

Appendix A

Corrosion Indices for the Precipitation of Protective Coatings

Many corrosion control programs for water utilities have targeted the protection of metal pipes through precipitation of calcium carbonate (CaCO_3). This process depends on the equilibrium reactions involving the calcium ion (Ca^{2+}), hydrogen ion (H^+), hydroxide-ion (OH^-), carbonic acid (H_2CO_3^*), carbon dioxide (CO_2), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). The objective of the process is to produce a finished water which will evenly precipitate calcium carbonate on the pipe walls within the distribution system. This means that the finished water should be supersaturated with respect to calcium carbonate to the extent that precipitation occurs.

A multitude of corrosion indices have been developed over the years to describe the precipitation of calcium carbonate. The recommended index is the Calcium Carbonate Precipitation Potential (CCPP) for use in evaluating the water quality goals necessary to successfully provide corrosion control protection through the formation of calcium carbonate films. The Langelier Saturation Index (LI) may also be used by PWSs due to its long history of application and the ability of some systems to develop reliable relationships between LI and corrosion control protection. Other corrosion indices are not recommended for determining

water quality goals generating calcium carbonate precipitation in distribution and home plumbing systems.

Calcium Carbonate Precipitation Potential.

The term calcium carbonate precipitation potential (CCPP) refers to the theoretical quantity of calcium carbonate that can be precipitated from waters that are super-saturated. A treated water CCPP of 4-10 mg/l (as CaCO_3) is typically required to promote formation of protective calcium carbonate deposits. For large systems, higher CCPPs may be required to ensure maintenance of calcium carbonate deposits throughout the distribution system.

CCPP has also been shown to relate directly to reaction kinetics as found by Nancollas and Reddy (1976) and presented by Rossum and Merrill (1983):

$$d[\text{Ca}^{2+}]/dt = -10^{-5} KS(\text{CCPP})^2$$

where K is the rate constant for crystalline growth and S is the surface area available for precipitation of a given particle size. When applying corrosion indices as a surrogate measure of corrosion control performance, it is important that the application be supported by additional information, such as distribution system monitoring, in-situ coupon testing, bench-scale corrosion testing, and inspection of pipe materials removed from the distribution system during maintenance and repair.

Determining the Calcium Carbonate Precipitation Potential

CCPP can be determined graphically through use of Caldwell-Lawrence diagrams, analytically through equilibrium equations, or by computer analysis.

$$\text{CCPP} = 50,000 * ([\text{Alk}]_i - [\text{Alk}]_{\text{eq}})$$

Theoretical basis for determining the amount of CaCO_3 precipitated or dissolved by waters depending on their saturation condition as presented by Merrill and Sanks (1977a, 1977b, 1978).

CCPP = 0: CaCO_3 saturated solution.

CCPP > 0: CaCO_3 supersaturated solution, and the CCPP value denotes the milligrams per liter of CaCO_3 which will be precipitated.

CCPP < 0: CaCO_3 undersaturated solution, and the CCPP value denotes the milligrams per liter of CaCO_3 needed to be dissolved into solution to bring to saturation.

Rule of Thumb Goal: 4-10 mg/L CaCO_3

CCPP Calculation Procedures:

A. Definition of Terms and Values of Constants

$[\text{Alk}]_i$ Measured value of alkalinity in the finished water,

representing the alkalinity of solution prior to precipitation of calcium carbonate.

$[\text{Alk}]_{\text{eq}}$ Equilibrium alkalinity resulting after precipitation of the calcium carbonate content beyond saturation. Calculation of this term requires an iterative solution for the hydrogen ion concentration at equilibrium. Once this is done, $[\text{Alk}]_{\text{eq}}$ can be calculated as follows:

$$[\text{Alk}]_{\text{eq}} = t_{\text{eq}}/p_{\text{eq}} * (\text{Acy}_i - s_{\text{eq}}) - s_{\text{eq}}$$

$$\text{where } t_{\text{eq}} = (2K_2' + [\text{H}^+]_{\text{eq}})/[\text{H}^+]_{\text{eq}}$$

$$p_{\text{eq}} = (2[\text{H}^+]_{\text{eq}} + K_1')/K_1'$$

$$s_{\text{eq}} = [\text{H}^+]_{\text{eq}} - K_w'/[\text{H}^+]_{\text{eq}}$$

and,

K_H = Henry's law constant for CO_2

K_w = dissociation constant for water

K_1' = first dissociation constant of carbonic acid.

K_2' = second dissociation constant of carbonic acid

$[\text{Acy}]_i$ = Acidity of the finished water.

$$= C_T * (a_1 + 2 * a_2) + [\text{H}^+] - [\text{OH}^-]$$

$$a_1 = ([\text{H}^+]/K_1' + 1 + K_2'/[\text{H}^+])^{-1}$$

$$a_2 = (1 + K_1'/[\text{H}^+] + K_1' * K_2'/[\text{H}^+])^{-1}$$

The equilibrium constants used in the above equations are given in Table A-1 for various temperature conditions.

Table A-1. Equilibrium Constants for Carbonate-Water System

Temp °C	pKsp ¹	pK _w	pK _H	pK ₁ '	pK ₂ '
0	8.03	14.93	1.11	6.579	10.625
5	8.09	14.73	1.19	6.517	10.557
10	8.15	14.53	1.27	6.464	10.490
15	8.21	14.35	1.32	6.419	10.430
20	8.27	14.17	1.41	6.381	10.377
25	8.33	14.00	1.47	6.352	10.329
30	8.38	13.83	1.53	6.327	10.290

¹ Derived from equation, $pK_{sp} = 0.01183 \cdot (\text{Temp}) + 8.03$, Larson and Boswell, 1942.

B. Algorithm for Iterative Solution

The CCPP represents in mg/L as CaCO₃ the saturation state of calcium carbonate with respect to existing conditions (Alk_i) and the equilibrium conditions which would exist after the water's potential to precipitate or dissolve calcium carbonate had occurred (Alk_{eq}). During this process, the equivalents of calcium precipitated (or dissolved) must be equal to the equivalents of alkalinity precipitated (or dissolved). However, the acidity of the water remains constant and therefore can be used to determine the equilibrium alkalinity conditions as described below.

$$Acy_i = Acy_{eq} = [(Alk_i + s_i)/t_i] \cdot p_i + s_i$$

where s_i, t_i, and p_i are defined as follows:

$$s_i = [H^+] - K_w/[H^+]$$

$$t_i = (2 \cdot K_2' + [H^+])/[H^+]$$

$$p_i = (2 \cdot [H^+] + K_1')/K_1'$$

Since acidity remains conservative through the precipitation/dissolution of calcium carbonate, the actual acidity of the water (Acy_i) may be used to define the

equilibrium alkalinity (Alk_{eq}) as shown below:

$$Alk_{eq} = t_{eq}/p_{eq} \cdot (Acy_i - s_{eq}) - s_{eq}$$

The equilibrium alkalinity condition may also be related to the initial calcium and alkalinity through the following equation:

$$2 \cdot [Ca^{2+}]_i - Alk_i = 2 \cdot K_{sp}' \cdot r_{eq} / (Alk_{eq} + s_{eq}) - Alk_{eq}$$

$$\text{with } r_{eq} = ([H^+]_{eq} + 2 \cdot K_2')/K_2'$$

Substituting $Alk_{eq} = f(Acy_i)$ into the above equation yields the relationship below:

$$2 \cdot [Ca^{2+}]_i - Alk_i = [(2 \cdot K_{sp}' \cdot r_{eq} \cdot p_{eq}) / (t_{eq} \cdot (Acy_i - s_{eq}))] - [t_{eq} \cdot (Acy_i - s_{eq}) / p_{eq}] + s_{eq}$$

If we let TERM0 equal the left side of the above equation, and TERM1 and TERM2 equal the first two terms on the right side of the above equation, then this reduces to:

$$TERM0 = TERM1 - TERM2 + s_{eq}$$

To solve for the equilibrium terms, H_{eq} is assigned a value initially. The above equation is tested to determine whether the

assigned value satisfies the conditions (i.e., does $TERM0 = TERM1 - TERM2 + s_{ca}$?). If not, then iterate the process by assigning a new value for H_{ca} until an adequate degree of accuracy is reached. In the following examples, this method of solving for CCPP was used with a tolerance of 0.001 for the above equation.

Spreadsheet formats are provided to assist in the design and development of a CCPP calculation tool.

C. Finding the CCPP Value for a Specific Water Quality Condition

A PWS performing lime softening has a finished water with the following characteristics: pH = 8.6; alkalinity = 90 mg/L as $CaCO_3$; and calcium hardness = 100 mg/L as $CaCO_3$. The worksheet presented on the following page (Exhibit A-1) calculates the CCPP (6.6 mg/L as $CaCO_3$) for this supply using the iterative solution discussed above.

D. Finding the Water Quality Conditions for a Desired CCPP.

To achieve a desired CCPP, any one or more of the three key water quality parameters may be modified. Exhibits A-2 and A-3 demonstrate this by modifying pH and alkalinity, respectively, to achieve a desired CCPP of 8.0 mg/L as $CaCO_3$ for the same water described above (Part B). When pH and calcium held constant, the required alkalinity is 101.8 mg/L as $CaCO_3$ for the targeted CCPP; with alkalinity and calcium contents are held constant, the resultant pH of 8.8 is required to achieve the desired CCPP.

Langelier Saturation Index. A commonly used measure of a water's

ability to deposit calcium carbonate is Langelier's Saturation Index (LI). This value is determined by subtracting the pH of saturation (known as pH_s , and dependent upon the calcium ion concentration, alkalinity, temperature, and dissolved solids concentration of the water) from the actual pH (pH_a).

A negative LI value indicates under-saturation and a tendency for the water to dissolve calcium carbonate. A positive value indicates supersaturation and a tendency for the water to deposit calcium carbonate. A value of zero indicates that the water is in chemical balance with respect to calcium carbonate.

While the LI is widely used, it has several notable shortcomings. Due to its qualitative nature, it indicates only the tendency or direction of calcium carbonate precipitation. It cannot predict the actual precipitation potential, or the amount of excess calcium carbonate available for precipitation.

For example, it has often been found that although a positive LI was maintained, severe corrosion had occurred in the distribution system, and inspections of pipe and fittings revealed no evidence of a coating of calcium carbonate. In other situations, however, PWSs have had limited corrosion problems with slightly negative LIs. In these instances, the amount of alkalinity may have been sufficient for carbonate passivation to reduce corrosion activity. In practice, the appropriate LI for a given system is highly site-specific, and is dependent upon treated water composition and distribution system size and complexity.

