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Lead Corrosion Inhibitors in Drinking Water

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LEAD CORROSION INHIBITORS IN DRINKING WATER

by

Seyedsoheil Hosseinibalajadeh

A Thesis Submitted in

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ABSTRACT

LEAD CORROSION INHIBITORS IN DRINKING WATER

by

Seyedsoheil Hosseinibalajadeh

The University of Wisconsin-Milwaukee, 2018
Under the Supervision of Professor Yin Wang

Lead-containing materials that include lead pipes, fittings, solder, and fixtures are widely present in drinking water distribution systems in North America and Europe. Their internal corrosion provides the most significant source of lead in drinking water. Several mechanisms contribute to the corrosion of lead-containing materials, including material heterogeneity, galvanic interaction, and reaction with progressively water constituents and to protect consumers from lead exposure, the Lead and Copper Rule (LCR) set the lead action level to 15 μg/L for a 1-L first-draw sample of tap water. Today more than half of the water treatment utilities in the U.S. are using phosphates as a corrosion inhibitor for lead release in plumbing systems. Despite good efficiency, phosphate found in the effluent of water treatment plants may have negative impacts on the environment. Also, to comply with disinfection byproduct regulations, many utilities have chosen to use chloramines rather than chlorine for residual maintenance. However, the switch to chloramines may expose these systems to another health risk, increased concentrations of lead.

This project investigated the capability of a suite of low-cost, environmentally friendly, and phosphate-free inorganic inhibitors in mitigating lead release from aged metallic lead materials under conditions relevant to Chicago and Milwaukee drinking water distribution in 2 phases, literature review and batch experiments on corrosion inhibitors including (1) metal sulfates: $SnSO_4$ (2 mg/L as Sn) and $ZnSO_4$ (2 or 4 mg/L as Zn), (2) sodium oxyanions: Na_2SiO_3, $Na_2Si_3O_7$ (20 mg/L as SiO_2), and $Na_2B_4O_7$ (5 mg/L as BO_3)and also pH adjustment.

The results showed that pH adjustment on 9.2 would decrease the lead release significantly. However, it could trigger some other reactions in the system which increase the concentration of iron, copper, magnesium, manganese, etc and the taste, color and odor of drinking water could be affected. Therefore, further investigation regarding pH adjustment may be needed.

Sodium silicate showed the capability of decreasing lead leaching in the system over time. Probably the reasons could be pH increase in the system and the creation of a protective layer on the surface of pipe. Also, Tin sulfate showed the capability of decreasing the lead leaching in the system.

Based on the experimental results, pH adjustment, silicate addition, and use of $SnSO_4$ were promising in minimizing lead release. Further recommendation includes

(1) identifying the optimum inhibitor formulations in a wide range of environmental matrices that are relevant to drinking water distribution,

(2) evaluating the long-term performance of the optimum inhibitor formulations

(3) conducting pilot-scale pipe loop studies to better represent the scenarios in real distribution systems.

Also, it will be beneficial to determine the combinative use of phosphate and phosphate-free inhibitors that may effectively mitigate lead release in tap water and reduce the loads of phosphate in wastewater utilities in the meantime. Cost-benefit analysis and life cycle assessment may also be needed to promote the technology adoption in the field.

DEDICATION

To my family; may God continue to bless our family and show us favor.

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ACKNOWLEDGEMENTS

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I am grateful to all of those with whom I have had the pleasure to work during this and other related projects. Each of the members of my Dissertation Committee, Professor Yin Wang, Professor Qian Liao and Professor Shangping Xu, has provided me extensive personal and professional guidance and taught me a great deal about both scientific research and life in general. I would especially like to thank my lab mates who have given me more than I could ever give them credit for here.

Nobody has been more important to me in the pursuit of this project than the members of my family. I would like to thank my parents; whose love and guidance are with me in whatever I pursue. They are the ultimate role models. Most importantly, I wish to thank my loving and supportive sister, Sahar, and my brother in law, Rahi, who provide unending inspiratio

Chapter 1 Introduction

1.1 Lead in drinking water

Lead is a chemical element which was discovered in the Middle East, and it was used mostly for making fishing nets, glazes glasses, and enamels. It is mostly found as lead mineral and remained on the crust of the earth (Emsley, J., 2011). Over time because of its physical and chemical characteristics, lead has been used for some other aspects as well. Some characteristics like malleability, durability, and resistance to corrosion and the cost of production made it an essential and common material for plumbing and painting industry in late 18th, 19th and even 20th and 21st century.

For years, lead has been used as a suitable material for the conveyance of water in large scale. Large amount facets, lead service pipes, plumbing fittings or fixture and solder were made by a portion of the lead. In 1924, 539 cities were surveyed, and 51% of them had used lead service line (Diven et al., 1924). Another survey in 1990 showed that about 6.4million lead connection and 3.3 million service line had been used in the US community water system (Hozalski et al., 2005; Economic&Engineering services, 1990). Another survey in 1991 showed that the estimation of the number of lead service lines could be in the range of 7 million to 10.2 million (Cornwell et al., 2016). The most recent survey done by American Water Works Association (AWWA) in 2016 indicates that there are still 6.1 million lead service lines in the drinking water system(Cornwell et al., 2016).

Although lead seems an ideal material for plumbing systems, over time further investigations proved that using lead materials in plumbing system causes unhealthy consequences. Kidney damage, impaired cognitive performance, impaired reproductive function, anemia, elevated blood pressure, delayed neurological and physical development are some of the health effects of lead exposure(Tate et al., 1990). Investigation showed that lead exposure could result in the potential for mild mental retardation (due to IQ point decrease) and cardiovascular problems(due to increase in blood pressure)(Fewtrell et al., 2004). However, maybe the most important problem related to lead exposure would be the problems could occur to children including behavior and learning problems, lower IQ and hyperactivity, slowed growth, hearing problems and anemia. It is essential that a dose of lead that would be a little effective on adults could be significantly effective on children. Lead can also have a serious effect on pregnant women and their fetus. Because of the accumulation of lead in pregnant women bodies, reduced growth of the fetus and premature birth would be probable (Lanphear et al., 2000; Jusko et al., 2008; US EPA; Edwards et al., 2009).

Recent events like lead poisoning in Greenville, N.C. in which no other source of lead was realized except drinking water (Allegood, J., 2005), high level of lead in the water (Renner, R.,2004), Elevated Blood Lead in Young Children Due to Lead-Contaminated Drinking Water Washington., in 2004 in which tap water was considered as the possible source (Edwards, et al., 2009), brought the importance of lead release in water into consideration. Before these events and investigations, most of the focus for lead exposure was on painting materials, dust and air. EPA estimates that more than 20 percent of total lead exposure results from drinking water and this amount could be raised to 40 percent and 60 percent for infants (US EPA). Studies indicate that the amount of the lead in natural water and outlet of water treatment plant is very little. Lead service lines, lead-based solder and brass faucet are considered as significant source of lead release in drinking water and amount of lead release depends on the age of the plumbing system (Hozalski et al., 2005; Karalekas Jr et al., 1983; Health Canada's Water Quality, HC Pub., 2016).

Using pipe, solder or flux in public water system which is not lead-free was prohibited by Congress safe water act Amendment of 1986(P.L.99-339). According to The Safe Drinking Water Act (SDWA), ‘’Lead-Free’’ content is one that contains an average of 0.25 percent calculated across the wetted surfaces of pipes, pipe fittings, plumbing fittings, and fixtures and 0.2 percent for solder and flux(US EPA, 1989). Moreover, In 1991 EPA required water distribution systems to install corrosion control measures by Jan 1997, Jan 1998, and Jan 1999 for large, medium and small systems respectively. According to that, Water systems are required to find the optimal method to measure the lead concentration in drinking water, and 90th percentile of all sample measurements must not exceed 0.015 mg/L for Lead (HEADQUARTERS, C. and MEXICO, 1997; Regulations, E.D.W., 1991).

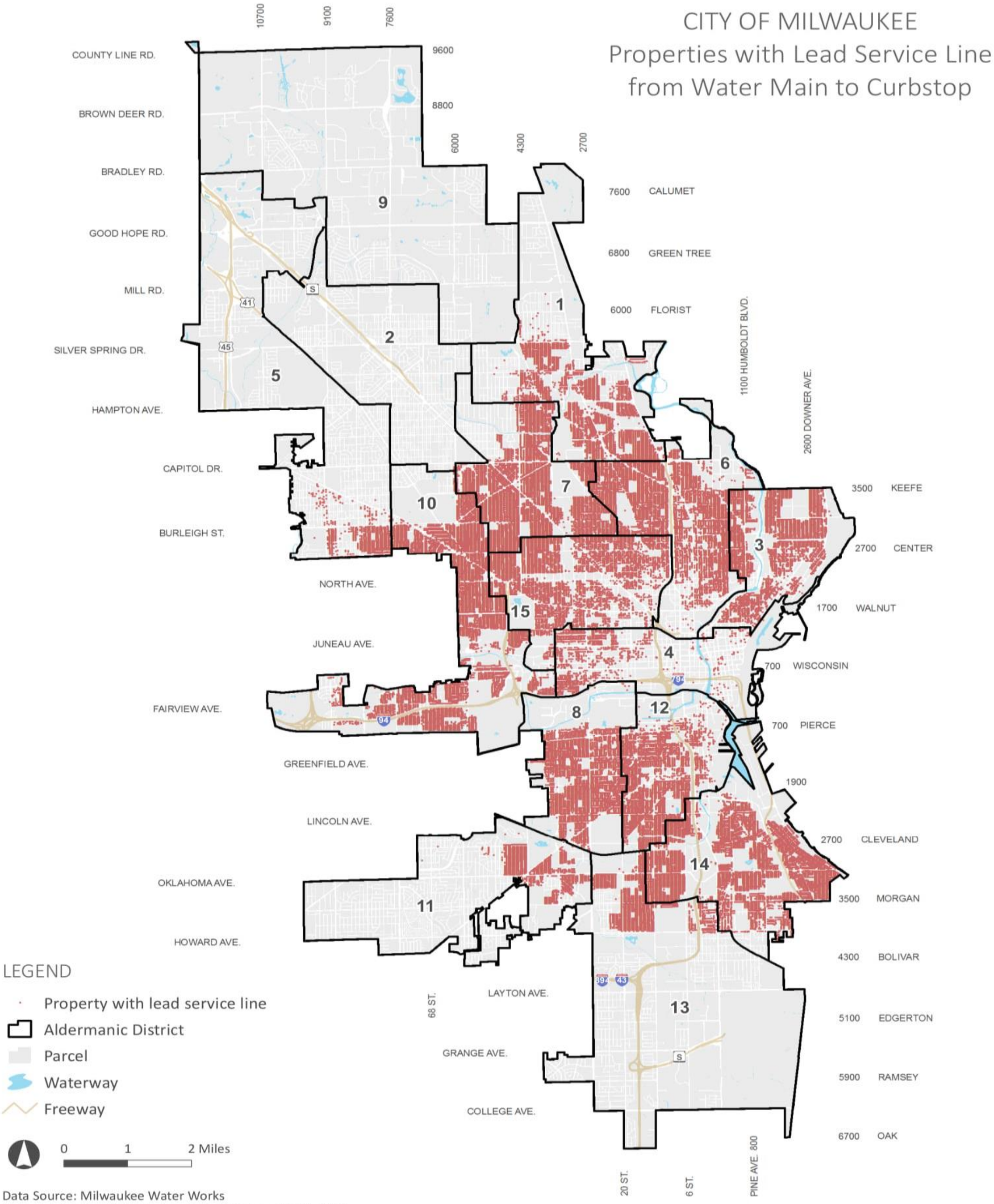
1.2 Milwaukee Water Works Statistics

Milwaukee Water Works (MWW), who was organized on April 18, 1871, serve as the operating water utility in Wisconsin. The City of Milwaukee owns the utility, and they follow the regulations of the Environmental Protection Agency (EPA) and the Wisconsin Department of Natural Resources (DNR) for facilities, operations, and water quality. They treat the Lake Michigan water and provide fresh drinking water to 865000 people in 16 communities in Milwaukee, Ozaukee and Waukesha Counties. Below is some statistics according to their annual reports.

Since many years ago lead service lines have been used in a large scale in the Greater Milwaukee Area. Figure 1.1 shows the geographical distribution of the lead service line in this area.

Milwaukee Water Works Utility Statistic	
Average daily pumpage in 2017(MG)	**96.1**
Average daily pumpage in 2016(MG)	97
Average daily pumpage in 2015(MG)	98
Number of Service connections	168738
Number of Lead service lines(Residential properties)	**70000**
Number of Lead service lines(Commercial properties)	**6000**
Daily per-person, indoor and outdoor use in Milwaukee(G)	41

Table 1-1. Milwaukee Water Works Utility Statistic (http://City.milwaukee.gov/water)



Data Source: Milwaukee Water Works
Prepared by City of Milwaukee DOA-BMD-kqp, 05/31/2016

Figure 1-1. Properties with Lead Service Line (http://City.milwaukee.gov/water)

1.3 Milwaukee Water Works treatment and Water Quality

Lake Michigan is the only resource for drinking water. Linnwood treatment plant and Howard treat lake Michigan's water and pump it into the distribution system. Below is the summary of the treatment process.

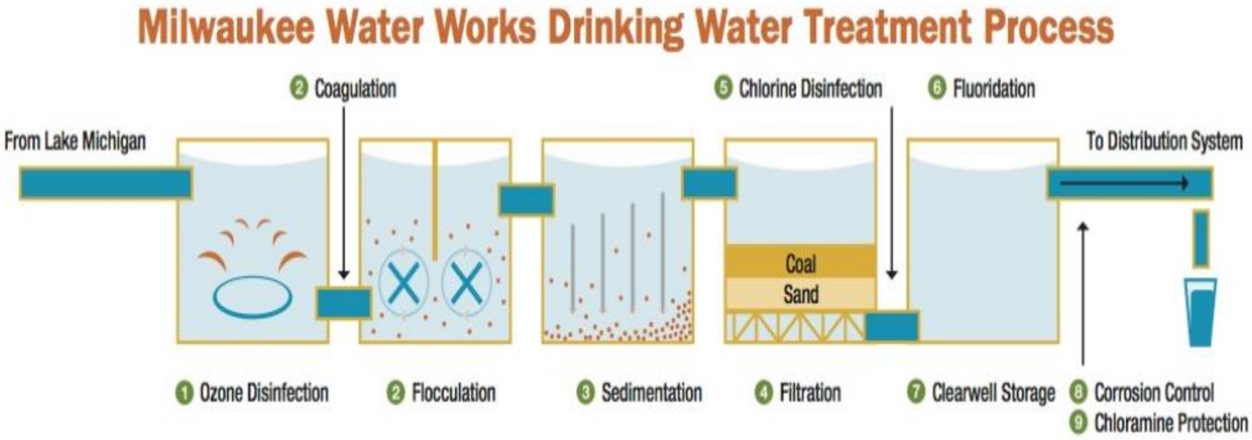


Figure 1-2. Treatment process at Linwood and Howard treatment plant (http://City.milwaukee.gov/water)

1-Ozone Disinfection: Ozone gas is used to make the drinking water free of disease-causing microorganisms like Giardia and Cryptosporidium. It also controls the taste, odor, and chlorinated disinfection byproducts

2-Coagulation and Flocculation: In order to neutralize the charge on microscopic particles Aluminum sulfate ($Al_2(SO_4)_3$) is used and as a result suspended particles will stick together and forms floc during the gently mixing of water.

