

Oxidant/Disinfectant Chemistry and Impacts on Lead Corrosion

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Background

In response to continued elevated lead levels throughout the District of Columbia's distribution system, a collaboration was begun with the District of Columbia's Water & Sewer Authority (WASA) and Water Resources Division of U. S. Environmental Protection Agency's (USEPA) Office of Research and Development in late winter of 2004 to investigate the causes of the sudden increases in lead release. Lead levels had been slightly above the Action Level in 1991 through 1994. Although increases in pH and the addition of orthophosphate were investigated in pilot studies and desktop corrosion studies at that time, the 90th percentile lead levels dropped to below 0.012 mg/L throughout the mid- to late 1990s. This coincided with a program of increased flushing and considerably elevated free chlorine dosages (often as high as 4 mg/L) to provide improved control of biofilms and bacterial regrowth. However, by 2000, concern with the upcoming increases in stringency of disinfection byproduct regulations led to a decision to change to chloramination in an attempt to keep trihalomethane (THM) levels below the new standards. The change was made in November of 2000, and in the next Lead and Copper Rule (LCR) monitoring round, the 90th percentile lead level surprisingly was found to have jumped to over 0.07 mg/L. Subsequent LCR 90th percentile results have remained over 0.04 mg/L. The general history of lead levels is illustrated in Figure 1, keeping in mind that some sampling periods are represented by some different monitoring sites in the site pool, and there were also differences in the number of sampling sites required.

Although there was considerable skepticism that chloramination could have been the cause of the sudden elevation of lead levels, some apparent increases of lead and copper release and attack on brass had been reported before in several investigations (Larson et al., 1956; James M. Montgomery Consulting Engineers, 1982; Francis, 1985a, 1985b; James M. Montgomery Consulting Engineers, 1985; Schock, 1999). In fact, reviews of general aspects of the redox chemistry of disinfectants and consideration of the different chemical behavior of metals in their different common valence states (eg. Fe, Mn, Cu, Pb) do suggest that any substantial change in the oxidation/reduction potential (ORP) could substantially alter the behavior of pipe scales and

the potential for corrosion byproduct or contaminant release (AWWARF-TZW, 1996; Schock, 2000; Schock & Holm, 2003).

While most water treatment and water chemistry specialists are very familiar with the radically different solubilities and scale formation properties of ferrous iron versus ferric iron, or cuprous copper versus cupric copper, there is much less realization of the same potential behavior of lead. Potential-pH diagrams for the lead system going back many years have a prominent stability field for the highly insoluble lead dioxide (PbO_2) solid (Delahay et al., 1951; Pourbaix et al., 1966; Pourbaix, 1973; Schock, 1980, 1981; Schock & Wagner, 1985; Schock et al., 1996; Schock, 1999). Thus, an analogy can be drawn between the $\text{Pb(IV)}\text{-Pb(II)}$ redox couple and the $\text{Fe(III)}\text{-Fe(II)}$ redox couple. The higher valence state forms oxide or oxyhydroxide scale phases of much lower solubility than those of the lower valence state. In the case of lead, however, the ORP required for the transformation of Pb(II) to Pb(IV) is much higher than for the ferrous to ferric iron transformation. Because of typical free chlorine dosages, consumer dislike of chlorinous tastes and odors, normal water residence times, and the usual pipe wall and bulk water oxidant demands, such highly oxidizing conditions will not be common amongst public water systems in the United States.

USEPA analyses of scales from lead pig-tails and service lines in the late 1980's and early 1990's verified that one or both of the common polymorphs of PbO_2 (plattnerite and scrutinyite) were present in varying degrees on the pipes from several different water systems (Schock et al., 1996). Thus far, of more than 85 lead pipe specimens obtained from 34 water systems, at least 16 specimens representing 9 systems have either $\alpha\text{-PbO}_2$, or $\beta\text{-PbO}_2$, or both present in clearly identifiable quantities. More samples may have trace amounts that are hard to positively confirm. Usually, the PbO_2 exists in the form of patches or a thin surficial layer at the water boundary. PbO_2 comprises nearly the entire scale material in the pipe samples from WASA and Cincinnati, and the majority of the scale material in some Oakwood, OH specimens. In Madison, WI, it formed a rather distinct surficial layer in contact with the water. The presence of PbO_2 is associated with waters of persistently high ORP. The elevated ORP could be caused by any of several mechanisms. For example: pristine low-NOM ground waters with little bulk oxidant demand allowing significant persistence of free chlorine; waters that very effectively passivate iron and remove its oxidant demand (such as hard waters with high buffering intensity); waters with low oxidant demand resulting from oxidative treatments such as greensand filtration (enabling the stability of high ORP); and many other possible scenarios. An additional cause can be the use of very high dosages of free chlorine to combat biofilm problems or to overcome corrosivity towards iron and its pipe wall demand.

More pipe analysis investigations by the U. S. Environmental Protection Agency in 2000 and 2001 revealed much more evidence for the importance of tetravalent lead compounds as very large primary components of lead service line scale material, particularly those in Cincinnati, Ohio and Madison, Wisconsin (Schock et al., 2001). In the Cincinnati pipe, representing long periods of relatively high disinfectant concentrations, followed by a combination of granular activated carbon and free chlorine treatment, essentially the entire scale was composed of the two PbO_2 polymorphs, with only traces of basic lead carbonate. It is not known when the PbO_2 scale formed in the Cincinnati pipe, as there were no historical scale analyses during several earlier treatment schemes. For the distribution system area where the Cincinnati pipe specimens

were obtained, it has employed elevated pH (8.5 to 9.2) since the 1980s for corrosion control. The lead service line specimens from Madison had a thin layer of PbO_2 at the water interface, with PbCO_3 making up the bulk of the underlying scale. An important amount of tetravalent lead scale material was also found in pipe from Oakwood, Ohio (another pH 7 high alkalinity water where greensand filtration for iron removal is employed). Taken in combination, these observations finally provide a reasonable hypothesis to explain the apparent anomaly observed in many field studies in which high alkalinity waters did not tend to produce nearly as high levels of lead release as would be expected from the knowledge of lead solubility chemistry and bench-scale tests (Dodrill & Edwards, 1994; Dodrill, 1995; Dodrill & Edwards, 1995; Edwards et al., 1999).

Pipe Scale Analyses Results

Lead service line specimens from residential homes in the District were shipped to the WSWRD, U. S. Environmental Protection Agency lab in Cincinnati, with their ends sealed to preserve humidity and moisture. The specimens were cut longitudinally with a band saw having a fine metal-cutting blade, and were photographed with a stereomicroscope at 6 to 66 X. Figures 2 and 3 illustrate some of the specimens from the WASA system that were analyzed, and how they compare to similar scales composed of large amounts of tetravalent lead compounds from other water systems.

Scale was removed and analyzed by X-ray powder diffraction using the same procedures as described previously (Schock et al., 2001). When lead carbonate and hydroxycarbonate solid phases are present, the positive identification of PbO_2 can be somewhat problematic, because some of the significant diffraction peaks of $\beta\text{-PbO}_2$ and $\alpha\text{-PbO}_2$ overlap with some of the peaks from PbO (litharge) and PbCO_3 (cerussite). While the d-space accuracy of the carefully-calibrated diffractometer should be more than sufficient to positively identify the phases of interest, the naturally-formed solids tend to have lattice distortions and peak broadening from small crystallite sizes. Both of these factors complicate the positive identification of PbO_2 polymorphs.

Therefore, to confirm the existence of tetravalent lead phases and corroborate the XRD results, the Pb pipe scales were additionally analyzed by X-ray absorption near edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopies. For XANES and XAFS studies, a thin layer of a Pb scale was smeared onto Kapton tape and folded back on itself. Pb (13035 eV) L_{III} -XANES and XAFS data were collected at Sector 20-BM (Pacific Northwest Consortium - Collaborative Access Team (PNC-CAT)) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The electron storage ring operated at 7 GeV. Three scans were collected at ambient temperature in fluorescence mode with an Ar-purged Lytle detector. A 0.5 mm premonochromator slit width and a Si(III) double crystal monochromator detuned by 20% to reject higher-order harmonics was employed. The beam energy was calibrated by assigning the first inflection of the absorption edge of lead metal foil to 13 035 eV. Reference samples of PbO (massicot), PbCO_3 (cerussite), $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite), $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (chloropyromorphite), $\text{Pb}(\text{NO}_3)_2$, $\beta\text{-PbO}_2$ (plattnerite), and Pb_3O_4 were commercially obtained

for comparison with the XANES and XAFS spectra. The phase identities were confirmed by XRD. The collected scans for a particular sample were averaged, the data were then normalized, and the background was removed by spline fitting using WinXAS 2.0 (Ressler, 1998).

