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Revised Guidance Manual for Selecting Lead and Copper Control Strategies

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# List of Acronyms and Abbreviations

C/L	Carbon per liter
Ca	Calcium
CaCO <sub>3</sub>	Calcium carbonate
ССТ	Corrosion control treatment
CO <sub>3</sub> <sup>2-</sup>	Carbonate ion
Cu	Copper
DIC	Dissolved inorganic carbon
DBP	Disinfection byproduct
HCO <sub>3</sub> -	Bicarbonate ion
LCR	Lead and Copper Rule
MDBP	Microbial and Disinfection Byproducts Rules
mg/kg	Milligrams per kilogram
μg/L	Micrograms per liter
mg/L	Milligrams per liter
OGWDW	Office of Ground Water and Drinking Water
Р	Phosphate
Pb	Lead
$\mathrm{PO}_4^{-}$	Orthophosphate
THMs	Trihalomethanes
WQP	Water quality parameter

# **Revised Guidance Manual for Selecting** Lead and Copper Control Strategies

### Foreward

In 1996, the Office of Ground Water and Drinking Water (OGWDW) of the U.S. Environmental Protection Agency was interested in developing a simple guidance that could be used by regulators, small water systems, and their engineers to aid in initially determining what treatment approaches for lead and copper control would have the best chance of success. The original document, *Guidance Manual for Selecting Lead and Copper Control Strategies*, was prepared in January of 1997.

In the five years since the completion of the manual, many water systems have successfully employed corrosion control treatment to achieve compliance with the Lead and Copper Rule. However, the information in the manual is still timely and relevant, because some systems still have difficulty in sufficiently reducing lead and copper corrosion, and other systems may need to change water treatment approaches because of other regulatory issues or changes in water sources. In particular, groundwater systems in the midwest with neutral pH value, high hardness, and high alkalinity water have had difficulty meeting the copper action level. Thus, corrosion control for lead and copper has been revisited in the context of these considerations.

EPA decided to take advantage of the considerable corrosion control treatment experience that had been gained over the past five years to refine (or even sometimes correct) the recommendations for treatment selection. The manual has been updated with:

- Information on aeration and limestone contactors for corrosion control;
- The most successful treatments for copper corrosion control in high alkalinity/high dissolved inorganic carbonate (DIC) waters;
- Tradeoffs of corrosion control with iron and manganese removal; and
- Considerations for corrosion control in light of the new (1994) water quality based standards for wastewater treatment.

In addition, the document has been streamlined to make it more responsive to users. Thus, this manual has been revised and edited to help provide readers with the best general screening-level guidance that current knowledge permits.

Data were gathered from a number of sources and State contacts were very valuable to this effort. We would like to acknowledge:

- Ron Cramer, Kansas Department of Health
- Steve Jillson, Environmental Engineer I and Steve Drda, Monitoring and Compliance Coordinator, Nebraska Health and Human Services
- James Melstad, Montana Department of Environmental Quality
- Robin Michaels, Arkansas Department of Health
- John R. Payne, Colorado Department of Health
- Lih-In Rezania, P.E., Public Health Engineer, Minnesota Department of Health.

#### Introduction

The objective of this manual is to assist water systems and regulatory agencies with selecting and approving effective treatment strategies for controlling lead and copper in drinking water. The selection of a treatment strategy for lowering lead, copper, or lead and copper levels in drinking water from corrosion of plumbing materials depends on numerous site-specific factors that cannot be addressed in this manual. Therefore, to address these site-specific factors, water systems should seek out the advice of water treatment professionals when selecting a treatment strategy.

### Why should we monitor for lead and copper?

The National Primary Drinking Water Regulations for Lead and Copper (also called the Lead and Copper Rule or LCR) became effective in 1991. The LCR requires all community and non-transient non-community water systems to monitor for lead and copper at a specified number of taps within homes and/or buildings served by that water system. It also establishes treatment technique requirements including corrosion control treatment, source water treatment, lead service line replacement, and public education. These requirements may be triggered if more than 10 percent of tap water samples collected during any monitoring period exceed the lead action level and/or the copper action level. The action level for lead is 0.015 mg/L. The copper action level is 1.3 mg/L.

Lead and copper are being regulated because of the possible negative health effects associated with drinking water containing these two contaminants. Health effects associated with exposure to lead in infants and young children include lower birth weight and a slowing down of normal physical and mental development which may result in lower IQ levels, damaged hearing, reduced attention span and poor classroom performance. Impacts to adults may include kidney damage, slight increases in blood pressure, and damage to the reproductive system. In addition, high levels of nitrate may magnify these adverse health effects.