3-Sedimentation: In the sedimentation tank, over time, floc will settle out and removed.

4-Biologically Active Filtration: At this step, 24 inches of anthracite coal and 12 inches of crushed sand are used.

5-Chlorine Disinfection: In order to destroy harmful microorganisms, chlorine is added to water.

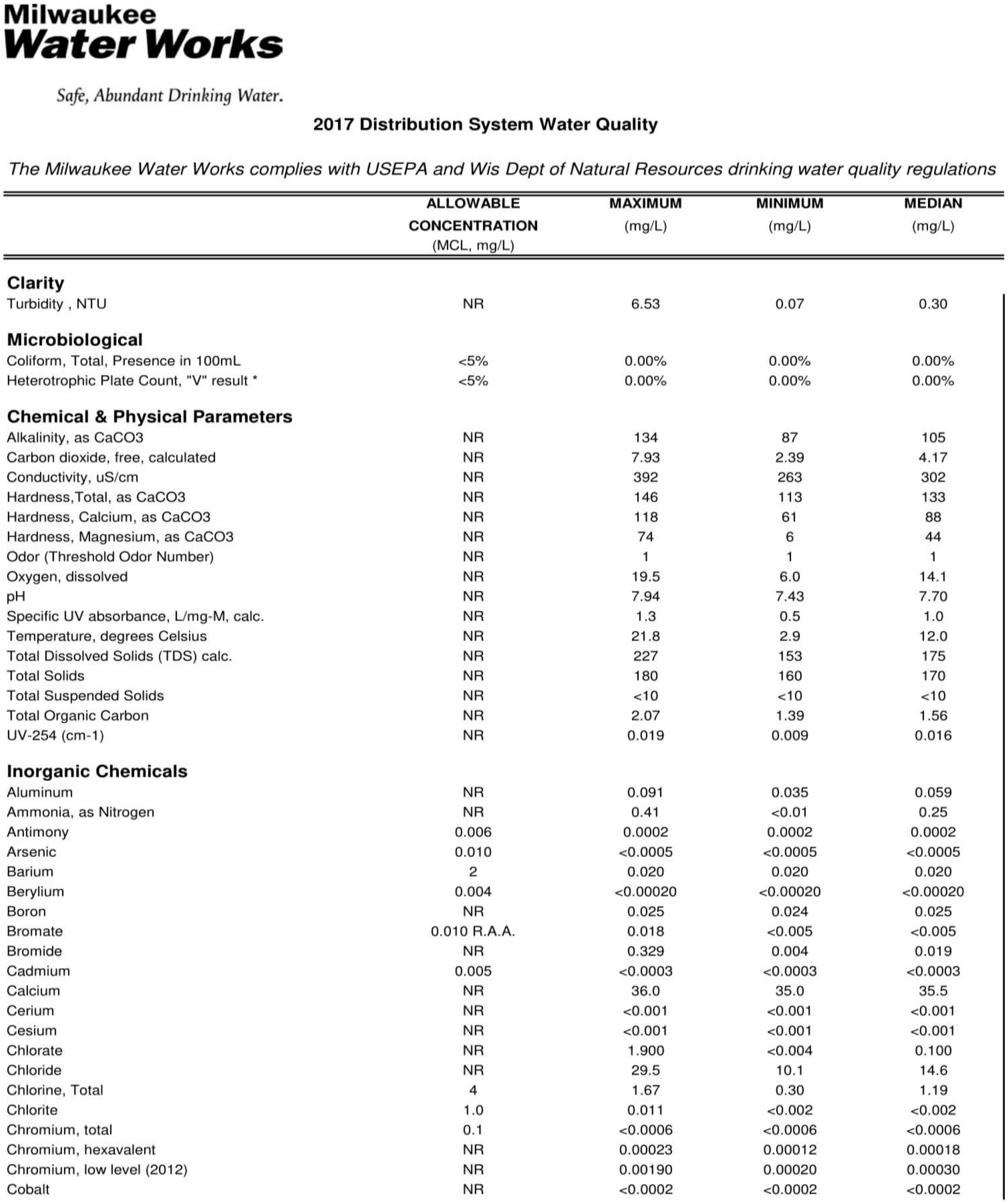
6-Fluoridation: Flouride at low level is added to water to prevent tooth decay.

7-Clearwell Storage: The storage of the treated water in underground tanks and pumpage to the distribution system is done at this level.

8-Corrosion Control: In order to meet the lead and copper regulation and prevent lead and copper leaching from pipes into the water, phosphorous compound is added to the water.

9-Chloramine Protection: By adding Ammonia in the water, chlorine will be changed to chloramine and maintain longer bacteriological protection in the system (http://City.milwaukee.gov/water).

Using this treatment method and implementation of the Water Quality Monitoring Program, made MWW able to provide safe and high-quality drinking water.



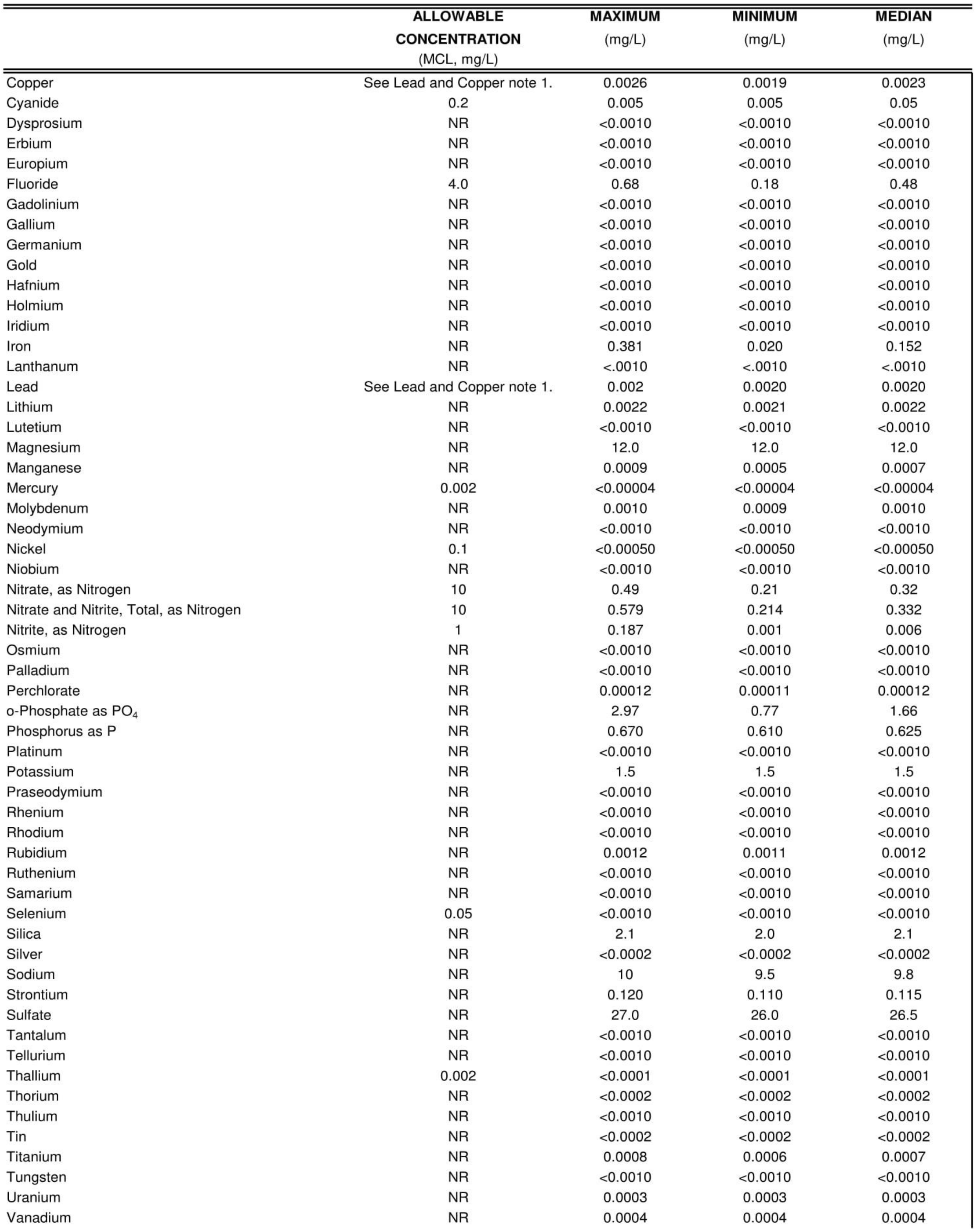
Milwaukee Water Works

Safe, Abundant Drinking Water.

2017 Distribution System Water Quality

The Milwaukee Water Works complies with USEPA and Wis Dept of Natural Resources drinking water quality regulations

	ALLOWABLE CONCENTRATION (MCL, mg/L)	MAXIMUM (mg/L)	MINIMUM (mg/L)	MEDIAN (mg/L)
Clarity				
Turbidity , NTU	NR	6.53	0.07	0.30
Microbiological				
Coliform, Total, Presence in 100mL	<5%	0.00%	0.00%	0.00%
Heterotrophic Plate Count, "V" result *	<5%	0.00%	0.00%	0.00%
Chemical & Physical Parameters				
Alkalinity, as CaCO3	NR	134	87	105
Carbon dioxide, free, calculated	NR	7.93	2.39	4.17
Conductivity, uS/cm	NR	392	263	302
Hardness,Total, as CaCO3	NR	146	113	133
Hardness, Calcium, as CaCO3	NR	118	61	88
Hardness, Magnesium, as CaCO3	NR	74	6	44
Odor (Threshold Odor Number)	NR	1	1	1
Oxygen, dissolved	NR	19.5	6.0	14.1
pH	NR	7.94	7.43	7.70
Specific UV absorbance, L/mg-M, calc.	NR	1.3	0.5	1.0
Temperature, degrees Celsius	NR	21.8	2.9	12.0
Total Dissolved Solids (TDS) calc.	NR	227	153	175
Total Solids	NR	180	160	170
Total Suspended Solids	NR	<10	<10	<10
Total Organic Carbon	NR	2.07	1.39	1.56
UV-254 (cm-1)	NR	0.019	0.009	0.016
Inorganic Chemicals				
Aluminum	NR	0.091	0.035	0.059
Ammonia, as Nitrogen	NR	0.41	<0.01	0.25
Antimony	0.006	0.0002	0.0002	0.0002
Arsenic	0.010	<0.0005	<0.0005	<0.0005
Barium	2	0.020	0.020	0.020
Berylium	0.004	<0.00020	<0.00020	<0.00020
Boron	NR	0.025	0.024	0.025
Bromate	0.010 R.A.A.	0.018	<0.005	<0.005
Bromide	NR	0.329	0.004	0.019
Cadmium	0.005	<0.0003	<0.0003	<0.0003
Calcium	NR	36.0	35.0	35.5
Cerium	NR	<0.001	<0.001	<0.001
Cesium	NR	<0.001	<0.001	<0.001
Chlorate	NR	1.900	<0.004	0.100
Chloride	NR	29.5	10.1	14.6
Chlorine, Total	4	1.67	0.30	1.19
Chlorite	1.0	0.011	<0.002	<0.002
Chromium, total	0.1	<0.0006	<0.0006	<0.0006
Chromium, hexavalent	NR	0.00023	0.00012	0.00018
Chromium, low level (2012)	NR	0.00190	0.00020	0.00030
Cobalt	NR	<0.0002	<0.0002	<0.0002



	ALLOWABLE CONCENTRATION (MCL, mg/L)	MAXIMUM (mg/L)	MINIMUM (mg/L)	MEDIAN (mg/L)
Copper	See Lead and Copper note 1.	0.0026	0.0019	0.0023
Cyanide	0.2	0.005	0.005	0.05
Dysprosium	NR	<0.0010	<0.0010	<0.0010
Erbium	NR	<0.0010	<0.0010	<0.0010
Europium	NR	<0.0010	<0.0010	<0.0010
Fluoride	4.0	0.68	0.18	0.48
Gadolinium	NR	<0.0010	<0.0010	<0.0010
Gallium	NR	<0.0010	<0.0010	<0.0010
Germanium	NR	<0.0010	<0.0010	<0.0010
Gold	NR	<0.0010	<0.0010	<0.0010
Hafnium	NR	<0.0010	<0.0010	<0.0010
Holmium	NR	<0.0010	<0.0010	<0.0010
Iridium	NR	<0.0010	<0.0010	<0.0010
Iron	NR	0.381	0.020	0.152
Lanthanum	NR	<.0010	<.0010	<.0010
Lead	See Lead and Copper note 1.	0.002	0.0020	0.0020
Lithium	NR	0.0022	0.0021	0.0022
Lutetium	NR	<0.0010	<0.0010	<0.0010
Magnesium	NR	12.0	12.0	12.0
Manganese	NR	0.0009	0.0005	0.0007
Mercury	0.002	<0.00004	<0.00004	<0.00004
Molybdenum	NR	0.0010	0.0009	0.0010
Neodymium	NR	<0.0010	<0.0010	<0.0010
Nickel	0.1	<0.00050	<0.00050	<0.00050
Niobium	NR	<0.0010	<0.0010	<0.0010
Nitrate, as Nitrogen	10	0.49	0.21	0.32
Nitrate and Nitrite, Total, as Nitrogen	10	0.579	0.214	0.332
Nitrite, as Nitrogen	1	0.187	0.001	0.006
Osmium	NR	<0.0010	<0.0010	<0.0010
Palladium	NR	<0.0010	<0.0010	<0.0010
Perchlorate	NR	0.00012	0.00011	0.00012
o-Phosphate as PO_4	NR	2.97	0.77	1.66
Phosphorus as P	NR	0.670	0.610	0.625
Platinum	NR	<0.0010	<0.0010	<0.0010
Potassium	NR	1.5	1.5	1.5
Praseodymium	NR	<0.0010	<0.0010	<0.0010
Rhenium	NR	<0.0010	<0.0010	<0.0010
Rhodium	NR	<0.0010	<0.0010	<0.0010
Rubidium	NR	0.0012	0.0011	0.0012
Ruthenium	NR	<0.0010	<0.0010	<0.0010
Samarium	NR	<0.0010	<0.0010	<0.0010
Selenium	0.05	<0.0010	<0.0010	<0.0010
Silica	NR	2.1	2.0	2.1
Silver	NR	<0.0002	<0.0002	<0.0002
Sodium	NR	10	9.5	9.8
Strontium	NR	0.120	0.110	0.115
Sulfate	NR	27.0	26.0	26.5
Tantalum	NR	<0.0010	<0.0010	<0.0010
Tellurium	NR	<0.0010	<0.0010	<0.0010
Thallium	0.002	<0.0001	<0.0001	<0.0001
Thorium	NR	<0.0002	<0.0002	<0.0002
Thulium	NR	<0.0010	<0.0010	<0.0010
Tin	NR	<0.0002	<0.0002	<0.0002
Titanium	NR	0.0008	0.0006	0.0007
Tungsten	NR	<0.0010	<0.0010	<0.0010
Uranium	NR	0.0003	0.0003	0.0003
Vanadium	NR	0.0004	0.0004	0.0004

Figure 1-3. 2017 Milwaukee Water Works Distribution System Water Quality (http://City.milwaukee.gov/water)

Regarding Lead and Copper Rule(LCR), water sampling from the beginning of the LCR in 1993 through 2017 shows the efficiency of phosphorous compound used in the water. Orthophosphate has been the main phosphorous compound has been used in the system. As seen in figure 1-4, using phosphorous had low efficiency. One possible reason for that could be the time-related effect of the compound on lead release.