Langelier Index (LI) = pH - pH_s

**Developed by W.F. Langelier
(1936)**

LI = 0: CaCO₃ saturation

LI > 0: CaCO₃ supersaturation

LI < 0: CaCO₃ undersaturation

Rule of Thumb Goal: +0.8 - +1.0

Calculation Procedure

A. Definition of Terms

pH_s Saturation pH for calcium carbonate calculated as follows:

$$\text{pH}_s = -\log_{10} [\text{H}^+] - \log_{10} f_m$$
$$[\text{H}^+] = (-B \pm \sqrt{B^2 - 4AC})/2A$$

where:

$$A = 1 - [\text{Ca}^{2+}]K_2'/K_1'$$

$$B = K_2'(2 - [\text{Ca}^{2+}][\text{Alk}]/K_1')$$

$$C = K_1'K_2'[\text{Ca}_2]/K_1'$$

and,

K_w' = Dissociation constant for water

K_s' = Solubility product constant for calcium carbonate.

K₂' = Second dissociation constant for carbonic acid.

f_m = activity coefficient for the monovalent ions. This term is normally neglected in calculating LI.

Conversion Between Total Alkalinity and Dissolved Inorganic Carbonate. To more easily utilize the solubility contour diagrams presented in Chapter 2.0 of this volume, Table A-2 provides a conversion chart for total alkalinity (Talk) and dissolved inorganic carbonate (DIC) by water temperature and pH. To use Table A-2, a PWS with a known Talk (expressed as mg CaCO₃/L), pH, and water temperature, find the factors A and B corresponding to their conditions. The

equivalent DIC level for that water supply can be calculated as follows:

$$\text{DIC (mg CaCO}_3\text{/L)} = [(\text{Talk}/50,000) + A] \cdot B$$

The resulting DIC can be used in finding the lead or copper solubility for the defined condition per Figures 2-2, 2-3, and 2-5 in this volume.

References

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- Schock, M.R. 1990. Internal Corrosion and Deposition Control. *Water Quality and Treatment*, 4th Ed. AWWA (Denver, Colorado 80235).

Exhibit A-2. CCCP Calculation Procedures

Example 2 – Spreadsheet for Calculating Alkalinity for Given CCCP

NO	Variable	Definition	Comments	Input	Output
Determine Alkalinity (Based on information from Example 1)			Given: CCCP=8 mg/l pH=8.6 Cal=100 mg/l as CaCO3 Temp=20 C		
1	Alki = Alkalinity, equiv/l	(1) (2)	vary	2.0E-03	
2	Ca = Calcium, moles/l	(1)	given	1.0E-03	
3	Hi = Hydrogen Ion, moles/l	(1)	given	2.5E-09	
4	K'sp = Solubility Constant, CaCO3		Table 2	5.4E-09	
5	K'w = Dissociation Constant for Water		Table 2	6.8E-15	
6	K'1 = 1st Carbonic Dissociation Constant		Table 2	4.2E-07	
7	K'2 = 2nd Carbonic Dissociation Constant		Table 2	4.2E-11	
8	Req = (Heq - 2*K'2)/K'2		calculated		3.3E+02
9	Peq = (2*Heq + K'1)/K'1		calculated		1.1E+00
10	Teq = (2*K'2 + Heq)/Heq		calculated		1.0E+00
11	Seq = Heq - K'w/Heq		calculated		-4.7E-07
12	Pi = (2*Hi + K'1)/K'1		calculated		1.0E+00
13	Si = Hi - K'w/Hi		calculated		-2.7E-06
14	Ti = (2*K'2 + Hi)/Hi		calculated		1.0E+00
15	Acyi = ((Alki + Si)/Ti)*Pi + Si		calculated		2.0E-03
16	Term1 = 2*K'sp*Req*Peq/T/(Acyi - Seq)		calculated		1.8E-03
17	Term2 = (Acyi - Seq)*Teq/Peq		calculated		1.9E-03
18	Alkeq = Teq/Peq*(Acyi-Seq) - Seq, mg/l(4)		calculated		93.7
19	Heq = Equilibrium H, moles/l	(3)	iterate	1.4E-08	
20	Term0 = 2*Ca - Alki		calculated		-3.5E-05
21	Right = Term1 - Term2 + Seq		calculated		-3.5E-05
22	CCCP = Alk - Alki, mg/l		calculated		8.0
23	Alki = Alkalinity, mg/l as CaCO3	(4)	calculated		101.8

- (1) Convert given information into proper units of moles/l and equiv/l.
- (2) Enter in values for alkalinity (moles/l) and then iterate Heq as in Example 1. Continue this process until CCCP converges to the targeted goal value (8 mg/l for Example 2).
- (3) Iteration can be accomplished by several procedures. Manual iteration requires the user to input various values of Heq until rows 20 and 21 converge. Another option in spreadsheets such as Lotus 123 and Microsoft Excel, allow cells to be "dependant" on one another. In this case rows 20 and 21 could be equated and the recalculate key used to iterate. Macros could also be written that would iterate using a loop command.
- (4) Covert to mg/l by multiplying by 50,000.

Exhibit A-3. CCCP Calculation Procedures

Example 3 – Spreadsheet for Calculating pH for Given CCCP

NO	Variable	Definition	Comments	Input	Output
Determine pH (Based on information from Example 1)					
			Given: CCCP=8 mg/l		
			Alk=90 mg/l as CaCO ₃		
			Cal=100 mg/l as CaCO ₃		
			Temp=20 C		
1	Hi	Hydrogen Ion, moles/l	(1) (2) vary	1.8E-09	
2	Ca	Calcium, moles/l	(1) given	1.0E-03	
3	Alki	Alkalinity, equiv/l	(1) given	1.8E-03	
4	K'sp	Solubility Constant, CaCO ₃	Table 2	5.4E-09	
5	K'w	Dissociation Constant for Water	Table 2	6.8E-15	
6	K'1	1st Carbonic Dissociation Constant	Table 2	4.2E-07	
7	K'2	2nd Carbonic Dissociation Constant	Table 2	4.2E-11	
8	Req	$(\text{Heq} - 2 \cdot \text{K}'2) / \text{K}'2$	calculated		2.9E+02
9	Peq	$(2 \cdot \text{Heq} + \text{K}'1) / \text{K}'1$	calculated		1.1E+00
10	Teq	$(2 \cdot \text{K}'2 + \text{Heq}) / \text{Heq}$	calculated		1.0E+00
11	Seq	$\text{Heq} - \text{K}'w / \text{Heq}$	calculated		-5.3E-07
12	Pi	$(2 \cdot \text{Hi} + \text{K}'1) / \text{K}'1$	calculated		1.0E+00
13	Si	$\text{Hi} - \text{K}'w / \text{Hi}$	calculated		-3.8E-06
14	Ti	$(2 \cdot \text{K}'2 + \text{Hi}) / \text{Hi}$	calculated		1.0E+00
15	Acyi	$((\text{Alki} + \text{Si}) / \text{Ti}) \cdot \text{Pi} + \text{Si}$	calculated		1.7E-03
16	Alkeq	$\text{Teq} / \text{Peq} \cdot (\text{Acyi} - \text{Seq}) - \text{Seq}$, mg/l(4)	calculated		82.0
17	Term1	$2 \cdot \text{K}'sp \cdot \text{Req} \cdot \text{Peq} / \text{Ti} / (\text{Acyi} - \text{Seq})$	calculated		1.8E-03
18	Term2	$(\text{Acyi} - \text{Seq}) \cdot \text{Teq} / \text{Peq}$	calculated		1.6E-03
19	Heq	Equilibrium H, moles/l	(3) iterate	1.2E-08	
20	Term0	$2 \cdot \text{Ca} - \text{Alki}$	calculated		2.0E-04
21	Right	$\text{Term1} - \text{Term2} + \text{Seq}$	calculated		2.0E-04
22	CCCP	$\text{Alki} - \text{Alkeq}$, mg/l	(4) calculated		8.0
23	pH	$\text{pHi} = -\log \text{Hi}$	calculated		8.8

- (1) Convert given information into proper units of moles/l and equiv/l.
- (2) Enter in values for Hi (moles/l) and then iterate Heq as in Example 1. Continue this process until CCCP converges to the targeted goal value (8 mg/l for Example 3).
- (3) Iteration can be accomplished by several procedures. Manual iteration requires the user to input various values of Heq until rows 20 and 21 converge. Another option in spreadsheets such as Lotus 123 and Microsoft Excel, allow cells to be "dependant" on one another. In this case rows 20 and 21 could be equated and the recalculate key used to iterate. Macros could also be written that would iterate using a loop command.
- (4) Covert to mg/l by multiplying by 50,000.

Table A-2

Total Alkalinity (TALK) to Dissolved Inorganic Carbonate (DIC) Conversion Variables

Determine A & B via the below table. Then compute DIC as follows:

$$\text{DIC as ppm CaCO}_3 = [(\text{TALK in ppm CaCO}_3/50,000) + A] \cdot B$$

pH	T=0 (deg. C)		T=5 (deg. C)		T=10 (deg. C)		T=15 (deg. C)		T=20 (deg. C)		T=25 (deg. C)	
	A	B	A	B	A	B	A	B	A	B	A	B
6.0	9.99E-07	2.40E+05	9.98E-07	2.14E+05	9.97E-07	1.96E+05	9.96E-07	1.81E+05	9.93E-07	1.70E+05	9.90E-07	1.62E+05
6.1	7.93E-07	2.01E+05	7.92E-07	1.81E+05	7.91E-07	1.66E+05	7.89E-07	1.54E+05	7.86E-07	1.45E+05	7.82E-07	1.39E+05
6.2	6.29E-07	1.70E+05	6.28E-07	1.54E+05	6.26E-07	1.42E+05	6.24E-07	1.33E+05	6.20E-07	1.26E+05	6.15E-07	1.21E+05
6.3	4.99E-07	1.45E+05	4.97E-07	1.32E+05	4.95E-07	1.23E+05	4.92E-07	1.16E+05	4.88E-07	1.10E+05	4.81E-07	1.06E+05
6.4	3.95E-07	1.25E+05	3.93E-07	1.15E+05	3.91E-07	1.08E+05	3.87E-07	1.02E+05	3.81E-07	9.78E+04	3.73E-07	9.48E+04
6.5	3.13E-07	1.10E+05	3.10E-07	1.02E+05	3.07E-07	9.60E+04	3.02E-07	9.15E+04	2.95E-07	8.80E+04	2.85E-07	8.55E+04
6.6	2.47E-07	9.76E+04	2.44E-07	9.13E+04	2.39E-07	8.65E+04	2.33E-07	8.29E+04	2.24E-07	8.02E+04	2.11E-07	7.82E+04
6.7	1.94E-07	8.78E+04	1.90E-07	8.28E+04	1.85E-07	7.90E+04	1.77E-07	7.62E+04	1.66E-07	7.40E+04	1.49E-07	7.24E+04
6.8	1.51E-07	8.00E+04	1.47E-07	7.60E+04	1.40E-07	7.30E+04	1.30E-07	7.08E+04	1.16E-07	6.90E+04	9.54E-08	6.78E+04
6.9	1.17E-07	7.39E+04	1.11E-07	7.07E+04	1.02E-07	6.83E+04	9.04E-08	6.65E+04	7.22E-08	6.51E+04	4.65E-08	6.41E+04
7.0	8.83E-08	6.89E+04	8.14E-08	6.64E+04	7.05E-08	6.45E+04	5.53E-08	6.31E+04	3.24E-08	6.20E+04	1.53E-08	6.12E+04
7.1	6.46E-08	6.50E+04	5.60E-08	6.30E+04	4.23E-08	6.15E+04	2.32E-08	6.04E+04	-5.68E-09	5.95E+04	-4.65E-08	5.89E+04
7.2	4.45E-08	6.19E+04	3.36E-08	6.03E+04	1.63E-08	5.91E+04	-7.70E-09	5.82E+04	-4.41E-08	5.75E+04	-9.54E-08	5.70E+04
7.3	2.67E-08	5.95E+04	1.30E-08	5.82E+04	-8.77E-09	5.73E+04	-3.90E-08	5.65E+04	-8.48E-08	5.60E+04	-1.49E-07	5.56E+04
7.4	1.03E-08	5.75E+04	-6.96E-09	5.65E+04	-3.43E-08	5.57E+04	-7.24E-08	5.52E+04	-1.30E-07	5.47E+04	-2.11E-07	5.44E+04
7.5	-5.53E-09	5.60E+04	-2.73E-08	5.51E+04	-6.17E-08	5.45E+04	-1.10E-07	5.41E+04	-1.82E-07	5.37E+04	-2.85E-07	5.35E+04
7.6	-2.17E-08	5.47E+04	-4.90E-08	5.41E+04	-9.24E-08	5.36E+04	-1.53E-07	5.32E+04	-2.44E-07	5.29E+04	-3.73E-07	5.27E+04
7.7	-3.89E-08	5.37E+04	-7.34E-08	5.32E+04	-1.28E-07	5.28E+04	-2.04E-07	5.25E+04	-3.19E-07	5.23E+04	-4.81E-07	5.21E+04
7.8	-5.83E-08	5.29E+04	-1.02E-07	5.25E+04	-1.70E-07	5.22E+04	-2.66E-07	5.20E+04	-4.11E-07	5.18E+04	-6.15E-07	5.16E+04
7.9	-8.07E-08	5.23E+04	-1.35E-07	5.20E+04	-2.22E-07	5.17E+04	-3.42E-07	5.15E+04	-5.24E-07	5.13E+04	-7.82E-07	5.12E+04
8.0	-1.07E-07	5.18E+04	-1.76E-07	5.15E+04	-2.85E-07	5.13E+04	-4.37E-07	5.11E+04	-6.66E-07	5.10E+04	-9.90E-07	5.09E+04
8.1	-1.40E-07	5.13E+04	-2.26E-07	5.11E+04	-3.64E-07	5.09E+04	-5.54E-07	5.08E+04	-8.43E-07	5.07E+04	-1.25E-06	5.06E+04
8.2	-1.80E-07	5.10E+04	-2.89E-07	5.08E+04	-4.81E-07	5.07E+04	-7.02E-07	5.05E+04	-1.07E-06	5.04E+04	-1.58E-06	5.03E+04
8.3	-2.29E-07	5.07E+04	-3.67E-07	5.05E+04	-5.84E-07	5.04E+04	-8.86E-07	5.03E+04	-1.34E-06	5.02E+04	-1.99E-06	5.01E+04
8.4	-2.91E-07	5.05E+04	-4.64E-07	5.03E+04	-7.37E-07	5.02E+04	-1.12E-06	5.01E+04	-1.69E-06	5.00E+04	-2.51E-06	4.99E+04
8.5	-3.68E-07	5.02E+04	-5.86E-07	5.01E+04	-9.30E-07	4.99E+04	-1.41E-06	4.98E+04	-2.13E-06	4.97E+04	-3.16E-06	4.96E+04
8.6	-4.65E-07	5.00E+04	-7.39E-07	4.99E+04	-1.17E-06	4.97E+04	-1.78E-06	4.96E+04	-2.69E-06	4.95E+04	-3.98E-06	4.94E+04
8.7	-5.87E-07	4.98E+04	-9.31E-07	4.96E+04	-1.48E-06	4.95E+04	-2.24E-06	4.94E+04	-3.39E-06	4.92E+04	-5.01E-06	4.91E+04
8.8	-7.40E-07	4.96E+04	-1.17E-06	4.94E+04	-1.86E-06	4.92E+04	-2.82E-06	4.91E+04	-4.26E-06	4.89E+04	-6.31E-06	4.88E+04
8.9	-9.32E-07	4.93E+04	-1.48E-06	4.91E+04	-2.34E-06	4.90E+04	-3.55E-06	4.88E+04	-5.37E-06	4.86E+04	-7.94E-06	4.84E+04

Table A-2

Total Alkalinity (TALK) to Dissolved Inorganic Carbonate (DIC) Conversion Variables

Determine A & B via the below table. Then compute DIC as follows:

$$\text{DIC as ppm CaCO}_3 = [(\text{TALK in ppm CaCO}_3/50,000) + A] \cdot B$$

pH	T=0 (deg. C)		T=5 (deg. C)		T=10 (deg. C)		T=15 (deg. C)		T=20 (deg. C)		T=25 (deg. C)	
	A	B	A	B	A	B	A	B	A	B	A	B
9.0	-1.17E-06	4.90E+04	-1.86E-06	4.88E+04	-2.95E-06	4.86E+04	-4.47E-06	4.84E+04	-6.76E-06	4.82E+04	-1.00E-05	4.80E+04
9.1	-1.48E-06	4.87E+04	-2.34E-06	4.85E+04	-3.71E-06	4.82E+04	-5.62E-06	4.80E+04	-8.51E-06	4.77E+04	-1.26E-05	4.74E+04
9.2	-1.86E-06	4.84E+04	-2.95E-06	4.81E+04	-4.68E-06	4.78E+04	-7.08E-06	4.74E+04	-1.07E-05	4.71E+04	-1.58E-05	4.68E+04
9.3	-2.34E-06	4.79E+04	-3.71E-06	4.78E+04	-5.89E-06	4.72E+04	-8.91E-06	4.68E+04	-1.35E-05	4.65E+04	-2.00E-05	4.61E+04
9.4	-2.95E-06	4.74E+04	-4.68E-06	4.70E+04	-7.41E-06	4.66E+04	-1.12E-05	4.61E+04	-1.70E-05	4.57E+04	-2.51E-05	4.53E+04
9.5	-3.72E-06	4.68E+04	-5.89E-06	4.63E+04	-9.33E-06	4.58E+04	-1.41E-05	4.53E+04	-2.14E-05	4.48E+04	-3.16E-05	4.43E+04
9.6	-4.68E-06	4.61E+04	-7.41E-06	4.55E+04	-1.17E-05	4.49E+04	-1.78E-05	4.43E+04	-2.69E-05	4.38E+04	-3.98E-05	4.32E+04
9.7	-5.89E-06	4.52E+04	-9.33E-06	4.46E+04	-1.48E-05	4.39E+04	-2.24E-05	4.32E+04	-3.39E-05	4.26E+04	-5.01E-05	4.20E+04
9.8	-7.41E-06	4.43E+04	-1.17E-05	4.35E+04	-1.86E-05	4.28E+04	-2.82E-05	4.20E+04	-4.27E-05	4.14E+04	-6.31E-05	4.07E+04
9.9	-9.33E-06	4.32E+04	-1.48E-05	4.24E+04	-2.34E-05	4.15E+04	-3.55E-05	4.07E+04	-5.37E-05	4.00E+04	-7.94E-05	3.93E+04
10.0	-1.17E-05	4.20E+04	-1.86E-05	4.11E+04	-2.95E-05	4.02E+04	-4.47E-05	3.94E+04	-6.76E-05	3.86E+04	-1.00E-04	3.79E+04
10.1	-1.48E-05	4.07E+04	-2.34E-05	3.97E+04	-3.72E-05	3.88E+04	-5.62E-05	3.79E+04	-8.51E-05	3.72E+04	-1.26E-04	3.65E+04
10.2	-1.86E-05	3.93E+04	-2.95E-05	3.83E+04	-4.68E-05	3.73E+04	-7.08E-05	3.65E+04	-1.07E-04	3.57E+04	-1.58E-04	3.51E+04
10.3	-2.34E-05	3.78E+04	-3.72E-05	3.69E+04	-5.89E-05	3.59E+04	-8.91E-05	3.51E+04	-1.35E-04	3.43E+04	-2.00E-04	3.37E+04
10.4	-2.95E-05	3.64E+04	-4.68E-05	3.54E+04	-7.41E-05	3.45E+04	-1.12E-04	3.37E+04	-1.70E-04	3.30E+04	-2.51E-04	3.25E+04
10.5	-3.72E-05	3.50E+04	-5.89E-05	3.41E+04	-9.33E-05	3.32E+04	-1.41E-04	3.25E+04	-2.14E-04	3.18E+04	-3.16E-04	3.13E+04
10.6	-4.68E-05	3.37E+04	-7.41E-05	3.28E+04	-1.17E-04	3.20E+04	-1.78E-04	3.13E+04	-2.69E-04	3.08E+04	-3.98E-04	3.03E+04
10.7	-5.89E-05	3.24E+04	-9.33E-05	3.16E+04	-1.48E-04	3.09E+04	-2.24E-04	3.03E+04	-3.39E-04	2.98E+04	-5.01E-04	2.94E+04
10.8	-7.41E-05	3.13E+04	-1.17E-04	3.06E+04	-1.86E-04	2.99E+04	-2.82E-04	2.94E+04	-4.27E-04	2.90E+04	-6.31E-04	2.86E+04
10.9	-9.33E-05	3.02E+04	-1.48E-04	2.96E+04	-2.34E-04	2.91E+04	-3.55E-04	2.86E+04	-5.37E-04	2.83E+04	-7.94E-04	2.80E+04
11.0	-1.17E-04	2.94E+04	-1.86E-04	2.88E+04	-2.95E-04	2.83E+04	-4.47E-04	2.80E+04	-6.76E-04	2.77E+04	-1.00E-03	2.74E+04
11.1	-1.48E-04	2.86E+04	-2.34E-04	2.81E+04	-3.72E-04	2.77E+04	-5.62E-04	2.74E+04	-8.51E-04	2.72E+04	-1.26E-03	2.70E+04
11.2	-1.86E-04	2.79E+04	-2.95E-04	2.76E+04	-4.68E-04	2.72E+04	-7.08E-04	2.70E+04	-1.07E-03	2.67E+04	-1.58E-03	2.66E+04
11.3	-2.34E-04	2.74E+04	-3.72E-04	2.71E+04	-5.89E-04	2.68E+04	-8.91E-04	2.66E+04	-1.35E-03	2.64E+04	-2.00E-03	2.63E+04
11.4	-2.95E-04	2.69E+04	-4.68E-04	2.67E+04	-7.41E-04	2.64E+04	-1.12E-03	2.63E+04	-1.70E-03	2.61E+04	-2.51E-03	2.60E+04
11.5	-3.72E-04	2.66E+04	-5.89E-04	2.63E+04	-9.33E-04	2.62E+04	-1.41E-03	2.60E+04	-2.14E-03	2.59E+04	-3.16E-03	2.58E+04
11.6	-4.68E-04	2.63E+04	-7.41E-04	2.61E+04	-1.17E-03	2.59E+04	-1.78E-03	2.57E+04	-2.69E-03	2.57E+04	-3.98E-03	2.57E+04
11.7	-5.89E-04	2.60E+04	-9.33E-04	2.59E+04	-1.43E-03	2.57E+04	-2.24E-03	2.57E+04	-3.39E-03	2.56E+04	-5.01E-03	2.55E+04
11.8	-7.41E-04	2.58E+04	-1.17E-03	2.57E+04	-1.86E-03	2.56E+04	-2.82E-03	2.55E+04	-4.27E-03	2.55E+04	-6.31E-03	2.54E+04
11.9	-9.33E-04	2.56E+04	-1.48E-03	2.56E+04	-2.34E-03	2.55E+04	-3.55E-03	2.54E+04	-5.37E-03	2.54E+04	-7.94E-03	2.53E+04
12.0	-1.17E-03	2.55E+04	-1.86E-03	2.54E+04	-2.95E-03	2.54E	-4.47E-03	2.53E+04	-6.76E-03	2.53E+04	-1.00E-02	2.53E+04