While drinking water with high levels of copper should not cause long-term health effects like lead, high copper levels in drinking water can cause very uncomfortable gastrointestinal effects such as nausea and diarrhea, and can magnify adverse effects of nitrate ingestion, especially in children.

## Why do we need to sample tap water?

High levels of lead and copper are rarely found in the water that a water system provides to its customers. The main sources of lead and copper in drinking water usually are plumbing materials made from copper; lead service lines and lead solder, commonly used before 1990 to join lengths of copper pipe together; and faucets containing brass or bronze internal parts, which usually contains lead impurities. Under the 1996 Amendments to the Safe Drinking Water Act, "lead free" brass can contain as much as 8 percent lead by weight, which is enough to contribute significant amounts to lead to tap water samples. If the water provided by your water system is highly or even moderately corrosive, some of the lead and/or copper in the plumbing materials may be released into the drinking water in houses or buildings served by your water system.

A sampling program that measures lead and copper levels at the tap helps to determine if a water system is providing corrosive water. Those water systems found to be providing corrosive water are required to install corrosion control treatment to lower the corrosivity of the water, which should then result in lower lead and copper levels at the users' taps.

## What do we do next?

The federal Lead and Copper Rule requires all water systems that have exceeded the lead action level, the copper action level, or both action levels to recommend a corrosion control treatment method that will minimize lead and copper levels at users' taps. In addition, water systems may be required to perform corrosion control studies to evaluate the most effective corrosion control treatment method. The objective of this guidance manual is to assist small water systems with selecting the appropriate treatment strategy and to provide assistance to State regulatory agencies that approve treatment plans for the water systems within their jurisdiction.

# Background on Corrosion Control for Lead and Copper

Lead and copper entering drinking water from household plumbing materials such as pipes, lead solder and faucets containing brass or bronze, can be controlled by changing water quality characteristics. The water quality factors that have the greatest affect on lead and copper corrosion are pH, dissolved inorganic carbonate (DIC), orthophosphate concentration, alkalinity, and buffer intensity. Dissolved oxygen and/or chlorine residual are also important considerations for copper. There are many other factors that affect the corrosion of lead and copper, but they cannot be easily altered by a water system and have a lesser effect on corrosion. Alkalinity, which is interrelated with pH and DIC, is often measured by water systems. Buffer intensity, which is also interrelated with pH and DIC, is an additional parameter that is very important in maintaining optimal corrosion control and water quality out in the distribution system.

#### pН

The pH of a water is a measure of acidity, otherwise known as hydrogen ion concentration (H<sup>+</sup> or H<sub>3</sub>O<sup>+</sup>). pH values can range from 0 to14, and the lower the value the more acidic the water. Most drinking waters range from 6 to 10. One common corrosion control treatment strategy is to raise the pH of the source water. This can be done through chemical or non-chemical means. Any increase in pH within the pH range of 5 to 10 should result in a decrease in lead and copper levels. At the higher pHs, there is less tendency for lead and copper to dissolve and enter drinking water. The pH of water can vary significantly as water moves through the distribution system. Although the pH measured at the pump station or treatment facility may appear to be stable, as it passes through the distribution system, flow rate, age and type of plumbing material. It is important to maintain the target pH throughout the distribution system, so that lead and copper levels can be minimized at the tap.

#### Alkalinity

Alkalinity is the capacity of water to neutralize acid. It is the sum of carbonate, bicarbonate and hydroxide anions. Alkalinity is typically reported as mg/L "as calcium carbonate" (CaCO<sub>3</sub>). Low alkalinity water will not neutralize acids well, while high alkalinity water will. For most surface waters, alkalinity varies with the seasons as snow melt or spring rain runoff decreases alkalinity; algal growth can affect alkalinity as can drought. Groundwater alkalinity tends to be more stable. Waters with high alkalinities also tend to have high buffering capacities, or in other words, a strong ability to resist changes in pH brought about by chemical dosing or water quality changes in the distribution system.

