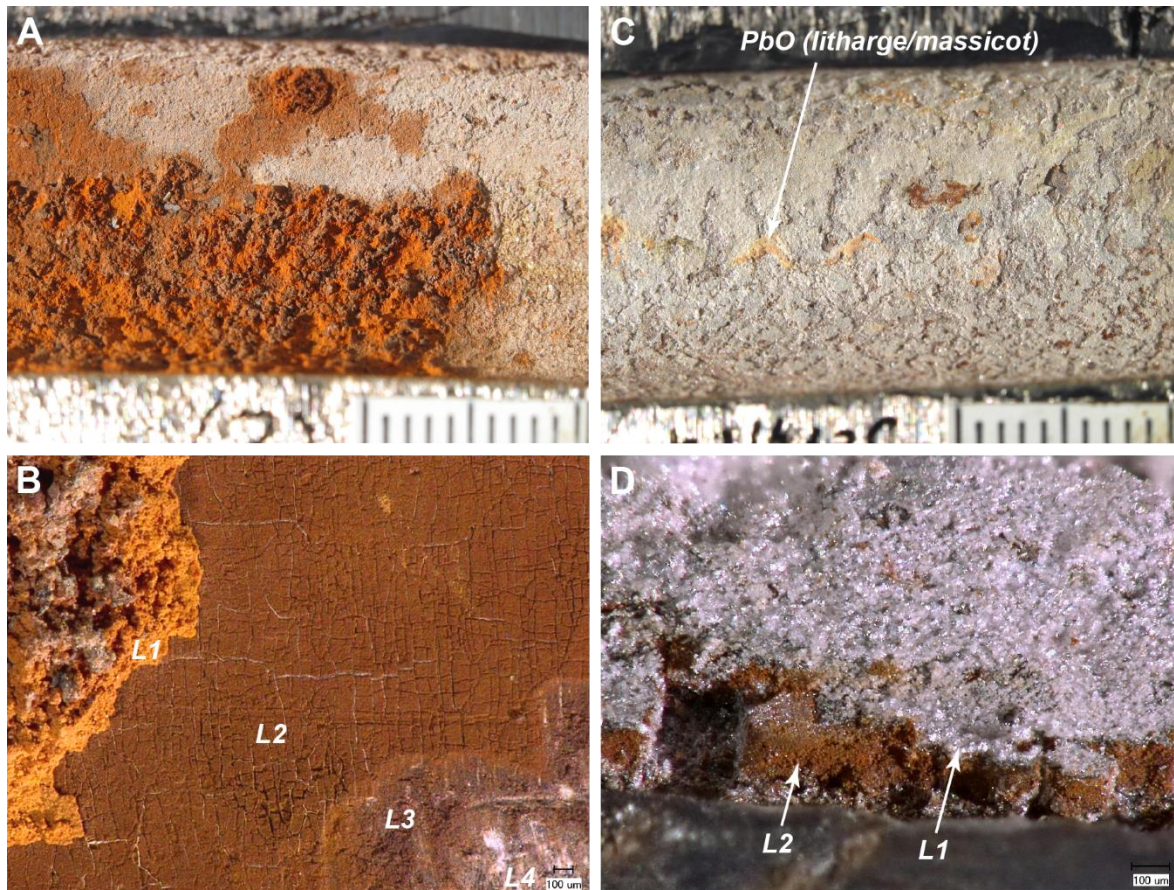


Figure S5. PXRD patterns for LSL layers L1-L5 in Utility C. Note the dominance of plattnerite in L4 and the Ca-Pb phosphate in L5.

