Lead and Copper Corrosion Control in Potable Water

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PREFACE

This report entails water quality (WQ) analysis for four potable water supply sources located in the vicinity of Pampa, Grey County, Texas. For the purpose of this report, they were grouped together and compared to each other because all of them used chlorine gas for disinfection. The data analysis, done by the author, was part of a much broader project and study of lead and copper corrosion for several public utility districts in the Northern Texas on which the author was Principal Technical Consultant. The entire WQ data cited in this report was obtained from and is publicly available on the Texas Commission on Environmental Quality (TCEQ) Drinking Water Watch (DWW) website. There is no confidentiality and non-disclosure agreement between the author and any of the parties involved. The report including data analysis has not been published anywhere else.

INTRODUCTION

The main sources of lead and copper (Pb & Cu) in drinking water are the materials used for pipes delivering water from the supply well to the buildings and building plumbing and fixtures. Water pH, alkalinity, chlorine, etc. may cause this material, especially in old plumbing systems, to release Pb & Cu. The report examines the range of WQ parameters that suppress or promote the release of Pb & Cu using the four water systems as an example of a desktop study and defines the USEPA suggested Pb & Cu treatment methods. The data analysis is the report entails a 1-year data set for the four systems from July 2016 to June 2017.

Researchers showed that free chlorine gas used for potable water disinfection creates sufficient oxidation-reduction potential (ORP) to promote PbO_2 scale formation on the inner surfaces of pipe and plumbing fixtures. This scale prevents lead from dissociating. This report demonstrates that long (above 4 days) water stagnation times result in free chlorine dissipation and, consequently, reduction in ORP that, in turn, stimulates lead release from the PbO_2 scales at pH as high as pH8.5. This was the dominant mechanism causing the NOV (one of the four systems examined in this report) lead action level (AL) exceedance on 6/17/2016 rather than pH variations from 7 to 8 (as claimed by TCEQ), chloride, alkalinity, chlorine feed rate or any other contributing factor.

PROJECT BACKGROUND

In 2017, the author was Principal Technical Consultant and Advisor on several WQ Pb & Cu corrosion projects in Texas. In accordance with Title 30 of the Texas Administrative Code (30 TAC) §290.117, PWSs are required to control levels of Pb & Cu by controlling water corrosivity. When an ALE of a routine tap sample occurs, the PWS must investigate the cause of the exceedance and propose treatment to prevent future exceedances. The investigation includes an assessment of the source water prior to entering the system and the water already within the system to determine the likely source of elevated Pb & Cu.

TCEQ requires the facilities that exceed Pb & Cu Action Levels to prepare and submit a so-called desktop Corrosion Control Study, normally done by professional engineers on behalf of PWSs. As an option, an expensive coupon or pipe loop study can be performed to demonstrate that the potable water distribution system in question has no potential for further Action Level Exceedances (ALEs) of Pb & Cu or, if such cannot be demonstrated, propose a treatment method.

In all cases for the four systems, the ALEs were caused by lead leaching from plumbing fixtures and not from the groundwater source. In many cases especially with the plumbing systems installed 30-40 years ago, water stagnation and a consequent reduction in water ORP due to reduction in free chlorine supply was the major reason of lead leaching from the pipe PbO_2 scales. The report discusses the leaching mechanism and Pb & Cu treatment options for the 4 example systems.

CORROSION CONTROL TREATMENT

Alkalinity and pH adjustment have been used by many systems for corrosion control. This method has been expanded to include dissolved inorganic carbon (DIC) adjustment because all three parameters are a better indicator of corrosion control effectiveness than pH and alkalinity alone.

DIC is an estimate of the total amount of inorganic carbon as shown in equation below:

$$DIC = CO_2 + H_2CO_3 + CO_3^{2-} + HCO_3^{-}$$

Information on the use and effectiveness of silicate-based corrosion inhibitors continues to be limited and more research is needed. Calcium hardness adjustment is not discussed in this report because newer research has shown that calcium carbonate films only rarely form on lead and copper pipe and are not considered an effective form of corrosion control. Calcium hardness is, however, important in evaluating the level of pH adjustment that can be made without causing calcium carbonate precipitation and resultant scaling problems in the distribution system.

Adjustment of pH/alkalinity/DIC can be accomplished by chemical or non-chemical means. Typical chemicals used for pH/alkalinity/DIC adjustment for corrosion control are listed in **Table 4-1**.

Table 4-1

Typical Chemicals Used for pH/Alkalinity/DIC Adjustment for Corrosion Control

Chemical	Use	Composition	Alkalinity Change	DIC Change	Notes
Baking Soda, $NaHCO_3$, (sodium bicarbonate)	Increases alkalinity with moderate increase in pH.	95% purity. Dry storage with solution feed.	0.60 mg/L as $CaCO_3$ alkalinity per mg/L as $NaHCO_3$	0.14 mg/L as C per mg/L as $NaHCO_3$	Good alkalinity adjustment chemical but expensive.
Carbon Dioxide, CO_2	Lowers pH. Converts hydroxide to bicarbonate and carbonate species.	Pressurized gas storage. Fed either through education or directly.	None	0.27 mg/L as C per mg/L as CO_2	Can be used to enhance NaOH or lime feed systems.
Caustic Soda, NaOH (sodium hydroxide) Or KOH (potassium hydroxide)	Raises pH. Converts excess carbon dioxide to carbonate alkalinity species.	93% purity liquid bulk, but generally shipped and stored, at < 50% purity to prevent freezing. KOH has a higher freezing point and may be stored at higher concentrations.	1.55 mg/L as CaCO3 alkalinity per mg/L as NaOH	None	pH control is difficult when applied to poorly buffered water. Is a hazardous chemical, requires safe handling and containment areas
Hydrated Lime, $Ca(OH)_2$ (calcium hydroxide)	Raises pH. Increases alkalinity and calcium content (i.e., hardness).	95 to 98% purity as $Ca(OH)_2$. 74% active ingredient as CaO. Dry storage with slurry feed.	1.21 mg/L as $CaCO_3$ alkalinity per mg/L as $Ca(OH)_2$	None	pH control is difficult when applied to poorly buffered water. Slurry feed can cause excess turbidity. O&M is intensive.

Chemical	Use	Composition	Alkalinity Change	DIC Change	Notes
Soda Ash, Na_2CO_3 (sodium carbonate) Or Potash, KCO_3 (potassium carbonate)	Increases alkalinity with moderate increase in pH.	95% purity. Dry storage with solution feed.	0.90 mg/L as $CaCO_3$ alkalinity per mg/L as Na_2HCO_3	0.11 mg/L as C per mg/L as Na_2CO_3	More pH increase caused compared with $NaHCO_3$, but less costly. Has increased buffer capacity over hydroxides.
Sodium Silicates Na_2SiO_3	Moderate increases in alkalinity and pH	Available in liquid form mainly in 1:3.2 or 1:2 ratios of Na_2O:SiO_2	Depends on formulation	None	More expensive than other options but easier to handle than lime and other solid feed options. Has additional benefits in sequestering or passivating metals.