Appendix B

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: Bennington, Vermont

Item	Description
I	Case Study Number 1
II	PWS Description
a.	Raw Water Supply Surface water
b.	Water Quality
1.	Raw Low pH, alkalinity and calcium content.
2.	Treated Coagulated water pH 4.5 - 5.0, alkalinity < 5 mg CaCO ₃ /L.
c.	Treatment Filtration, chlorination.
III	Corrosion Control Study Elements
a.	Desk-top Evaluation <ul style="list-style-type: none"> Community blood lead monitoring program revealed elevated levels in 1977. Material survey of the distribution system found that one-third of the system was served by lead service lines. Tap samples were collected, finding lead levels as high as 0.86 mg/L. Theoretical performance of carbonate passivation.
b.	Demonstration Testing
1.	Flow-Through NA
2.	Static NA
3.	Full-Scale Implemented pH and alkalinity adjustment treatment.
c.	Full-Scale Confirmation
1.	Tap sampling Monthly first-draw and running tap samples from 10 targeted sites.
2.	WQP-DIS pH, alkalinity, and scale analysis using X-ray diffraction.
3.	WQP-POE pH and alkalinity
IV	Testing Program Description
a.	Constraints Due to the elevated blood lead levels in the population, treatment installation had to be easily and quickly installed and operable.
b.	Priorities
1.	Primary Reduce lead levels in consumers' tap water.
2.	Secondary
c.	Treatment Alternatives pH and alkalinity adjustment: Increase pH to 8.0-8.5 and increase alkalinity to above 25 mg CaCO ₃ /L.
d.	Monitoring programs <ul style="list-style-type: none"> Tap monitoring for lead in first-draw and running samples: 1977-1991. pH and alkalinity monitoring in distribution system and at the POEs: 1977-1991. Evaluate scale on lead service line pipes using X-ray diffraction: 1977.
e.	QA/QC Elements See Reference

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: Bennington, Vermont

Item	Description						
V	<p>Testing Results</p> <table border="1"> <tr> <td data-bbox="224 395 522 583">a. Corrosion Control Performance</td> <td data-bbox="522 395 1500 583"> <ul style="list-style-type: none"> Average monthly lead levels in first-draw tap samples were reduced from a high of 250 ug/L to approximately 20 ug/L lead within six-months of operations. Ongoing monitoring has showed a continual decline in lead levels in first-draw tap samples with early 1991 data indicating lead levels less than 10 ug/L. X-ray diffraction analysis confirmed scale formation consisting of cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂). </td> </tr> <tr> <td data-bbox="224 583 522 629">b. Secondary Impacts</td> <td data-bbox="522 583 1500 629">NA</td> </tr> <tr> <td data-bbox="224 629 522 729">c. Treatment Issues</td> <td data-bbox="522 629 1500 729">Initial operation of the sodium bicarbonate and sodium hydroxide feed systems was manual, and targeted values for pH and alkalinity were not always achieved. To improve treatment consistency, automated operational controls were installed in 1990.</td> </tr> </table>	a. Corrosion Control Performance	<ul style="list-style-type: none"> Average monthly lead levels in first-draw tap samples were reduced from a high of 250 ug/L to approximately 20 ug/L lead within six-months of operations. Ongoing monitoring has showed a continual decline in lead levels in first-draw tap samples with early 1991 data indicating lead levels less than 10 ug/L. X-ray diffraction analysis confirmed scale formation consisting of cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂). 	b. Secondary Impacts	NA	c. Treatment Issues	Initial operation of the sodium bicarbonate and sodium hydroxide feed systems was manual, and targeted values for pH and alkalinity were not always achieved. To improve treatment consistency, automated operational controls were installed in 1990.
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VI	Notes/Qualifications NA						
VII	Reference(s) Vinci, A. 1992. Bennington, Vermont Corrosion Control Studies with the Bicarbonate/pH System. Technical comments submitted to USEPA in response to the proposed Lead and Copper Rule from Church & Dwight, Company, 469 N. Harrison St., Princeton, NJ, 08543-5297.						

PWS Characterization: *Low pH, Alkalinity, & Calcium*
PWS Name & Location: *MWRA, Boston, Massachusetts*

Item	Description																				
I	<table border="1"> <tr> <td data-bbox="236 351 527 401">Case Study Number</td> <td data-bbox="527 351 1505 401">2</td> </tr> </table>	Case Study Number	2																		
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PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: MWRA, Boston, Massachusetts

Item	Description						
V	<p>Testing Results</p> <table border="1"> <tr> <td data-bbox="240 409 524 743"> <p>a. Corrosion Control Performance</p> </td> <td data-bbox="524 409 1512 743"> <ul style="list-style-type: none"> • Six-month trial full-scale treatment using zinc orthophosphate: <ol style="list-style-type: none"> 1. Initial passivation dose of 13 mg/L used for several weeks, then reduced the dosage to between 3.2 and 4.5 mg/L. 2. Initial increase in tap lead levels observed, then slow decline in lead noted toward the end of the six month period. 3. Algal growth appeared to be stimulated in the open, finished water storage reservoirs due to the additional phosphate content. • pH Adjustment using sodium hydroxide was subsequently installed. <ol style="list-style-type: none"> 1. Lead and copper levels in first-draw samples were reduced by increased pH. 2. Researchers noted that when the pH dropped from pH 9 to below pH 8, the lead levels increased. </td> </tr> <tr> <td data-bbox="240 743 524 840"> <p>b. Secondary Impacts</p> </td> <td data-bbox="524 743 1512 840"> <ul style="list-style-type: none"> • Algal growth was stimulated in the open, treated water reservoirs when zinc orthophosphate was used. • Dirty water complaints arose with the introduction of the phosphate inhibitor. </td> </tr> <tr> <td data-bbox="240 840 524 916"> <p>c. Treatment Issues</p> </td> <td data-bbox="524 840 1512 916"> <ul style="list-style-type: none"> • A high pH at the POE was necessary to maintain targeted pH values throughout the distribution system. </td> </tr> </table>	<p>a. Corrosion Control Performance</p>	<ul style="list-style-type: none"> • Six-month trial full-scale treatment using zinc orthophosphate: <ol style="list-style-type: none"> 1. Initial passivation dose of 13 mg/L used for several weeks, then reduced the dosage to between 3.2 and 4.5 mg/L. 2. Initial increase in tap lead levels observed, then slow decline in lead noted toward the end of the six month period. 3. Algal growth appeared to be stimulated in the open, finished water storage reservoirs due to the additional phosphate content. • pH Adjustment using sodium hydroxide was subsequently installed. <ol style="list-style-type: none"> 1. Lead and copper levels in first-draw samples were reduced by increased pH. 2. Researchers noted that when the pH dropped from pH 9 to below pH 8, the lead levels increased. 	<p>b. Secondary Impacts</p>	<ul style="list-style-type: none"> • Algal growth was stimulated in the open, treated water reservoirs when zinc orthophosphate was used. • Dirty water complaints arose with the introduction of the phosphate inhibitor. 	<p>c. Treatment Issues</p>	<ul style="list-style-type: none"> • A high pH at the POE was necessary to maintain targeted pH values throughout the distribution system.
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<p>c. Treatment Issues</p>	<ul style="list-style-type: none"> • A high pH at the POE was necessary to maintain targeted pH values throughout the distribution system. 						
VI	<p>Notes/Qualifications</p> <p>The poor performance of the zinc orthophosphate inhibitor is most likely the result of an excessively low pH for its effectiveness. Had the treated water pH been increased to above 7, it is likely that the performance results would have been improved.</p>						
VII	<p>Reference(s)</p> <p>Karalekas, P.C. et al. 1983. Control of Lead, Copper, and Iron Pipe Corrosion in Boston. <i>Journal AWWA</i> 75(2):92-95.</p>						

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: FCWD, Fort Collins, Colorado

Item	Description
I	Case Study Number 3
II	PWS Description
	a. Raw Water Supply Poudre River & Horsetooth Reservoir
	b. Water Quality
	1. Raw Cold, low turbidity, moderate pH, low alkalinity and low calcium
	2. Treated Coagulated Water: pH = 5.8 - 7.2, Alkalinity = 5-25 mg CaCO ₃ /L, and Calcium = 20-30 mg CaCO ₃ /L
	c. Treatment Alum coagulation, fluoridation, and chlorination
III	Corrosion Control Study Elements
	a. Desk-top Evaluation Analogous Systems: Seattle, WA and Bennington, VA Theoretical: Evaluation of carbonate passivation Process Testing: Marble Chip Testing
	b. Demonstration Testing
	1. Flow-Through NA
	2. Static NA
	3. Full-Scale Implemented pH/alkalinity adjustment full-scale in two stages to optimize treatment.
	c. Full-Scale Confirmation
	1. Tap sampling First-draw samples from public taps: 1981 - 1992.
	2. WQP-DIS WQP-DIS for pH, alkalinity and calcium: 1981 - 1992. WQP-DIS for pH, alkalinity and calcium: 1981 - 1992.
IV	Testing Program Description
	a. Constraints <ul style="list-style-type: none"> Brewery which required consistent, moderate pH. Land application of sewage sludge limited by copper. Use of phosphate inhibitor questionable due to wastewater treatment requirements and public acceptance.
	b. Priorities
	1. Primary Reduce copper levels in tap water and sewage sludge.
	2. Secondary No adverse effects on other water treatment goals or aesthetic quality of the treated water.
	c. Treatment Alternatives pH and alkalinity adjustment using lime and sodium bicarbonate. Stage 1: pH Goal = 7.6-7.8 & Alk Goal > 30 mg CaCO ₃ /L Stage 2: pH Goal = 7.8-8.0 & Alk Goal = 35-45 mg CaCO ₃ /L
	d. Monitoring programs <ul style="list-style-type: none"> In-line pH monitors located after stabilization chemical feed points. Alkalinity measured at POE every 4-hours. 8-10 sampling stations monitoring monthly for first-draw copper and WQP-DIS.
	e. QA/QC Elements Process controls.

