

Overview of Lead Scale Formation and Solubility

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The response of lead source materials in premise and distribution systems to changes in water treatment is strongly dependent on the mineralogy of the corrosion scales attached to various parts of the system. These determinations are particularly critical for lead compounds, of which there have been many reported. Knowledge of the crystal form and the degree of crystallinity of these compounds is a key contribution to models of lead behavior and understanding of lead control via passivation. Accordingly it is critical to develop an understanding of the chemical processes at work involving Pb components in distribution systems.

For Pb, the dominant minerals found in distribution systems (DS) are simple oxides and carbonates. Phosphates are also found, and are increasingly relevant as systems turn to orthophosphate dosing to stabilize Pb scales. Table 1 presents a list of common minerals and their chemical formulas. There are many others however, and substitutions of other cations or anions are possible, particularly with phosphate compounds.

Table 1. Some common Pb minerals and their chemical formulas			
Major Group		Chemical Formula	Comments
<i>Oxides</i>			
	Plattnerite	PbO ₂	Rare in nature, common in DS
	Minimum	PbOPbO ₂	Rare in DS
	Litharge	PbO (tetragonal)	Common in nature and DS
	Massicot	PbO (orthorhombic)	Rare in DS
<i>Carbonates</i>			
	Cerussite ¹	PbCO ₃	Common in nature and DS
	Hydrocerussite ¹	Pb ₃ (CO ₃) ₂ (OH) ₂	Common in nature and DS
	Plumbonacrite	Pb ₁₀ O(CO ₃) ₆ (OH) ₆	Very rare in nature, sometimes seen in DS
<i>Phosphates-Vanadates</i>			
	Hydroxypyromorphite	Pb ₅ (PO ₄) ₃ OH	Common in nature and DS
	Chloropyromorphite	Pb ₅ (PO ₄) ₃ Cl	Common in nature and DS
	Fluoropyromorphite	Pb ₅ (PO ₄) ₃ F	Rare in nature, sometimes seen in DS with fluoridation
	Apatite	Ca ₅ (PO ₄) ₃ X (X = OH, Cl, or F)	Very common in nature, may occur in DS as Pb-substituted apatite
	Vanadinite	Pb ₅ (VO ₄) ₃ X (X = OH, Cl, or F). As can substitute for V	Rare in nature, sometimes seen in DS using elevated pH for corrosion control
<i>Sulfates</i>			
	Anglesite	PbSO ₄	Common in nature, rare in DS
	Leadhillite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂ (monoclinic)	Rare in nature, sometimes found in DS
	Susannite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂ (trigonal)	Forms from Leadhillite on heating. More common in hotter climates?
	Lanarkite	PbOPb(SO ₄)	Rare in nature. Not reported so far in DS

¹(misspelled *cerrusite* and *hydrocerrusite* in the PHREEQC databases)

This array of minerals differs widely in solubility in water depending on the presence of H⁺, HCO₃⁻, PO₄³⁻, SO₄²⁻, and the total charge in the solution. Because Pb can occupy three oxidation states (Pb⁰, Pb²⁺, and Pb⁴⁺), the oxidation level of the water is also critical. This parameter is usually expressed as Eh, or the potential relative to a standard hydrogen electrode.

Metallic Pb itself reacts readily with water to produce soluble products and it is only the formation of protective scales that brings the concentration of Pb in lead piping down into reasonable ranges from a health perspective. Probably the most common

protective scales under water distribution system conditions are the two lead carbonates: cerussite and hydrocerussite.

The Carbonates

Many distribution systems have calcium carbonate scales, usually as the mineral calcite, which does not present a health problem, but can cause serious problems for equipment maintenance. Carbonate minerals are also widely distributed in nature and accordingly have been thoroughly studied. There are several Pb carbonates but two are dominant, [cerussite](#), which has an orthorhombic crystal structure, and [hydrocerussite](#) which is trigonal. The orthorhombic form is more symmetrical and cerussite tends to form elongate, blocky crystals, whereas hydrocerussite tends to form in intersecting plates. Both minerals are frequently found as weathering products of Pb ore minerals, so again there is a wide literature on their mineralogy and chemistry.