In addition to chemical methods, pH/alkalinity/DIC adjustment can be accomplished using limestone contactors or aeration. Limestone contactors, which are enclosed filters containing crushed high-purity limestone, have been used at small systems because they are relatively easy to operate. As the water passes through the limestone, the limestone dissolves, raising the pH, alkalinity, DIC, and calcium of the water. An empty bed contact time of 20 to 40 minutes is typically used to optimize pH and alkalinity adjustment. If a high pH is needed, other media types (e.g., dolomite, dolomitic materials) may be available regionally. When using limestone contactors, the influent should have pH < 7.2, calcium < 60 mg/L, alkalinity < 100 mg/L, and DIC < 10 mg/L. For influent pH >7.2, carbon dioxide can be added prior to the contactors. Limestone contactors can also be used for iron removal but require backwash capabilities to remove iron that accumulates on the limestone. Recommendations on the design and application of limestone contactors can be found on the following USEPA-funded Web site:

http://www.unh.edu/wttac/WTTAC_Water_Tech_Guide_Vol2/limestone_intro.html.

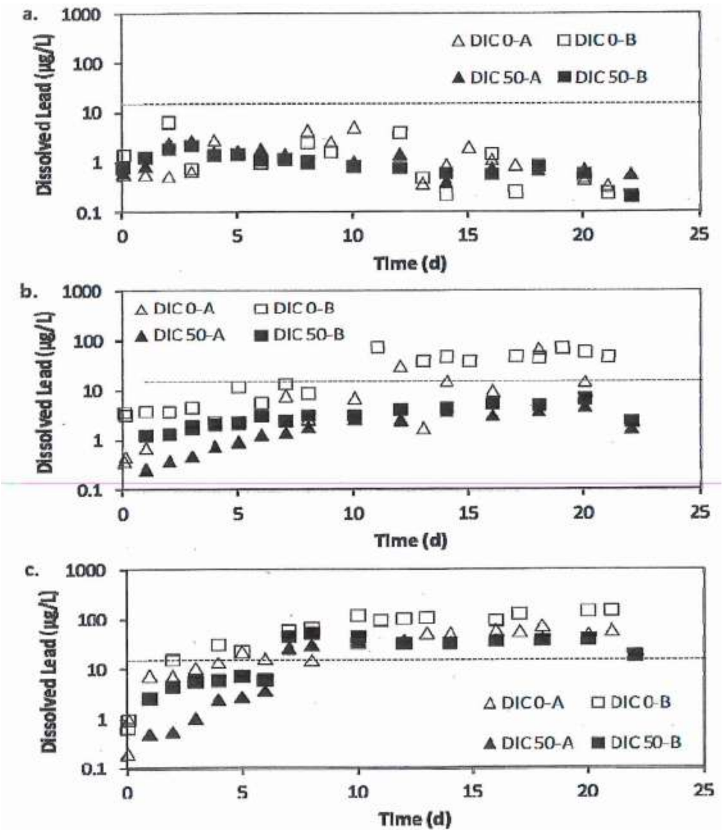
Aeration is a non-chemical method for adjusting pH where air is introduced into the water. Aeration is the only method that reduces excess DIC by removing carbon dioxide, which results in an increase in pH. Aeration systems include Venturi injector systems, tray systems, packed tower systems, and diffuse bubble systems. They can be designed to remove other constituents such as iron, manganese, radon, volatile organic compounds (VOCs) and hydrogen sulfide

(H2S). Aeration is most effective when there is an adequate carbon dioxide concentration in the water (4 - 10 mg/L CO_2), and the pH is < 7.2 (Ref. 5). Phosphate-based corrosion inhibitors have been widely used to control lead release. They are briefly described in this report as well.

EFFECT OF WATER STAGNATION TIME ON LEAD DISSOLUTION

Even in the presence of free chlorine and fluoride which increase ORP, measurable amounts of lead can be released from PbO_2 after long stagnation times at conditions relevant to drinking water. Dissolved lead increases with increasing stagnation time and reaches plateaus after 10 days of reaction as shown in **Figure** Error! No text of specified style in document.**-1**. The total lead concentrations exceed the action level after 10 days at pH8.5 and 4 days at pH7.5. At pH6.0, lead concentrations do not increase with time. In Fig. 4-1, dashed line is the lead AL of 15 ppb, a., b., and c. are at pH of 6, 7.5 and 8.5, and open and closed symbols are with free chlorine and DIC and without free chlorine and DIC, respectively.

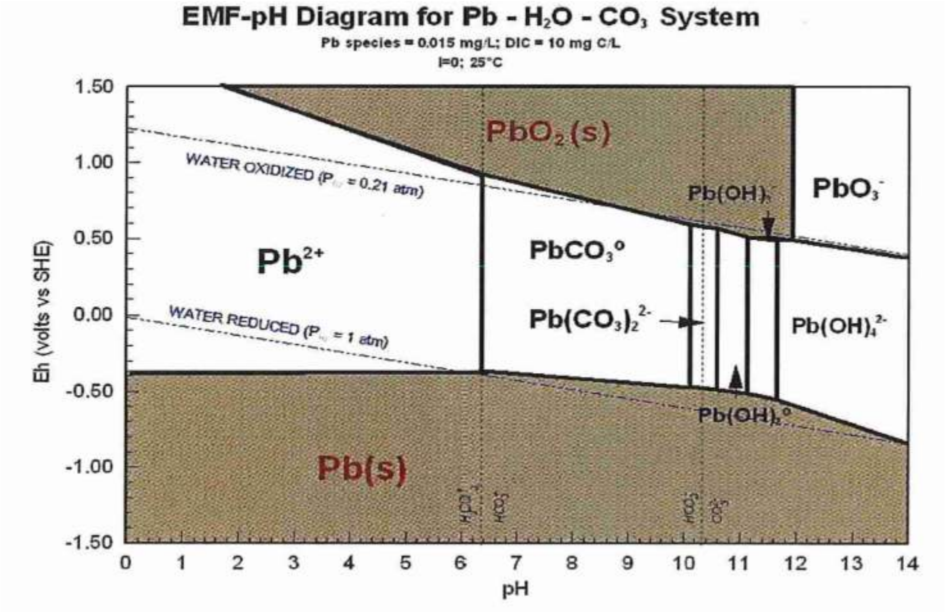
Figure Error! No text of specified style in document.**-1**
Dissolved Lead Concentration with Time at 50 ppm DIC and 2 ppm Cl_2/L



Stagnation results in lowering ORP provided by free chlorine which, in turn, leads to transformation from low solubility PbO_2 to high solubility lead(II) carbonates. The lead carbonate species such as $Pb_3(CO_3)_2(OH)_2$, $PbHCO_3^-$ and $PbCO_3$ are indicative of corrosion of the PbO_2 layer. **Figure** Error! No text of specified style in document.**-2** shows that for normal drinking water pH, lead (IV) from the PbO_2 scales dissociates as lead (II) in lead carbonates.