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: FCWD, Fort Collins, Colorado

Item	Description						
V	<p>Testing Results</p> <table border="1"> <tr> <td data-bbox="225 411 514 513">a. Corrosion Control Performance</td> <td data-bbox="514 411 1495 513"> <ul style="list-style-type: none"> • Tap copper levels were reduced from high levels ranging between 0.8-1.0 mg/L to maximum values between 0.2-0.4 mg/L. • Sludge metal content reduced: Copper 20%; Lead 30-50%. </td> </tr> <tr> <td data-bbox="225 513 514 648">b. Secondary impacts</td> <td data-bbox="514 513 1495 648"> <ul style="list-style-type: none"> • Post-filtration turbidity spikes with lime addition • Elevating pH caused post-precipitation of manganese during period of reservoir stratification. This caused brown water complaints. FCWD installed potassium permanganate pretreatment to control soluble manganese present after filtration. </td> </tr> <tr> <td data-bbox="225 648 514 892">c. Treatment Issues</td> <td data-bbox="514 648 1495 892"> <ul style="list-style-type: none"> • Process control for stable and consistent final pH took between one and two years to debug. • FCWD has been able to achieve the pH and alkalinity goals over 90 percent of the time. • For more cost-effective treatment, FCWD is installing carbon dioxide in lieu of sodium bicarbonate. • Redundant feed systems are being installed for lime and carbon dioxide to ensure continuous operation. </td> </tr> </table>	a. Corrosion Control Performance	<ul style="list-style-type: none"> • Tap copper levels were reduced from high levels ranging between 0.8-1.0 mg/L to maximum values between 0.2-0.4 mg/L. • Sludge metal content reduced: Copper 20%; Lead 30-50%. 	b. Secondary impacts	<ul style="list-style-type: none"> • Post-filtration turbidity spikes with lime addition • Elevating pH caused post-precipitation of manganese during period of reservoir stratification. This caused brown water complaints. FCWD installed potassium permanganate pretreatment to control soluble manganese present after filtration. 	c. Treatment Issues	<ul style="list-style-type: none"> • Process control for stable and consistent final pH took between one and two years to debug. • FCWD has been able to achieve the pH and alkalinity goals over 90 percent of the time. • For more cost-effective treatment, FCWD is installing carbon dioxide in lieu of sodium bicarbonate. • Redundant feed systems are being installed for lime and carbon dioxide to ensure continuous operation.
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VI	<p>Notes/Qualifications</p> <p>During the first incident of manganese post-precipitation, FCWD stopped the pH adjustment portion of their corrosion control program. Within days of this, copper levels began to increase in first-draw tap samples, and the copper and lead content of the sewage sludge increased during the period when pH adjustment was not being practiced. This indicated to FCWD that (1) effective corrosion control could only be assured if continuously practiced; and (2) while the loss of corrosion protection became apparent in a matter of days, it took several weeks to months to regain the control conditions experienced prior to the treatment interruption.</p>						
VII	<p>Reference(s)</p> <p>Smith, M. et al. 1992. <i>Corrosion Control Studies and Strategies - Fort Collins, Colorado</i>. AWWA Corrosion Control Seminar (Denver, CO).</p> <p>Kuchenrither, R.D. et al. 1988. <i>Sludge Quality Benefits Realized from Drinking Water Stabilization</i>. Proc. Annual WPCF Conference.</p> <p>Elmund, G.K. et al. 1986. <i>Stabilization of a Finished Water: Fort Collins, Colorado</i>. Proc Joint Regional AWWA-WPCA Conference.</p>						

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: Bureau of Water, Portland, Oregon

Item	Description
I	Case Study Number 4
II	PWS Description a. Raw Water Supply Unfiltered surface water supply b. Water Quality 1. Raw Low pH, alkalinity, and calcium 2. Treated Finished water quality: pH 6.9; Total hardness 14 mg CaCO ₃ /L; Alkalinity 10 mg CaCO ₃ /L; Total dissolved solids 24 mg/L. c. Treatment Chlorination/chloramination.
III	Corrosion Control Study Elements a. Desk-top Evaluation Theoretical: Carbonate passivation Analogous Systems: Seattle, Washington b. Demonstration Testing 1. Flow-Through Coupons and copper tubing 2. Static NA 3. Full-Scale NA c. Full-Scale Confirmation 1. Tap sampling NA 2. WQP-DIS NA 3. WQP-FOE NA
IV	Testing Program Description a. Constraints Compatibility with unfiltered surface water treatment facilities. b. Priorities 1. Primary Assess the corrosion rates of domestic plumbing materials. 2. Secondary Determine the most cost effective approach to treatment. c. Treatment Alternatives Existing treatment at two locations in the distribution system: 1. Pipe rig consisted of coupon (6) flow-through units with black iron, galvanized steel, copper, lead, lead:tin solder-coated copper, and asbestos-cement. 2. A single loop (220 feet) of lead:tin soldered copper tubing was also included in the pipe rig. Soldered joints were placed every 20-feet. 3. Pipe rig 1 was located at the source of supply with a free chlorine residual of 1 mg/L 4. Pipe rig 2 was located several miles from the source and chloramines were added. d. Monitoring programs Metal leaching and water quality parameters entering the pipe loops systems. e. QA/QC Elements NA

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: Bureau of Water, Portland, Oregon

Item	Description						
V	<p>Testing Results</p> <table border="1"> <tr> <td data-bbox="241 426 539 670"> <p>a. Corrosion Control Performance</p> </td> <td data-bbox="539 426 1515 670"> <ul style="list-style-type: none"> • Equilibrium corrosion rates appeared to result after six months of operation for all of the materials. • Based on the test coupons, lead corrosion rates increased with free chlorine as compared to chloramines. • All other materials experienced comparable corrosion rates (on the basis of coupons) regardless of the disinfectant present. • The copper tubing with lead:tin solder showed increased corrosion activity with chloramines as compared to the free chlorine loop. </td> </tr> <tr> <td data-bbox="241 670 539 720"> <p>b. Secondary Impacts</p> </td> <td data-bbox="539 670 1515 720"> <p>NA</p> </td> </tr> <tr> <td data-bbox="241 720 539 849"> <p>c. Treatment Issues</p> </td> <td data-bbox="539 720 1515 849"> <p>The source of lead in first-draw tap samples appeared to be the lead-based solder as confirmed by the pipe loop testing program. No treatment was recommended since the City of Portland had instituted a lead ban on plumbing materials for domestic supply systems.</p> </td> </tr> </table>	<p>a. Corrosion Control Performance</p>	<ul style="list-style-type: none"> • Equilibrium corrosion rates appeared to result after six months of operation for all of the materials. • Based on the test coupons, lead corrosion rates increased with free chlorine as compared to chloramines. • All other materials experienced comparable corrosion rates (on the basis of coupons) regardless of the disinfectant present. • The copper tubing with lead:tin solder showed increased corrosion activity with chloramines as compared to the free chlorine loop. 	<p>b. Secondary Impacts</p>	<p>NA</p>	<p>c. Treatment Issues</p>	<p>The source of lead in first-draw tap samples appeared to be the lead-based solder as confirmed by the pipe loop testing program. No treatment was recommended since the City of Portland had instituted a lead ban on plumbing materials for domestic supply systems.</p>
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<p>c. Treatment Issues</p>	<p>The source of lead in first-draw tap samples appeared to be the lead-based solder as confirmed by the pipe loop testing program. No treatment was recommended since the City of Portland had instituted a lead ban on plumbing materials for domestic supply systems.</p>						
VI	<p>Notes/Qualifications</p> <p>Portland has participated in the AWWARF Pipe Loop Study, and more information on the corrosion behavior of it system, especially as it relates to first-draw tap samples will be available in the final report.</p>						
VII	<p>Reference(s)</p> <p>Treweek, G.P. et al. 1985. Pilot-plant Simulation of Corrosion in Domestic Pipe Materials. <i>Journal AWWA</i> 77(10):74-82.</p>						

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: SWD, Seattle, Washington

Item	Description	
I	Case Study Number 5	
II	PWS Description	
	a. Raw Water Supply	Two unfiltered surface water supplies - Tolt & Cedar Rivers
	b. Water Quality	
	1. Raw	Low pH, alkalinity, calcium and mineral content.
	2. Treated	Finished water quality: pH 5.7-6.2; Alkalinity 3-5 mg CaCO ₃ /L; Chlorine residual 0.2-0.4 mg/L.
	c. Treatment	Chlorination and fluoridation.
III	Corrosion Control Study Elements	
	a. Desk-top Evaluation	Theoretical: Carbonate passivation
	b. Demonstration Testing	
	1. Flow-Through	Series of pilot loop tests conducted prior to full-scale treatment installation.
	2. Static	NA
	3. Full-Scale	Corrosion rate and metal leaching studies conducted after installing treatment.
	c. Full-Scale Confirmation	
	1. Tap sampling	First-draw tap samples collected from 300 homes in service area.
	2. WQP-DIS	pH, alkalinity, chlorine residual, dissolved oxygen, conductivity
	3. WQP-POE	pH, alkalinity, chlorine residual
IV	Testing Program Description	
	a. Constraints	Compatibility with unfiltered, surface water facilities.
	b. Priorities	
	1. Primary	Reducing the corrosion activity in the distribution system toward lead, copper, zinc (galvanized piping) and iron.
	2. Secondary	Reliability and operational feasibility of the selected treatment process.
	c. Treatment Alternatives	<p>Pipe loop testing evaluated pH/alkalinity alternatives and orthophosphate corrosion inhibitors:</p> <ol style="list-style-type: none"> 1. Recirculating pipe loops were constructed using 1/2-inch copper tubing in which a bead of 50:50 lead:tin solder was attached longitudinally in the piping. 2. Copper tubing lengths were 6-8 inches individually; then several were connected using plastic tubing. 3. Treated water was circulated through a test loop using a peristaltic pump cyclically. <p>Corrosion rate testing was performed using linear polarization techniques once full-scale treatment was installed.</p>
	d. Monitoring programs	Metal leaching, corrosion rates, and water quality parameters were monitored in the flow-through testing apparatus and in the full-scale systems once the recommended treatment was installed.
e. QA/QC Elements	See Reference Materials.	