A useful way to compare different Pb minerals is to use concentration vs pH diagrams (Figure 1). These assume equilibrium between the mineral and the solution and also require mathematically solving a set of simultaneous equations involving ion-pair formation in the solution. These equations are embodied in computer codes such as PHREEQC, which is the code used for this set of diagrams. The y-axis is total Pb, which comprises Pb^{2+} , Pb^{4+} , $PbCO_3^0$, $PbCl^+$, etc. Moving up on the diagram, there is first a region of solution only, with no minerals stable. At about 10^{-6} moles/liter, one or the other of the carbonates should precipitate. At this point, Pb levels in the solution should not go any higher, because any addition of Pb would be compensated by growth of additional Pb carbonate. If for some reason the carbonate does not form (for example in very low alkalinity waters), the solution continues to increase in Pb content until litharge forms at Pb concentrations in the neighborhood of 10^{-3} moles/liter. This Pb level is high and most utilities strive to convert any PbO in the distribution system into one of the carbonates. Even equilibrium values with respect to the lead carbonates are still above the LCR action limit, however. In practice, a well-developed lead carbonate scale does provide protection, because only a portion of the water in the system is in contact with the lead service lines or Pb-containing plumbing materials. Normally, utilities with well-developed lead carbonate scales will be able to keep lead levels at the tap below the action level. Pb in equilibrium with $PbCO_3$ is virtually independent of pH at dissolved inorganic carbonate (DIC) levels of 60 mgC/L and higher. However, at 20 mg C/L, there is a strong solubility minimum at pH about 9.8 (Schock et al 1996, their fig. 4-14). Also note that if there is an underlayer of litharge, mechanical removal of the cerussite layer could lead to a sudden increase in Pb levels.

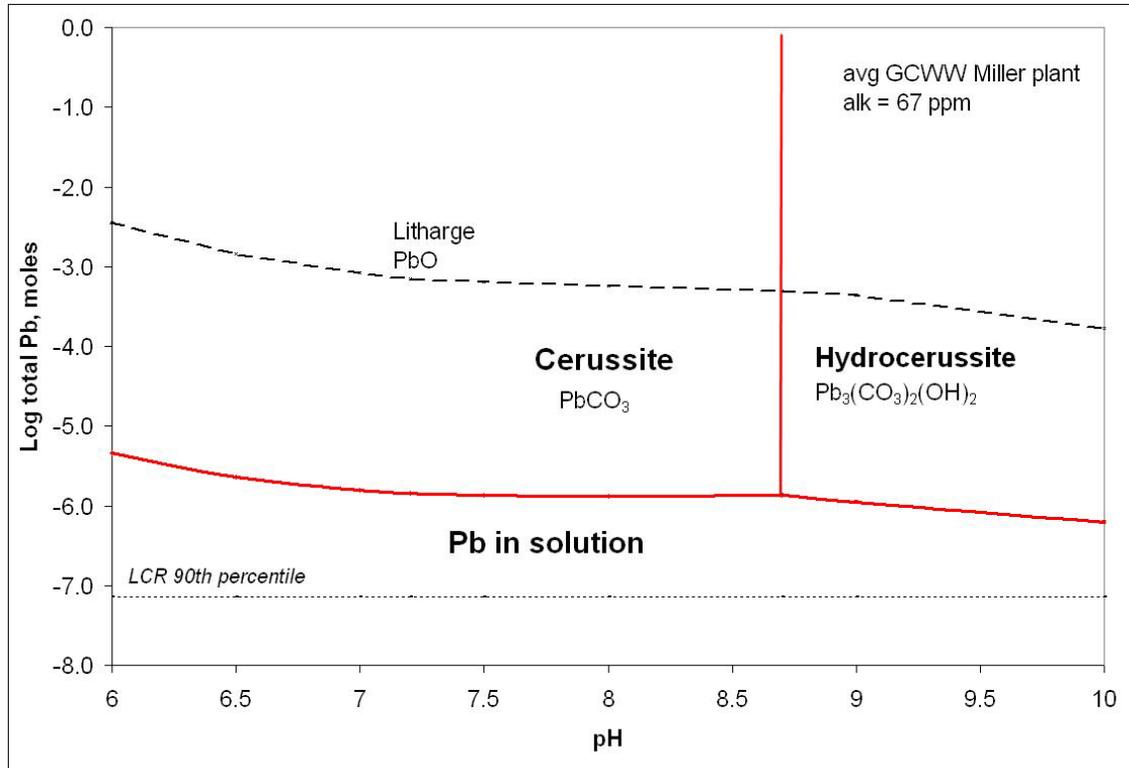


Figure 1. pH-concentration diagram for the Pb carbonates in alkaline distribution water. (PbO is shown for comparison. Speciation based on the PHREEQC code using the MINTeq database and the solution parameters given in Table 2.)