Because the scales were very thin and tenaciously adherent to the pipe surfaces, only small amounts (tens of milligrams) were available for analysis. Subsamples have also been sent by USEPA to the U. S. Geological Survey laboratory in Denver, for digestion and elemental analysis to investigate general scale chemistry and to try to help identify some of the other trace compounds present in the diffraction patterns.

Figures 4 and 5 show examples of the XRD and XANES patterns that confirmed that the WASA lead pipes are coated with a thin and uniform layer of α - and β -PbO₂.

Discussion

Conventional lead corrosion control theory, which is normally based on divalent lead chemistry, would predict solubility behavior approximately as represented in Figure 6. This was done using the LEADSOL computer program (Schock, 1980; Schock et al., 1996) with some representative concentrations for chloride, sulfate and total inorganic carbon. Figure 7 illustrates the difference in trends and order of magnitude of solubility for tetravalent lead as opposed to divalent lead.

Trying to model Pb(IV) solubility is full of difficulties, as there is little relevant data appropriate to potable water systems. Some of these issues have been addressed previously (Schock et al., 2001). Due to lack of stability constant data and speciation data, the model followed suggestions of Pourbaix (1966) as a first approximation. Only PbO₃²⁻ and PbO₃⁴⁻ complexes were included. The accuracy of the thermodynamic data and the proper species to choose for the aqueous model is highly questionable. However, even if considerably off, it still strongly argues that tetravalent solubility is remarkably lower than in well-treated systems working with divalent lead scales. Using the existing tentative aqueous solution model for Pb(IV), tetravalent lead solubility is predicted to be at its lowest level at a pH even below neutrality. Hence, the solubility minimization trend with pH is intriguingly opposite that of Pb(II) in the normal pH range for controlling corrosivity to metallic materials, approximately pH 7 to 10.

No specific information on identified Pb(IV) orthophosphate or carbonate-containing solids has been uncovered so far. Whether or not orthophosphate interacts with tetravalent lead is also hard to determine reliably, because of conflicting published interpretations of experimental results from lead-acid battery performance investigations (Voss, 1988). At very high phosphoric acid concentrations, some evidence has been found for some stable Pb(IV)-orthophosphate complexes or poorly-crystalline materials (Amlie & Berger, 1972). Some research suggests that orthophosphate facilitates reversibility of oxidation and reduction by surface sorption and modification of the PbO₂ phases, while other research suggests that the orthophosphate could bind with Pb(II) and reduce the formation of PbSO₄ (Bullock & McClelland, 1977; Bullock, 1979a; Bullock, 1979b, 1980; Voss, 1988). The high acidity and extremely high concentrations of sulfuric and phosphoric acids present in such systems cannot be directly applied to estimate the relative impacts at concentrations thousands of times lower in drinking water solutions. One

of the most interesting aspects of the literature, however, is that PbO_2 solids may readily function as semiconductors (Greninger et al., 1975). Thus, there is likely considerable electrochemical reversibility and ease of electron transport between the water and the underlying lead metal of the pipe, making responses of the scale to changes in ORP rather fast and measurable.

The critical role that the concentration and type of disinfection plays in the formation and solubility of passivating films on lead service line piping is clarified by Figure 8. The top figure is a simple potential-pH diagram for 1 mg/L free chlorine, showing the speciation of the chlorine system and the high ORP necessary for free chlorine stability. These fields are considerably above the thermodynamic water stability boundary. The bottom two graphs show the comparison of ORP values obtained using different concentrations of monochloramine solution and free chlorine in recent USEPA laboratory studies by James, et. al. (2004). Note the ORP produced by monochloramine concentrations are far lower than those produced by the same concentration of free chlorine. Referring to the potential-pH diagram for lead (Figure 9), it can be seen that free chlorine at high dosages can produce sufficiently high ORP to form PbO_2 . These experimental data are in good agreement with values extracted from the research literature in papers relating to virus inactivation studies or breakpoint chlorination studies (Schock et al., 1996).

There are some uncertainties in the PbO_2 field boundary because of the imprecision and possible inaccuracy of the tabulated free energy of formation data, although it is qualitatively consistent with the analyzed scale material and the solubility behavior in the actual lead piping. The boundary would shift upward (higher ORP needed) if the PbO_2 material is less soluble than predicted by the published data. However, there is clearly a straightforward mechanism that can readily explain the sudden rise in dissolved lead release (as well as some particulates) when the ORP is lowered. In the pH range of normal operation (high 7's to low 8's), divalent lead solubility is considerably higher than the Action Level, and observed lead levels in targeted samples representing water in direct contact with the lead service lines for "overnight" standing periods were in an amazingly similar range (100 to 200 $\mu\text{g/L}$) to that predicted by the solubility model. Unfortunately, specific lead service line sample data was not available from the late 1990's when the 90th percentile values were very low and the ORP was very high from the use of free chlorine. However, given the first-draw relationships to the service line concentrations in the current sampling (post-chloramination), the lead levels were probably very low during that time period, consistent with tetravalent lead solubility trends. Note that of 5 second-draw sample collections in 1997-2000, the 90th percentile for the second-draws were equal or lower than the 90th percentiles for the first draws in 3 cases and only slightly higher in the other two cases. Since the change to chloramination and the lead scale destabilization, the 90th percentile of the second draw samples has always been at least approximately 50% higher than the 90th percentile of the first draw samples, and has generally been 2 to 4 times the Action Level.

Two other lines of investigation further corroborate the operation of the Pb(IV) to Pb(II) conversion mechanism as being the cause of the sudden increase in lead levels. During April of 2004, the normal springtime seasonal switch to 1 month of free chlorine residual (4 mg/L) was made. After 3 weeks of going back to free chlorine, several lead profiles were conducted in residential homes containing lead service lines that previously had lead profiles conducted during

chloramination. In all cases, lead levels decreased substantially over that time frame (Figures 10 & 11), showing the reversibility of the lead redox reaction.

Support is also provided by data from the exhumed pipe section used in one of the “stagnation” loop tests described by Thomas et al, (2004), shown in Figure 12. After equilibrating with the chloramines “control” condition, the disinfection was changed to hypochlorite solution (dashed reference line). The lead concentrations immediately began to drop. After about a month of operation at approximately 5 mg/L free chlorine dosage, the dosage was approximately doubled (solid reference line). As was demonstrated in the USEPA laboratory experiments (Figure 13), the ORP did not change significantly by the additional free chlorine addition. Lead levels continued to nearly linearly decrease. It is hard to tell from the data if the trend was beginning to reduce in slope after about 3 weeks of this elevated ORP when approximately 10 mg/L (as PO₄) was added to test its effect (dot/dashed line). Therefore, it is not possible at this time to unambiguously determine if the apparent stabilization is caused by interference with the oxidation of existing Pb(II) solids in the scale to PbO₂, or not. In comparison to the “control” experiment with chloramine only (not shown), the lead concentration after 2 months of return to free chlorine was more than a factor of 15 times lower. Interestingly, the total lead concentration in the control loop is similar (particularly within modeling uncertainty) or slightly higher than that predicted by the diagram in Figure 6, and the dissolved lead concentrations in orthophosphate-dosed chloraminated loops were mostly between approximately 45 and 80 µg/L, again consistent with model trend predictions, though slightly higher.