#### Dissolved Inorganic Carbonate (DIC)

DIC is an estimate of the amount of total carbonates in the form of carbon dioxide gas (CO<sub>2</sub> or  $H_2CO_3$ ), bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), and carbonate ion (CO<sub>3</sub><sup>-2</sup>) in a particular water. It is measured as milligrams of carbon per liter (mg C/L). DIC is related to alkalinity in that if you know the pH and alkalinity of a water, you can predict the DIC. The level of DIC affects levels of lead and copper and affects the stability of the pH. The amount of DIC relates to the buffering of the water. The buffering of a water is its ability to resist a change in pH. If a water has minimal DIC, then the pH may fluctuate significantly. Because of the high sensitivity of copper and lead to pH, the improved pH control of a minor DIC increase to raise buffering (i.e., 3-6 mg C/L) offsets potential increases in copper levels. Therefore, balancing the amount of DIC for lead, copper, and buffering is an important part of corrosion control.

At a constant pH, as the DIC increases, copper levels should increase. The effect of DIC is not as strong as the effect of pH until high (> 30 mg C/L) levels of DIC are reached, when pH adjustment stops being an effective treatment approach. Increases in DIC of 3-6 mg C/L will typically have minimal impact on copper levels, particularly with respect to the regulatory action level. In contrast, for control of lead, as the DIC increases the lead concentration decreases or remains essentially unchanged within the pH range of about 7.0 to 8.0. At higher pHs there will

be very little impact of DIC on lead levels or there may be a very slight increase in lead levels with increasing DIC.

#### Hardness

Hardness is a measure of the amount of calcium and magnesium in the water. Hardness is usually measured with the combined calcium and magnesium and reported "as CaCO<sub>3</sub>", that is as calcium carbonate. Obtaining calcium data as mg/L is also very helpful or an estimate of calcium levels can be made from hardness "as CaCO<sub>3</sub>" data by dividing the hardness number by 2.5. The calcium and magnesium compounds can interfere with corrosion control efforts because they are less soluble at higher pH values than at lower pHs. Hardness must be taken into consideration when corrosion control is selected and implemented because it can cause unintended side affects such as increased scaling, both within the pump station/treatment plant or out in the service area.

#### Orthophosphate

Orthophosphate ( $PO_4$ ) added as a corrosion control treatment chemical can combine with lead and copper in plumbing materials to form several different compounds. These compounds do not have a strong tendency to dissolve. As a result, lead and copper levels in the water will remain low. The key to ensuring that orthophosphate will reduce lead and copper levels is to maintain the proper pH and orthophosphate residual. Residual orthophosphate is the free amount of orthophosphate measured in the distribution system. It is very important for most water systems to maintain a residual of at least 0.5 mg/L orthophosphate as phosphate (P) and if, possible a residual of 1 mg/L as P is preferable. In many cases, water systems maintain a residual that is too low, thus making the orthophosphate treatment ineffective. When using orthophosphate for lead and copper control, the pH should be maintained within the range of 7.2-7.8. If the pH is too low, even high dosages of orthophosphate will not work. At high pH, poor corrosion-protecting film stability has often been observed. Much higher concentrations are often needed to resolve copper problems than lead problems. Treatment chemicals containing zinc will help protect cement and cement mortar-lined pipes. When copper or zinc concentrations in wastewater discharge or sludge are of concern, pH/DIC adjustment to control copper corrosion is usually preferable if feasible for the water quality.

#### **Buffer Intensity**

Buffer intensity is a measure of the resistance of a water to changes in pH, either up or down. Bicarbonate and carbonate ions are the most important buffering species in almost all drinking waters. At high pH (over 9), silicate ions also supply buffering. Phosphate contributions are normally insignificant as long as DIC is approximately 5 mg/L as C or greater. Buffering is normally greatest at approximately pH 6.3, decreases towards a minimum at a pH of between about pH 8 and 8.5, and then again gets increasingly higher as pH goes above 9. Thus, treated waters in this very low buffer intensity pH range (8 - 8.5) tend to have highly variable pH in the distribution network. This is aggravated in waters that have very low amounts of DIC (less than about 10 mg C/L). Waters with low buffer intensity are prone to pH decreases from such sources as uncovered storage, nitrification, corrosion of cast iron pipe, and pH increases from

contact with cement pipe surfaces. Maintaining sufficient buffering is very important when using orthophosphate addition or pH adjustment, because copper and lead control require particular pH ranges to be effective. Even if the pH of the water leaving the treatment plant is correct, pH changes in the distribution system may nullify the intended corrosion control treatment.