Pb oxides

The most common Pb oxide seen in distribution systems is [litharge](#), which is quite soluble (Figure 1), but often occurs as a layer between the metal surface and an overlayer of Pb carbonate. Possibly it forms within the scale by reaction between native lead and the carbonate layer.

The Pb^{4+} oxide, [plattnerite](#) is much less soluble (Figure 2), but is stable only at very high Eh values (Schock et al., 2001; Schock and Giani, 2004). Such conditions can be achieved in distribution systems with high chlorine residuals throughout and with very low concentrations of organic matter (see Table 3). If a protective plattnerite layer is present, Pb levels can be improved by raising the pH above about 8.5. Note, however, that supersaturation with respect to $CaCO_3$ as calcite occurs in this model system at pH 8.01. Therefore raising the pH beyond the low 8s is likely to result in an increase in $CaCO_3$ scale formation.

Table 2. Solution parameters used in generating equilibrium diagrams. Based on average Greater Cincinnati Water Works finished water from Miller plant

Units	
Temperature	23.0 degrees C
Alkalinity, mg/L	67.0 as CaCO ₃
Na ⁺ , mg/L	28.0
Cl ⁻ , mg/L	28.0
SO ₄ ²⁻ , mg/L	74.0
Ca ²⁺ , mg/L	37.0
Mg ²⁺ , mg/L	8.6

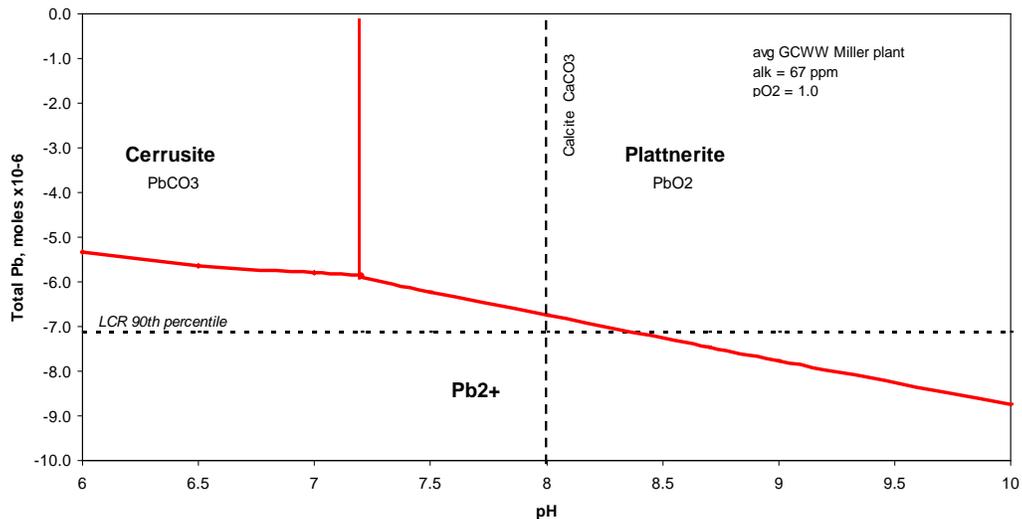


Figure 2 Plattnerite-cerussite relations at very high Eh. The Eh values for this diagram correspond to the upper stability limit for water at a given pH. Waters with free chlorine would have slightly higher Eh.

The importance of plattnerite is that it can revert to more soluble Pb minerals if the Eh subsequently drops (Figure 3). Lytle and Schock (2005) presented experimental evidence for ready reversibility of the plattnerite-cerussite transition.