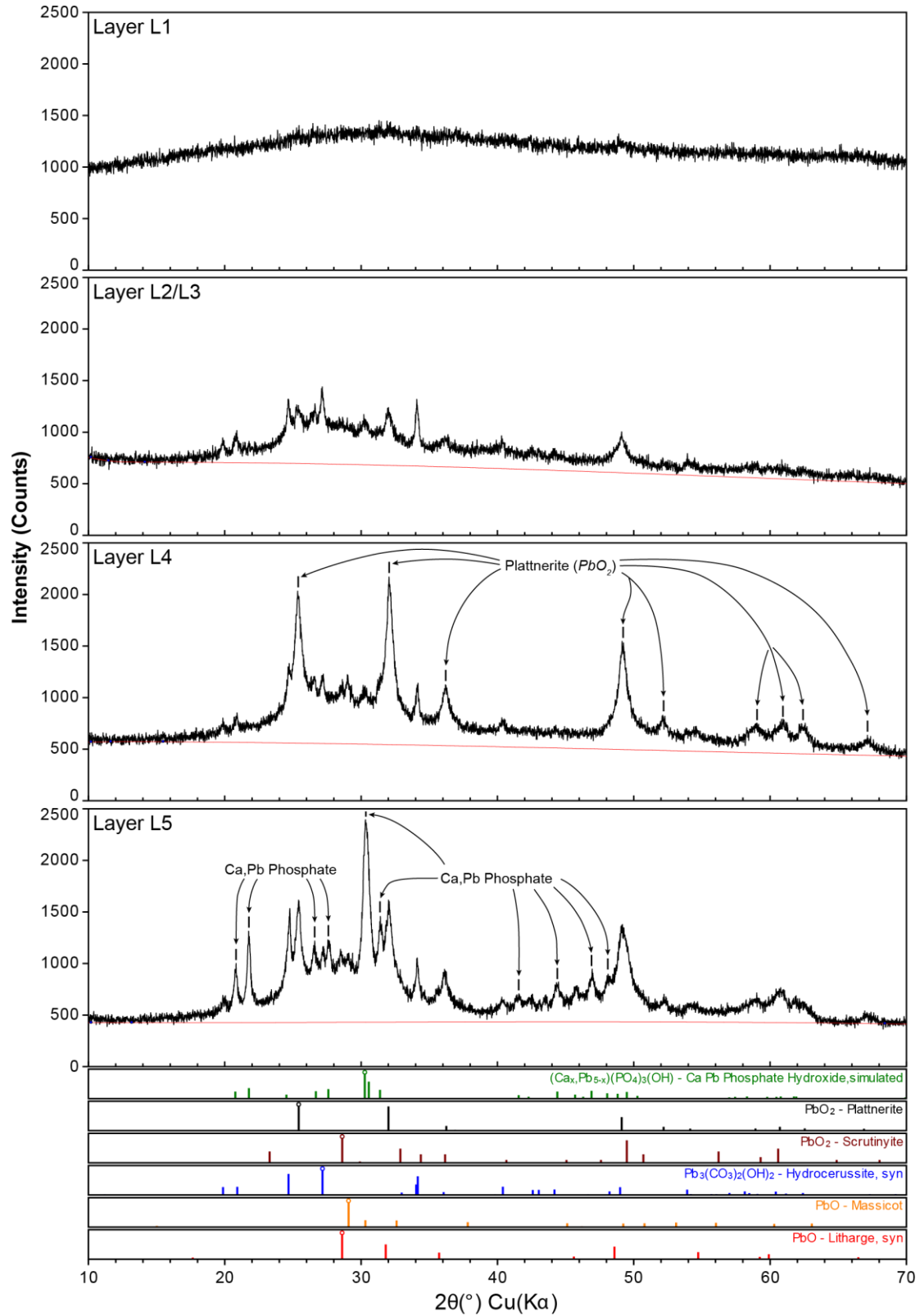


Figure S6. SEM back scatter detection image with associated elemental maps for the LSL scale from Utility C characterized by PXRD in Figure S5. Scale bar = 250 μm .