Figure Error! No text of specified style in document.**-2**

ORP-pH Diagram for a Lead-Water Carbonate System in the Presence of Free Chlorine



The dissolution rate and not the equilibrium solubility of PbO_2 controls dissolved lead concentrations in water that is in contact with PbO_2.

Lead dissolution is strongly inhibited by free chlorine even at concentrations as low as 0.2 ppm. The threshold above which the formation of PbO_2 is favored is less than 4 ppm of Cl_2. The average rate of chlorine feed at the four systems examined in this report is around 1-1.5 ppm of chlorine which is within the optimal chlorine range preventing lead dissolution. Increased DIC results in reduced dissolved lead which is also consistent with the findings of this report.

6. WQ DATA REVIEW

6.1. NOV WQ

Table 6-1 shows NOV's tap water quality parameters averaged for the period from mid-2016 to mid-2017.

Table 6-1

NOV Tap WQ Concentration

WQ Parameter	**C, ppm**
Sulfate	154.6
Aluminum	0.0094
Calcium as Ca^{2+}	76.7
Copper	0.056
Fluoride	0.89
Chloride	205.6
Magnesium	33.9
Nitrogen oxides	1.66
Iron	0.062
Lead (1), ppb	*7*
Hardness$^{\text{as CaCO3}}$	321
Alkalinity$_{\text{Total}}^{\text{as CaCO3}}$	151
Manganese	0.0005
TDS	796
El.conductivity umho/cm	1396
pH (2) S.U.	7.92
Sodium	136
TTHM, ppb	17.6

6.2. WQ DATA COMPARISON

When Pb & Cu exceed the limits, two Corrosion Control Study options are given as follows:

1. A desktop study based on the facility's supply and distribution system water and direct comparison with a similar in size and WQ;
2. A real-time Pb & Cu release study based on testing a system's prototype or a bench scale laboratory study using coupons/plates of the PWS's solder or equal pipe/fittings construction material.

For the purpose of this report and the lack of systems' pipe and fittings material samples, Option 1 was chosen. The general data for the four systems is shown in Table 6-2 for comparison. As of 2017, none of the PWS systems listed in **Table 6-**2 employed a disinfection method other than chlorine. None of these systems used alkalinity/pH adjustment or orthophosphate addition.

Table 6-2

Studied PWSs

Facility	**TX PWS ID.**	**County**	**Water Source**	**Treatment**	**Depth, ft**	**Population served**	**Average daily consumption, MGD**	**Lead violation**
NOV	0900012	Gray, TX	Groundwater	Chlorine gas	730	100	0.016	Yes
City of McLean	0900002	Gray, TX	Groundwater	Chlorine gas	165	770	0.177	No
Cabot Corp.	0900022	Gray, TX	Groundwater	Chlorine gas	420	100	0.25	No
Smithfield Premium Genetics	0900044	Gray, TX	Groundwater	Chlorine gas	NA	50	0.084	No

Table 6-3 compares the average WQPs concentrations for the major potable WQ parameters. The average concentrations in the table are the arithmetic averages of the tap WQ mid-2016 to mid-2017 data found on the TCEQ Drinking Water Watch Web site.

Table 6-3

WQ Parameter Concentrations Comparison for PWSs in Table 6-2

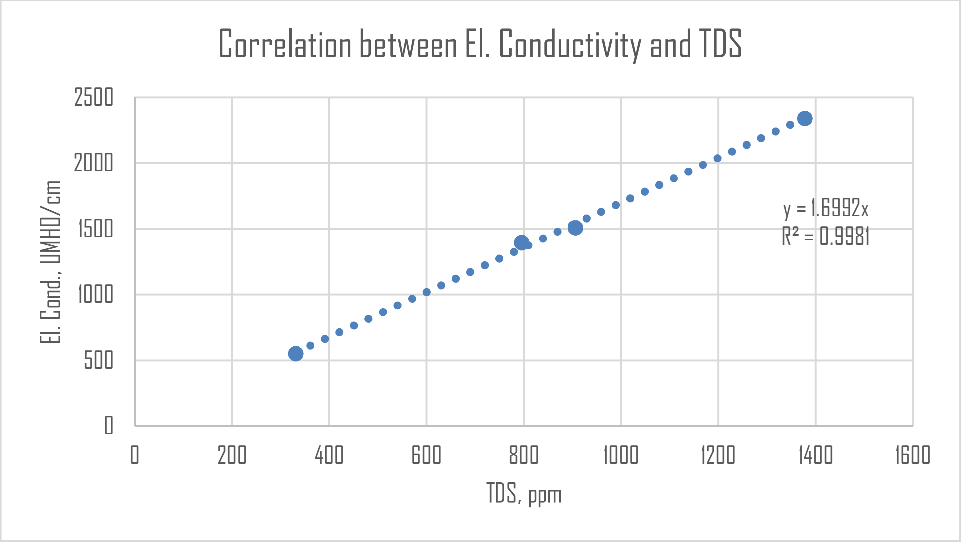
WQ Parameter (WQP)	**PWS Facility WQP concentration, ppm, unless noted otherwise**			
	0900012	**0900002**	**0900022**	**0900044**
Sulfate	154.6	68.4	360	200.5
Aluminum	0.0094	0.028	NA	0.007
Calcium $^{\text{as }Ca2+}$	76.7	73.6	144.4	83.1
Copper	0.056	0.027	0.043	0.04
Fluoride	0.89	0.337	0.785	0.697
Chloride	205.6	4.972	435.3	275.5
Magnesium	33.9	0.0875	57.7	38.8
Nitrogen oxides	1.66	4.972	1.25	1.44
Iron	0.062	0.0875	0.0684	0.33
Lead (1), ppb	*7*	*0.94*	*2*	*3.4*
Hardness$^{\text{as }CaCO3}$	321	227	789	400
Alkalinity$_{\text{Total}}^{\text{as }CaCO3}$	151	212	193	180
Manganese	0.0005	0.0009	0.0037	0.0022
Total dissolved solids	796	331	1378	906
El. conductivity$^{25\text{ DC}}$ UMHO/cm	1396	552	2340	1507.5
pH (2) S.U.	7.92	7.36	7.49	7.65
Sodium	136	22	259	163
TTHM, ppb	17.6	10.2	1.1	6.3

Notes: (1) Lead Action Level = 15 ppb; (2) Approximate values

6.3. DATA ANALYSIS

By examining **Table 6-**3, the reader will agree that all four systems have very similar tap WQ except for chlorides, and consequently, TDS and electrical conductivity. Electrical conductivity is a function of TDS which includes chlorides. **Figure 6-3** shows a 99.9% correlation between the average TDS and electrical conductivity values for the 4 PWSs when the intercept is set at (0,0). This shows that the systems raw WQ is practically identical. The Tap WQ varies due to small variations in chlorine injection rates, pipe and fittings material and age and, to a higher degree, system detention (stagnation) times. For this set of data, according to **Figure 6-3**, TDS equals conductivity divided by 1.7.