PWS Characterization: Low pH, Alkalinity, & Calcium
PWS Name & Location: SWD, Seattle, Washington

Item	Description						
V	<p>Testing Results</p> <table border="1"> <tr> <td data-bbox="243 409 537 679">a. Corrosion Control Performance</td> <td data-bbox="537 409 1503 679"> <ul style="list-style-type: none"> pH and alkalinity adjustment was the recommended treatment on the basis of the flow-through testing program. After installation, reductions in tap lead and copper levels (as first-draw samples) of 12 and 60 percent were found within the first year of operation. Electrochemical testing results showed a 50% decrease in corrosion rates on new copper plumbing with greater decreases in aged materials. Short-term variations in copper corrosion rates were found to be strongly correlated to free chlorine (direct relationship), and to a lesser degree with pH (inverse relationship). </td> </tr> <tr> <td data-bbox="243 679 537 722">b. Secondary Impacts</td> <td data-bbox="537 679 1503 722">NA</td> </tr> <tr> <td data-bbox="243 722 537 819">c. Treatment Issues</td> <td data-bbox="537 722 1503 819">pH and alkalinity adjustment took place gradually over the first year of operations, increasing the average pH to 7.8-8.3 and the average alkalinity to 15-17 mg CaCO₃/L.</td> </tr> </table>	a. Corrosion Control Performance	<ul style="list-style-type: none"> pH and alkalinity adjustment was the recommended treatment on the basis of the flow-through testing program. After installation, reductions in tap lead and copper levels (as first-draw samples) of 12 and 60 percent were found within the first year of operation. Electrochemical testing results showed a 50% decrease in corrosion rates on new copper plumbing with greater decreases in aged materials. Short-term variations in copper corrosion rates were found to be strongly correlated to free chlorine (direct relationship), and to a lesser degree with pH (inverse relationship). 	b. Secondary Impacts	NA	c. Treatment Issues	pH and alkalinity adjustment took place gradually over the first year of operations, increasing the average pH to 7.8-8.3 and the average alkalinity to 15-17 mg CaCO ₃ /L.
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VI	Notes/Qualifications						
VII	<p>Reference(s)</p> <p>Reiber, S.H. et al. 1987. Corrosion Monitoring and Control in the Pacific Northwest. <i>Journal AWWA</i>. 79(2):71-74.</p> <p>Stone, A. et al. 1987. The Effects of Short-term Changes in Water Quality on Copper and Zinc Corrosion Rates. <i>Journal AWWA</i>. 79(2):75-82.</p> <p>Reiber, S.H. et al. 1987. <i>Corrosion in Water Distribution Systems of the Pacific Northwest</i>. EPA 600/S2-87-042.</p> <p>Herrara, C.E. et al. 1984. <i>Seattle Distribution System Corrosion Control Study - Volume 2: Tolt River Water Pilot Plant Study</i>. EPA 600/2-84-065.</p> <p>Hoyt, B.P. et al. 1982. <i>Seattle Distribution System Corrosion Control Study - Volume 1: Cedar River Water Pilot Plant Study</i>. EPA 600/2-82-026.</p>						

PWS Characterization: Low pH, High Alkalinity & Calcium
PWS Name & Location: Oakwood, Ohio

Item	Description
I	Case Study Number 6
II	PWS Description
	a. Raw Water Supply Two well-fields
	b. Water Quality
	1. Raw Lower pH, High alkalinity and calcium, elevated iron.
	2. Treated Finished water quality: pH 7.1; Total hardness 200 mg CaCO3/L; Alkalinity 370 mg CaCO3/L.
c. Treatment Water from one well-field removes iron through green-sand filtration and is then softened using zeolite softening. The treated water is then blended with water from the other well-field and chlorinated prior to distribution.	
III	Corrosion Control Study Elements
	a. Desk-top Evaluation NA
	b. Demonstration Testing
	1. Flow-Through Pipe loop study to evaluate corrosion rates before and after softening.
	2. Static NA
	3. Full-Scale Tap sampling before and after softening to determine difference in corrosion activity.
	c. Full-Scale Confirmation
	1. Tap sampling First-draw tap samples at sites receiving water only from Well-field 1 prior to being blended with water from the second well-field.
	2. WQP-DIS pH, alkalinity, hardness
	3. WQP-POE pH, alkalinity, hardness

PWS Characterization: Low pH, High Alkalinity & Calcium
PWS Name & Location: Oakwood, Ohio

Item	Description
IV	Testing Program Description
a. Constraints	NA
b. Priorities	
1. Primary	Determine if softening would impact corrosion rates.
2. Secondary	
c. Treatment Alternatives	<ul style="list-style-type: none"> • Flow-through testing program: <ol style="list-style-type: none"> 1. Two pipe rigs were constructed with one receiving unsoftened water and the other receiving softened water. 2. Each rig had three test loops: black iron, lead, and pipe sleeves consisting of black iron, copper, lead:tin solder-coated copper, and galvanically coupled (copper and lead solder) coupons (4 coupons of each). 3. Each pipe loop (black iron and lead) was pre-conditioned by receiving only hard water for 7-months. 4. The pipe sleeves received hard and soft water throughout the entire testing period. 5. Flowrate conditions for the pipe sleeves were: 0.5 gpm at 5 psi for six days, with one day of standing time. 6. Flowrate conditions for the pipe loops were: Iron pipe, recirculating rate of 1 gpm with an effluent rate of 0.0172 gpm; Lead pipe flow-through rate of 0.5 gpm for 16 hours with an 8-hour standing time cyclically operated. 7. Each pipe rig operated two lead loops: one was of new material and the second was excavated (old material) from the distribution system. • Full-scale evaluation testing program consistent of sampling consumers' homes for metals and water quality parameters while receiving hard and softened water.
d. Monitoring programs	<ul style="list-style-type: none"> • Flow-through testing program: In addition to the WQP monitoring performed were the following: Pipe loops: Metal leaching Pipe Sleeves: Metal leaching and coupon weight-loss Dissolved oxygen: depletion was used to calculate the corrosion rates in the iron pipe loops. • Full-scale evaluation: First-draw samples for lead, copper, pH, alkalinity, and hardness.
e. QA/QC Elements	See Reference

PWS Characterization: Low pH, High Alkalinity & Calcium
PWS Name & Location: Oakwood, Ohio

Item	Description
V	<p>Testing Results</p> <p>a. Corrosion Control Performance</p> <ul style="list-style-type: none"> • Flow-through testing program: <ol style="list-style-type: none"> 1. <i>Coupon results</i>: no difference was observed on the basis of weight-loss between hard and softened water, except in the case with galvanically-coupled coupons where a modest increase in corrosion rate was noted for the softened condition. Generally, corrosion rates did decrease over time. 2. <i>Iron pipe loop results</i>: At the end of the 7-month pre-conditioning period, the iron loops produced similar corrosion rate results. 3. <i>Lead pipe loop results</i>: At the end of the 7-month pre-conditioning period, significant variability in the performance of loops were observed as follows: <ul style="list-style-type: none"> New & Old did not perform alike; Old & Old did not perform alike; While the two new loops behaved statistically comparable, the variability was high with 90% confidence intervals ranging between 32 and 72 percent of the mean values of lead. • Full-scale evaluation - No significant difference in metal concentrations were found before and after the installation of softening treatment. <p>b. Secondary Impacts NA</p> <p>c. Treatment Issues NA</p>
VI	<p>Notes/Qualifications</p> <ul style="list-style-type: none"> • Flow-through testing program: <ol style="list-style-type: none"> 1. Replicate performance of pipe loops showed a large variability in metal leaching. 2. Results from the evaluation of hard and softened water conditions have yet to be published. • Full-scale evaluation - 23 homes were included in the tap monitoring program. Of these, 12 had point of entry softeners which were to be bypassed during the sampling day. However, this means that about 50 percent of the sites had already been exposed to softened water prior to the utility installing its ion exchange treatment unit.
VII	<p>Reference(s)</p> <p>Wysock, B.M. et al. 1991. A Study of the Effect of Municipal Ion Exchange Softening on the Corrosion of Lead, Copper, and Iron in Water Systems. Proc. Annual AWWA Conference (Philadelphia, PA).</p>

PWS Characterization: Moderate pH, High Alkalinity & Calcium
PWS Name & Location: Fort Shawnee, Ohio

Item		Description
I	Case Study Number	7
II	PWS Description	
	a. Raw Water Supply	Groundwater
	b. Water Quality	
	1. Raw	Moderate pH, high alkalinity and hardness, and elevated iron and hydrogen sulfide levels.
	2. Treated	Final water quality: pH 7.3-8.0; Total hardness 250-300 mg CaCO ₃ /L; Alkalinity 290-350 mg CaCO ₃ /L; sulfate 206-330 mg SO ₄ /L; chloride 16-45 mg Cl/L; and carbon dioxide 18-28 CO ₂ mg/L.
	c. Treatment	Well water is aerated and filtered for iron and hydrogen sulfide removal; split treatment for zeolite softening.
III	Corrosion Control Study Elements:	
	a. Desk-top Evaluation	<ul style="list-style-type: none"> • Copper pitting failures occurring in domestic cold water piping in relatively new condominiums. • Investigators determined that excessive carbon dioxide and oxygen primarily responsible for corrosive behavior of the treated water. This was thought to be exacerbated by the higher sulfate and chloride content of the water supply. • Raising the pH to approximately 8.3 would reduce the carbon dioxide content of the finished water.
	b. Demonstration Testing	
	1. Flow-Through	Pipe loop testing was performed.
	2. Static	NA
	3. Full-Scale	NA
	c. Full-Scale Confirmation	
	1. Tap sampling	NA
	2. WQP-DIS	NA
	3. WQP-POE	NA

PWS Characterization: Moderate pH, High Alkalinity & Calcium
PWS Name & Location: Fort Shawnee, Ohio

Item	Description
IV	<p>Testing Program Description</p> <p>a. Constraints</p> <ul style="list-style-type: none"> • Treatment facility was not continuously staffed. • Chemical storage was located in an unheated building, so that freezing was a concern for the winter months. <p>b. Priorities</p> <p>1. Primary: Reduce the copper pitting failures in home-owners' plumbing systems.</p> <p>2. Secondary: Operational feasibility.</p> <p>c. Treatment Alternatives</p> <ul style="list-style-type: none"> • Two pipe loops constructed of 50-by-1 meter lengths of type L copper tubing - 3/4 inch diameter, soldered with 50:50 lead:tin solder. • Pipe loop 1 received existing finished water; Pipe loop 2 received finished water treated with soda ash to raise the pH to approximately 8.3. • Loops were operated cyclically: running for 10-minutes; standing for 110-minutes for sixteen hours; then standing for 8-hours. <p>d. Monitoring programs</p> <ul style="list-style-type: none"> • Water quality parameters were measured entering the pipe loops, but no metal leaching data was collected. • After one-year's operation, the tubes were removed and physically inspected for corrosion activity. • Energy dispersive spectroscopy (EDS) and microchemical analysis were used to confirm the corrosion byproducts present on the interior walls of the copper piping. <p>e. QA/QC Elements: NA</p>
V	<p>Testing Results</p> <p>a. Corrosion Control Performance</p> <p>EDS and microchemical analyses confirmed that pipe loops treated with soda ash showed cuprous oxide and calcium carbonate coatings on the surface of the pipe walls. No pitting corrosion was evident in any of the pipes extracted from the soda ash-treated loop.</p> <p>Pitting corrosion was evident in pipes exposed to water not treated with soda ash based on visual inspection. EDS and microchemical analysis confirmed the following:</p> <ol style="list-style-type: none"> 1) Green tubercles overlaying pits consisted principally of copper carbonate (malachite) mixed with copper sulfate; 2) Pits examined by scanning electron microscopy were found to contain cubic crystalline byproducts. EDS findings indicated that these byproducts contained major quantities of copper with semiminor quantities of sulfate, and trace amounts of chloride. <p>Tap sampling was not performed, but following installation of soda ash treatment, the pitting failures of copper, domestic piping ceased within 6-months.</p> <p>b. Secondary Impacts: NA</p> <p>c. Treatment Issues: Average dosage of soda ash was 35 mg/L for a pH goal of 8.1-8.3.</p>
VI	Notes/Qualifications
VII	Reference(s) Cohen, A. and J.R. Meyers. 1987. Mitigating Copper Pitting through Water Treatment. <i>Journal AWWA</i> . 79(2):58-61.