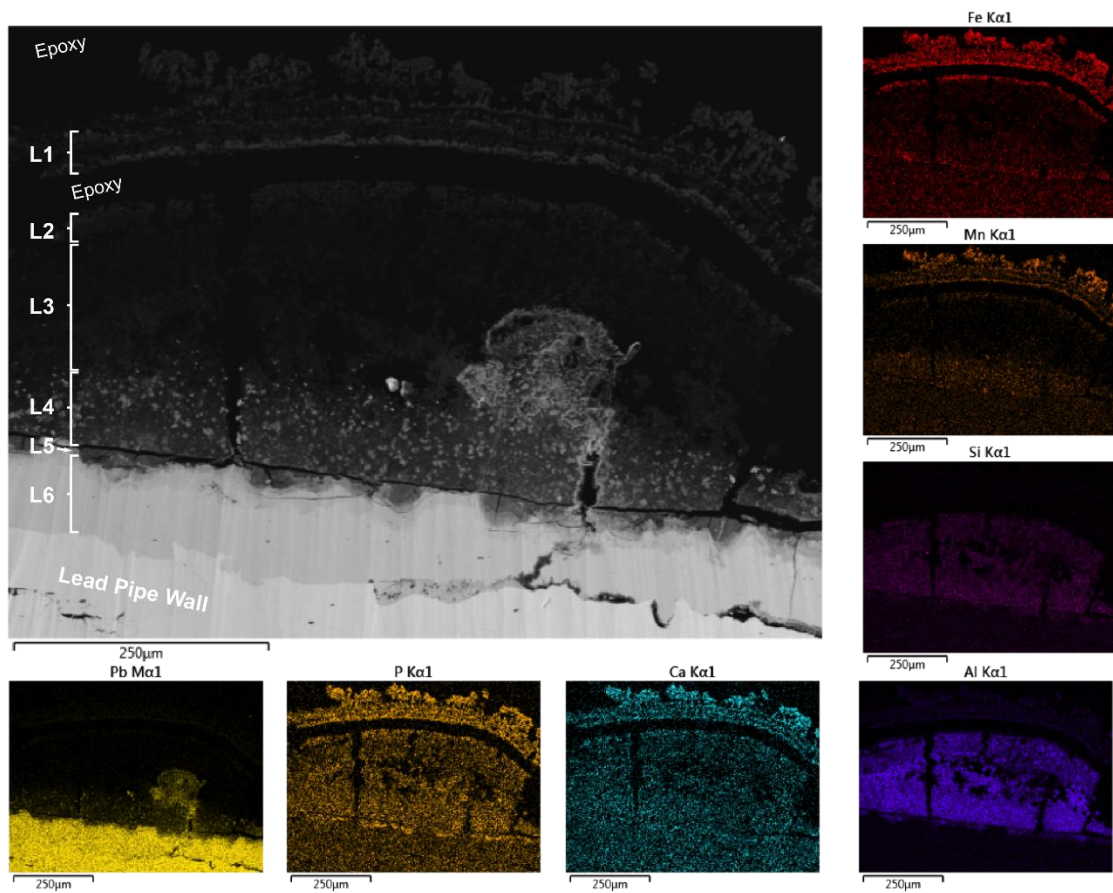
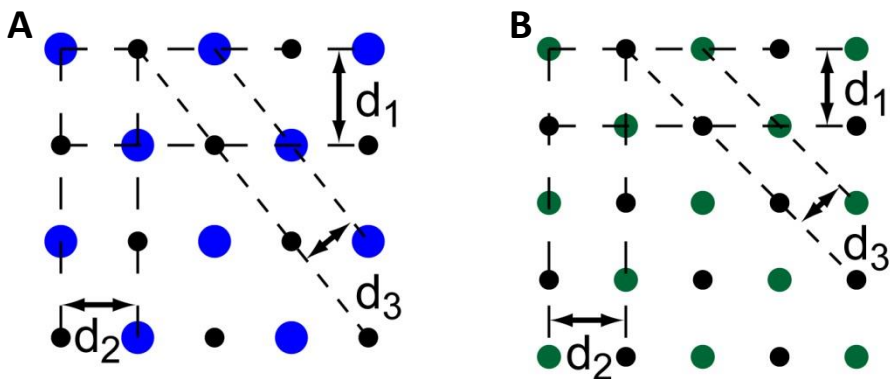


Figure S7. Schematic illustrating crystal lattice plane spacings (d_1 , d_2 , d_3) for A) lead phosphate and B) calcium lead phosphate



Methods

The lead service lines (LSLs) were shipped devoid of water, but with their ends sealed to prevent the scales from drying out. Samples were received at US EPA's Andrew W. Breidenbach Environmental Research Center in Cincinnati, Ohio. On receipt the exterior surfaces of the pipes were cleaned with a wire brush and rinsed with de-ionized water. The ends were then uncapped, and the scales dried under ambient air conditions overnight. A bandsaw was used to cut each LSL into approximately 12-inch long sections which were then split longitudinally. Each section was carefully cleaned of lead shavings introduced by the cutting process and representative sections were photographed and set aside for archive. Each section of the LSL was examined, and scale layers were determined based on color and textural details. Once all layers were identified and described a variety of paintbrushes and metal picks were used to harvest each individual scale layer as has been described elsewhere (1-8). Once sampled each layer was crushed and passed through a 75 μm sieve to achieve relative particle size uniformity.

Representative sections of each LSL were selected and the scales were set with Buehler Epo-Heat epoxy resin (Lake Bluff, IL). The resulting epoxied LSLs were trimmed into approximately 1 cm^2 blocks that served as an illustrative example of the scale layers present in each sample. Each block was polished using a JEOL SM09010 cross-section polisher at 5.5 kV for 8 hours. These cross-sections were then analyzed on a JEOL JEM 6490LV scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Energy-Dispersive Spectroscopy (EDS) elemental analysis was performed using an Oxford X-Act analytical drift detector (Oxford Instruments, Concord, MA). The EDS system was calibrated using a 99.9% cobalt reference sample prior to spectra collection as suggested by Oxford Instruments. At the operating accelerating voltage of

15 kV X-ray lines detected included: *Pb Ma₁*; *O, P, Ca, Fe, Al, and Si Ka₁*; and *C Ka_{1&2}*. C was detected in all scans; however, it is not shown in the line scans or elemental data because the primary signature from the scale is overprinted by C in the epoxy used to stabilize the sample for cutting and polishing. Oxygen was calculated by stoichiometry and the data were normalized to 100%. This standardless elemental analysis was done using the phi(pz) algorithm used by Oxford's INCA software version 18.1 (Concord, MA).