Figure 6-3
Correlation between El. Conductivity and TDS



Chlorides and TDS concentrations may vary depending on the chlorine gas feed rate. Sulfate concentrations for all 4 systems are around 200 ppm. Alkalinity, calcium hardness and pH are also in the same range for all four facilities as shown in

Table 6-4.

Table 6-4
Major WQPs

Fac.	Cl	SO_4	Cl/SO_4	Pb, ppb	ALK	pH	HARD	DIC
NOV	206	155	1.33	7	151	7.94	321	37
COM	20	68	0.29	0.94	212	7.36	227	54
CAB	435	360	1.21	2	193	7.49	789	48
SPG	276	201	1.37	3.4	180	7.65	400	45

The WQPs in

Table 6-4 were correlated against each other. The correlation coefficients are shown in **Table 6-**5.

Table 6-5

Correlation Coefficients for Major WQPs

	Cl	**SO_4**	**Cl/SO_4**	**Pb**	**ALK**	**HARD**	**DIC**	**pH**	**Cu**
Cl	1			0.106					
SO_4		1							
Cl/SO_4			1	0.655	-0.773				0.813
Pb	0.106		0.655	1	-0.986		-0.979	0.995	0.909
ALK			-0.773	-0.986	1	0.0067		-0.996	-0.945
HARD				-0.202	0.067	1			
DIC				-0.979			1		-0.958
pH				0.995	-0.996			1	0.915
Cu			0.813	0.909	-0.945		-0.958	0.915	1

A negative 98% and 96% correlation is observed between dissolved lead and copper and DIC, respectively. A positive 99.5% correlation exists between dissolved lead and pH. Surprisingly, a negative 99.6% correlation is shown between pH and ALK. A positive 65.5% correlation was calculated between dissolved lead and the Cl/SO_4 ratio. **Figure 6-4** and

Figure 6-5 present these correlations graphically. The correlation coefficients for dissolved copper followed the same trend as lead. It is important to note that copper was better correlated to the Cl/SO_4 ratio than did lead (81% vs 66%).

Figure 6-4
Dissolved Lead Concentration as Function of Alkalinity and DIC

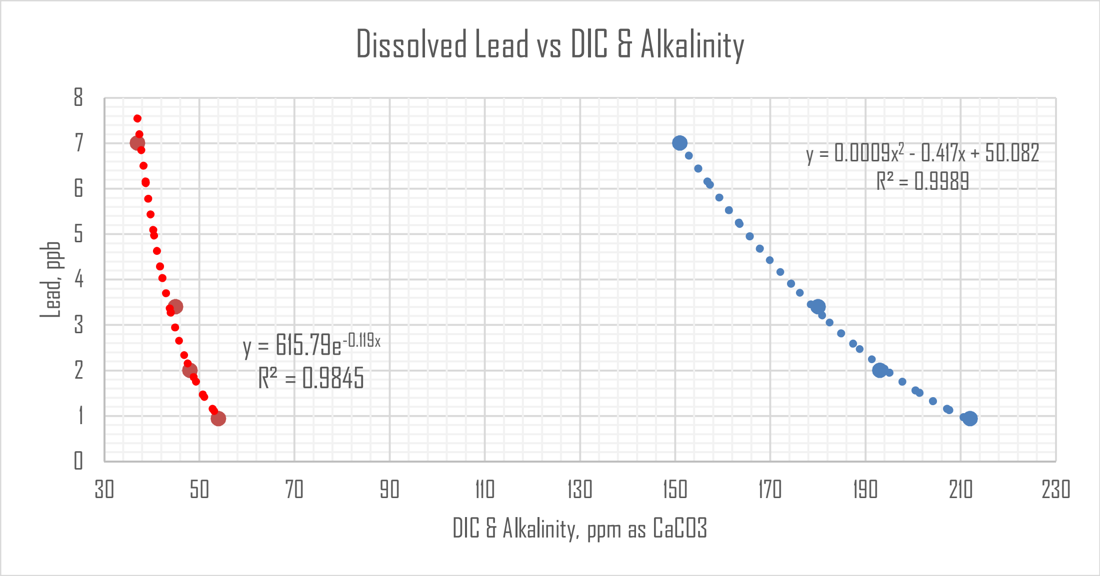
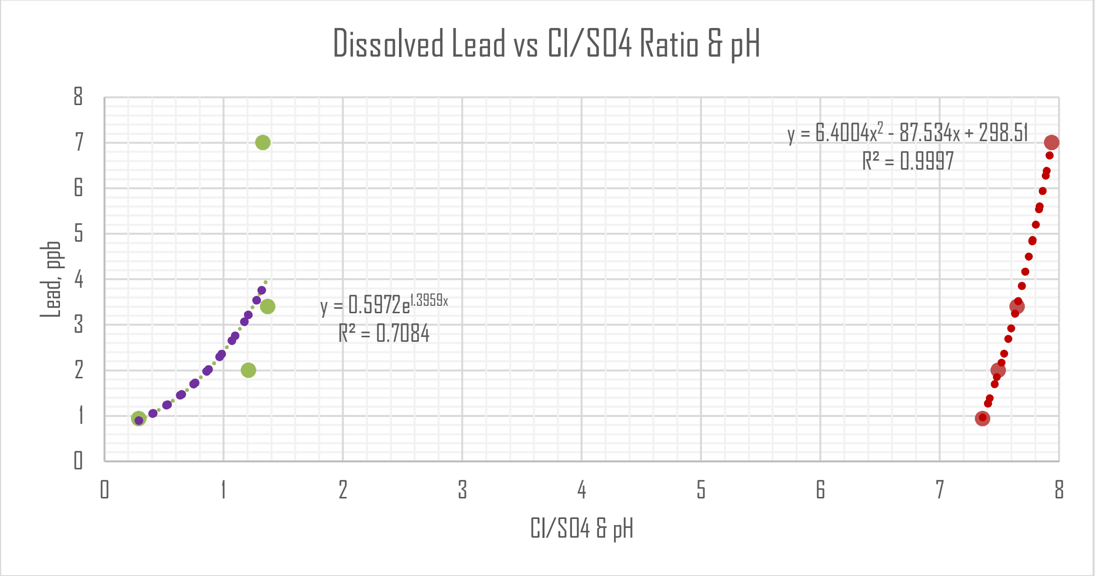


Figure 6-5
Dissolved Lead Concentration as Function of pH and Cl/SO_4 Ratio



Based on these relationships, the following limiting factors for these facilities not to exceed the 15 ppb (MCL = 15 ppb) action level for lead can be projected:

Alkalinity > 110 ppm
pH < 8.4
DIC > 31.2 ppm
Cl/SO_4 < 1.