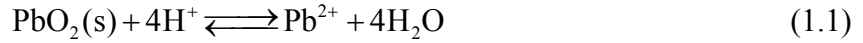
The plausibility of relatively rapid (months) formation of PbO₂ under drinking water conditions (DIC = 10 mg/L, free chlorine residual, pH 6.5 – 10) from the addition of lead chloride to water has been proven in bench experiments at USEPA (Lytle & Schock, 2004). The PbO₂ evolved from a hydrocerussite or cerussite precursor phase, and when the ORP decreased after the chlorine residual was reduced or lost, the PbO₂ decomposed. The phase transformations were observed to follow the expected trends, i.e. decreasing dissolved lead concentration during PbO₂ formation, and increases back to the carbonate phase equilibrium values after oxidant depletion and reversion. The induction period for PbO₂ formation varied with pH, but was generally only a few weeks. Decomposition after the loss of sufficient ORP was similarly only a few weeks in duration.

Future Research Needs

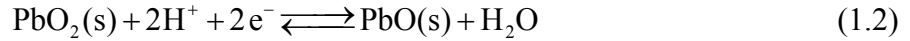
More lead pipe specimens will be collected and analyzed from both the service line removal program, and also from the laboratory test systems, to get an even better understanding of the scale transformations taking place.

The field data and the chemical models show that high ORP conditions will mitigate the lead solubility problem caused by the breakdown of the PbO₂ passivating scale. However, if the maintenance of high ORP conditions through free chlorine are not desired for other reasons, there is relatively little firm information upon which to base the development of an alternative treatment strategy that would be as effective against lead release.

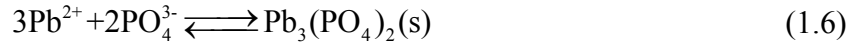
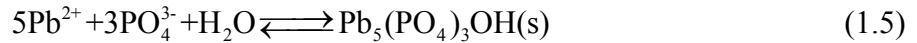
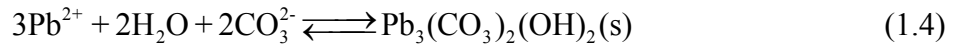
The viability of different alternate treatment schemes are totally dependent upon the exact reaction pathway of the chemical reduction/breakdown pathway of the PbO₂, and the relative rates of the breakdown reaction(s) versus the rates of formation reactions for divalent lead compounds. For example, the breakdown of PbO₂ could follow any of several reaction paths to release lead into solution, such as (but not confirmed to be)



or



Pb(II) oxide and hydroxide are both extremely soluble at any drinking water pH, so other precipitation reactions would have to be operative to limit lead levels. Once in solution, the activity of the free lead ion will be governed by the amount of complexation, primarily by bicarbonate, carbonate, and hydroxide ions (Hunt & Creasey, 1980; Schock, 1981; Schock & Gardels, 1983; Schock et al., 1996; Schock, 1999). The free lead ion can then react with carbonate or orthophosphate in the water to precipitate one of the conventional passivating solids. For example:



Presumably, these reaction rates would necessarily be very dependent upon pH and the activities of the passivating and complexing ligands, such as bicarbonate and orthophosphate. Unfortunately, kinetic information for these dissolution and precipitation reactions is almost completely lacking, making *a priori* estimates of lead levels and time to achieve them very unreliable. If the existing scale dissolves faster than the released aqueous lead(II) species can re-precipitate into a sufficiently insoluble passivating film, then prolonged elevated lead levels will persist, until all of the prior scale is converted. If the precipitation reactions are as fast or potentially faster than Pb²⁺ ions are released from the PbO₂ breakdown, and if the scale material adheres to the pipe surface, then the lead concentrations in the pipes will stabilize in the usual timeframes typified by the experiences of many other water systems that have successfully used pH/carbonate adjustment or orthophosphate passivation.

The current hardness of the water and the use of lime for pH adjustment essentially precludes the pH/alkalinity/TIC adjustment approach, because the necessary pH (over 9 based on theory and the experiences of other water systems) could not be achieved without major scaling problems in the filters and distribution system. Supplemental softening or some kind of carefully balanced threshold sequestration would be needed. The remaining alternative approach, using orthophosphate dosing, needs to be investigated to determine empirically what the relative rates

of divalent lead passivation reactions are in comparison to the breakdown of the existing pipe scale. As noted above, if the reaction of the Pb(II) released from the breakdown of the PbO₂ scale with orthophosphate in the water (equations 1.5 and 1.6) is equal to or faster than the rate of dissolution and release into the water, then it should be possible to achieve sufficiently low lead levels in the water relatively quickly. If it is not, there is not a good basis to estimate the length of time it would take to achieve complete conversion of PbO₂ to the passivating divalent lead phosphate solids.

Very basic questions pertaining to Pb(IV) chemistry are critical to answer to provide important information necessary for revisions to lead corrosion control guidance, and to properly evaluate disinfection alternatives. These fundamental questions include:

- What are the solubility constants for the α -PbO₂ and β -PbO₂ polymorphs?
- What factors govern the formation of one polymorph as opposed to the other?
- What are the important aqueous complexes of Pb⁴⁺ (e.g. PO₄, SO₄, Cl, HCO₃, CO₃, OH⁻)?
- What are the stability constants of those complexes?
- What reaction pathways are taken for formation and breakdown of PbO₂ phases?
- Are there other important Pb(IV) solid phases for drinking water conditions?

Little is known about the passivation mechanism for exposed soldered joints and brass devices. Whether or not PbO₂ solids can form and be stable on these kinds of surfaces is another important question, because of its relevance to the origin of lead concentrations caught in 1-liter first-draw samples.

Several studies to shed light on some of the aspects of tetravalent lead chemistry are currently underway at WASA and at USEPA. Corrosion control is intimately interrelated with other finished water quality objectives, for consumer satisfaction and regulatory compliance. Therefore, these recent discoveries of the importance of Pb(IV) chemistry in some water systems support the idea that more resources need to be mobilized quickly to gather the information needed to provide timely guidance for water systems confronted with needing to evaluate complex and costly major treatment upgrades to meet new regulatory requirements.

Disclaimer

Any opinions expressed in this paper are those of the author(s) and do not, necessarily, reflect the official position and policies of the EPA. Any mention of products or trade names does not constitute recommendation for use by the EPA.

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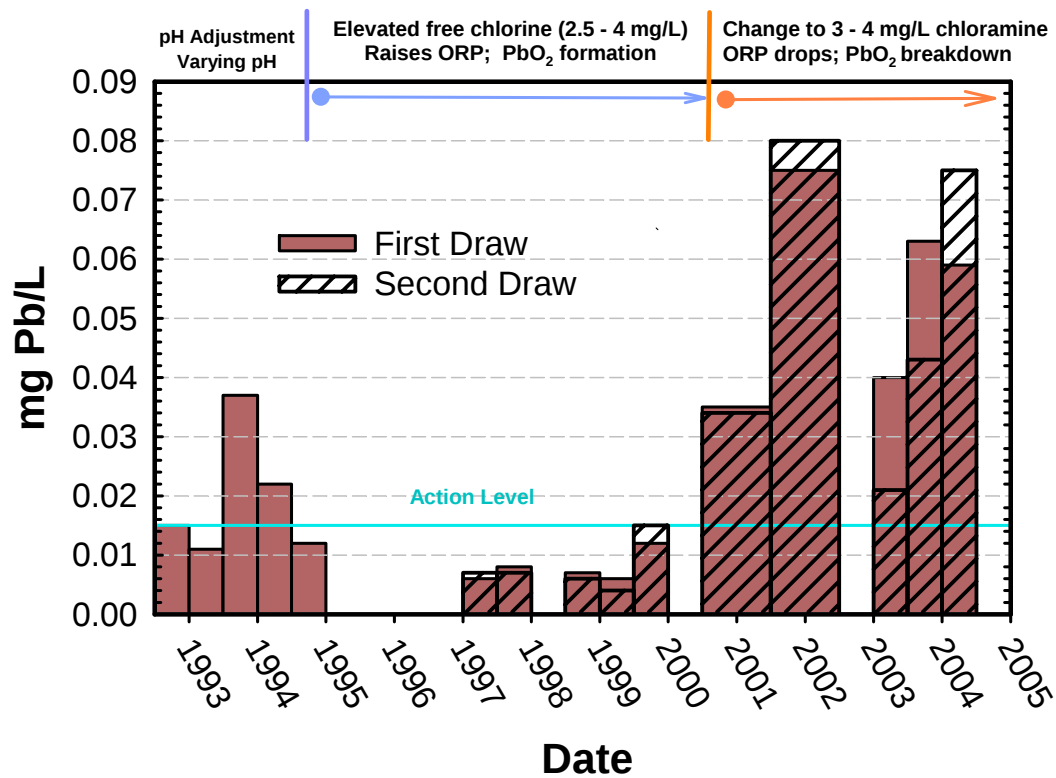


Figure 1. DC WASA lead history timeline.