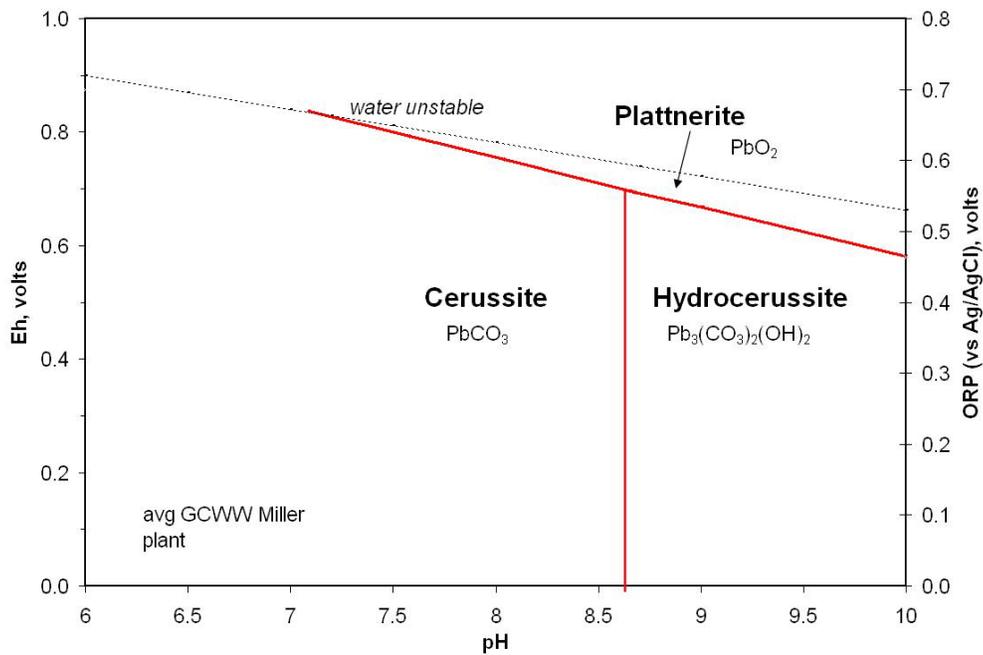


Figure 3. Eh-pH diagram for the Pb carbonates and the oxide plattnerite under alkaline conditions.

Effect of disinfection technique

Eh in distribution systems is controlled largely by the choice of disinfectant (Figure 4). Chlorine yields very high values, above the stability limit for water. For this reason chlorine is metastable out in the system, and tends to decay with time.

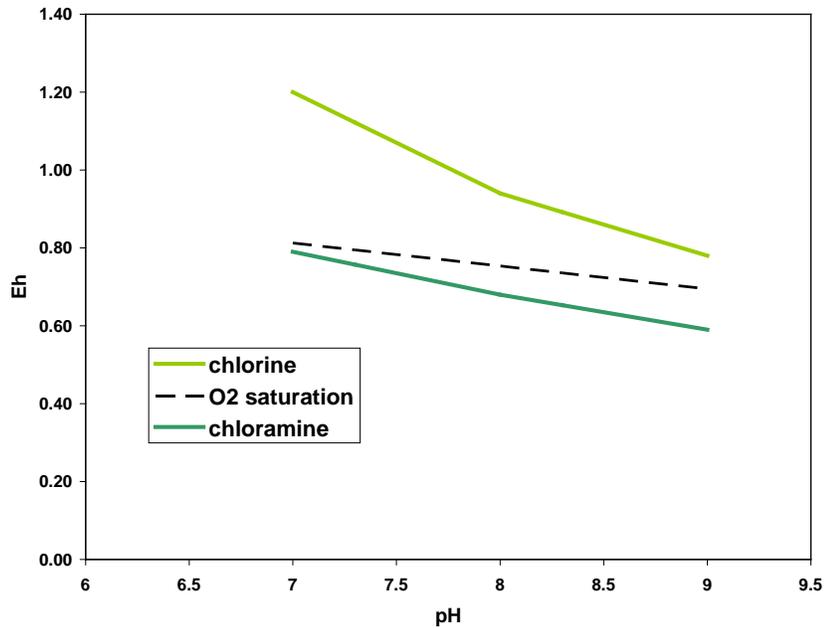


Figure 4. Eh-pH diagram for the disinfectants. Chloramine produces a substantially lower Eh than does chlorine.

Chloramine, which is often chosen to reduce the production of toxic chlorinated C_1 organic compounds (or halomethanes), yields a substantially lower Eh. A change from chlorine to chloramine disinfection, while it has little effect on the Pb carbonates, has a drastic effect on the Pb oxides (Figure 5).