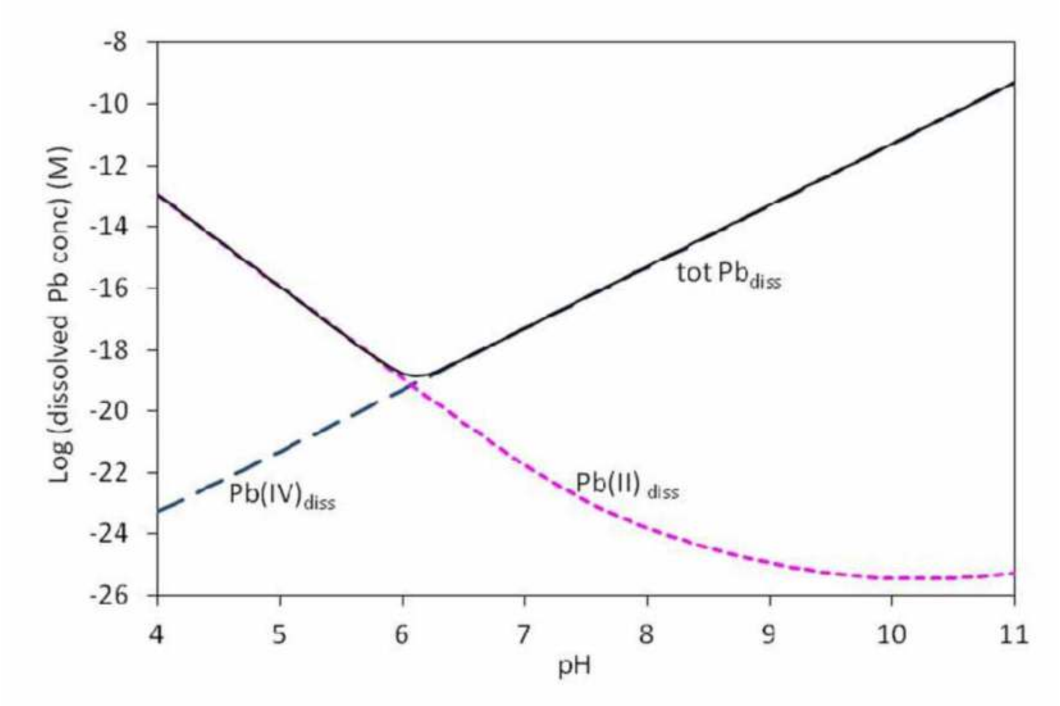
The limiting factors for copper (MCL = 1.3 ppm) can be defined in a similar manner. The finding that dissolved lead is inversely proportional to both the DIC and alkalinity is consistent with those found in Ref. 1 as the effect of increasing alkalinity is determined by the solubility of lead carbonate. The stability of these carbonate solids is determined by the activity of the carbonate ion, which is defined by both the DIC and pH. The presence of DIC accelerates the formation of PbO_2. The DIC concentrations fall within a typical range of DIC in drinking water of 0-50 ppm. In the presence of free chlorine, increased DIC results in higher rate of PbO dissolution and greater production of PbO_2.

Ref. 6 cites the optimal Cl/SO_4 ratio for lead control as less than 0.58. If this is true, then the only facility with no risk of plumbosolvency, i.e. lead release, would be 0900002 (**Table 6-**2). However, the other two facilities, 0900022 and 0900044 (CAB & SPG, Table 6-4), had never exceeded the lead action level (AL) of 15 ppb albeit their Cl/SO_4 ratios are above 1. Despite this disagreement, the finding of this report that dissolved lead would exceed action level after a certain threshold Cl/SO_4 ratio has been reached is consistent with the discussion in Ref. 6. For the 4 systems examined in this report, this threshold Cl/SO_4 ratio is above 1.0 due to similarity in source water quality and disinfection method.

The finding that dissolved lead increases with increasing pH may not appear to be consistent with the general notion that increased pH would always results in reduced dissolved lead. This result, however, is consistent with the data shown in **Figure 6-6**.

Figure 6-6

Dissolved Lead Concentration in the Presence of Free Chlorine and DIC



Based on Fig. 6-4, Pb(IV) species become dominant above pH6 and the total dissolved lead concentration increases with increasing pH despite a decrease in Pb(II) species. The half reaction can be presented as follows:

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

For the normal potable water pH range, the total dissolved lead can be found as a sum of lead carbonates, chloride, oxides and hydroxides. Lead concentrations in Fig. 6-4 are below AL.

7. CAUSES OF ELEVATED LEAD CONCENTRATION

Normally, the following factors and their combinations contribute to lead AL exceedance:

- Plumbing fixtures
- Pipe material/solder
- Well/source water
- Storage tank material
- pH
- pH variability
- Disinfectant feed rate variability
- Water use pattern which may result in stagnating conditions.

A low pH (6-7) and its variations (6-8) are, perhaps, the most common causes. A pH below 7 would generally result in decreased chlorine ORP (below 0.2 ppm) and, consequently, decreased germicidal capacity. Normally, there is at least 0.5 ppm of chlorine in the tap water. The loss of free chlorine in conduits can be defined as follows:

$$C_t = C_0 e^{-kt}$$

where C_t – chlorine concentration in distribution system at time t

C_0 – initial chlorine concentration in distribution system

k - chlorine decay coefficient, day^{-1}

t – time of water parcel to travel inside a conduit, days.

For $C_0 > 0.6$ ppm, $k = 0.6$ and $t \leq 0.008$ days (maximum system length of 3000 ft), the value of C_t is above 0.5 ppm.

8. ASSSEMENT OF CORROSION CONTROL TECHNOLOGIES

8.1. SCALING POTENTIAL DETERMINATION

Table 8-2 lists calculated Langelier Saturation and Ryznar Stability Indices (LSI & RSI). According to several state environmental protection agencies, LSI and RSI cannot be used to evaluate the degree of corrosion but can be used for scaling potential determination.

LSI ($\mathrm{LSI} = \mathrm{pH} - \mathrm{pH}_s$) uses the following classification:

$\mathrm{LSI} \approx 0$	The water is in equilibrium with calcite
$\mathrm{LSI} < -0.3$	The water tends to be corrosive
$\mathrm{LSI} > 0.3$	The water tends to be scale forming.

RSI ($\mathrm{RSI} = 2\mathrm{pH}_s - \mathrm{pH}$) uses the following classification:

$\mathrm{RSI} \ll 6$	The scale tendency increases as the index decreases
$\mathrm{RSI} \gg 7$	The calcium carbonate formation probably does not lead to a protective corrosion inhibitor film
$\mathrm{RSI} \gg 8$	Mild steel corrosion becomes an increasing problem.

pH and pH_s are the actual and saturation pH values.