#### Dissolved Oxygen/Chlorine Residual

Dissolved oxygen is a measure of the amount of oxygen dissolved in water. Oxygen is slightly soluble in water, seldom reaching concentrations exceeding 15 mg/L and in some ground waters, it is absent or below detection levels. However, adding dissolved oxygen can have a great effect on water quality as it oxidizes dissolved reduced iron and manganese (more slowly) and forms more soluble copper compounds than waters with no dissolved oxygen. This is a consideration for aeration for either iron oxidation or for corrosion control. The benefits of carbon dioxide removal and pH rise from aeration must be balanced against the possibility of creating soluble copper in the distribution system from increased dissolved oxygen addition.

The addition of chlorine to a groundwater source that has low dissolved oxygen has the same effect as adding dissolved oxygen on the chemistry of the water. Systems that have to add chlorine to meet the Groundwater Disinfection Rule may find increased copper corrosion, necessitating a revision of corrosion control.

# **Directions for Making Treatment Determinations**

Selecting viable a treatment option for controlling lead and copper is a five-step process:

- **Step 1: Examine the lead and copper data.** Because small water systems collect so few samples, it is important to ensure that an action level exceedance is due to corrosive water, rather than some other cause. Water with pHs greater than 7.8 and with alkalinities between 30 and 100 mg  $CaCO_3/L$  would generally not be considered corrosive. (Water with an alkalinity greater than 100 mg  $CaCO_3/L$  is frequently highly corrosive toward copper.) If the water quality data are in the non-corrosive range but there are some unusual lead or copper numbers, then the possibility of re-sampling or materials replacement should be discussed with the primacy agency. A few minutes educating customers regarding proper sampling for lead and copper may save extensive and expensive adjustment of the treatment.
- Step 2: Collect accurate and sufficient background chemistry information to characterize the water and anticipate future regulatory requirements. Although it initially appears to be expensive to collect many water samples and analyze a broad range of water quality constituents, doing so can save tens or hundreds of thousands of dollars of added expenses later in revising treatment plants or adding new processes that were not anticipated. Having very accurate pH and alkalinity/DIC data is absolutely necessary to know the feasibility of such simple treatments as aeration or limestone contactors, and also the cost associated with chemical additions and chemical delivery systems. Having good calcium, magnesium, sulfate, iron, manganese, and other water quality data may help in defining constraints to pH adjustment, phosphate dosing, use of packed tower aerators, membranes or other processes, because of scale buildup issues. Knowing whether or not arsenic or radon are present in the source water will dictate corrosion control treatments which are compatible with the removal processes, and this can be planned and done at once. For example, radon can readily be removed by aeration, which can also be used for substantial pH adjustment for corrosion control, so chemical feeds may not be necessary. However, a complication to both might be the presence of iron or manganese, so a combination of a removal process or filtration following oxidation (aeration/disinfection) might be cost-effective and would eliminate the need for sequestration. Similarly, some arsenic removal processes may coincide with iron removal and simplify the corrosion control chemistry treatment. For surface water or blended surface/ground water systems, knowledge of the potential for disinfection byproduct formation or microbial concerns could change the corrosion control approach. There are many other possible interactions, and the water system should try to anticipate as many future regulatory water quality requirements and treatment selection influences as possible.
- Step 3: Once accurate water quality data are known, a) look up the DIC of your water in Table 3 on pages 13 - 17 based on raw water pH and alkalinity; b) Determine the highest pH that you can achieve with your water without creating scaling conditions using your hardness data and Figure 1 on page 18; and c) Use one of the five attached sets of treatment recommendation flow chart sheets to select treatment options (see Section 1). The treatment recommendation flow charts suggest appropriate

water quality modifications based on the limited amount of water quality information available to the water system. Treatment strategies not suggested by the flow charts for a particular set of water quality characteristics should be avoided.

Increasing the pH of a water that contains calcium may promote the precipitation of calcium carbonate. In some circumstances, precipitation of calcium carbonate can clog hot water heaters and produce cloudy water. To limit the problems associated with calcium precipitation, the pH at which calcium is likely to precipitate can be estimated by use of Figure 1. The pH of calcium precipitation is estimated by finding the point on the figure that corresponds to the DIC and calcium level. The calcium must be expressed as calcium (Ca) and not calcium carbonate (CaCO<sub>3</sub>). Note that maintaining the pH below the level estimated on the chart should minimize, not eliminate, the potential for precipitating calcium carbonate. In many cases, it will be possible to exceed the estimated pH levels without having a calcium precipitation problem because the precipitation of calcium is affected by many factors, such as temperature and other dissolved metals.