Figure 2. Lead service line scale from 4 different locations in WASA distribution system.

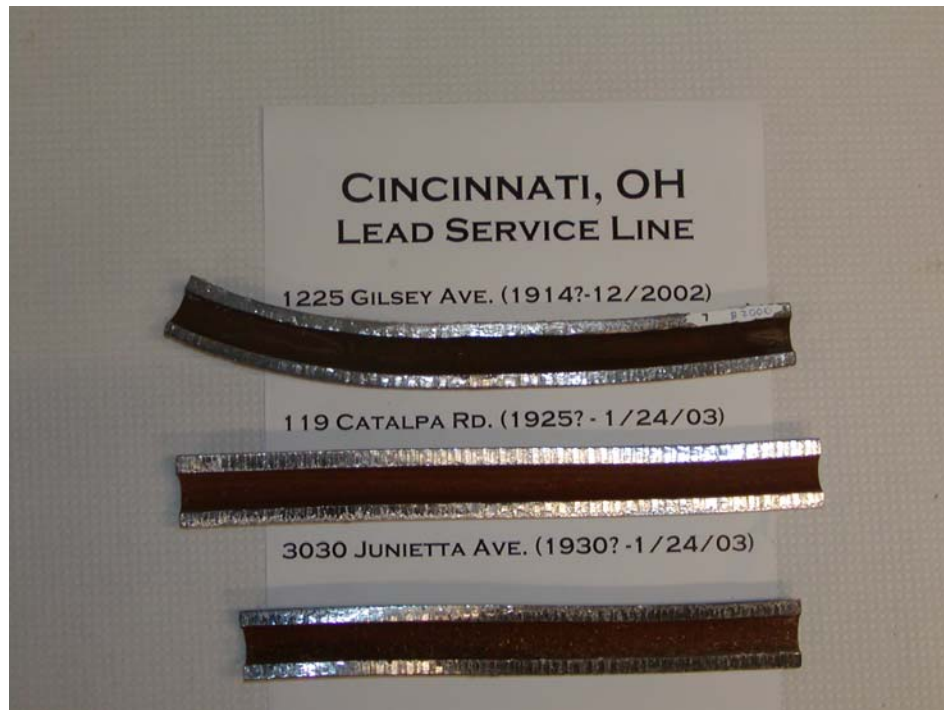


Figure 3. Comparison of similar PbO_2 -rich scales in two other water systems, showing the similarity to the DC-WASA pipe scales.

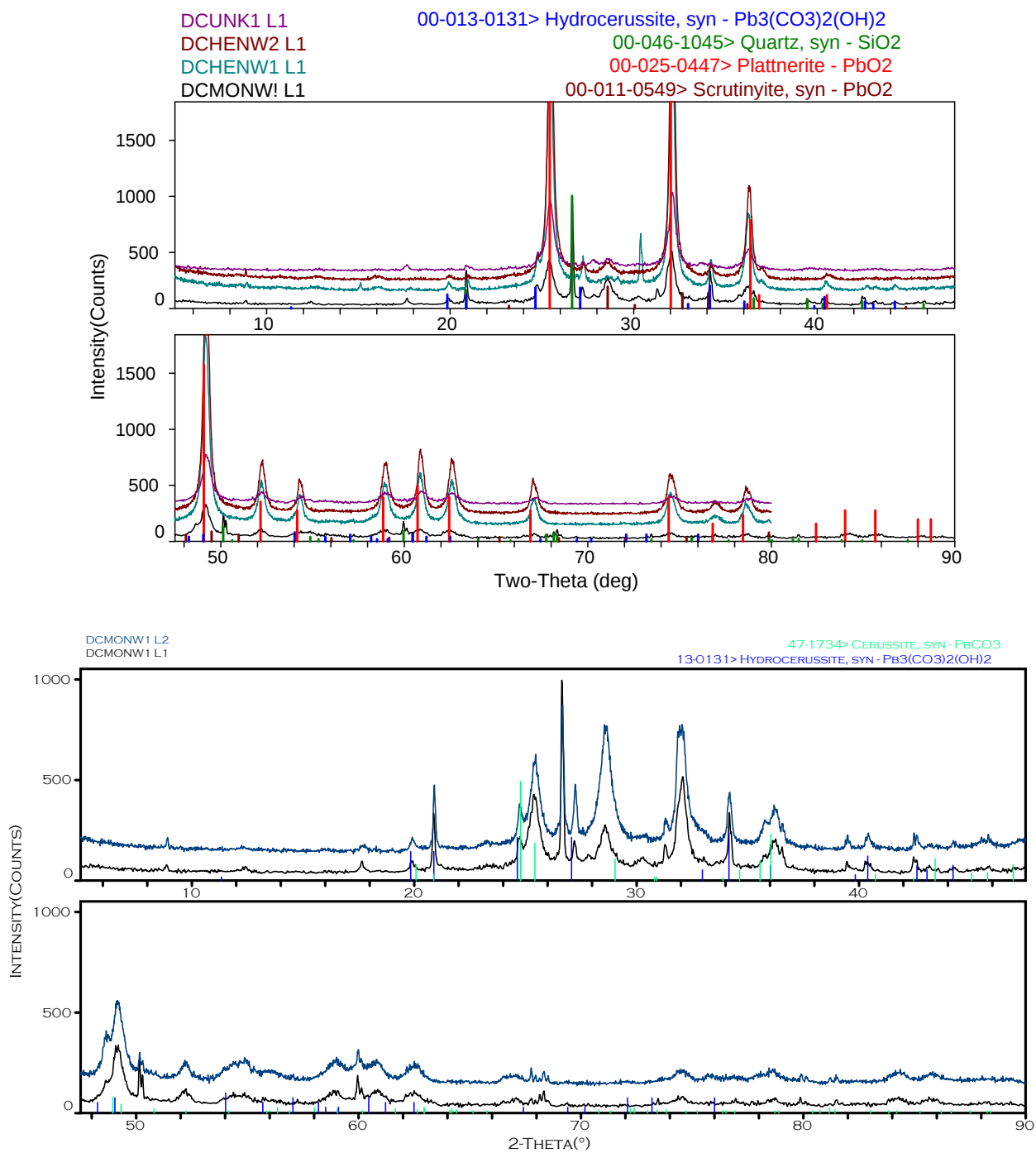


Figure 4. X-ray diffraction patterns of lead service line specimens from the WASA system. (Top) Predominance of plattnerite and scrutinyite phases in four samples and similarity of mineralogical compositions in the different locations. Hydrocerussite and quartz are minor phases on some specimens. (Bottom) Reference lines for cerussite and hydrocerussite for two scale layers (L1 nearest water), showing potential peak overlap for PbCO_3 with PbO_2 and the minor amount of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ present. Large peak near 27° is quartz (SiO_2).