Table 8-2
WQPs Used for Scaling and Corrosion Potential Determination

WQ Parameter	Temp. F°	TX PWS Facility Corrosion/Scaling Indices			
		0900012	0900002	0900022	0900044
Langelier Saturation Index (LSI)	60	+0.40	+0.07	+0.28	+0.23
	70	*+0.48*	*+0.15*	*+0.36*	*+0.31*
	80	+0.56	+0.23	+0.44	+0.39
Ryznar Stability Index (RSI)	70	*6.96*	*7.08*	*6.77*	*7.04*
Cl/SO_4 ratio		1.33	0.29	1.21	1.37
DIC $^{\text{as CaCO3}}$, ppm		37	54	48	45

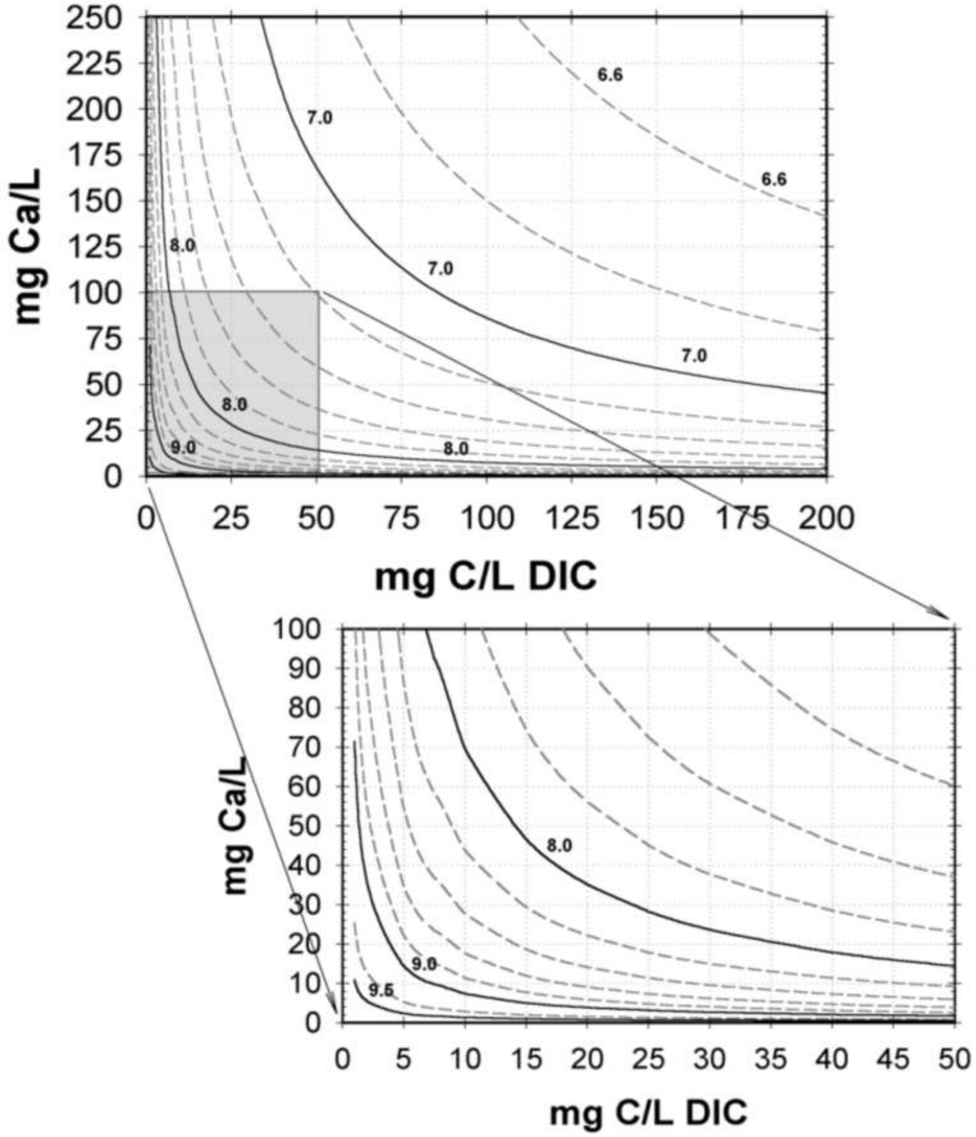
Based on the LSI values, all systems produce potable water that is not corrosive, nearly balanced and has some PbO_2 scale forming potential. Based on the RSI values, the tap water is only "slightly corrosive".

8.2. SATURATION pH DETERMINATION

The presence of calcium in the water may limit the system's ability to raise the pH due to scaling problems in the distribution system. Scaling can clog pipes, reduce carrying capacity, and cause the water to be cloudy. Before selecting possible treatments, USEPA recommends that systems and primacy agencies identify the saturation pH (pHs) for calcium carbonate for the system. Maintaining the pH below the saturation pH should help to minimize, although not eliminate, the potential for precipitating calcium carbonate.

The Saturation pH value determination is done based on the recommended EPA procedure found in Ref. 6. For concentrations of calcium and DIC as 77 ppm and 37 ppm, respectively, saturation pH is 7.42 as found from **Figure 8-7**.

Figure 8-7
Theoretical Saturation pH for $CaCO_3$ Precipitation (Ref. 6)



As an example, based on Fig. 7-1, the NOV $pH_s \leq 7.42$.

8.3. TREATMENT METHOD SELECTION

The treatment method for NOV as an example is chosen based on the USEPA lead corrosion manual (Ref. 6). The method is dependent on pH and DIC. **Table 8-3** lists saturation pH and DIC values for the 4 PWS facilities. These values were computed based on the procedures given in Ref.6.

In this report, the corrosion and scaling indices are presented as the ratio of the average actual PWS pH to the saturation pH (Table 7-2). It is then obvious that the water is well balanced if this ratio is equal 1.0. Likewise, it has scaling potential if this ratio is over 1.0 and tends to be corrosive if the ratio is less than 1.0. Out of the 4 facilities examined, the NOV system has the lowest corrosion potential but also has the highest scaling potential which is in good agreement with LSI and RSI (Table 7-1).

Treatment method in **Table 8-3** was selected based of the EPA selection procedure shown in

Figure 8-8 and **Figure 8-9**. For DIC over 25 ppm and pH below 7.8, the only treatment method option is orthophosphate (

Figure 8-8). For DIC above 5 ppm and pH above 7.8, caustic soda treatment is alternative to orthophosphate (**Figure 8-9**). These options are shown in **Table 8-3**.