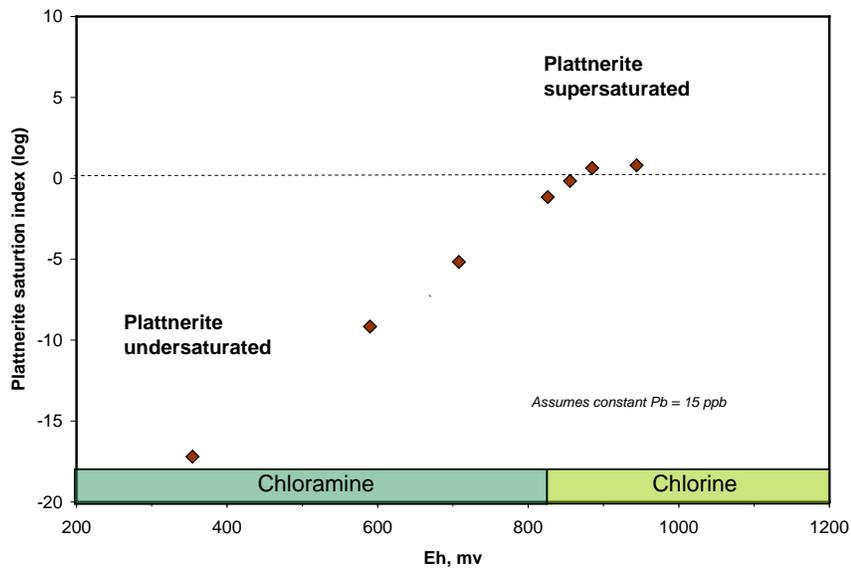


Figure 5. Eh v solubility diagram for the plattnerite. This mineral is only stable in the presence of chlorine.

A possible explanation for the increase in Pb in the DCWASA system was that the change from chlorine to chloramine disinfection reduced the Eh below the stability level of plattnerite and allowed litharge to temporarily control Pb levels (Edwards and Dudi, 2004; Schock and Giani, 2004).

Pb phosphates

A popular strategy for control of Pb release is addition of phosphate, either as orthophosphate, Zn-orthophosphate, or as polyphosphate. Schock et al. (1996) contains a detailed discussion of historic experience with phosphate and of equilibrium modeling. Figure 4 presents a simplified view of phosphate behavior using hydroxypyromorphite as an example. Adding orthophosphate greatly reduces the equilibrium solubility of phases like hydroxypyromorphite and its Cl and F cousins and should therefore reduce Pb at the tap. Similar results are sometimes obtained with polyphosphate addition by utilities with high pH distribution water, possibly because the polyphosphates revert to the monomeric orthophosphate in the distribution system (Schock and Clement, 1998, p. 21). However, in the absence of reversion, polyphosphate may well be detrimental because it prevents the formation of insoluble lead compounds (AwwaRF 1990) or enhances release of Pb particulates (Cantor et al. 2000; Edwards and McNeil, 2002).

Note that the amount of Pb in solution at equilibrium with [pyromorphite](#) is appreciably lower than for equilibrium with the carbonates and that the levels approach the LCR limit. However, there is a pronounced solubility minimum and much of the benefit could be lost by raising the pH beyond 8 when using orthophosphates. Chloropyromorphite is appreciably less soluble than hydroxypyromorphite in the MINTEQ database (Hopwood et al., 2002), so the incorporation of even small amounts of Cl- or F- into the structure could change the solubility behavior appreciably. Likewise, the vanadate ion (VO_4^{2-}) substitutes readily for phosphate, and the mineral [vanadinite](#) is known from some distribution systems. Finally, PHREEQC modeling shows strong supersaturation with hydroxyapatite at all levels of orthophosphate addition for the whole pH range in Figure 4. It may be possible that the first phase to form is actually an apatite that subsequently reacts to adsorb Pb from solution. This, however, takes us into the realm of kinetics, which is not well understood for mineral systems in general, and is particularly poorly understood for the time frame and solution conditions presented by distribution systems.