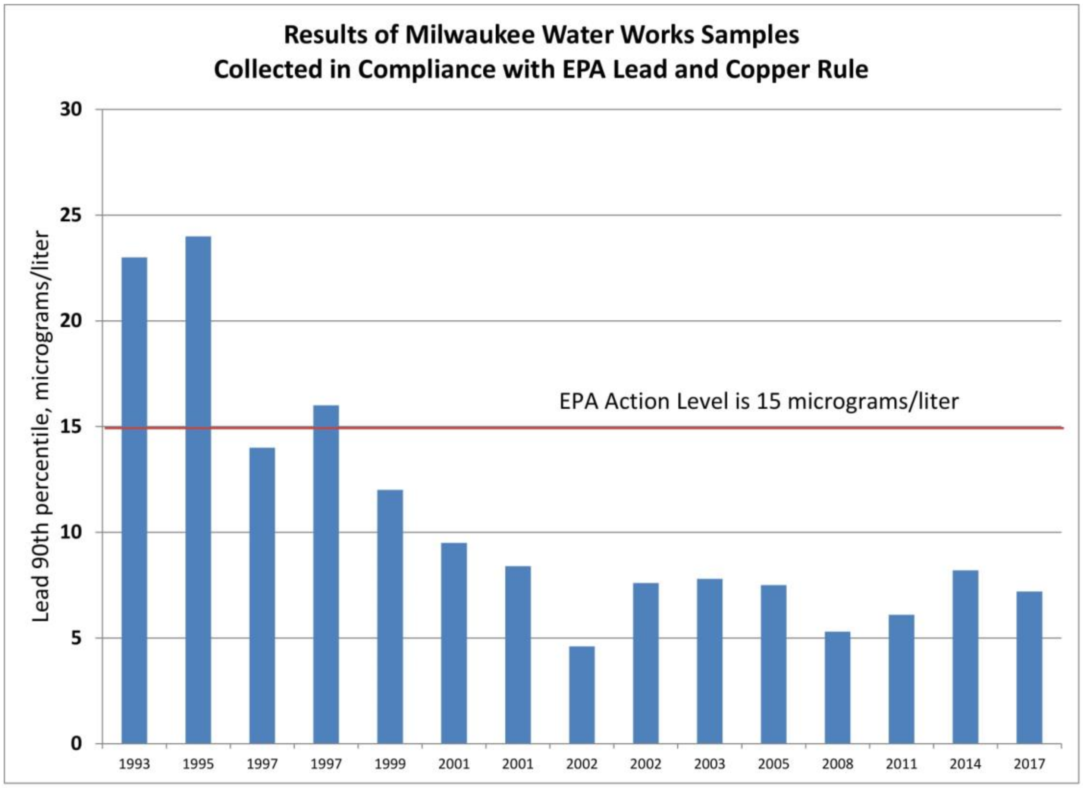


Figure 1-4. Efficiency of the phosphorous compound in the drinking water (http://City.milwaukee.gov/water)

1.4 Research project introduction

To comply with disinfection byproduct regulations, many utilities have chosen to use chloramines rather than chlorine for residual maintenance in drinking water distribution systems. However, the switch to chloramines may expose these systems to another health risk, increased concentrations of lead (Switzer et al., 2006). Today more than half of the water treatment utilities in the U.S. are using phosphates as a corrosion inhibitor for lead release in plumbing systems. Despite good efficiency, phosphate found in the effluent of water treatment plants may have negative impacts on the environment. Therefore, it would be highly desired to find phosphate-free inorganic inhibitors to prevent lead release in tap water.

As mentioned above, in step 8 of the treatment process, phosphorous compound is added to the water and in step 9 ammonia is added into the water in order to change chlorine to chloramine.

According to Figure 1-3, the median concentration of orthophosphate (PO_4) in the water is 1.66 mg/L. Also, the annual water pumpage is 96.1 million gallon (MG) * 365=35076 MG (132777 million liters).

Therefore the total annual addition of O-phosphate in the drinking water would be 1.66(mg/L)* 132777(ML)= $220410 * 10^6$ mg= 220 Tons

Water quality is a concern in greater lakes (Khazaei, et al, 2018) and nutrient loading have made problems (Hamidi, et al, 2017). Phosphorous loading from wastewater treatment plants to the lakes (Khazaei, et al, 2017; Bravo, et al, 2017) or rivers (Khazaei, et al, 2018) is an example which has a great role in this concern. Chapter NR 217 of the Wisconsin Department of Natural Resources (WDNR) establishes phosphorus limits for point source discharges at 1.0 mg/L. Therefore, a significant amount of the phosphate is removed in wastewater treatment process which raises the burden of the treatment. It is also worth mentioning that the wastewater may also have stormwater and runoff.

This project investigated the capability of a suite of low-cost, environmentally friendly, and phosphate-free inorganic inhibitors in mitigating lead release from aged metallic lead materials under conditions relevant to Chicago and Milwaukee drinking water distribution. Three classes of inorganic compounds were evaluated, including (1) metal sulfate: $SnSO_4$ and $ZnSO_4$, (2) sodium oxyanion: Na_2SiO_3, $Na_2Si_3O_7$, and $Na_2B_4O_7$ and (3) pH/alkalinity adjusting agents: NaOH and $NaOH/Na_2CO_3$ (1:1 molar ratio).

Chapter 2 Literature Review

2.1 Formation & Dissolution of lead corrosion products

2.1.1 Formation of lead corrosion products

Water chemistry has an important role in the formation of lead corrosion products. There are many lead phases formed inside the lead pipe in drinking water distribution system but the most common products are Lead(II)carbonates ‘’ $PbCO_3$’’, Lead(II)oxides ’’PbO’’, lead(IV) oxides ’’PbO_2 ’’, and plumbonacrite ($Pb_{10}(CO_3)_6 (OH)_6O$), (Xie et al., 2010; Wang et al., 2010).

PbO_2 is one of the most important and effective solid which has an important role in a lead release. Shock (Schock et al., 1996; Regulations, E.D.W., 1991) has published reports regarding the presence of Pb(IV) oxides in drinking water distribution systems and experimental pipe loop rig systems. More scale analyses have been performed by USEPA researchers from 42 domestic water systems. Plattnerite(β- PbO_2) and scrutinyite(α- PbO_2) were two types of Pb(IV) oxides observed in one or more specimen from 14 of those systems (Lytle, 2009). Moreover, it has been shown that lead (IV) oxides will be formed in drinking water in realistic conditions and redox conditions have an important role in equilibrium between lead(IV) and lead(II) solids(Schock et al., 1983; Lytle, 2005; Switzer et al.,2006).

As a result of the oxidation of the original pipe (Pb) with oxic or chlorinated water, Lead(II) products are produced. These products will be oxidized by free chlorine to form scrutinyite(α-PbO_2) and plattnerite(β- PbO_2). Depending on the concentration of free chlorine, high oxidation-reduction potential(ORP) could be maintained which lead to stable lead(IV) species formation like scrutinyite (α-PbO_2) and plattnerite (β-PbO_2) (Wang et al., 2010; Wang et al., 2013) and reducing the concentration of free chlorine could lead to unstable lead(IV) species formation. According to

Lytle study, the first eight days after chlorination would be the critical time for losing free chlorine in water (Lytle et al., 2009). Although high ORP could be achieved in other conditions including pristine low-natural organic matter(NOM) ground waters with little bulk oxidant demand allowing significant persistence of free chlorine; waters that 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 (Lytle et al., 2005), chlorinated water is one of the most common conditions we are dealing with in drinking water distribution systems. As high ORP is needed for stable lead(IV) oxides, in drinking water with lower ORP lead(II) solids are dominant (Lytle et al., 2005; Wang et al., 2012; Wang et al., 2010). Although the free chlorine concentration in water distribution system is typically in the range of 0.5-1.5mg/L as Cl_2, PbO_2 formation at this concentration is thermodynamically possible.

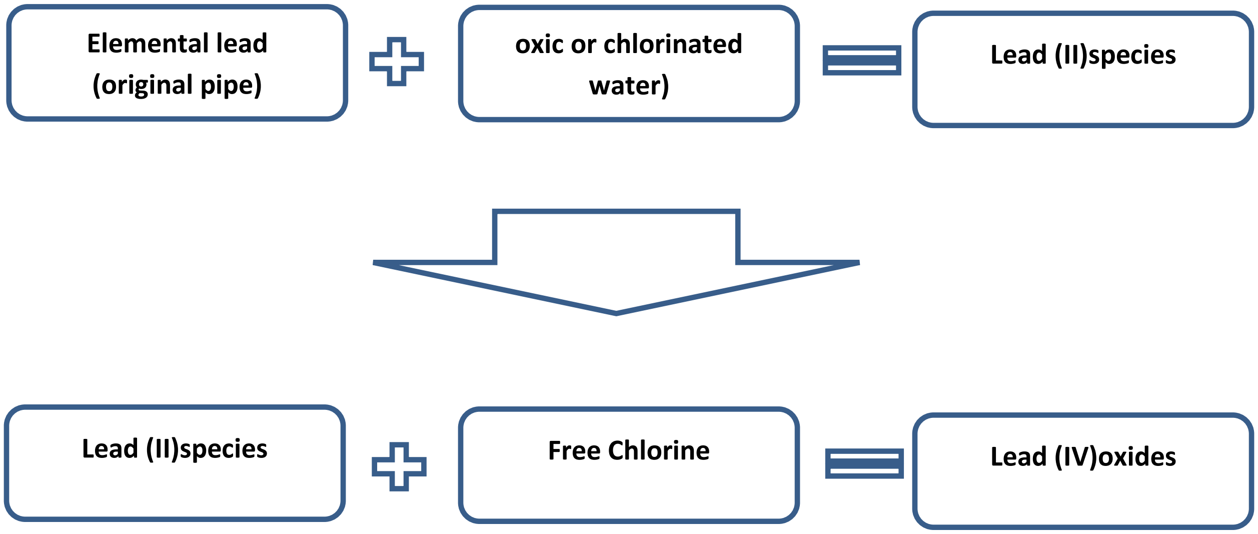


Figure 2-1. Oxidation of lead species in drinking water

This process could be defined in two steps. The first step is the oxidation of Pb(0) and the second step is oxidation of Pb(II) species.

$Pb+HOCl+H^+ \rightarrow Pb^{2+}+Cl^-+H_2O$

$HOCL+Pb^{2+}+H_2O \rightarrow PbO_2+Cl^-+3H^+$

Half reactions:

$Pb^{2+}+2e^- \rightarrow Pb(0)$ E_h=-0.123 (Xie, Y., 2010)

$HOCl+2e^- \rightarrow Cl^-+2H_2O$ E_h=+1.63 or 1.48

$PbO_2+4H^++2e^- \rightarrow Pb^{2+}+2H_2O$ E_h=1.458

To stabilize the lead (IV) oxides, high ORP is needed (Wang et al., 2013). In the actual distribution system, it is provided from free chlorine, but depending on other parameters it varies. Below are two diagrams (Figure 2.2) showing the dominant lead solid phase or dissolved species as a function of pH and ORP.

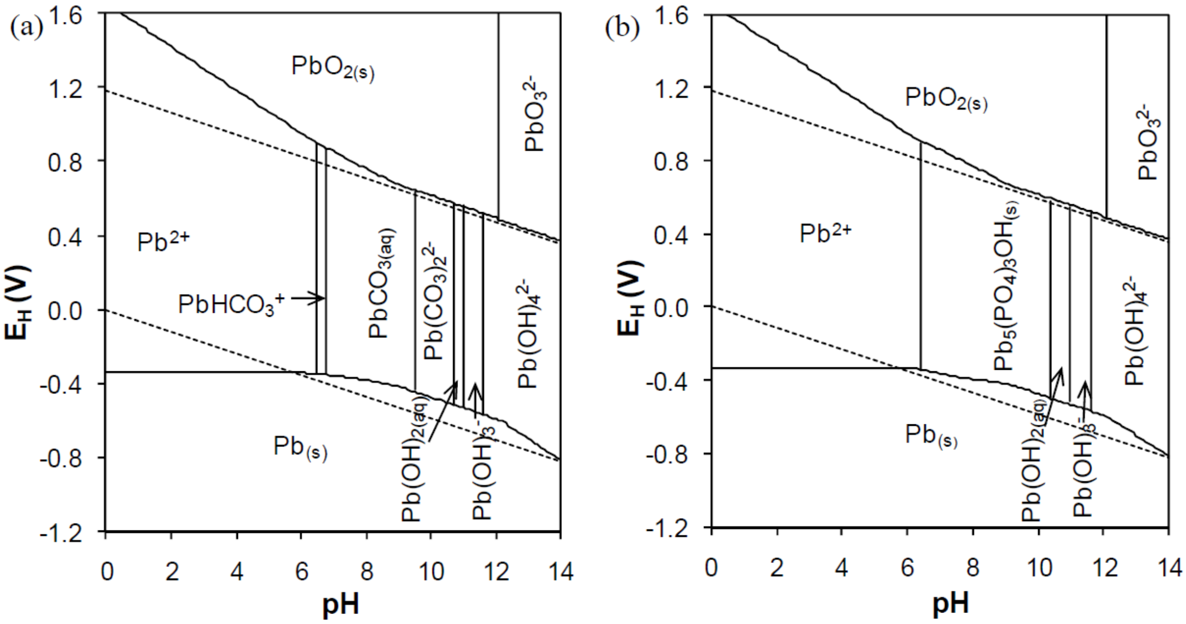


Figure 2-2. Dominant lead solids phase or dissolved species for (a) 30 mg C/L dissolved inorganic carbon (DIC) (2.5×10^{-3} M) and (b) 3 mg C/L DIC (2.5×10^{-4} M) plus 3mg/L dissolved orthophosphate (9.7×10^{-5} M). The diagrams are constructed for a total lead concentration of 15

µg/L. The dashed lines represent the stability limits of water (PO_2 =0.001 atm and P_{H2} = 1 atm). (Xie et al., 2010).

According to Wang and Xie study (Wang et al., 2010), when massicot(β-PbO) is used as PbO_2 precursor, raising the concentration of free chlorine, in the presence of dissolved inorganic carbon (DIC) (later will be discussed in this section), could accelerate the formation of PbO_2 but in the absence of DIC, lower concentration of free chlorine (4mg/L) will result in more PbO_2 formation than the higher one(20mg/L). Two possible way for this would be:

1-Direct oxidation of massicot: $PbO_{(s)} + HOCl = PbO_{2(S)} + H^+ + Cl^-$

2-Dissolution of massicot and after that oxidation of dissolved lead(II): $PbO_{(s)} + 2H^+ = Pb^{2+} + H_2O$, $Pb^{2+} + HOCl + H_2O = PbO_{2(s)} + Cl^- + 3H^+$

In a solution with higher concentration of free chlorine(20mg/L) the first equation could be favored, and as a result, a possible layer of PbO_2 could be formed on the surface of massicot. Over time when more PbO_2 is formed, the possible contact of free chlorine with massicot will be limited. Therefore PbO_2 formation will be inhibited.