Table 8-3
Treatment Options According to USEPA

WQ Parameter	TX PWS Facility Corrosion Potential and Scaling Indices			
	0900012	0900002	0900022	0900044
Saturation pH_S	7.42	7.57	7.09	7.32
Calcium, ppm	77	74	144	83
pH	7.92	7.36	7.49	7.65
DIC $^{\text{as CaCO3}}$, ppm	37	54	48	45
pH/pH_S	1.07	0.97	1.06	1.05
Treatment Method	Orthophosphate or caustic soda	Orthophosphate	Orthophosphate	Orthophosphate

Figure 8-8
Selecting Lead Treatment for pH from 7.2 to 7.8

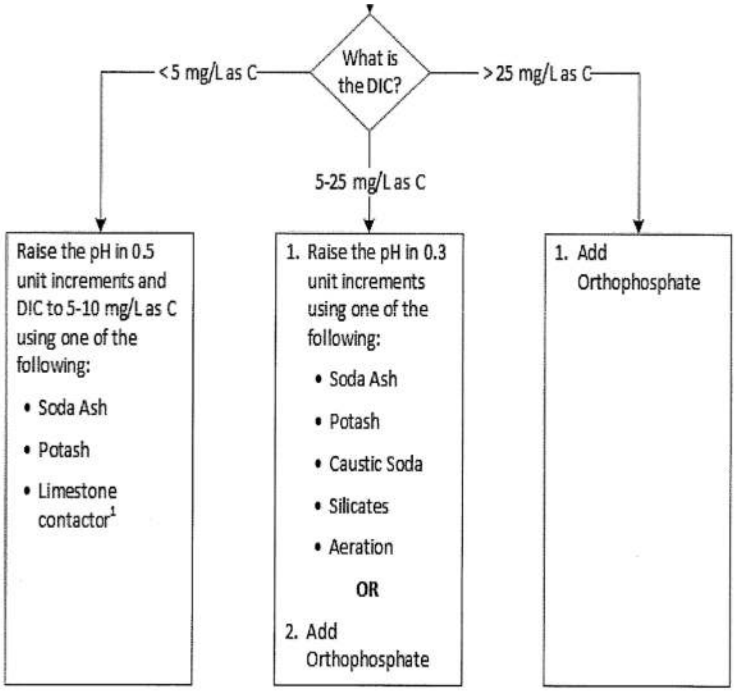
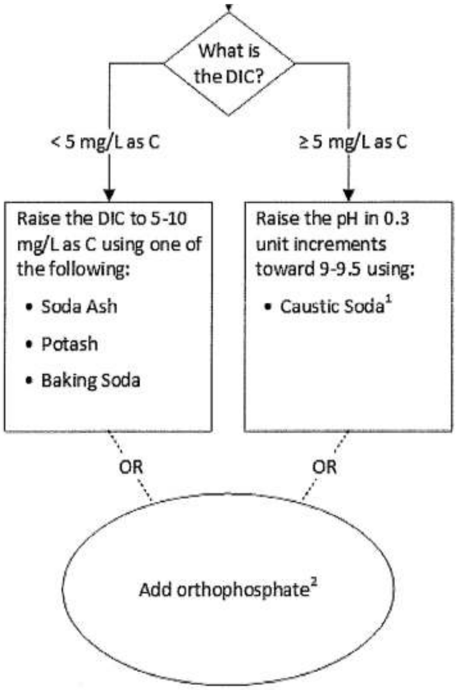


Figure 8-9
Selecting Lead Treatment for pH from 7.8 to 9.5



Caustic soda (NaOH) and caustic potash (KOH) raise pH. Since the system pH should be kept below 7.4 theoretical saturation pH (and above 7) in the case of NOV, caustic soda addition as a treatment method for NOV should be avoided despite that gaseous chlorine lowers the pH. Soda ash (sodium carbonate) could be a better choice as it results in moderate pH increase if it was allowed by USEPA. Orthophosphate, therefore, is the only treatment method to satisfy all of the conditions and limitations discussed in this report. Application of the phosphate-based lead inhibitors including orthophosphate are described in more detail in the following section.

9. PHOSPHATE-BASED LEAD INHIBITORS

Phosphate-based corrosion inhibitors have been widely used to control lead release.

Phosphate-based corrosion inhibitors are chemicals that have orthophosphate in their formulation. Orthophosphate reacts with lead (II) to form compounds that have a strong tendency to stay in solid form and not dissolve into water. The extent to which orthophosphate can control lead release depends on the orthophosphate concentration, pH, DIC, and the characteristics of the existing corrosion scale (e.g., whether it contains other metals such as iron or aluminum).

Orthophosphate is available as phosphoric acid, in salt form (potassium or sodium), and as zinc orthophosphate. Phosphoric acid (H_3PO_4) is a common form that is available in concentrations between 36 and 85 percent. Because it is an acid, it requires special handling and feed facilities. Zinc orthophosphate inhibitors typically have zinc: phosphate weight ratios between 1:1 and 1:10. Recent research found that zinc orthophosphate did not provide additional lead control compared to orthophosphate (Ref. 6). The zinc did, however, provide better corrosion protection for cement at low alkalinity/hardness/pH conditions. Blended phosphates are a mix of orthophosphate and polyphosphate, with the orthophosphate fraction ranging from 0.05 to 0.7. It is possible that blends can provide both sequestration of metals and reduce metals release (Ref. 5). It is important to note that blended phosphates may not function as corrosion inhibitors strictly on the basis of concentration and relative amount of orthophosphate.

The effectiveness of orthophosphate treatment depends on many factors, including phosphate dose, pH, DIC, and other constituents in the water (e.g., iron, manganese). Polyphosphates alone should not be used to treat for lead and copper; they are mainly used to sequester iron and manganese. Conventional practice is that orthophosphate treatment for controlling lead should target residual concentrations of 0.33 to 1.0 mg/L as P (1.0 to 3.0 mg/L as PO_4) at the tap when pH is within the range of 7.2 to 7.8. Higher orthophosphate doses (1.0-1.2 mg/L as P, or 3-3.5 mg/L PO_4) may be required to control lead release at higher pH. Whilst the pH range of 7.2 to 7.8 is still considered optimal, systems should not automatically reduce the pH of their water if it is 8 or higher when starting orthophosphate treatment. Orthophosphate may be effective at pH as high as 9. Laboratory results suggest albeit that less effective control of lead release occurs between pH 8 and 8.5 than either above or below that range. Systems should therefore avoid operating between pH 8 and 8.5, if possible, to control for lead release. In general, orthophosphate is more effective at low DIC (<10 mg C/L). Also, the pH is less important for lead control in low DIC waters.

The target orthophosphate concentration is the level needed to control corrosion in premise plumbing. Because orthophosphate will react with metals and other compounds, the concentration leaving the treatment plant may need to be higher to achieve the target concentration at the tap. During start-up, systems should be prepared to adjust the dose at the treatment plant to meet the target dose at the tap throughout the distribution system. See Ref. 6 for additional recommendations on start-up of orthophosphate treatment.