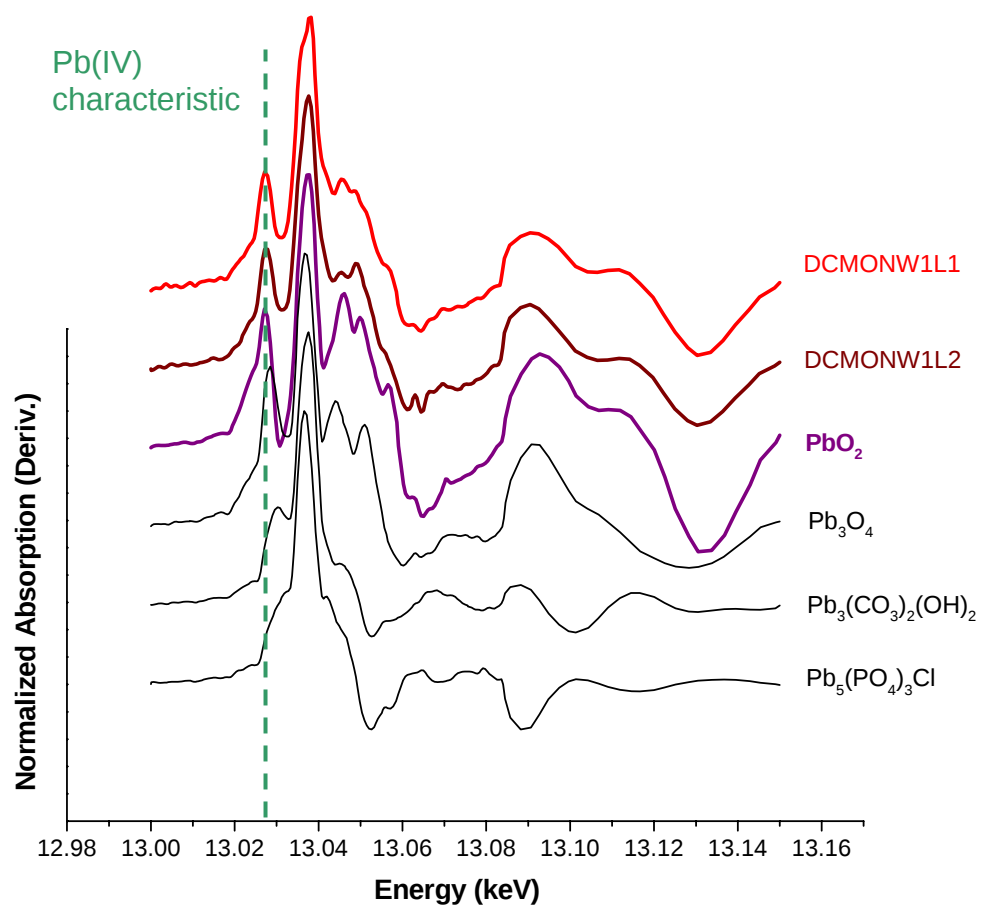


Figure 5. XANES spectra example showing uniformity of scale sample from 1083 Monroe St. NW (two layers scraped) and similarity to reference spectrum for $\beta\text{-PbO}_2$.

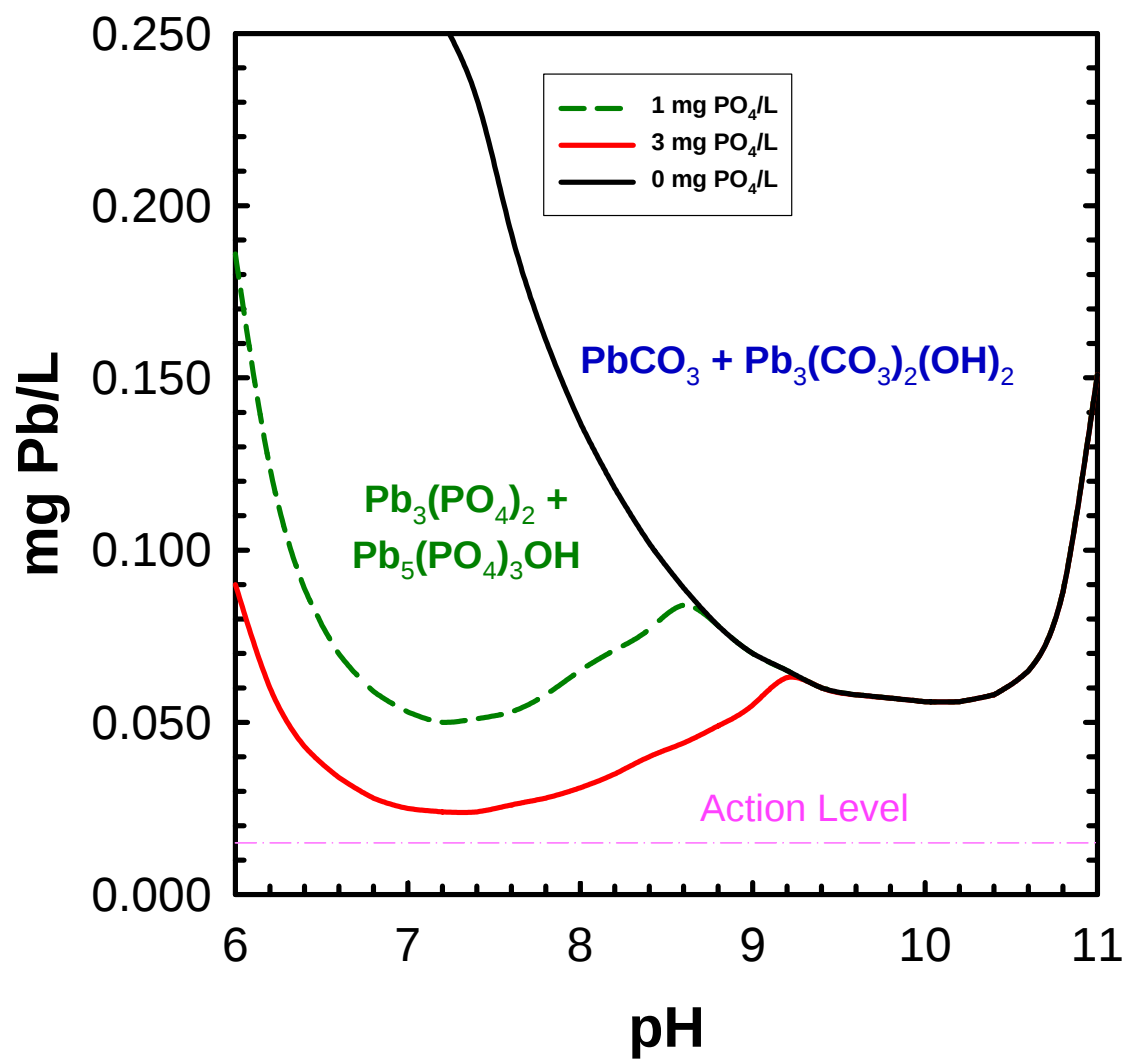


Figure 6. Solubility diagram for the impact of orthophosphate on Pb(II) species for DIC = 18 mg C/L, Cl^- = 31 mg/L, SO_4^{2-} = 44 mg/L, 0.005 M ionic strength, and 25°C.

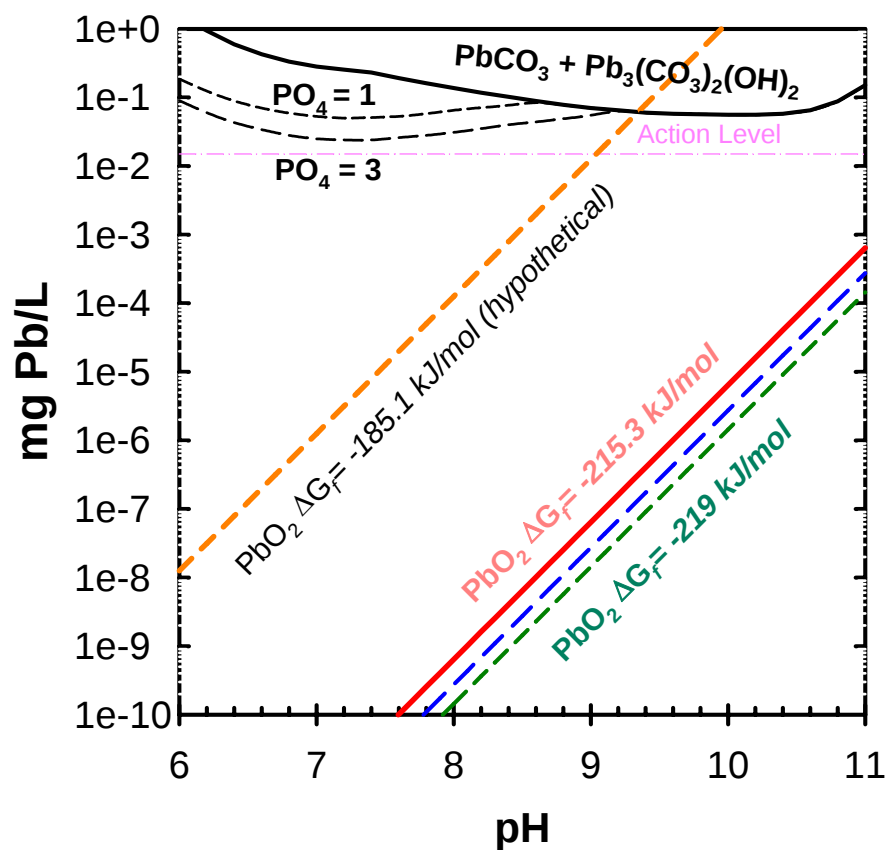


Figure 7. Computed solubility diagram for PbO_2 , using several tabulated Gibbs free energy of formation values to compute the solubility constants. Shown also is the relationship to divalent lead solubility for the same water.