According to Lytle and Schock ’s study (Lytle et al., 2005), the higher the pH, the more scrutinyite will be formed from lead(II)chloride and the lower the pH, the more plattnerite. More studies(Wang et al., 2010) showed that pH affects the PbO_2 formation both in the presence and absence of DIC by using massicot as a PbO_2 precursor. In the presence of free chlorine, DIC and after almost a month of reaction plattnerite could be considered as a dominant product at pH 7.5 and scrutinyite at pH 10.5(Table 2-1). However, they did not find a dominant product in the absence of DIC. They also find that rasing the pH could accelerate the fromation of PbO_2. Probably by raising the pH more ion of lead (II) will be available in the solution and then PbO_2 could be formed by either of the pathways below:

1-Dissolved Pb(II) →Aqueous phase oxidation→ Dissolved Pb(IV)→Heterogeneous nucleation→Pb(IV) solids

2- Dissolved Pb(II) →Aqueous phase oxidation→DissolvedPb(IV)→Homogenous nucleation →Pb(IV) solids

Also, studies have shown that DIC could cause the transformation of hydrocerussite to cerussite during the PbO_2 formation process(Liu et al., 2008; Lytle et al., 2009) and lead(II) carbonates could be considered as intermediate in this process. (Lytle, et al., 2009; Lytle et al., 2005; Liu et al., 2008). It is notable that although lead (II) carbonates could be considered as PbO_2 precursors, PbO_2 formation does not require them or their intermediate phases. However, the presence of DIC could help the formation of PbO_2. Studies(Wang et al., 2010; Lytle et al., 2009) shows that in the presence of DIC, lead(II) carbonates like cerussite and hydrocerussite are some intermediate solids in the formation of PbO_2. As discussed earlier, PbO_2 could be formed by oxidation of Pb(II) ions by free chlorine. As mentioned, DIC forms lead(II) carbonates as intermediate solids and these solid provide more lead(II) ion in water and finally the more ion of lead(II) the more PbO_2 formation(in the presence of free chlorine), and the related reaction would be:

$$Pb^{2+}+HOCl+H_2O=PbO_{2(s)}+Cl^{-}+3H^{+}$$

Although PbO is an important precursor of PbO_2, as mentioned above, there are some other corrosion products which could be considered as PbO_2 precursors including cerussite Hydrocerussite.

Also, PbO_2 can be directly formed from soluble Pb(II). Wang and Xie studied the formation of PbO_2(Wang et al., 2010) using $PbCl_2$ in the presence of free chlorine. They found that high concentration of free chlorine(20 mg/L) would result in pure plattnerite formation in a week and by using low concentration of free chlorine(4 mg/L) lead(II) oxide chloride ($Pb_4O_3Cl_2.H_2O$) was observed as an intermediate solid and finally after a month of reaction pure plattnerite formation was seen.

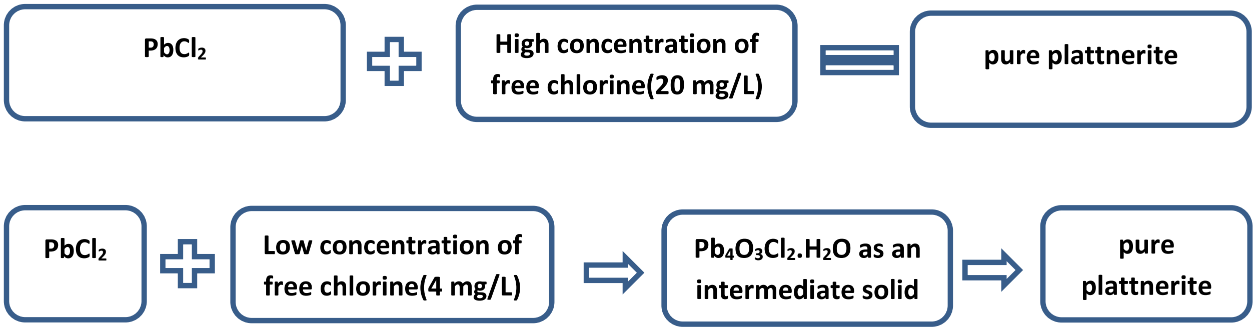


Figure 2-3. Oxidation of $PbCl_2$ with high and low concentration of free chlorine in drinking water

found that formation of a mixture of scrutinyite and plattnerite after a month of reaction is possible (Wang et al., 2010). However, plattnerite formation as a dominant product at pH 6.7-7.8 was found by Lytle and shock (Lytle et al., 2005).

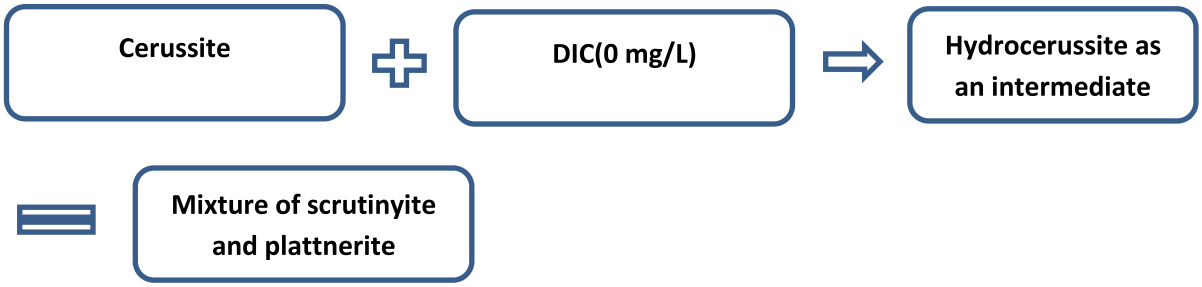


Figure 2-4. Transformation of Cerussite to hydrocerussite

Using hydrocerussite as a PbO_2 precursor results in pure scrutinyite after 28 days and in the absence of DIC and without any intermediate solid and also the oxidation product in the presence of DIC may be the same (Liu et al., 2008; Wang et al., 2010). Therefore, most probably, in the case cerussite is the precursor(in the absence of DIC) quick transformation of cerussite to hydrocerussite at higher pH could be the reason for having a mixture of scrutinyite and plattnerite as a result.

In many water treatment plants, chloramines is another type of disinfectant used in drinking water, and they do not oxidize Pb and lead(II) species to lead(IV). The ORP provided by chloramines is from 0.6 V to 0.9 V whereas free chlorine provides the ORP of 1.2 to 1.3 V. Therefore the ORP from chloramine is not high enough to maintain the Pb(IV) oxides (Switzer et al., 2006; Rajasekharan et al., 2007).

$NH_2Cl+H_2O+2e^- \rightarrow Cl^-+OH^-+NH_3$ Eh=0.69 V (Xie, Y., 2010)

In this condition, pure water may reduce PbO_2 to Pb(II) species. $PbO_{2(s)}+H_2O=Pb^{2+}+0.5O_2+2OH^-$

The possible effect of different parameters on PbO2 formation from different precursors

No	precursor	Low pH	High pH	DIC(0-50mg/L)	w/o intermediate solids	free chlorine	chloramine	Phosphate
1	Massicot			Increase PbO_2 formation	"mix of scrutinyite & plattnerite"	Forms more PbO_2	Destabilize PbO_2	
2	lead(II) chloride	Favors scrutinyite formation	Favors scrutinyite formation	lead carbonate as intermediate solids	mix of scrutinyite & plattnerite			Inhibits the PbO2 formation
3	Hydrocerussite			Pure scrutinyite in presence and absence of DIC	Pure scrutinyite			
4	Cerussite	Plattnerite as a dominant product	Transformation to Hydrocerussite and result in scrutinyite and plattnerite formation					
5	PbCl2					pure plattnerite		

Table 2-1. Possible effect of different parameters on PbO_2 formation from different precursors (Wang et al., 2010; Lytle et al., 2005; Xie, Y., 2010)

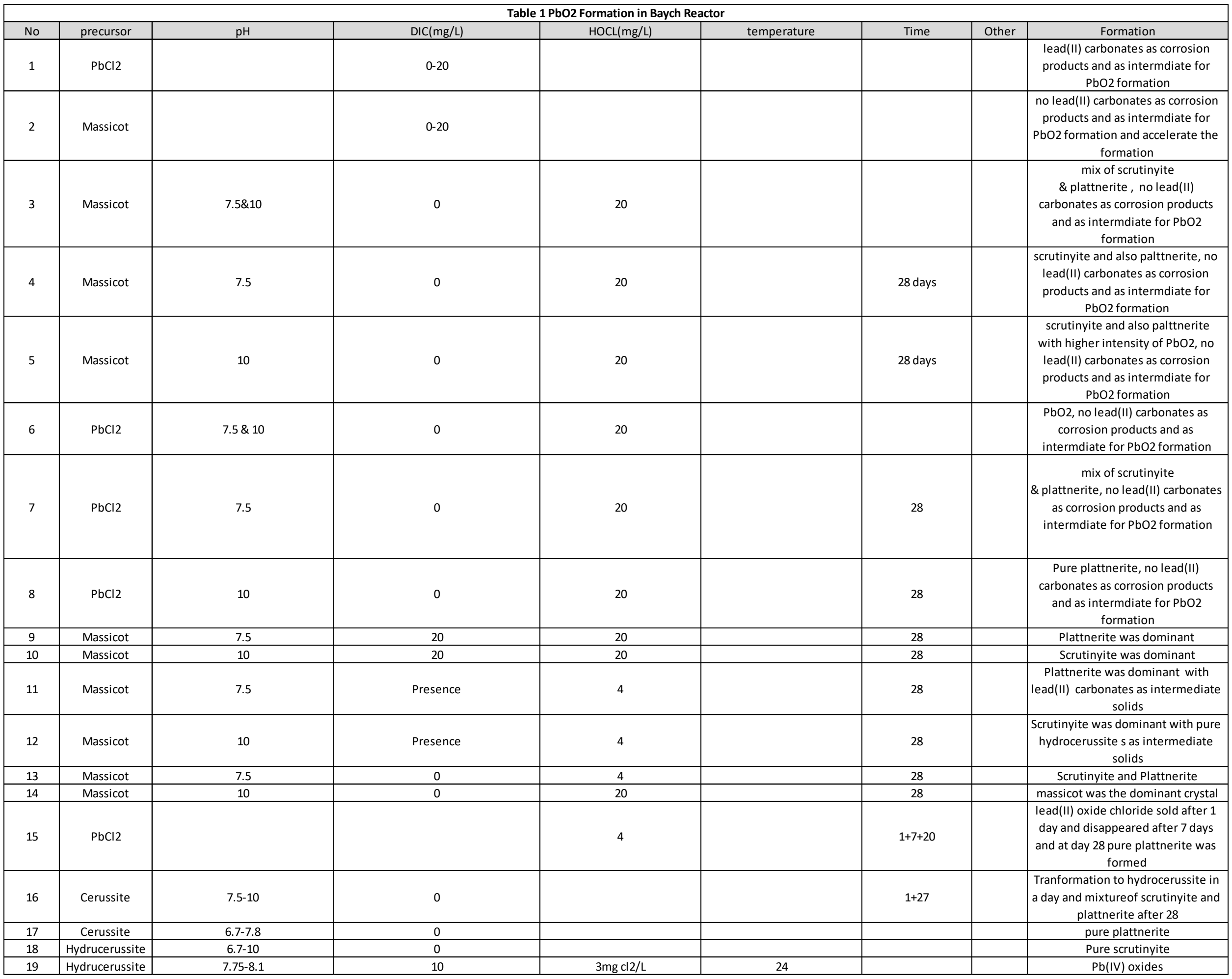


Table 1 PbO2 Formation in Baych Reactor

No	precursor	pH	DIC(mg/L)	HOCL(mg/L)	temperature	Time	Other	Formation
1	PbCl2		0-20					lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
2	Massicot		0-20					no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation and accelerate the formation
3	Massicot	7.5&10	0	20				mix of scrutinyite & plattnerite , no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
4	Massicot	7.5	0	20		28 days		scrutinyite and also palttnerite, no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
5	Massicot	10	0	20		28 days		scrutinyite and also palttnerite with higher intensity of PbO2, no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
6	PbCl2	7.5 & 10	0	20				PbO2, no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
7	PbCl2	7.5	0	20		28		mix of scrutinyite & plattnerite, no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
8	PbCl2	10	0	20		28		Pure plattnerite, no lead(II) carbonates as corrosion products and as intermdiate for PbO2 formation
9	Massicot	7.5	20	20		28		Plattnerite was dominant
10	Massicot	10	20	20		28		Scrutinyite was dominant
11	Massicot	7.5	Presence	4		28		Plattnerite was dominant with lead(II) carbonates as intermediate solids
12	Massicot	10	Presence	4		28		Scrutinyite was dominant with pure hydrocerussite s as intermediate solids
13	Massicot	7.5	0	4		28		Scrutinyite and Plattnerite
14	Massicot	10	0	20		28		massicot was the dominant crystal
15	PbCl2			4		1+7+20		lead(II) oxide chloride sold after 1 day and disappeared after 7 days and at day 28 pure plattnerite was formed
16	Cerussite	7.5-10	0			1+27		Tranformation to hydrocerussite in a day and mixtureof scrutinyite and plattnerite after 28
17	Cerussite	6.7-7.8	0					pure plattnerite
18	Hydrucerussite	6.7-10	0					Pure scrutinyite
19	Hydrucerussite	7.75-8.1	10	3mg cl2/L	24			Pb(IV) oxides

Table 2-2. PbO_2 Formation in lab investigations (Wang et al., 2010; Lytle et al., 2009; Lytle et al., 2005)

2.1.2 Dissolution of lead corrosion products (the primary mechanism on the release of dissolved lead)

The lead concentration in tap water depends on the equilibrium of lead corrosion products which is potential to change by the existence of different individual products and water chemistry. The possible types of dissolved lead species would be Pb^{2+} or Pb^{4+} and their complexes (Xie Y., 2010).

Lead (IV) oxide (PbO_2) is a significant lead corrosion product, and its stability is a significant factor for lead release in drinking water distribution systems. As mentioned above, high ORP is needed to stabilize PbO_2 in the system, and it could be provided by free chlorine (Xie et al., 2010). However, even without free chlorine in the system dissolution of PbO_2 would be so slow (scales of pipes harvested from Washington, D.C, in 2011 contained PbO_2 even after ten years) (Welter et al., 2012) unless there is a reductant in the water. Also, during the stagnation of water when free chlorine residual is depleted, NOM could reduce PbO_2, and lead release could be increased tremendously (Xie et al., 2011; Lin et al., 2009).