PWS Characterization: Moderate pH, High Alkalinity & Calcium
PWS Name & Location: Pinellas County, Florida

Item		Description
I	Case Study Number	8
II	PWS Description	
	a. Raw Water Supply	Deep well water
	b. Water Quality	
	1. Raw	High hardness and alkalinity with elevated hydrogen sulfide
	2. Treated	Finished water quality: pH 7.6-7.85; Total hardness 200-214 mg CaCO ₃ /L; Alkalinity 200-211 mg CaCO ₃ /L; chlorine residual 2.5 mg/L
	c. Treatment	Reduced draft aeration of well water for hydrogen sulfide removal; pH adjustment using caustic soda, and chlorination.
III	Corrosion Control Study Elements	
	a. Desk-top Evaluation	NA
	b. Demonstration Testing	
	1. Flow-Through	Screening of options for full-scale evaluation and pipe rig operation using various water quality conditions to determine the cause and effect of corrosion problems as a function of dissolved oxygen, pH, and corrosion inhibitor.
	2. Static	NA
	3. Full-Scale	In-situ testing using pipe rig systems after full-scale treatment installation.
	c. Full-Scale Confirmation	
	1. Tap sampling	First-draw tap samples for copper.
	2. WQP-DIS	pH, dissolved oxygen, carbon dioxide, inhibitor residual
	3. WQP-POE	pH, dissolved oxygen, inhibitor dose
	IV	a. Constraints
Priorities		
1. Primary		Minimize copper corrosion.
2. Secondary		Not adversely affect lead corrosion.
c. Treatment Alternatives		<p>Screening testing evaluated four corrosion inhibitors, combinations of ortho- and polyphosphates for four months.</p> <p>Full-scale evaluation:</p> <ol style="list-style-type: none"> 1. Coupons and flow-through test racks were installed at 11 locations in the distribution system. 2. The test racks were operated at a flow of 2 gpm for a month at a time. 3. The recommended orthophosphate inhibitor treatment was installed full-scale. 4. Corrosion rates were evaluated for 6-months prior to installing phosphate treatment and 6-months after treatment was in-place. <p>Demonstration flow-through testing:</p> <ol style="list-style-type: none"> 1. Four pipe rigs were constructed with lead, copper, and mild steel flat coupons (4 each), and galvanized steel and copper pipe inserts (2 each). 2. Flow-through testing was conducted for 6-months under varying combinations of dissolved oxygen, pH, and inhibitor dosages.

PWS Characterization: Moderate pH, High Alkalinity & Calcium
PWS Name & Location: Pinellas County, Florida

Item	Description
d. Monitoring programs	<ul style="list-style-type: none"> • Screening tests utilized Virchem 2902 corrosion test units which measure corrosion rates through electrochemical measurements. • Full-scale evaluation: corrosion rates were measured via weight loss measurements for the coupons and pipe inserts. First-draw tap samples were also collected from 25 sites in the affected area of the distribution system. • Demonstration flow-through testing: corrosion rates were measured using weight loss. <p>Water quality parameters were measured throughout all phases of the testing program.</p>
e. QA/QC Elements	NA
V	Testing Results
a. Corrosion Control Performance	<p>Screening tests indicated that orthophosphate was most effective in controlling copper and lead corrosion.</p> <ul style="list-style-type: none"> • Full-scale evaluation: <ol style="list-style-type: none"> 1. Reductions in copper corrosion rate of 30% after adding 1 mg/L orthophosphate. 2. Lead corrosion reduction was nominal, approximately 10%. 3. Tap sampling results showed copper and lead reductions in first-draw samples of 47% and 40%, respectively. 4. Wastewater influent copper levels were noted to be reduced by 57%. • Demonstration flow-through testing <ol style="list-style-type: none"> 1. Optimum orthophosphate dose was 1.0 mg/L as PO₄. 2. Lead corrosion rates increased slightly when the pH was increased from 7.5 to 8.1. 3. A pH value of 7.7 was found to be optimum with dissolved oxygen concentrations of 0.4-6.0 mg/L. 4. Dissolved oxygen concentrations between 0.4 and 6 mg/L has little effect on corrosion rates in the presence of 1 mg/L orthophosphate.
b. Secondary Impacts	NA
c. Treatment Issues	NA
VI	Notes/Qualifications
VII	Reference(s) Powell, R.M. et al. 1991. Corrosion in Water Distribution Systems. AWWA/EPA Corrosion Control Seminar (Chicago, IL).

PWS Characterization: High pH, Alkalinity & Calcium
PWS Name & Location: Water District No. 1, Johnson County, Kansas

Item		Description
I	Case Study Number	9
II	PWS Description	
	a. Raw Water Supply	Kansas River and Missouri River
	b. Water Quality	
	1. Raw	High turbidity, hardness and alkalinity; Moderate pH.
	2. Treated	Finished water quality: pH 9.1, Total hardness 122 - 130 mg CaCO ₃ /L, Alkalinity 53 mg CaCO ₃ /L, TDS 300 mg/L, chloride 35-70 mg/L, sulfate 135-200 mg/L.
	c. Treatment	Lime softening, chloramination, and polyphosphate addition.
III	Corrosion Control Study Elements	
	a. Desk-top Evaluation	<ul style="list-style-type: none"> • Reviewed historical water quality data: raw, treated, and within the distribution system. • Removed several unlined fittings from the distribution system for visual inspection. • Reviewed technical literature about corrosion behavior for high pH waters. • Surveyed other lime softening utilities about corrosion problems encountered in their distribution systems. • Recommendation was to try to achieve calcium carbonate deposits for corrosion protection.
	b. Demonstration Testing	
	1. Flow-Through	NA
	2. Static	NA
	3. Full-Scale	Coupon inserts in distribution system during three phases of treatment modification.
	c. Full-Scale Confirmation	
	1. Tap sampling	NA
	2. WQP-DIS	NA
	3. WQP-POE	pH, alkalinity, calcium, temperature

PWS Characterization: High pH, Alkalinity & Calcium
PWS Name & Location: Water District No. 1, Johnson County, Kansas

Item	Description
IV	Testing Program Description
a. Constraints	Compatibility of treatment approach for lime softening facility. Polyphosphate addition was practiced for calcium sequestering prior to filtration to prevent excessive deposition on filter media.
b. Priorities	
1. Primary	Based on customer complaints, reduce iron corrosion.
2. Secondary	Determine if optimal corrosion for iron control would also benefit the District for lead and copper corrosion control.
c. Treatment Alternatives	Three phases of softening modification: 1. Phase 1 - Increase pH to 9.3; 2. Phase 2 - Increase pH to 9.5 and increase final alkalinity and calcium content to 140-160 mg CaCO ₃ /L and 90-110 mg CaCO ₃ /L, respectively. 3. Phase 3 - Increase pH to 9.8-10.0
d. Monitoring programs	Removal and replacement of mild steel coupons placed in-situ in the distribution system every 3-months. Finished water quality monitored to achieve goals of each treatment phase.
e. QA/QC Elements	NA
V	Testing Results
a. Corrosion Control Performance	<ul style="list-style-type: none"> • Phase 2 treatment corrosion rates were 35% lower than Phase 1 corrosion rates based on the mild steel coupon results. • A 40% decrease in customer complaints was observed overall (across Phases 1 and 2); however, complaints in areas of the service area composed of older, unlined cast iron mains showed little improvement.
b. Secondary Improvements	NA
c. Treatment Issues	NA
VI	Notes/Qualifications <ul style="list-style-type: none"> • The corrosion behavior of the distribution system is still be evaluated through the Phase 3 treatment modifications. • Elimination of the polyphosphate feed is being considered in order to improve the deposition of calcium carbonate.
VII	Reference(s) Goold, R.R. et al. 1991. Enhancing Distribution System Water Quality at Water District No. 1. Proc. Annual AWWA Conference (Philadelphia, PA).

Appendix C

Statistical Evaluation of Corrosion Control Performance Data

Non-parametric Statistics

The use of non-parametric statistical measures may assist PWSs in interpreting the findings of demonstration tests. These methods of data analysis are independent of the normality of data distributions, and provide measures of the relationship between distinct data populations. In applying the non-parametric methods to lead and copper testing results, the type of question which they may answer is: Is the population of lead levels from experimental condition 'A' higher, lower, or the same as those from experimental conditions 'B'?

The Wilcoxon Test (also known as the Mann-Whitney Test, the U-Test, or the Rank Sums Test) is a non-parametric alternative to the two sample Student's t-Test. Using the lead concentration data presented in the flow-through example in Section 4.9.1 (Table 4-8), the Wilcoxon Test may be used to select the treatment method which minimized lead levels in simulated first-flush samples. The problem may be stated as follows:

- Are the lead levels from Pipe Loop 1 larger than those from Pipe Loop 2?
- Are the lead levels from Pipe Loop 1 larger than those from Pipe Loop 3?
- Are the lead levels from Pipe Loop 2 larger than those from Pipe Loop 3?

By applying the Wilcoxon Test to answer the three questions above we

will be able to determine whether lime addition (Loop 2) or phosphate inhibitors (Loop 3) provide improvements in lead corrosion control, and whether either method is superior to the other.

The first step is to rank the two populations of data under evaluation as one set of data, from the smallest to the largest value. Table C-1 presents the results of ranking the lead concentration data for our three comparison conditions. Note that when a value occurs multiple times in the data base, the mean rank is assigned to each occurrence.

The next step is to sum the ranking for the data each of the populations. For example, Loop 1 and Loop 2 rankings were summed under the first comparison condition as shown in Table C-1, resulting in 1,504 and 979, respectively. The U-value may be calculated based on the sum of the ranks, W_i , and the number of observations, n_i , as follows:

$$U_i = W_i - n_i(n_i + 1)/2$$

with the statistic U being the smaller of U_1 and U_2 for any comparison condition. The mean and variance for any population of U values may be calculated as:

$$\text{Mean } U = n_1 * n_2 / 2$$

$$\text{Var } U = n_1 * n_2 * (n_1 + n_2 + 1) / 12$$

The U statistic approximates a normal distribution when both n_1 and n_2 are greater than 8.