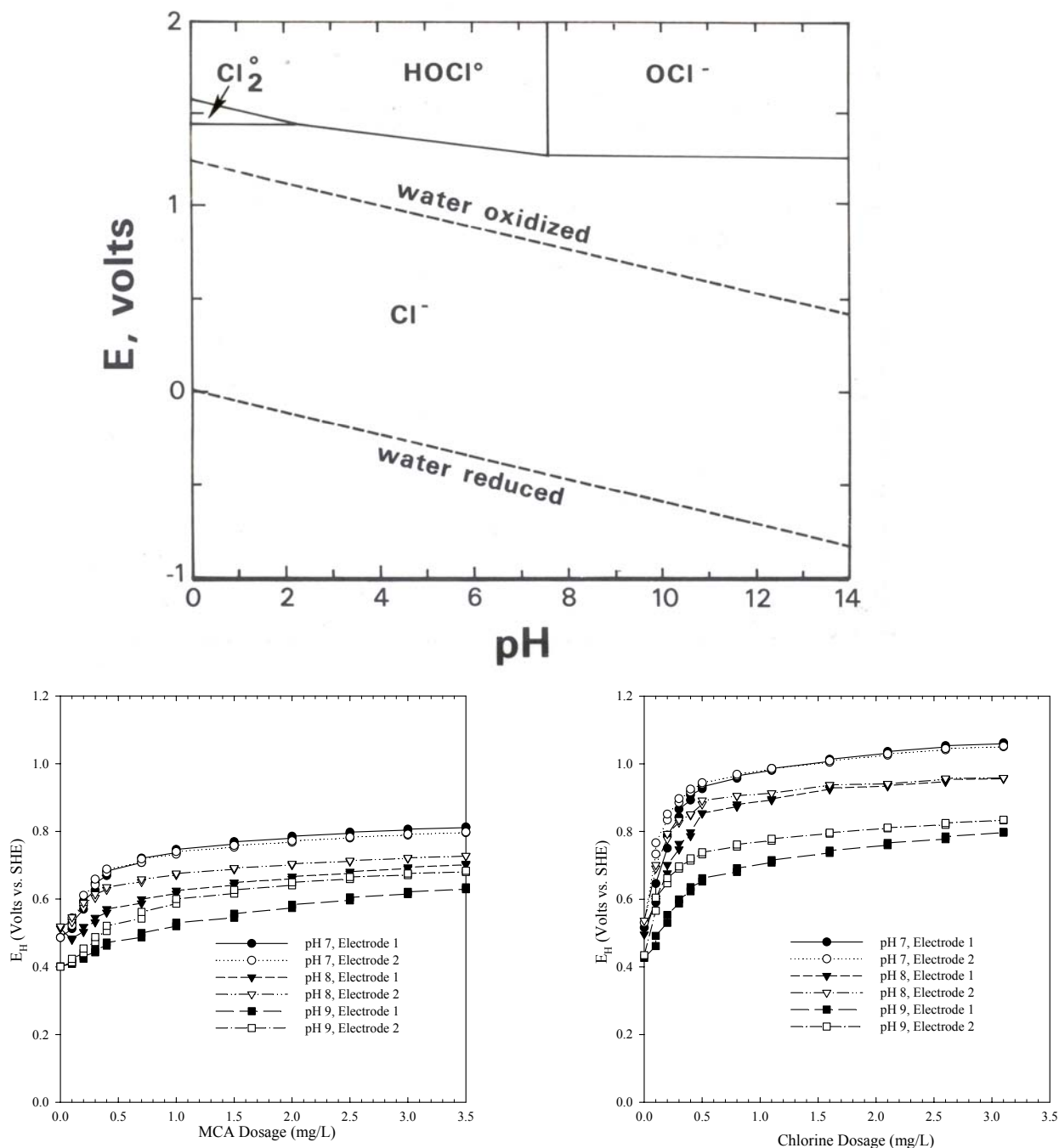


Figure 8. (Top) Potential-pH diagram for 1 mg/L free chlorine, showing the speciation of the chlorine system and the high ORP necessary for free chlorine stability, and the relationship to the water stability boundary. (Bottom) Comparison of ORP values obtained using different concentrations of monochloramine solution (left) and free chlorine (right) in USEPA laboratory studies by James, et. al. (2004). Note the consistently much lower ORPs produced by chloramines.