Compared to lead (II) solids, lead (IV) oxides have a lower solubility. Therefore, in drinking water in which lead (IV) is a dominant product, the lower lead concentration would be expectable. This fact also could be explained by considering the equilibrium calculations:

$$PbO_{2(s)}+4H^+=Pb^{4+}+2H_2O$$

$$K_{\text{sp,scrutinyite}}=\frac{[Pb^{4+}]}{[H+]^4}=10^{-8.26}$$

$$Pb^{4+}+3H_2O=PbO_3^{2-}+6H^+ \qquad \log(K_{eq})=-23.04$$

$$Pb^{4+}+4H_2O=PbO_4^{4-}+8H^+ \qquad \log(K_{eq})=-63.8$$

Reduction of PbO_2 to Pb(II) species could result in lead release (Wang et al., 2010). Reductants such as natural organic matter(NOM), Fe(II) and Mn(II) species, bromide and iodide can reductively dissolve PbO_2 (Wang, et al., 2013; Dryer, et al., 2007).

In studying the mechanisms of the PbO_2 dissolution. Lin and Valentine observed that in acidic conditions, increasing Br^- and H^+ would increase the dissolution rate of PbO_2 at pH 3.5-4.5. (Lin, et al., 2010) The mechanism is described in two steps:

1-Attacking the reductant to PbO_2 and reduce the surface Pb(IV) to Pb(II)

2-Detachment of the reduced surface to the water

This mechanism is for acidic condition whereas, in reality, we do not have this situation and pH usually would be 6.5-10. Iodide is found widely in water and could be considered as a reductant for modeling the PbO_2 reduction as below(Wang et al., 2012):

Half reactions:

$4H^++PbO_2+2e^-=Pb^{2+}+2H_2O$

$2I^-=I_2+2e^-$

Hydrolysis of I_2:

$I_2+H_2O=I^-+HOI+H^+$

Therefore the overall redox reaction between PbO_2 and I^- would be:

$PbO_2+2I^-+4H^+=Pb^{2+}+I_2+2H_2O$

Using previous studies (Lin et al., 2008; Shi et al., 2009) and their observation (Wang et al., 2012),Below is the comparison of different types of reductant ions on PbO_2 dissolution rate.

Dissolution rate of PbO_2			
Reductant conc	pH	DIC mg C/L	Rate(mol.m^{-2}.m^{-1})
Iodide 10 (μm)	7.6	10	4.70E-09
Iodide 10 (μm)	7		2.10E-09
NOM 20(mg/L)	7		4.00E-09
Ferous Ion 40(μm)	7.8		1.30E-06
Manganous Ion20(μm)	7.8		3.20E-06

Table 2-3. Dissolution rate of PbO_2 (Wang et al., 2012; Lin et al., 2008; Shi et al., 2009)

Therefore the dissolution rate order could be $NOM<I^{-}<Mn^{2+}<Fe^{2+}$

Decreasing the pH (Increasing H^+) would favor redox reaction of PbO_2. Considering the thermodynamics of this reaction, decreasing pH would increase the electrochemical potential of reaction, and it could be increased by 0.118V for a one pH unit decrease. From a kinetic point of view, increasing H^+ causes more iodide adsorption to the PbO_2 surface which results in the faster dissolution of PbO_2 (Wang et al., 2012; Wang et al., 2013; Xie et al., 2010).

According to several previous studies (Wang et al., 2012; Xie et al., 2010), in the presence of strong reductant like iodide, increasing the concentration of DIC could increase the dissolution of PbO_2. What is probably happening is that DIC carbonate complexes which result in a higher concentration of Pb(II) ion in drinking water.

Flow is another important factor in lead dissolution into drinking water. Xie (Xie et al., 2011) found that the dissolution rate for flowing water would be one order of magnitude higher than the stagnation system. The reason for it could be the acceleration of mass transfer made by the flow.

When lead(II) is dominant, Pb(II) carbonate, oxide, or phosphate can control the dissolved lead in water as Pb^{2+}.

$Pb_3(CO3)_2(OH)_{2(S)}+2H^+=3Pb^{2+}+2CO_3^{2-}+2H_2O$

$$k_{sp,hydrocerussite}=\frac{[Pb^{2+}]^3[CO_3^{2-}]^2}{[H^+]^2}=10^{-18.77}$$

$Pb_5(PO_4)_3OH_{(s)}+H^+=5Pb^{2+}+3PO_4^{3-}+H_2O$

$$k_{sp,hydrocerussite}=\frac{[Pb^{2+}]^5[PO_4^{3-}]^3}{[H^+]}=10^{-62.79}$$

As shown in Figure 2.4, the equilibrium with lead(II) carbonate or phosphate provides a much more dissolved lead in water. However, some other important parameters are affecting the concentration of lead in tap water. Hydraulic residence time is an important parameter for this issue because a significant amount of lead would be released in first 24 hours of stagnation (Lytle et al., 2000; Xie, Y., 2010). There are also some other noticeable parameters including flow velocity which could influence corrosion mechanisms (Schock, M.R., 1999), phosphate inhibitors which were demonstrated to inhibit lead release(Lehrman et al., 1952; Hozalski et al., 2005; Edwards et al., 2002; Larson T.E., 1957; McNeill et al., 2002; Holm et al., 1991; Schock et al. 2005; Mayne et al., 1954; Lytle et al.,009; McNeill et al., 2002) , and effect of pH and carbonates which depends on the exact condition and corrosion products (Schock M.R., 1999). In actual distribution system, by having insufficient hydraulic residence time the products could not be in equilibrium. Moreover, there are no accurate data regarding constants and transitions between scale types and reaction kinetics. Therefore, considering equilibrium-based models could not be entirely reliable (Edwards et al., 1999; Vasquez, F., 2005; Xie, Y., 2010).

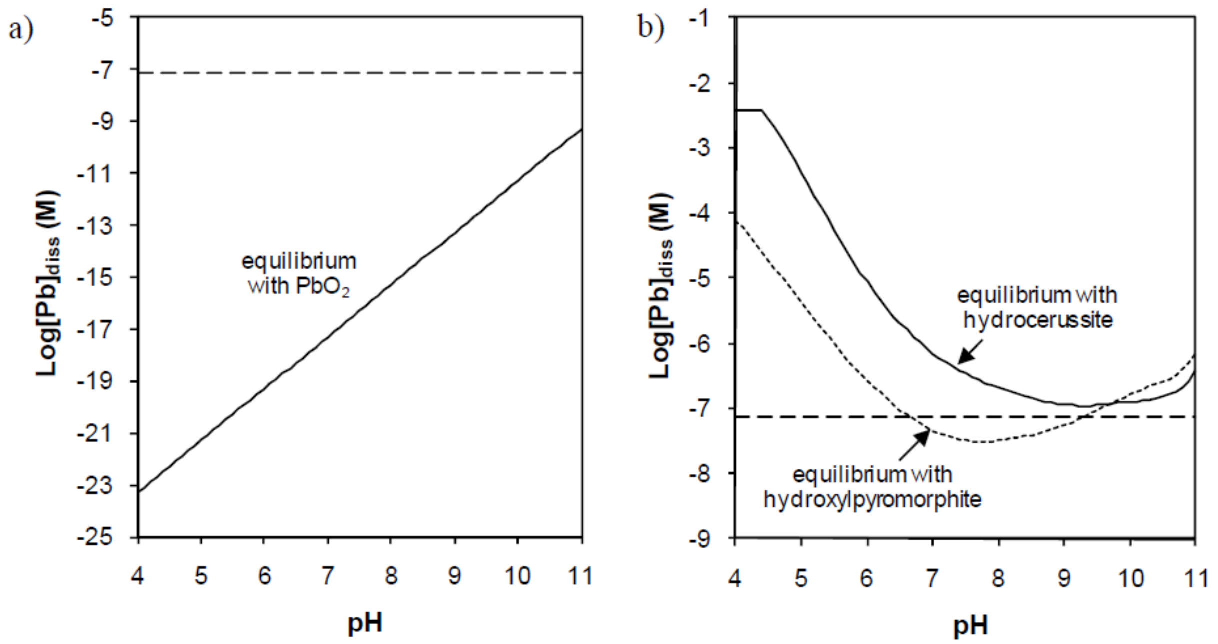


Figure 2-5. Dissolved lead concentration in equilibrium with (a) lead(IV) oxide at sufficiently oxidizing conditions that all lead is present as lead(IV) and (b) the lead(II) carbonate hydrocerussite with 30 mg/L DIC and the lead(II) phosphate hydroxylpyromorphite with 30 mg/L DIC and 3 mg/L orthophosphate. The long dashed line shows the lead action level of 15 µg/L. Note the difference in the y-axis ranges (Xie et al., 2010).

Type of the disinfectant is another important point which was mentioned in the formation section. As mentioned above, free chlorine would provide the high ORP which could make PbO_2 stable and switch to chloramine would decrease the ORP of the water which destabilizes PbO_2 and as a result of this destabilization, higher dissolution rate of plattnerite could be expected. (Xie et al., 2010) Below is plattnerite dissolution rates order according to the type of disinfectant used in drinking water:

No disinfectant>Monochloramine>Chlorine

2.1.3 Dissolved lead versus particulate lead

There are two main types of lead in drinking water distribution system resulted from lead release Soluble lead & particulate lead.

The soluble lead is the lead dissolved in the water, and particulate lead is like tiny grains of sand. The particulate lead fall of the pipe's wall into the drinking water which is retained by 0.45 µm filter.

Several factors affect the amount of soluble and particulate lead in drinking water including stagnation time, galvanic corrosion, pH, flow rate and inhibitors. These factors and their effects are discussed below:

Stagnation and galvanic corrosion:

Partial service line replacement is performed by replacing the service line from corporation stop to curb stop. Wang and Ye (Wang et al., 2012) found that using brass-coupled system between the copper and lead service lines could increase the particulate lead, especially for longer stagnation time and it could persist for about six months. Most likely, galvanic corrosion is the main reason for this release. In another study in which brass dielectric and brass coupling were used to connect the copper and lead pipes, the large particular lead release was observed(Wang et al., 2013). Experiments showed that using plastic-coupled system would dramatically decrease the lead release into the water.

Ph and flow rate:

pH is another important parameter in this discussion. According to Kim and Herrera's study(Kim et al., 2011), the particulate lead would be a significant amount of total lead in stagnated systems at higher pH but in lower pH particulate would be the more significant contributor to total lead concentration. In another study(McNeill et al., 2004) in the stagnated system(with pH 7.2 and alkalinity 15 mg/L), a large amount of particular lead was observed, but in a system, with higher alkalinity(45 mg/L) lower particulate lead was observed. Cartier and Dore (Cartier et al., 2013) study show that raising the flow rate, in flowing systems, and in existence of orthophosphate could increase the particulate lead tremendously.

Inhibitors:

Inhibitors are used in large scale in water distribution systems. Polyphosphate and orthophosphate are the most common inhibitors used for preventing the lead release by making a protection layer on the pipe's wall. However, they could affect the amount of particulate and soluble lead in the system. Compared to orthophosphates, which could increase the particulate lead(Cartier et al., 2012), using hexametaphosphate inhibitors in drinking water would increase the soluble and particulate lead (McNeill, L.S., 2000).Another study (Xie et al., 2011) in which PbO_2 and hydrocerussite were developed in lead pipes by using free chlorine for eight months(3.25 mg/L free chlorine, pH=10), showed that using orthophosphate would decrease the soluble lead release rate and increase the particulate lead release in the water in both flowing water and stagnation system. Probably the precipitation of lead phosphate solids is an essential contribution to the particulate lead concentration into the water.

Experiments (Xie et al., 2011) showed that most of the lead in stagnation system(2hrs) would be dissolved lead except the system in which orthophosphate is used. According to Xie and Giammar's experiments in stagnation systems, the particulate lead would be just 10% of the total lead whereas in the system with orthophosphate this value would be increased to 49%. Other studies also showed a high particulate lead fraction for a solution with phosphate(McFadden et al., 2011).

Galvanic corrosion	More particulate lead for longer stagnation time
Higher pH	More particulate lead in stagnation system
Polyphsphate	Increase both soluble and particulate lead
orthophosphate	Increase the particulate lead
Stagnation system	more dissolved lead(except the system with orthophosphate)

Table 2-4. Particulate and soluble lead in different systems (Wang, et al., 2012; Kim, et al., 2011; McNeill, L.S., 2000; Xie et al., 2011)

2.1.4 Galvanic corrosion

Drinking water is a weak electrolyte and when two dissimilar metals such as lead and copper are connected in the drinking water self-induced current (resulted from the electrical potential difference between the two metals) will be created.

$$CU^{2+}+2e \longleftrightarrow Cu \qquad E(Volts)=0.339$$

$$Pb^{2+}+2e^{-} \longleftrightarrow Pb \qquad E(Volts)=-0.126$$

This process is named Galvanic corrosion. Two dissimilar metals in physical contact or contact galvanically. In many water distribution system, copper service line from corp to curb stop and lead service line from curb stop to meter are prevalent. The connection of them at curb stop provide the condition which favors the galvanic corrosion. Although the affected zone probably is not more than a few inches, it could be a great contributor to lead release into the drinking water.

There are many factors which could affect the galvanic corrosion such as pH, free chlorine, monochloramine, alkalinity, etc. According to Cartier and Dore study's (Cartier et al., 2013) increasing the flow rate could result in the higher lead in the water especially in the form of particulate lead. Using two pipe-loop systems with two galvanic couples (lead-copper, lead-bronze) in a controlled water quality environment, Boyd and Reiber (Boyd, et al., 2012) used the tap water with a pH range of 7.98-8.36, a total alkalinity of 20 mg/L as $CaCO_3$, the hardness of 27 mg/L, total organic carbon of 1 mg/L and phosphate of less than 2 mg/L(Tap1) and changed the different factors to find their effect on galvanic corrosion. Increase in alkalinity (20mg/L to 140 mg/L) and the addition of phosphate showed a slight increase of lead release. Although there was a little change of lead release as a result of the disinfectant change, the most prominent increase of lead was observed at ph decreased from 8.3 to<7.5. Other studies showed that the type of connection is considered as a prominent factor in galvanic corrosion.Below could be considered as an order of lead increase for different connection:

Plastic<Plastic with external<Brass dielectric< Brass coupling< Brass coupling with higher Zinc(Wang et al., 2013; Wang et al., 2012; Clark et al., 2013).

Another important factor which could affect the intensity of lead release resulted from galvanic corrosion is the chloride-to-sulfate mass ratio (CSMR) (Hu et al., 2012; Cartier et al., 2012). A dramatic increase could happen by increasing CSMR to the range of 0.1 to 10.(Nguyen et al., 2011) One hypothesis about this phenomenon would be the stimulation of attack on lead when it is connected to copper whereas it tends to protect the lead when there is no connection to copper. Sulfate, on the other hand, was found to inhibit the lead corrosion by making a corrosion product layer. It changes the format of the layer from needle-like crystals to flat platelets which are considered more protective to lead corrosion (Edwards et al., 2007).

In experiments conducted by Clark and Cartier (Clark et al., 2013) the effect of distance and crevices on galvanic corrosion were examined. They found that increasing the distance would decrease the galvanic corrosion significantly (80% decrease at 12 inches). Also, they found that crevice creation at the connection would worsen the corrosion.