LSL Scale Descriptions

Individual scale layers for each LSL sample are sequentially numbered from the uppermost layer, which is always given the designation of L1 (layer 1) to the lowest layer (ex. L4). L1 represents the scale layer that is in direct contact with flowing drinking water, while the lowest layer identified (highest number) in a pipe is the scale layer immediately next to the lead pipe wall.

Utility A Scale Morphology

SI Figure 2A represents the scale observed in the LSL from prior to orthophosphate (A_prePO₄) from which two layers were sampled. The outermost layer (L1) was approximately 30-50 μm in thickness with a finely crystalline texture that created a relatively even yellowish red (Munsell value 5YR 5/6) coating along the length of the LSL, although there were areas where the coating was cracked and portions of the scale had flaked away revealing a dark reddish brown material underneath (Munsell value 5 YR 3/4). The layer directly against the lead pipe wall (L2) had a very thin surface layer of crystalline reddish black material (Munsell value 5R 2.5/1) which changed to a thicker dusky red crystalline material (Munsell value 5R 3/4). L2 is in total

approximately 125 μm thick and in places contains cracks filled with white (Munsell value N8) to pink (Munsell value 10R 8/3) crystalline material.

The LSL that had been exposed to the phosphate treatment in Utility A (A_postPO4) is pictured in SI Figure 2B. Four layers were harvested from this pipe. Layer 1 (L1) has a granular, rough bumpy surface texture and ranges in color from light olive brown (2.5 Y 5/3) at the surface to reddish yellow (7.5 YR 6/8) with depth. This layer is up to 100 μm thick and includes some white (N8) crystalline material that seems to extend up from layer 4 (L4). Layer 2 (L2) is finely crystalline and smooth in texture, creating a relatively uniform layer across the entire pipe surface and is dark red (10R 3/6) in color. The white patches and bands identified in L1 are also visible within L2. L3 is a dusky red (10R 3/3) color and is well adhered to the surface of L4. Combined, L2 and L3 are approximately 50 μm thick. The lowest layer is L4 which ranges in color from reddish black (10R 2.5/1) at the surface (L4a) to very dusky red (5R 2.5/4) (L4b) and is around 150-170 μm thick and very well adhered to the lead pipe wall.

Utility B Scale Morphology

The uppermost scale layer in Area 1 (L1) was identified as a porous friable layer with an uneven surface (B_area1 L1). Approximately 400-500 μm in thickness this strong brown (Munsell value 7.5 YR 5/8) colored layer was only identified in the region around the wiped joint and as shown in SI Figure 4A and 4B there is a shift in color at the base of L1 to a very pale brown (Munsell value 10 YR 8/4). The surface layer is poorly adhered to layer L2, such that there is a distinct detachment zone between L1 and the underlying material. The middle two layers form a

gradational succession of reddish-brown colored scale with a total thickness of approximately 80 μm . L2 is about 30 μm thick and finely crystalline, L3 is about 50 μm thick with a slightly different color and subtly coarser texture than L2. The lowest layer in Area 1 (L4) is very dusky red in color (Munsell value 2.5 YR 2.5/2). This layer is compact and forms a thin (~ 20 μm) hard surface adhered to the lead pipe wall.

The uppermost layer of B_area2 is starkly different from that in B_area1. Bearing a white to pinkish white crystalline appearance (Munsell value N8 to 2.5 YR 8/2) consisting mainly of small transparent/translucent platy crystals. L1 is approximately 10-30 μm thick with sporadic patches of pale yellow (Munsell value 2.5 Y 8/13) to reddish yellow irregularly shaped crystals (Munsell value 5 YR 7/8) exposed at the surface (SI Figure 4C and 4D). These patches appear to originate below L2, which is approximately 30 μm thick and comprised of a finely crystalline yellowish red (Munsell value 5YR 4/6) material similar to that of B_area1 L2 and L3 layers. In places the upper part of layer L2 has sloughed off, leaving a rough, irregularly channeled surface (SI Figure 4C). This disruption of L2 likely preceded or was contemporaneous with the formation of layer L1, as L1 overlies both high and low areas of L2. Layer L3 in sample B_area2 is identical to L4 from B_area1.

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