EMF-pH Diagram for Pb - H₂O - CO₂ System

Pb species = 0.015 mg/L; DIC = 18 mg C/L

I=0; 25°C

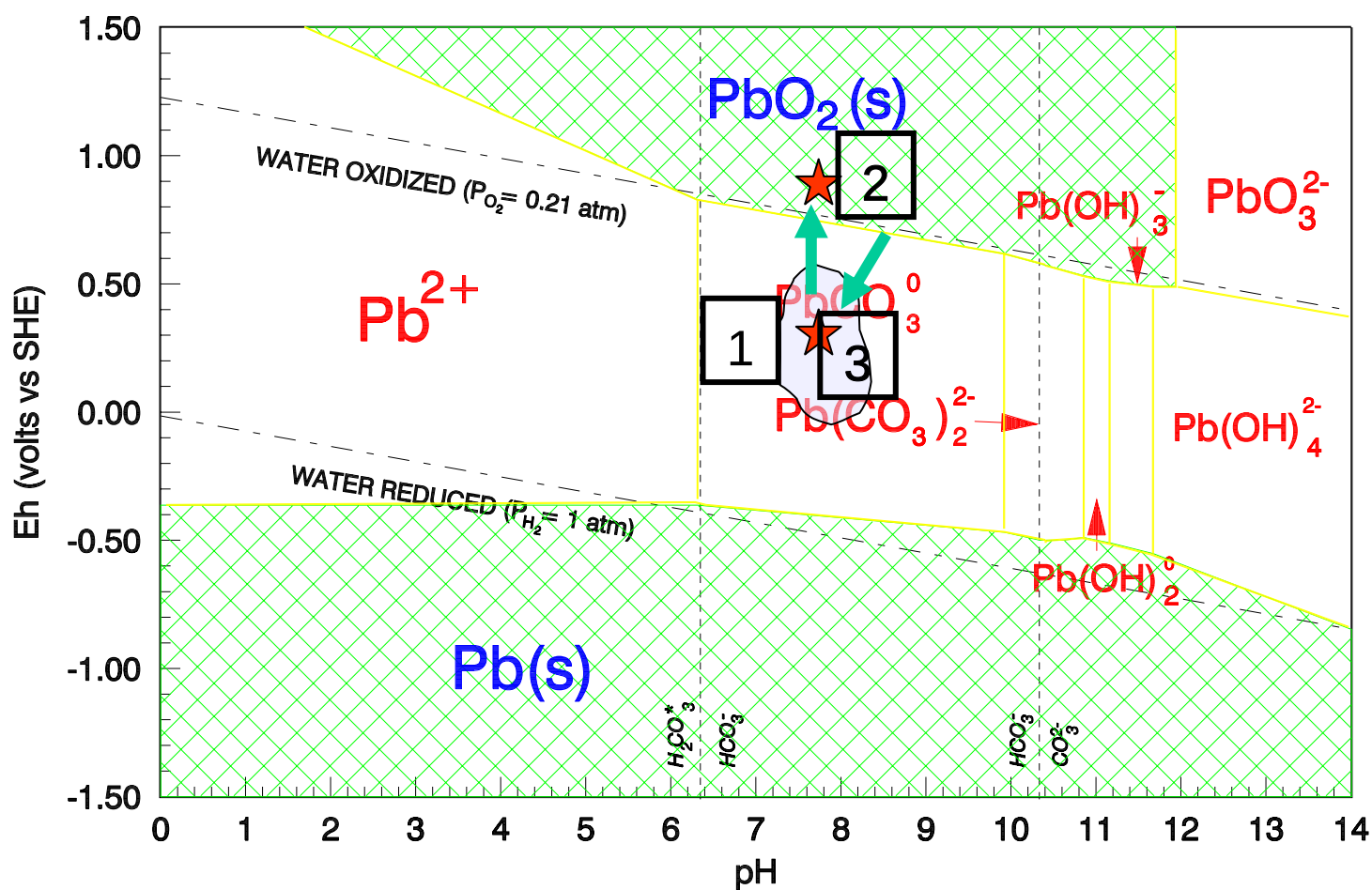


Figure 9. Potential-pH diagram for the lead system corresponding to DC-WASA water, showing how the sequence of treatment changes over the past decade formed and then destabilized the PbO₂ passivating film. (1) represents the initial conditions of the early 1990's where there were some lead release problems. The initiation of high free chlorine residuals and flushing in 1994 moved the system chemistry to approximately point (2). The change to chloramines secondary disinfection in 2001 moved the ORP back into approximately the area of (3).

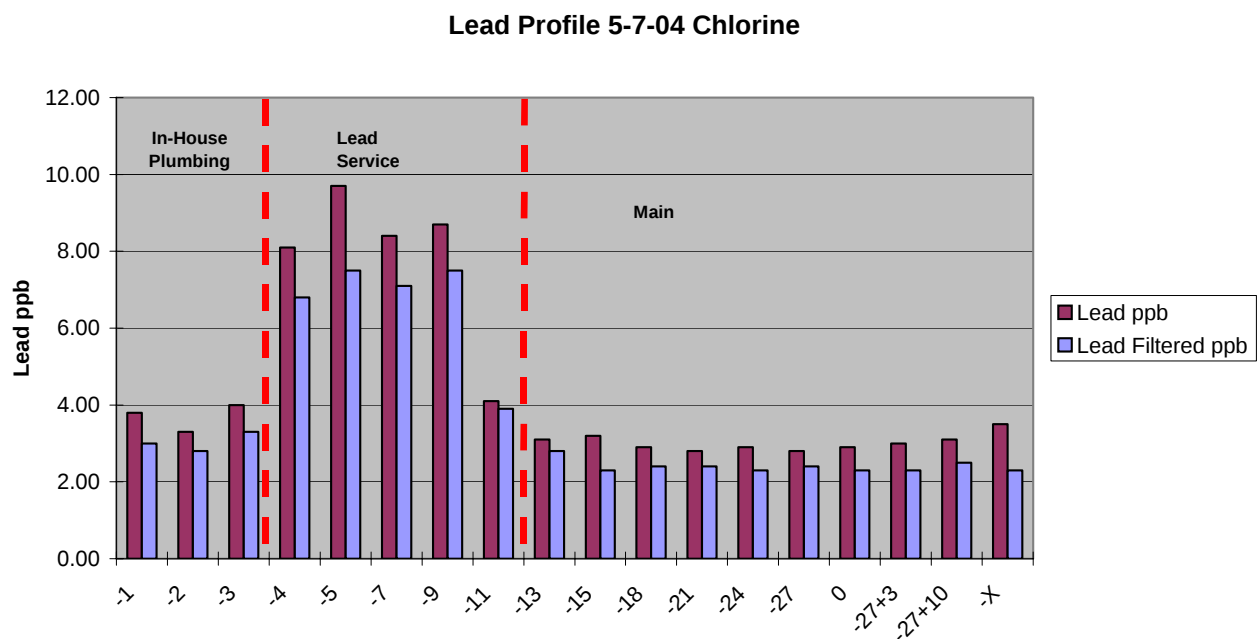
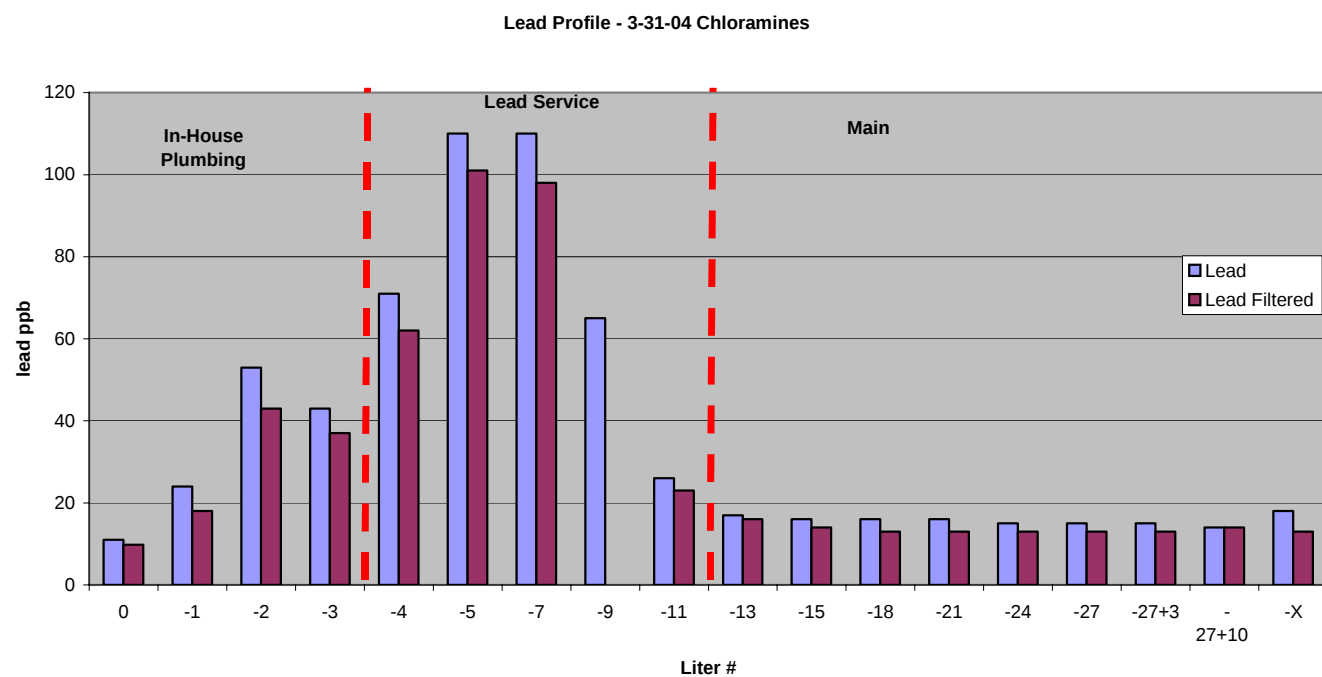


Figure 10. Lead profile conducted at the same home during chloramine (top) and chlorine. The x-axis represents the liter number taken from the tap into the main (i.e. 1 = first draw, 2 = 2nd liter, 27 = 27th liter. 27+3 represents 3 minutes after the 27th liter was taken, X = water hammer). Lead profile procedures taken from *Edwards, Giani et al 2004*)