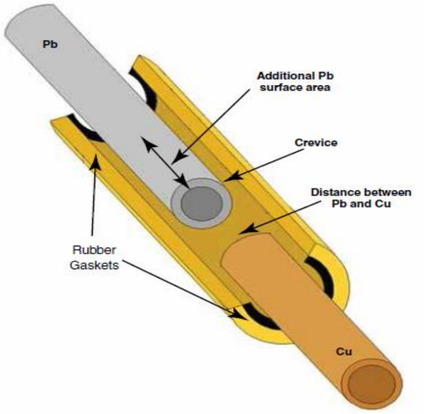


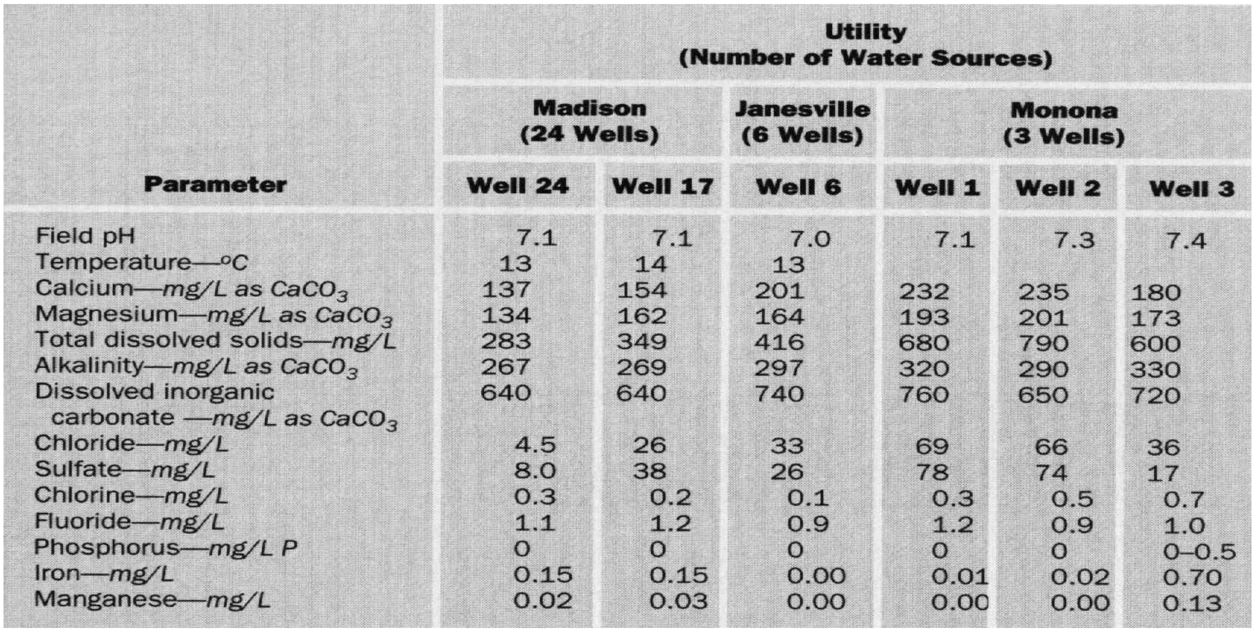
Figure 2-6. Distance between Pb and Cu (Clark et al., 2013)

2.2 Lead release inhibitors

2.2.1 Phosphate inhibitor addition

Many phosphate-based water treatment products are available which could be divided into three main parts: orthophosphates (trisodium orthophosphate Na_3PO_4, etc.), polyphosphates(sodium pyrophosphate $Na_4P_2O_7$, sodium tripolyphosphate $Na_5P_3O_{10}$) and blended phosphates. Inhibitor doses could range form 0.2 mg /L to 3mg/L as PO_4

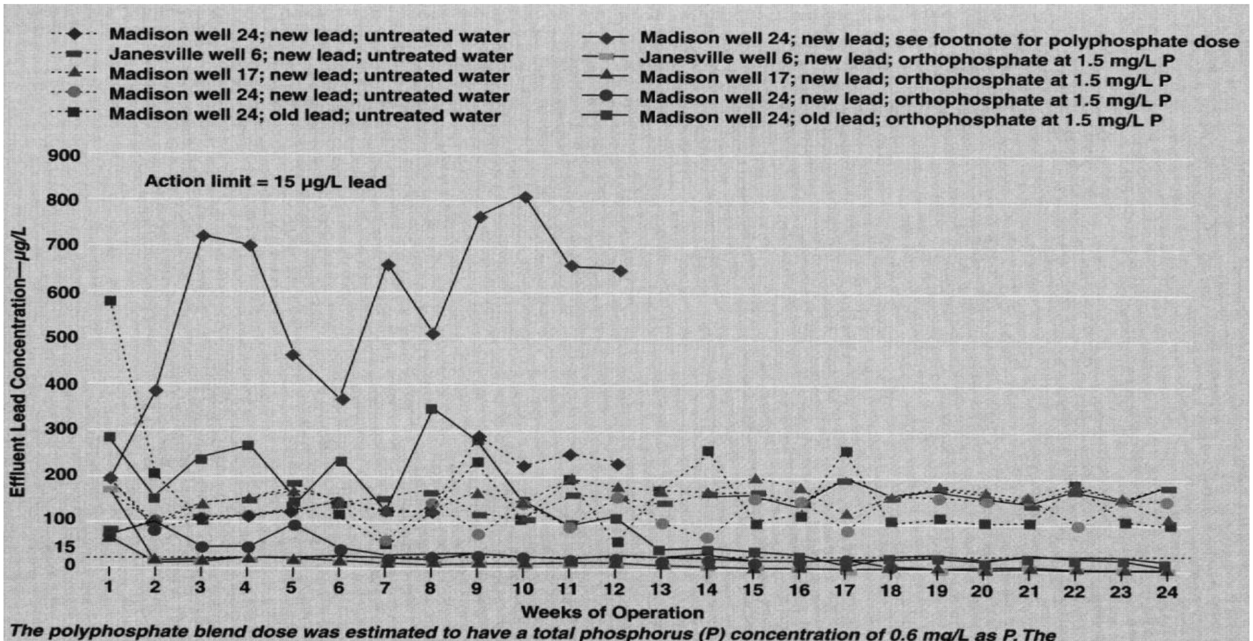
The effect of the polyphosphates addition is very complex because of the number of interactions when it is added to water to reduce the lead solubility. pH, alkalinity, temperature, the percentage of orthophosphate, the concentration of metals(e.g., Ca, Fe, Mn) and stability constants for the polyphosphate ligands are the important factor in the complexity of it. Also, one possible



Parameter	Madison (24 Wells)		Janesville (6 Wells)	Monona (3 Wells)		
	Well 24	**Well 17**	**Well 6**	**Well 1**	**Well 2**	**Well 3**
Field pH	7.1	7.1	7.0	7.1	7.3	7.4
Temperature—°C	13	14	13			
Calcium—*mg/L as $CaCO_3$*	137	154	201	232	235	180
Magnesium—*mg/L as $CaCO_3$*	134	162	164	193	201	173
Total dissolved solids—*mg/L*	283	349	416	680	790	600
Alkalinity—*mg/L as $CaCO_3$*	267	269	297	320	290	330
Dissolved inorganic carbonate —*mg/L as $CaCO_3$*	640	640	740	760	650	720
Chloride—*mg/L*	4.5	26	33	69	66	36
Sulfate—*mg/L*	8.0	38	26	78	74	17
Chlorine—*mg/L*	0.3	0.2	0.1	0.3	0.5	0.7
Fluoride—*mg/L*	1.1	1.2	0.9	1.2	0.9	1.0
Phosphorus—*mg/L P*	0	0	0	0	0	0–0.5
Iron—*mg/L*	0.15	0.15	0.00	0.01	0.02	0.70
Manganese—*mg/L*	0.02	0.03	0.00	0.00	0.00	0.13

Utility (Number of Water Sources)

Table 2-5. Water quality at distribution entry points in the Wisconsin corrosion control studies (Cantor et al., 2000)



The polyphosphate blend dose was estimated to have a total phosphorus (P) concentration of 0.6 mg/L as P. The orthophosphate contribution to the total averaged 0.2 mg/L as P and was found by analysis. The polyphosphate product had a polyphosphate-to-orthophosphate ratio of 2:1.

Figure 2-7. Wisconsin lead pipe loop test results (Cantor et al., 2000) hypothesis is polyphosphates require calcium ions to develop protective layer (Boffardi et al., 1991). There is not enough study regarding these factors and their effects and as a result, application of polyphosphate could be encountered with high risk (Holm et al., 1991)(Larson, T.E., 1957)(Boffardi et al., 1991). Above is the result of a study (Cantor et al., 2000) show that using polyphosphate tend to increase the lead concentration in the systems.

Also, some other studies showed that using polyphosphates could increase the concentration of lead in drinking water. For example, according to Edward's study (Edwards et al., 2002), hexametaphosphate could increase the release of soluble and particulate lead in drinking water. Based on their experiments, each mg/L of residual Hexametaphosphate could increase the soluble lead by 1.6 mg/L after three days of stagnation.

In a study done by Cartier (Cartier et al., 2012) the efficiency of Orthophosphate was surveyed. In his study, four different type of samples were tested including samples without treatment, with the addition of 0.8 mg P/L of orthophosphate, with pH adjustment to 8.4 and with adjustment to a higher chloride to sulfate mass ratio (CSMR; ratio from 0.3 to 2.9). Base on the results orthophosphate reduced the lead leaching 41% and 70% for double faucets. It also increases the percentage of particulate lead (>0.45 µm) from 31% to 54%.

Some other studies also showed an excellent efficiency of orthophosphate. For example, Edward's experiments results (Edwards et al., 2002) showed that orthophosphate dosing could reduce the soluble lead release by 70% , according to the characteristic of base water (Table 2.6). However, in new pipes, it could have less efficiency and could even increase the lead release. Most likely, in a new pipe, orthophosphate cannot increase the pH value enough to reduce the lead release. Experiments (Lytle et al., 2009) showed that in the absence of orthophosphate, transformation from Pb(II) mineral hydrocerussite could happen (DIC=10 C/L, pH 7.75-8.1, 3 mg/L Cl2) which could result in more lead release in the water. Interaction of orthophosphate with the lead surface (Boffardi et al., 1991) is also another type which could be taken into account.

Parameter(mg/L)	Value
Orthophosphate	<0.05
Iron	1.1
Lead	<0.003
Copper	<0.01
Natural Silica	5-8
Calcium	21
Magnesium	7.6
Chloride	6
Fluoride	1.1
Sulfate	6
Free chlorine	0
Total organic carbon	1.28

Table 2-6. Typical characteristics of base water (Edwards et al., 2002)

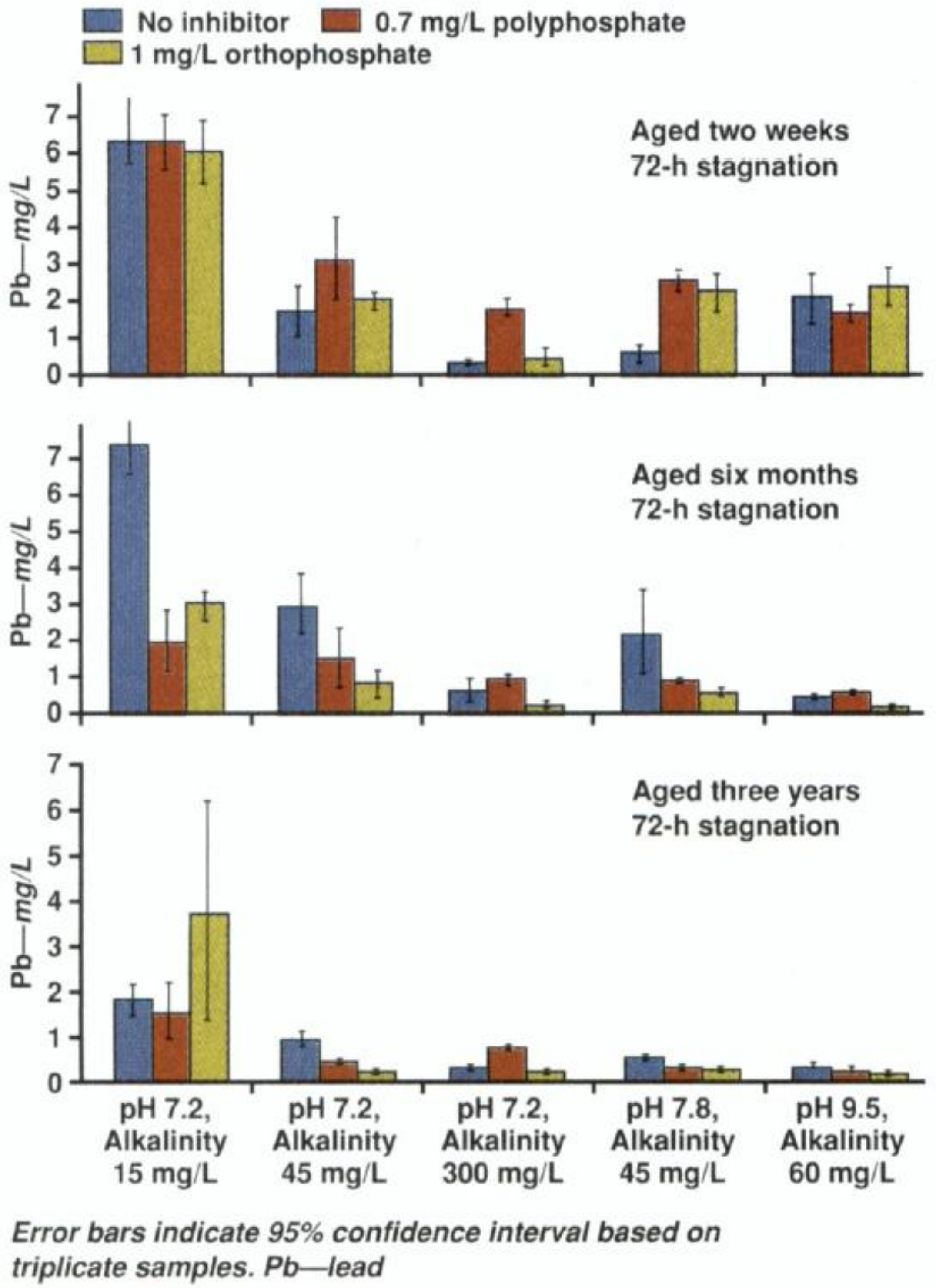
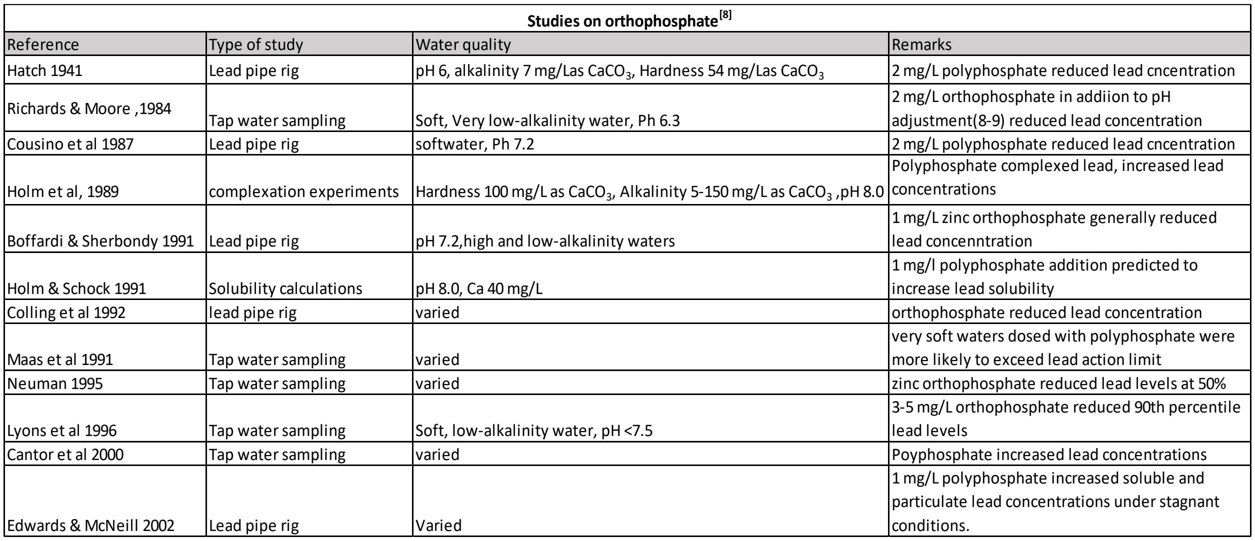


Figure 2-8. Total Pb Released during 72-h exposure (Edwards et al., 2002)

Observations (Schock et al., 2005) showed that in phosphate-treated systems there would be less deposition of PbO_2. Phosphate compounds can kinetically inhibit the formation of divalent metal carbonate, oxide and hydroxycarbonate minerals in different systems (Lytle et al., 2009).