To test the null hypothesis that the two data groups come from the same population, the z-statistic is calculated as a function of U, Mean U, and

Table C-1. Wilcoxon Test for Comparing Flow-Through Testing Results

Comparison 1 — Loop 1:2			Comparison 2 — Loop 1:3			Comparison 3 — Loop 2:3		
Pb.ppb	Rank	Loop	Pb.ppb	Rank	Loop	Pb.ppb	Rank	Loop
45	1	2	30	1	3	30	1	3
48	2	2	38	2	3	38	2	3
48	3	2	42	3	3	42	3	3
52	4	2	45	4	3	45	4.5	2
52	5	2	50	5	3	45	4.5	3
52	6	2	51	6	3	48	6.5	2
53	7	2	52	7	3	48	6.5	2
55	8	2	54	8	3	50	8	3
57	9	2	55	9	3	51	9	3
58	10	2	58	10	3	52	11.5	2
60	11.5	1	60	11	1	52	11.5	2
60	11.5	2	62	13	1	52	11.5	2
62	13	1	62	13	3	52	11.5	3
63	14	1	62	13	3	53	14	2
68	16	1	63	15	1	54	15	3
68	16	1	65	16.5	3	55	16.5	2
68	16	2	65	16.5	3	55	16.5	3
72	19.5	1	68	20.5	1	57	18	2
72	19.5	2	68	20.5	1	58	19	3
72	19.5	2	68	20.5	3	58	20.5	2
72	19.5	2	68	20.5	3	60	20.5	2
75	22.5	1	68	20.5	3	62	22.5	3
75	22.5	2	68	20.5	3	62	22.5	3
76	24	2	70	24	3	65	24.5	3
78	26	1	72	26	1	65	24.5	3
78	26	1	72	26	3	68	28	2
78	26	1	72	26	3	68	28	3
79	27.5	2	75	28	3	68	28	3
79	27.5	2	75	30	3	68	28	3
80	31	1	75	31	1	70	31	3
80	31	2	75	31	3	70	34	2
80	31	2	76	32	3	72	34	2
82	33	1	78	34.5	1	72	34	2
85	34.5	1	78	34.5	1	72	34	3
85	34.5	2	78	34.5	3	72	34	3
87	36.5	1	78	34.5	3	72	34	3
87	36.5	2	80	37.5	1	73	37	3
90	38	2	80	37.5	3	75	39	2
91	39	1	81	39	3	75	39	3
92	41	1	82	40.5	1	75	39	3
92	41	1	82	40.5	3	76	41.5	2
92	41	2	85	42	1	76	41.5	3

Table C Wilcoxon Tes for Comparing Flow-Through Testing Results (continued)

Comparison 1 — Loop 1:2			Comparison 2 — Loop 1:3			Comparison 3 — Loop 2:3		
Pb,ppb	Rank	Loop	Pb,ppb	Rank	Loop	Pb,ppb	Rank	Loop
95	43.5	1	87	43	1	78	43	3
95	43.5	2	91	44	1	79	44.5	2
96	45	2	92	45.5	1	79	44.5	2
97	46.5	1	92	45.5	1	80	47	2
97	46.5	2	95	47	1	80	47	2
100	48.5	1	97	48	1	80	47	3
100	48.5	2	98	49	3	81	49	3
103	50.5	1	100	50	1	82	50	3
103	50.5	2	102	51.5	3	85	51	2
107	52	1	102	51.5	3	87	52	2
108	53.5	2	103	53	1	90	53	2
108	53.5	2	107	54	1	92	54	2
110	55.5	1	109	55	3	95	55	2
110	55.5	2	110	56	1	96	56	2
112	57.5	1	112	57.5	1	97	57	2
112	57.5	1	112	57.5	1	98	58	3
115	59	1	115	59.5	1	100	59	2
118	60	1	115	59.5	3	102	60.5	3
125	61	1	118	61	1	102	60.5	3
126	62	1	125	62	1	103	62	2
130	63	2	126	63.5	1	108	63.5	2
132	64	1	126	63.5	3	108	63.5	2
135	65	2	132	65	1	109	65	3
138	66	1	138	66	1	110	66	2
162	67	1	162	67	1	115	67	3
175	68	1	175	68	1	126	68	3
190	69	1	190	69	1	130	69	2
205	70	1	205	70	1	135	70	2

StdDev U (STDDEV U = square root of Var U) as follows:

$$z = (U - \text{Mean } U) / \text{StdDev } U$$

Table C-2 presents sum of ranks, U values, and z values for the three comparison conditions for the lead concentration data from the flow through testing results using the above calculations.

To test the comparison conditions, the z values are evaluated with respect to z_α values for the alpha (i.e., α) level of significance desired. In the lead testing example, $Z_{\alpha,01} = 2.575$ was used to evaluate the three comparisons. When $z < -z_\alpha$, then the distribution of the data with the larger U value is said to be *stochastically* higher than the other population's distribution. For the first comparison condition, for example, the larger U value corresponded to Loop 1 data and the z value was less than $-z_\alpha$, then the lead levels found in the control loop (Loop 1) are higher than those found from the lime addition loop (Loop 2). Conversely, when $z > z_\alpha$, then the distribution of the data with the larger U value is said to be stochastically lower than the other population's distribution.

The results shown in Table C-2 indicate that Loop 2 and Loop 3 lead levels were significantly different from Loop 1 lead levels, but not significantly different from each other. Additionally, the z values show that Loop 1 (control) lead levels were higher than both Loop 2 and Loop 3 lead concentrations.

Parametric Statistics

Water quality measurements obtained during corrosion control studies will seldom represent the one true value

present at the time of sampling. Errors will be associated with both sampling techniques and analytical measurements. It is generally assumed that the errors indigenous to these measured values are random errors. Therefore, the mean of several values should be a better indicator of the true value than a single measurement.

The configuration in which the data are arranged is called its distribution, and many statistical procedures utilize a normal distribution in which the data are symmetrical and form a bell shaped curve. Parametric statistics make use of these procedures.

Most sample sets of water quality data do not exactly form a bell shaped curve, and they are sometimes "transformed" by the application of some mathematical function into another form which more closely follows a normal distribution. As an example of this procedure, the lead data used for the example of Section 4.9.1 (See Table 4-8) will be transformed into the log normal mode by using the log of the individual determinations.

Parametric statistics were used to compare the two treatments with the control. The data were investigated for skewness recognizing that as the moment coefficient of skewness approaches zero that the data approach a more normal distribution. If the distribution is normal, or can be made more normal by a transformation, the statistical techniques based on a normal distribution are appropriate; otherwise they are only approximations and the use of non-parametric statistics as presented previously in Appendix C may be more appropriate.

Table C-2. Summary of Wilcoxon Test Measures for Comparing the Performance of Lead Corrosion Control Alternatives

Condition	Measurements			
Sum of Ranks, W	Loop 1	Loop 2	Loop 3	
Comparison 1	1,504.0	979.0	----	
Comparison 2	1,612.5	----	874.5	
Comparison 3	----	1,366.0	1,199.0	
U — Values	Loop 1	Loop 2	Loop 3	Resultant
Comparison 1	874.0	349.0	----	349.0
Comparison 2	982.5	----	244.5	244.5
Comparison 3	----	736.0	569.0	569.0
Key Statistical Measures	Mean_U	Var_U	z	Finding
Comparison 1	612.5	7,248.0	-3.1	Loop 1 > Loop 2
Comparison 2	612.5	7,248.0	-4.3	Loop 1 > Loop 3
Comparison 3	612.5	7,248.0	-0.5	No Difference

The skewness coefficient, γ , is defined as:

$$\gamma = \frac{m_3}{m_2^{1.5}}$$

where:

$$m_2 = \frac{1}{n} \sum x_i^2 - \bar{x}^2$$

$$m_3 = \frac{1}{n} \sum x_i^3 - \frac{3}{n} \bar{x} \sum x_i^2 + 2\bar{x}^3$$

x_i = individual samples, $i = 1$ to n

\bar{x} = mean

Table C-3 gives the calculated means, moments, and skewness coefficients for the lead data of Table 4-8 for both normal and log normal distributions. The smaller coefficients for the log normal distribution were used as indicators that the data would more appropriately adapt to parametric statistics using a logarithmic transformation.

Table C-3. Skewness Coefficients

Normal:	Loop 1	Loop 2	Loop 3
mean	0.1038	0.0791	0.0711
m ₂	0.0012	0.0005	0.0005
m ₃	0.0001	5.83 x 10 ⁻⁶	5.76 x 10 ⁻⁶
γ	1.21	0.47	0.60
Log Normal:			
mean	-1.0058	-1.1204	-1.1683
m ₂	0.0182	0.0163	0.0178
m ₃	0.0013	-0.0001	-0.0007
γ	0.53	-0.04	-0.32

The student's t statistic was used to compare paired data among the three loops. These results are shown in both Table C-4 and Table 4-9. Student's t can be defined as:

$$t = \frac{\bar{d}}{s_d}$$

where the numerator represents the mean difference between paired sample data and the denominator represents the standard deviation appropriate to the difference between the sample means. These values are then compared to standard statistical tables to determine if there is a statistical difference in treatments.

Table C-4. Student's t Values

Comparison	t
Loop 1 and Loop 2	5.46***
Loop 1 and Loop 3	6.98***
Loop 2 and Loop 3	2.87**
Notes: All test data transformed to logarithmic values	
** Highly significant difference at the 0.01 level	
*** Extremely significant difference at the 0.001 level	

As indicated in the text of Section 4.9.1, the last 10 weeks of data were independently examined. These data are shown in Table C-5. Again, prior to conducting an examination of the data using the Student's t statistic, a log transformation was made, i.e.:

0.078 was used as $\log 0.078 = -1.1079$
 0.060 was used as $\log 0.060 = -1.2218$;
 etc.

Using Student's t and examining the paired data between loops for week 26 through week 35 gave the results

shown in Table C-6. Standard statistical tables were used to compare the t value against with the sign ignored, i.e., either a positive or negative value was acceptable. For 9 degrees of freedom (10 sets of data minus 1), the t statistics are:

- t @ 0.05 level = 2.262
Significant difference
- t @ 0.01 level = 3.250
Highly significant difference
- t @ 0.001 level = 4.781
Extremely significant difference

Table C-5. Lead Data from Final 10 Weeks of Testing

Week No.	Loop 1	Loop 2	Loop 3
26	0.078	0.080	0.080
27	0.060	0.052	0.062
28	0.092	0.058	0.054
29	0.075	0.045	0.058
30	0.087	0.053	0.045
31	0.063	0.060	0.052
32	0.072	0.055	0.068
33	0.068	0.052	0.030
34	0.080	0.048	0.051
		0.057	

Table C-6. Calculate Student's t Values for Final 10 Weeks

Comparison	t
Loop 1 and Loop 2	4.88**
Loop 1 and Loop 3	3.60**
Loop 2 and Loop 3	0.67, not significant
Notes: All test data transformed to logarithmic values	
** t value > 3.25, highly significant difference	

Thus the analysis shows that each treatment is significantly different from the control, but there is no apparent statistical difference between treatments.