Peak dissolved lead levels in homes during lead profiles

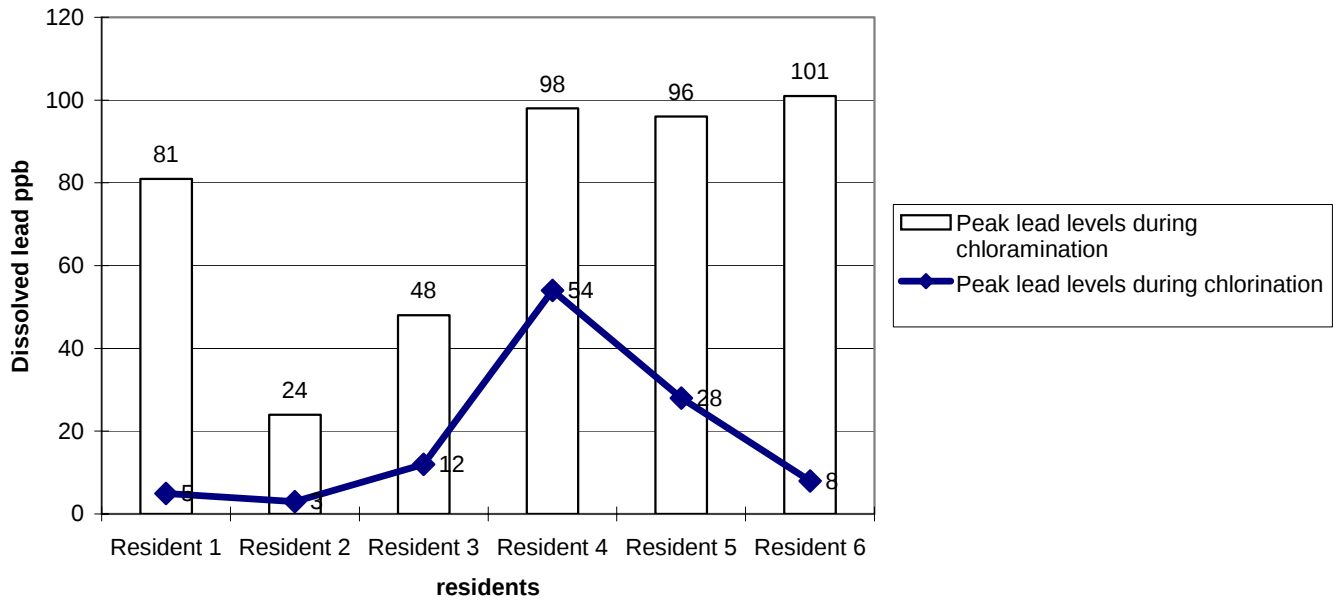


Figure 11. Peak dissolved lead concentrations taken from 6 residential homes during chloramination and chlorination.

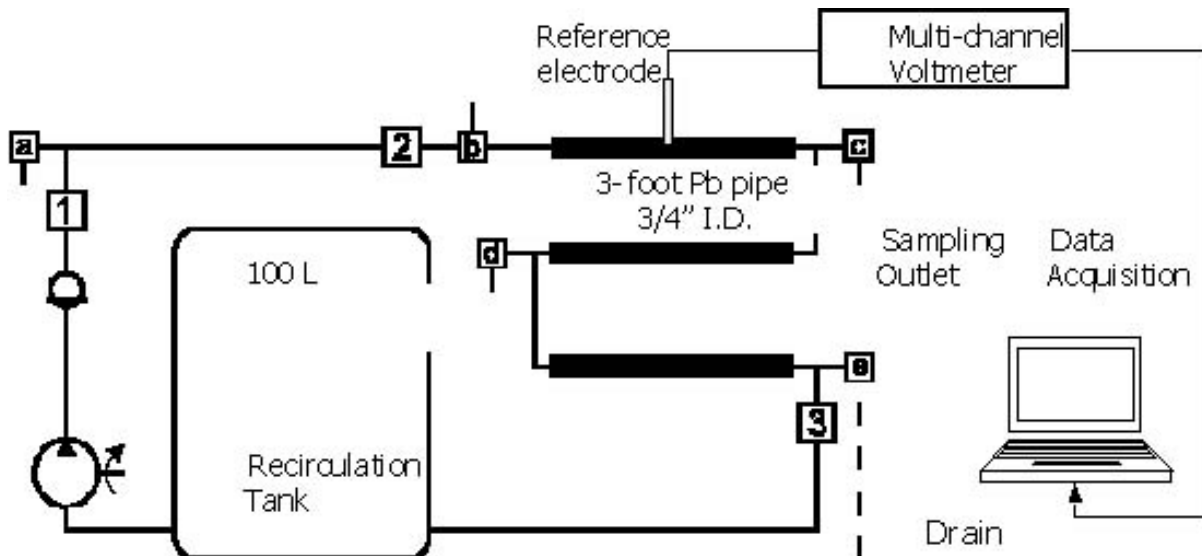


Figure 12. Stagnation loop setup diagram.

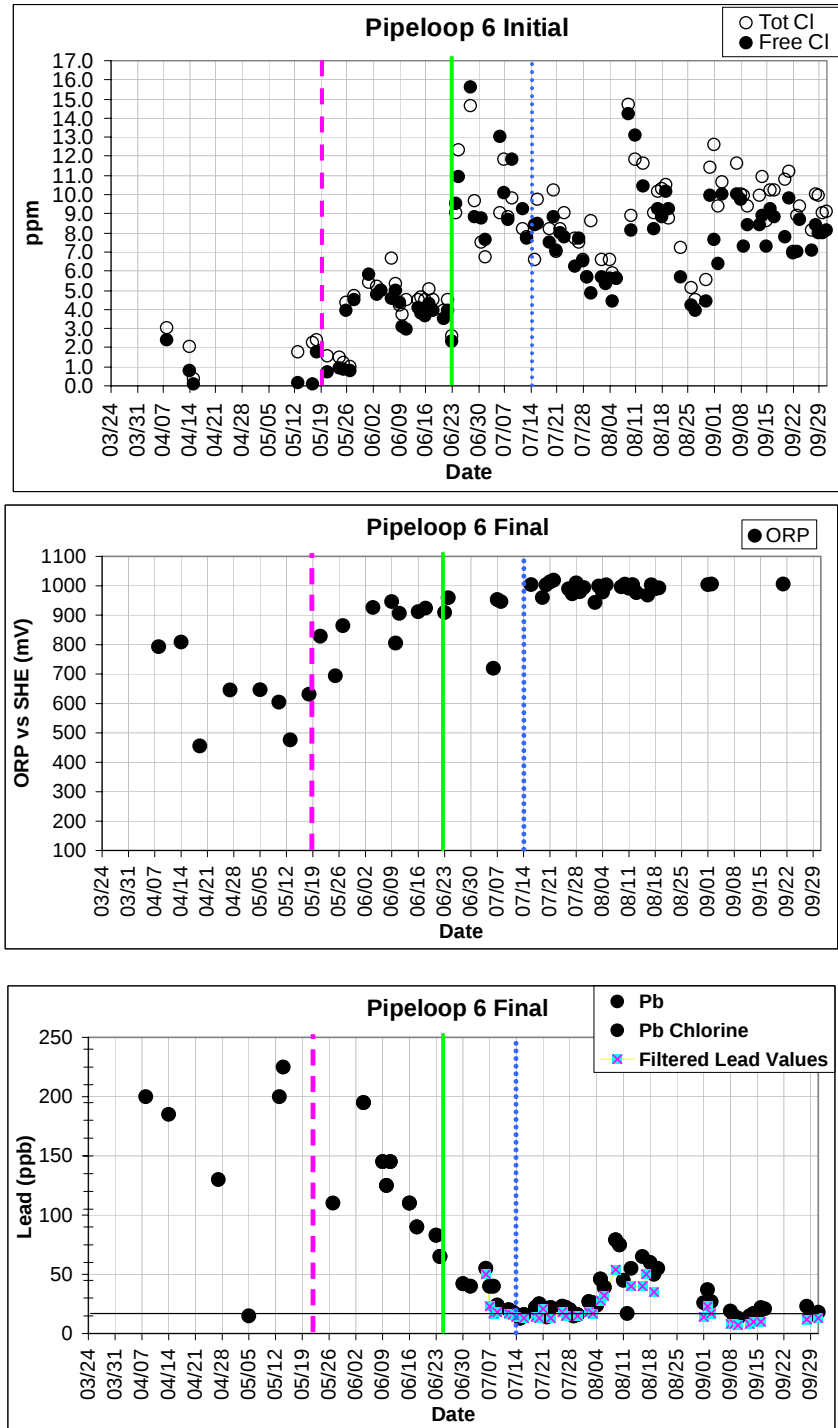


Figure 13. Laboratory “stagnation loop” data for actual removed pieces of service line, testing the effects of free chlorine and subsequent orthophosphate (10-15 mg/L as PO_4) addition on redox potential and lead release. The magenta reference line indicates the end of the conditioning period of exposure to chloraminated water, before shifting to free chlorine (top graph). The green line represents a boost in free chlorine concentration, and the blue dotted line represents the introduction of the orthophosphate dosing.