The formation of relatively insoluble compounds such as hydroxypyromorphite ($Pb_5(PO_4)_3(OH)$) and tertiary lead orthophosphate($Pb_3(PO_4)_2$) could be promoted by using orthophosphate in drinking water distribution systems. (Sheiham, et al., 1981)



Studies on orthophosphate[8]

Reference	Type of study	Water quality	Remarks
Hatch 1941	Lead pipe rig	pH 6, alkalinity 7 mg/Las $CaCO_3$, Hardness 54 mg/Las $CaCO_3$	2 mg/L polyphosphate reduced lead cncentration
Richards & Moore ,1984	Tap water sampling	Soft, Very low-alkalinity water, Ph 6.3	2 mg/L orthophosphate in addiion to pH adjustment(8-9) reduced lead concentration
Cousino et al 1987	Lead pipe rig	softwater, Ph 7.2	2 mg/L polyphosphate reduced lead cncentration
Holm et al, 1989	complexation experiments	Hardness 100 mg/L as $CaCO_3$, Alkalinity 5-150 mg/L as $CaCO_3$,pH 8.0	Polyphosphate complexed lead, increased lead concentrations
Boffardi & Sherbondy 1991	Lead pipe rig	pH 7.2,high and low-alkalinity waters	1 mg/L zinc orthophosphate generally reduced lead concenntration
Holm & Schock 1991	Solubility calculations	pH 8.0, Ca 40 mg/L	1 mg/l polyphosphate addition predicted to increase lead solubility
Colling et al 1992	lead pipe rig	varied	orthophosphate reduced lead concentration
Maas et al 1991	Tap water sampling	varied	very soft waters dosed with polyphosphate were more likely to exceed lead action limit
Neuman 1995	Tap water sampling	varied	zinc orthophosphate reduced lead levels at 50%
Lyons et al 1996	Tap water sampling	Soft, low-alkalinity water, pH <7.5	3-5 mg/L orthophosphate reduced 90th percentile lead levels
Cantor et al 2000	Tap water sampling	varied	Poyphosphate increased lead concentrations
Edwards & McNeill 2002	Lead pipe rig	Varied	1 mg/L polyphosphate increased soluble and particulate lead concentrations under stagnant conditions.

Table 2-7. Studies on Orthophosphate (McNeill et al., 2002)

2.2.2 Addition of other chemicals (e.g., silicates, tin chloride), and pH/alkalinity adjustment

Calcium is a chemical which may be potential to reduce the lead release by the addition to the drinking water. In a study (James et al., 2000) the formation of particulate lead in the system was surveyed by conducting batch and pipe-loop systems experiments. Results showed that addition of calcium at the level of 5 mg/L might reduce the zeta potential of lead-bound colloids and even total lead concentration.

The effect of the pH on the concentration of lead in drinking water has brought much attention. It is a strong hypothesis that raising pH in the range of 8.4-9.5 could control the lead release in the drinking water system. Batch, pipe loop and sentinel studies (Kim et al., 2011) showed that increasing pH value might decrease the solubility of lead corrosion scale and consequently decrease the concentration of lead in drinking water system. The stagnation time, flow rate, temperature, existence of other metals and chemicals are some other factors which could influence the effect of pH value in controlling the lead release.

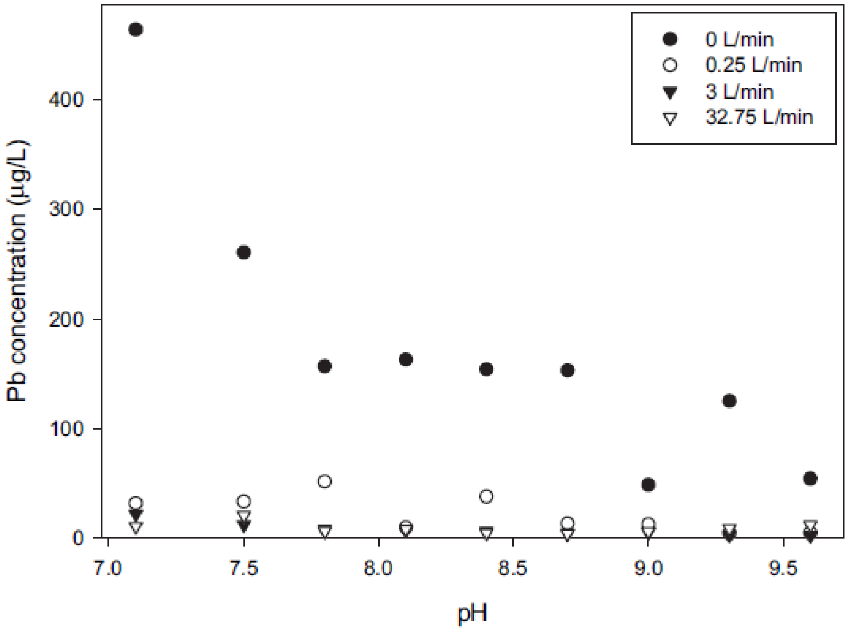


Figure 2-9. Total lead concentration observed during pipe loop test at different pH values and water flow rates (Kim et al., 2011)

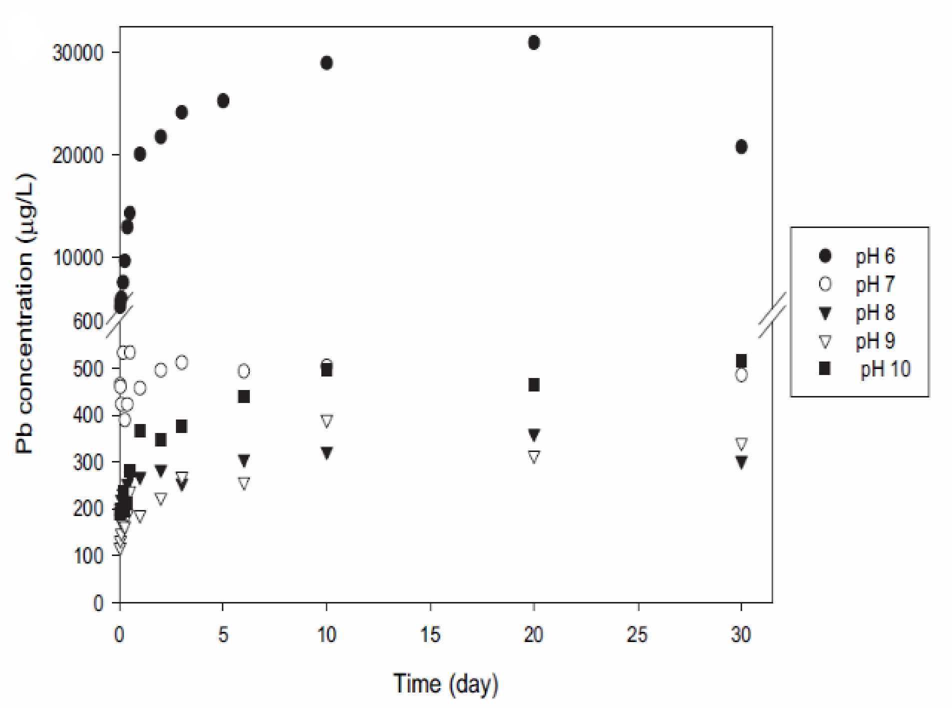


Figure 2-10. Contributions of soluble and particulate lead concentrations to total lead concentrations at various pH and flow rate of (a) 0 L/min (stagnation) and (b) 3 L/min. (Kim, et al., 2011)

Chloride and sulfate are common chemicals found in drinking water. Even though either of them itself may not have a significant contribution to lead release and concentration of lead in drinking water, but CSMR could be considered as an effective parameter in lead release. Anion exchange treatment, switch in coagulant type and some other treatment steps could increase the CSMR.According to Edwards and Nguyen bench-scale experiments, higher CSMR(>0.5) increased lead leaching from brass coupons and lead solder-copper pipe joints by the factor of 1.2-2.7 and 2.3-40 respectively. It has been mentioned that high chloride relative to sulfate (yielding CSMR>0.5) would increase the galvanic corrosion (Edwards et al., 2007; Nguyen et al., 2011). Other studies showed that the CSMR to the range of 0.1-1.0 could make a dramatic increase in lead leaching from lead-tin solder galvanically coupled to copper (Nguyen et al., 2011).

Observations from different water systems have provided some hypotheses regarding the relationship between alkalinity and lead release. According to this survey, keeping the pH value and alkalinity lower than 8.4 and in a range of 30-74 mg/L as CaCO3 respectively, could reduce the lead release significantly compared to lead release at alkalinity lower than 30 mg/L as CaCO3. The result also shows that inhibitors could improve the lead corrosion by-product release at alkalinity lower than 30 mg/L s CaCO3. (Dodrill et al., 1995).

2.2.3 Use free chlorine as a disinfectant

Free chlorine is present in drinking water as HOCl and OCl^- as a result of the addition of sodium hypochlorite (NaOCl) and chlorine gas(Cl_2) to water. Free chlorine could oxidizes lead (II) species to lead (IV) species (Xie, Y., 2010) and Because of the high (ORP) maintained by free chlorine, stable lead (IV) products will be formed in drinking water (Xie et al., 2010).

In some water treatment plant, in order to reduce the disinfectant by-product, chloramines (e.g.NH_2Cl) is used in drinking water. Chloramines are formed by reacting ammonia with free chlorine and generates less of disinfection byproducts like trihalomethanes and haloacetic acids. (Vasquez, F., 2005) ORP is lowered by switching the disinfectant from free chlorine to chloramine. Therefore lead(IV) species will be unstable in drinking water.

By using free chlorine, the system would have ORP of 1.2 to 1.3 V which is enough to maintain Pb(IV) oxides. However, when chloramine is used in the system, ORP will be 0.6 to 0.9 V which is not enough to stabilize lead (IV) oxides and consequently more lead (II) species will be seen in the system. In this condition, water may reduce lead (IV)oxides to lead(II) species (Xie, Y., 2010)

$$PbO_{2(s)}+H_2O=Pb^{2+}+0.5O_2+2OH^-$$

This process may be considered as the prominent cause of high lead levels in distribution system of the Washington D.C. wherein treatment plant free chlorine disinfectant was switched to chloramine, and as result of that, the lead concentration in tap water exceeded 0.015 mg/L. In one hundred homes, it even exceeded 0.3 mg/L.

As explained in part 2.1, maintaining ORP in the system is mostly related to free chlorine concentration. It could stabilize Pb(IV) oxides and as a result of this stabilization lead release would be decreased and controlled.(Lytle et al., 2009) found that in chlorinated water and in the presence of DIC, less free chlorine concentration drop and less OPR drop would be achieved by using very high concentration of Orthophosphate(30 mg/L).

Chapter 3 Experimental

3.1 Project objectives

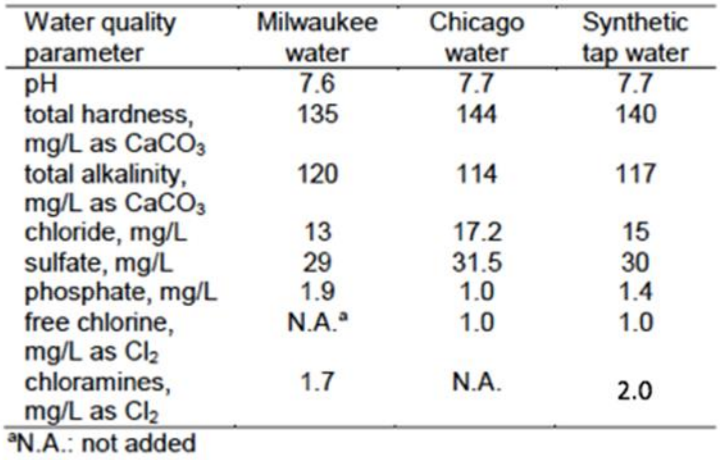
In this project, the overall objective was to systematically investigate the capability of a variety of phosphate-free inorganic inhibitors in minimizing lead release from aged metallic lead materials under conditions relevant to Chicago and Milwaukee drinking water distribution. The specific objectives of this work were to:

(1) identify the optimum inorganic inhibitor formulations and concentrations.

(2) determine the impact of disinfectant type on the performance of the inorganic inhibitors.

3.2 Research Methods

Three classes of phosphate-free inorganic compounds were selected as potential corrosion inhibitors, including: (1) metal sulfates: $SnSO_4$ (2 mg/L as Sn) and $ZnSO_4$ (2 or 4 mg/L as Zn), (2) sodium oxyanions: Na_2SiO_3, $Na_2Si_3O_7$ (20 mg/L as SiO2), and $Na_2B_4O_7$ (5 mg/L as BO_3), and (3) pH adjusting agents: NaOH (pH = 8.5 or 9.2). The effectiveness of the six inorganic inhibitor formulations in mitigating lead release from aged lead coupons was systematically evaluated by using aged lead coupons in 500-mL batch reactors with synthetic tap water at ambient temperature (20 ± 1 ^{o}C). Metallic lead coupons were prepared by cutting the lead sheet into pieces with about 4 cm^2 surface area. Synthetic tap water was prepared to simulate the chemistry of both Chicago and Milwaukee distribution systems (Table 3.1.).



Water quality parameter	Milwaukee water	Chicago water	Synthetic tap water
pH	7.6	7.7	7.7
total hardness, mg/L as $CaCO_3$	135	144	140
total alkalinity, mg/L as $CaCO_3$	120	114	117
chloride, mg/L	13	17.2	15
sulfate, mg/L	29	31.5	30
phosphate, mg/L	1.9	1.0	1.4
free chlorine, mg/L as Cl_2	N.A.[a]	1.0	1.0
chloramines, mg/L as Cl_2	1.7	N.A.	2.0

[a]N.A.: not added

Table 3-1. Water Quality parameter

Lead coupons were conditioned using a "dump-and-fill" mode by suspending in completely stirred batch reactors with 400 mL of synthetic tap water for about three months to develop the lead corrosion on the new coupon. After that, inhibitors were switched from phosphate to phosphate-free ones on week 1 (Mar 28, 2016) to evaluate their performance. To determine the impact of disinfectant type, disinfectant was changed from free chlorine (1 mg/L as Cl_2) to mono-chloramine (2 mg/L as Cl_2) on week 10 (May 30, 2016). Inhibitor concentrations or pH were also changed on week 19 (Aug 1, 2016) to identify their effects. Totally 22 weeks was taken for the experiments.