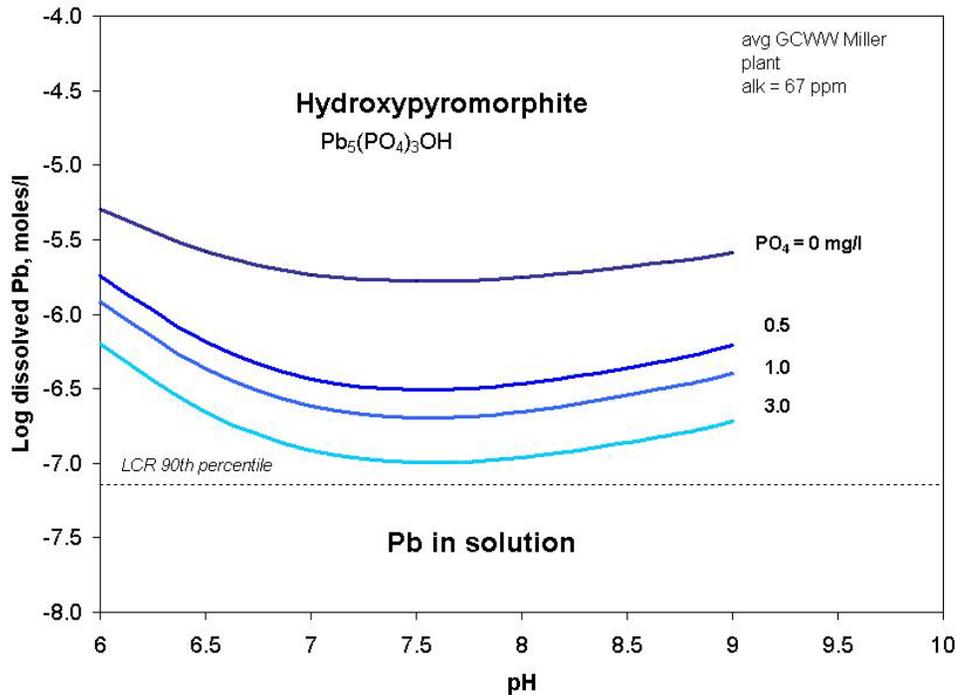


Figure 6. Effect of phosphate addition on Pb in equilibrium with hydroxypyromorphite.

Table 3. Effect of Water Quality on Pb Levels Associated with Certain Scale Minerals at Equilibrium (PHREEQC model)			
<i>Major Group</i>	<i>Chemical Formula</i>	<i>Equilibrium Pb, utility 1</i>	<i>Equilibrium Pb, utility 3</i>
<i>Oxides</i>			
Plattnerite	PbO ₂	3880 (µg/L)	0.796
Litharge	PbO (tetragonal)	201,000	42,000
<i>Carbonates</i>			
Cerussite	PbCO ₃	59	147
Hydrocerussite	Pb ₂ CO ₃ (OH) ₂	68	19
<i>Phosphates</i>			
OH-pyromorphite	Pb ₅ (PO ₄) ₃ OH	8	208
Cl-pyromorphite	Pb ₅ (PO ₄) ₃ Cl	0.06	6.9
<i>Sulfates</i>			
Lanarkite	PbO PbSO ₄	257	345
<i>Utility 1: chloramine disinfection; alkalinity = 83, pH=7.7; Utility 3: chlorine disinfection, alkalinity = 41, pH=9.8</i>			

References

AwwaRF **1990**. Lead Control Strategies. Awwa Research Foundation and American Water Works Association. Denver, CO

- Cantor, A.F., Denig-Chakroff, D., Vela, R.R., Oleinik, M.G., and Lynch, D.L. **2000**. Use of polyphosphate in corrosion control: *Jour. AWWA*, 92: 96-102.
- Edwards, M, and A. Dudi. **2004**. Role of chlorine and chloramines in corrosion of lead-bearing plumbing materials: *Jour. AWWA*, 96: 69-81.
- Edwards, M. and McNeil, L.S. **2002**. Effect of phosphate inhibitors on lead release from pipes: *Jour. AWWA*, 96: 69-81.
- Hopwood, J. D., R. J.Davey, M. O. Jones, R. G. Pritchard, P. T. Cardew, and A. Booth. **2002**, Development of chloropyromorphite coatings for lead water pipes: *Journal of Materials Chemistry*, v. 12, p. 1717-1723.
- Lytle, D.A. and Schock, M.R. **2005**. Formation of Pb(IV) oxides: *Jour. AWWA*, 97: 102-114.
- Schock, M. R., and J.A. Clement. **1998**. "Lead and copper control with non-zinc orthophosphate". *Journal New England Water Works Association*, v. 112, p. 20-42.
- Schock, M.R., and R. Giani. **2004**. "Oxidant/disinfectant chemistry and impacts on lead corrosion". *Proc. American Water Works Association, WQTC. American Water Works Association. Denver, CO.*
- Schock, M.R., I. Wagner, and R.J. Oliphant. **1996**. "Corrosion and solubility of lead in drinking water". Chapter 4 in *Internal Corrosion of Water Distribution Systems. American Water Works Association Research Foundation/ DVGW Forschungsstelle, Denver CO.*
- Schock, M.R., S.M. Harmon, J. Swertfeger, and R. Lohmann. **2001**. "Tetravalent lead: a hitherto unrecognized control of tap water lead contamination." *Proc. American Water Works Association, WQTC. American Water Works Association. Denver, CO.*