Some systems have started orthophosphate treatment using a higher passivation dose, followed by a lower maintenance dose for long-term treatment. Ref. 6 recommends that the passivation dose be 2 to 3 times higher than the target maintenance dose in order to build up a protective film as quickly as possible. The amount of time needed for the initial passivation dose to form adequate scale is unknown and will vary depending on the system's specific water quality. Also, the maintenance dosage may initially need to be higher to convert the existing scales on lead surfaces. Lead levels may continue to decline for years after an optimal orthophosphate dose has been applied, due to the slow rate of scale formation. As such, the facility should evaluate whether the orthophosphate dose is enough to passivate in a timely manner. Routine maintenance or repairs such as water main replacements, meter installations, service line and shut-off valve replacements, and leak repairs may disrupt scales and result in high lead levels. In addition, when establishing a maintenance dosage, it is important to consider other factors such as facilities with chronically low water use. Ongoing diagnostic monitoring at these sites before and after treatment installation or adjustment can provide useful information for establishing a proper maintenance dose.

Blended phosphates have been used for corrosion control and to sequester iron and manganese. Blended phosphates have been shown to be effective for reducing lead levels; however, the lead corrosion scale may not be as robust as the scale created by orthophosphate and, thus, may be more susceptible to physical disturbances and low water use conditions (Ref. 6). The effectiveness of blended phosphates cannot be based on the orthophosphate concentration in the blend for the following reasons:

- Blended phosphates control corrosion by creating a barrier film from the interaction of calcium and magnesium in the bulk water with phosphorus containing compounds. If the polyphosphate portion of the blend has a high affinity for sequestering lead, it may counteract the benefit of the orthophosphate portion in forming solid lead compounds.

- The percent of orthophosphate in the blend can vary widely (from 5 to 70 percent). Blended phosphate should contain a minimum orthophosphate concentration of 0.5 mg/L as P (1.5 mg/L as PO4) as a starting point for evaluation. The orthophosphate ratio in the blend and/or the dose may need to be increased to provide adequate lead control. In some cases, however, simply adding more blended phosphate may not be effective because, if there is excess polyphosphate available beyond what is bound up with other constituents in the water, it can sequester the lead. EPA recommends a demonstration study, additional monitoring, or both for systems that recommend blended phosphates to control lead release.

10. CONCLUSIONS AND RECOMMENDATIONS FOR NOV

The author examined all publicly available in 2017 WQ data covering a 1-year period for 4 potable water treatment facilities located in Grey County, Texas and came to the following conclusions and recommendations:

- Two potable water distribution system were installed in 1920-ths and probably had lead components in their pipe and plumbing fixtures. It is suggested that since then parts of the systems have been replaced with parts the material of which does not necessarily contain lead.

- The facilities data does not show appreciable quantities of NOM, ammonia and nitrate/nitrite to suspect anaerobic processes on pipe or plumbing fixtures internals leading to acidic conditions leading to Pb & Cu release or free chlorine consumption.

- Based on the tap water quality data, the average concentrations of manganese and iron are less than 0.05 ppm and 0.3 ppm, respectively, resulting in minimal deposition.

- Based on the tap water quality data, NOV pH varied from 7.6 to 8.26.

- Based on TCEQ records, the average system pH, alkalinity, DIC and lead concentrations were around 7.9, 151, 37 and 7 ppb, respectively, which, in general, indicates a non-corrosion prone PWS.

- Based on Langelier Saturation Index (LSI), the system water is a chemically well-balanced system with a slight scaling rather than corrosion tendency, if the breakpoint is 0.3.

- Based on Ryznar Stability Index (RSI), the system water is around 7 which is an indicative of a well-balanced system with a slight scale forming potential, if the breakpoint is 6.5.

- Based on the ratio of the annual average system's pH to the saturation pH (pH_a/pH_s) of around 1.07, the system shows a slight scaling potential. Ratios of less than 1 is an indicative of corrosion and 1.0 is the breakpoint.

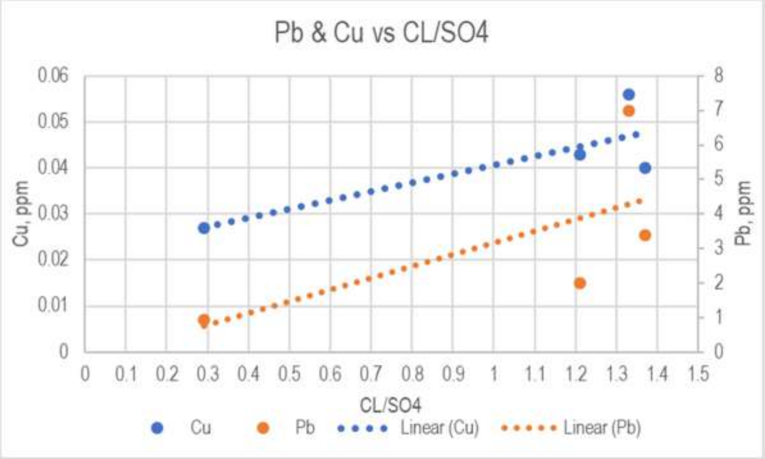
- The average hardness above 150 ppm indicates calcium deposition and contribution to scale formation. There was no evidence supporting a notion that increased calcium deposition may increase lead dissolution.

- For old plumbing systems, occasional Pb & Cu AL exceedances due to the building water usage patterns rather than minor pH fluctuations is a well documented fact. Long water stagnation times (over 4-10 days) result in lack of free chlorine normally delivered with flow. Consequently, a reduction of ORP leading to Pb & Cu dissociation from PbO_2 pipe and fixture scales occurs.

- NOV system must maintain alkalinity and DIC above 110 ppm and 31.2 ppm, respectively, to avoid AL exceedance. Online alkalinity analyzers are available now and can be installed to maintain alkalinity levels.

- The ideal system pH operating range is 7.0-7.4 for NOV.

- The lead release threshold Cl/SO_4 ratio for all four systems was found to be 1.0 vs 0.58 cited in Ref. 6. As such, this ratio may not be an exact indicative of lead corrosion potential albeit the ratio needs to be maintained as low as practical. Chloride is part of TDS the average NOV concentration for which is around 800 ppm whilst the secondary MCL is 500 ppm. For comparison, the average TDS for TX0900002 is 331 ppm. Lead (Pb) and copper (Cu) as a function of Cl/SO_4 followed the same trend as shown in the figure below.



- The applicability of lead corrosion control methods provided in Ref. 6 was examined. For the average NOV's pH and DIC (indicative of alkalinity), Ref. 6 guides to only two options which are caustic soda and orthophosphate. Since caustic soda increases pH, the only treatment option for NOV is, therefore, orthophosphate. Increasing pH prior to chlorine contact chamber, in general, reduces disinfection performance and requires an increase in chlorine dose or contact time to meet the USEPA's minimum contact time (CT) value. Part 8 discusses orthophosphate application in detail including recommended feed rates. Those may vary from 0.3 ppm to 3 ppm depending on the system's most remote fixture WQ.

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