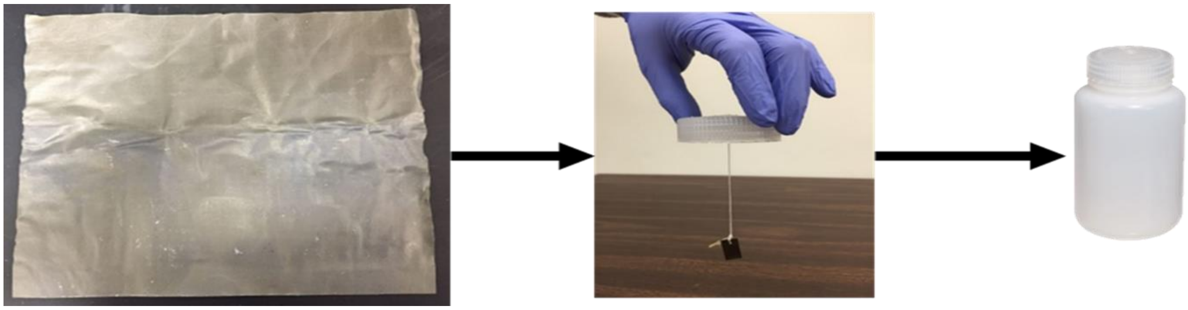


Figure 3-1 Aged lead coupon

There were 19 batch reactors in total (Figure 3-2). Each experimental condition was run in duplicates. Two reactors were blank without any inhibitor. Three reactors used phosphate inhibitor as a control. "Dump-and-fill" mode was used in the experiments: synthetic tap water was changed and replenished with freshly prepared ones three times a week (i.e., Monday, Wednesday, and Friday). The pH and disinfectant concentration was monitored and adjusted on a daily basis. pH meter was used to measure and adjust the pH and DPD method was used to measure the disinfectant concentration. For measuring the Pb concentration, 10 ml samples were collected twice per week for total lead analysis using inductively coupled plasma mass spectrometry (ICP-MS) which were acidified to 2% HNO_3 before analysis.

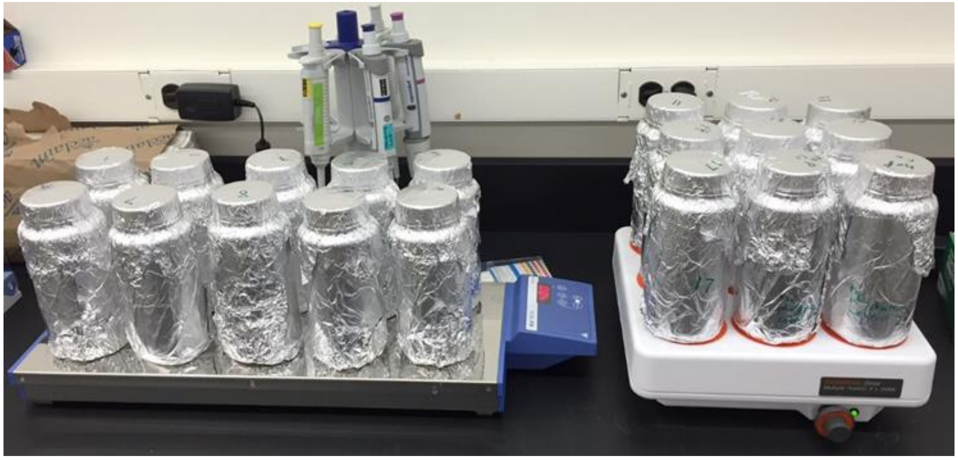


Figure 3-2. Batch reactors used in examining the performance of phosphate-free inhibitors

3.3 Results and discussion

3.3.1 Performance of Inhibitors

After about three months of conditioning for the new lead coupon, inhibitors were switched from phosphate to phosphate-free on week 1 to evaluate their performance. The pH was adjusted to 7.7 except for the condition that used pH adjusting agent as an inhibitor (pH 9.2). Free chlorine was used as the disinfectant. As shown in Figure 3-3, the X-axis is the number of the week, and the Y-axis is the total lead concentration after 48-hour stagnation. In the blank reactors without any inhibitor, the lead concentration was relatively high. The use of the phosphate inhibitor effectively prevented the lead release from aged lead coupons (with total lead concentration ~20 µg/L).

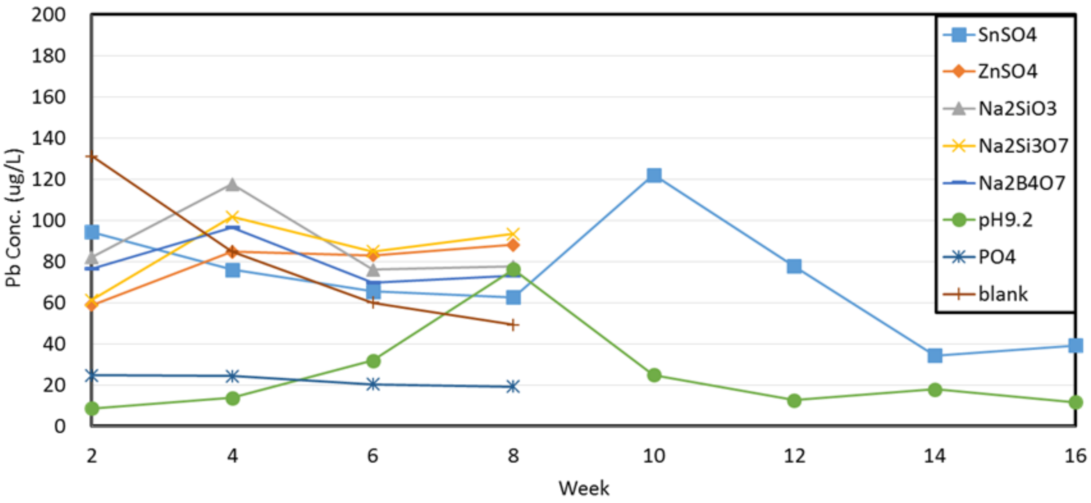


Figure 3-3. Total lead release with the use of different corrosion inhibitors as a function of time

Among different phosphate-free strategies, pH adjustment (pH 9.2) worked best. The possible reason is that increasing pH may decrease the solubility of certain lead corrosion products that control lead release in tap water. Although the unexpected lead release was observed from week 8 (corrosion scale not well developed and destabilization of the scale to release particulate lead), after the long-term experiment, the unexpected lead release disappeared. Another observation is that $SnSO_4$ exhibited some level of inhibition for lead release, but it also required more time to passivate the lead corrosion scales.

3.3.2 Effect of Disinfectant

To determine the impact of disinfectant type, disinfectant was switched from free chlorine (1 mg/L as Cl_2) to mono-chloramine (2 mg/L as Cl_2) from week 10. The total lead concentration after 48-hour stagnation was measured. As shown in Figure 3-4, the grey bars are the two weeks' average for lead concentration before switching disinfectant, and the blue bars are the two weeks' average for lead concentration after switching disinfectant.

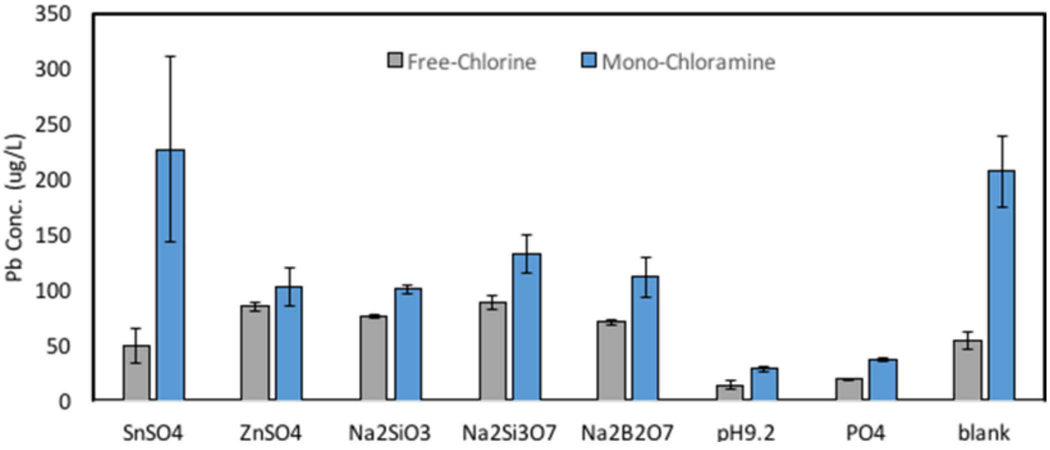


Figure 3-4. Average total lead concentration after 48 hours of stagnation with the use of free chlorine and mono-chloramine as disinfectants (Two weeks average)

In the conditioning experiments, free chlorine was used as the disinfectant, which may favor the formation of lead dioxide (PbO_2) on the surface of lead coupons. Switching free chlorine to mono-chloramine increased lead release, especially in blank and $SnSO_4$ conditions, due to the lower ORP and the destabilization of lead dioxide corrosion products. However, pH adjusting agent (pH 9.2) could effectively inhibit lead release in the presence of mono-chloramine as well as in the presence of free chlorine.

3.3.3 Effect of Silicates

At the beginning of the experiments, the pH was adjusted to 7.7 for all reactors except the pH adjusting agent (pH 9.2). Some unique aspects of silicates inhibitor were observed that the addition of silicates increased the pH of the solution to about 9.0. So from week 14, the pH was not adjusted back to 7.7 for reactors with sodium silicates as inhibitors. The experiments were conducted with mono-chloramine as the disinfectant. The total lead concentration after 48-hour stagnation was measured. Compared with phosphate control and inhibitor-free blank, the addition of silicates without adjusting pH back to 7.7 could effectively prevent lead release in relatively short-term experiments. The probable reason was the increase of solution pH (about pH 9.0) in the reactors with silicates as inhibitors.

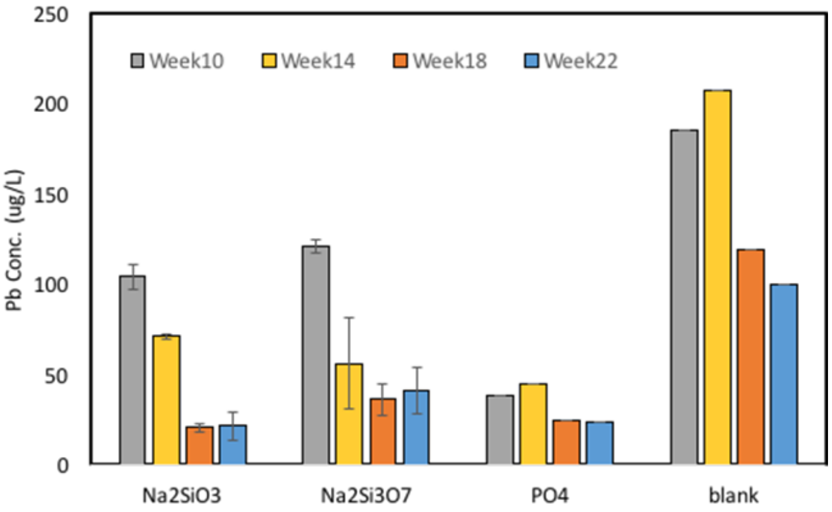


Figure 3-5. Effect of Silicates on total lead release after 48 hours of stagnation

3.3.4 Effect of $ZnSO_4$ Concentration and pH

To identify the effects of inhibitor concentration, the inhibitor concentration or pH was changed from week 19. The $ZnSO_4$ inhibitor concentration was increased from 2 mg/L to 4 mg/L as Zn with mono-chloramine as the disinfectant. Starting from week 19, the pH of pH adjusting agent inhibitor was decreased from 9.3 to 8.5 with free chlorine (F) and mono-chloramine (M) as disinfectants. The total lead concentration after 48-hour stagnation was measured. As shown in Figure 3-6, for the $ZnSO_4$ inhibitor, doubling ZnSO4 concentration inhibited lead release to some extent with mono-chloramine as the disinfectant. For the pH adjusting agent, decreasing pH worked well in the presence of free chlorine as the disinfectant, while it enhanced lead release with mono-chloramine as the disinfectant.

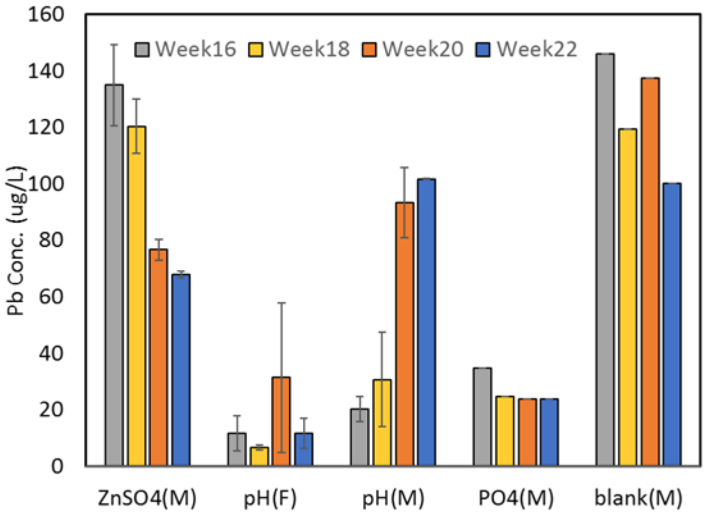


Figure 3-6. Effect of ZnSO4 Concentration and pH on total lead release after 48 hours of stagnation

Chapter 4 Conclusion and future work

This project investigated the capability of a suite of low-cost, environmentally friendly, and phosphate-free inorganic inhibitors in mitigating lead release from aged metallic lead materials under conditions relevant to Chicago and Milwaukee drinking water distribution.

The results showed that pH adjustment on 9.2 would decrease the lead release significantly. However, it could trigger some other reactions in the system which increase the concentration of iron, copper, magnesium, manganese, etc and the taste, color and odor of drinking water could be affected. Therefore further investigation regarding pH adjustment may be needed.

Sodium silicate showed the capacity of decreasing lead leach in the system over time. Probably the reasons could be pH increase in the system and the creation of a protective layer on the surface of the pipe. Also, $SnSO_4$ showed the capacity of decreasing lead in the system.

Based on the experimental results, pH adjustment, silicate addition, and use of $ZnSO_4$ were promising in minimizing lead release. Further recommendations will focus on

(1) identifying the optimum inhibitor formulations in a wide range of environmental matrices that are relevant to drinking water distribution,

(2) evaluating the long-term performance of the optimum inhibitor formulations

(3) conducting pilot-scale pipe loop studies to better represent the scenarios in real distribution systems.

Also, it will be beneficial to determine the combinative use of phosphate and phosphate-free inhibitors that may effectively mitigate lead release in tap water and reduce loads of phosphate in wastewater utilities in the meantime. Cost-benefit analysis and life cycle assessment may also be needed to promote the technology adoption in the field.

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