- Step 4: Once the treatment option(s) are selected from the treatment recommendation flow charts, use the "Water Treatment Considerations" (see Section 2) to determine if there are other restricting factors. If all of the conditions are not met for a particular treatment, then that strategy should be discarded.
- Step 5: If there is more than one viable treatment option remaining, examine each option with regard to secondary impacts, the operability of the system (see Section 3) and costs. In some cases, several different treatment options will be available to a particular water supply. As a result, some water systems will be able to select the most appropriate treatment option based on system configuration, economics, simplicity, reliability, operations, and other site-specific factors. Consideration will also need to be given to impacts of drinking water treatment chemicals on wastewater discharge limits, or concentrations of metals in sludge.

As EPA has moved toward water quality-based limits for wastewater treatment plant effluents since 1994, permissible levels of many of the metals in effluents have been reduced to well below the drinking water standards. Example water quality based effluents for copper, lead, and zinc are listed in Table 1 with the drinking water standards for these metals presented for contrast. The range in limits permitted for these metals are based on the designated use for the receiving water and the total hardness of the receiving water.

Table 1: Metals Limits in Drinking Water and Wastewater Effluents*							
Metal	Drinking Water Limit (μg/L)	Wastewater Limit (µg/L)					
Copper	1,300	6.4 - 65					
Lead	15	1.3 - 956					
Zinc 5,000 59 - 758							
*From NPDES Permit Writers Manual, 1996							

Removal of metals from the waste water to the sludge does provide some way to reduce metals in the wastewater effluent but, depending on the final residual (sludge) disposal method, there are limits for metals in sludges also. Land applied residuals must meet the pollutant concentration limits outlined in Table 2.

Table 2: Metals Limits in Land Residual*								
Metal	Pollutant Concentration Limit (mg/kg)							
Arsenic	41							
Cadmium	39							
Chromium	1,200							
Copper	1,500							
Lead	300							
Mercury	17							
Nickel	420							
Selenium	36							
Zinc	2,800							
*From A Plain English Guide to Part 503 Rule, 1994								

Thus, many wastewater utilities have found that preventing metals from getting into the wastewater stream has proven more cost-effective than trying to remove them. Some wastewater utilities have gone so far as to provide some of the funding to their water utility to support corrosion control efforts rather than construct improved metals removal treatment at the wastewater treatment plant.

Another consideration for wastewater treatment plants is nutrient limits in wastewater effluents. Nutrients are nitrogen and phosphates in the wastewater effluents that can promote overgrowth of algae or aquatic plants in receiving waters. On the other hand, phosphate inhibitor addition can be a significant benefit for corrosion control for water utilities.

Detailed discussion of all aspects pertinent to selection of optimal corrosion control are beyond the scope of this document, but should be thoroughly addressed by all water systems as appropriate.

#### Section 1 – Flow Chart Treatment Determinations

At the end of this section, the user will find five sets of flow charts that can be used to determine treatment approaches depending on whether the system has exceeded the lead action level, the copper action level or both and whether the system treats for iron/manganese removal. Select the set that corresponds to your system as follows:

- 1. Exceeded lead and copper action level sheets 1A, 2A, 3A
- 2. Exceeded lead action level sheets 1B, 2B, 3B
- 3. Exceeded copper action level sheets 1C, 2C, 3C
- 4. Exceeded either of the action levels, have elevated source water iron and manganese levels, and iron and manganese removal treatment sheets 1D and 2D
- 5. Exceeded either of the action levels, have elevated source water iron and manganese but do not have iron/manganese removal treatment sheets 1E and 2E.

Before using the flow charts, you will need to read the following information and calculate the DIC and highest treatment pH value for your water hardness as described below. The selection of a corrosion control treatment option will be dependent on the pH, alkalinity, DIC, and other water quality data such as calcium, iron, and manganese. Invalid water quality data can result in the misapplication of a treatment strategy. Note that as treatments are applied, particularly pH adjustment, your position and choices may move to another chart. Note also that the presence of iron or manganese removal treatment alters the proposed corrosion control treatment for those systems with iron and/or manganese in the raw water. At higher pH values, both iron and manganese oxidation rates rise dramatically, with the potential to improve removal of these metals if the pH is raised before the filtration step.

**pH Measurements** – field pH is the most critical variable for determining treatment options. Many factors affect pH measurements. The following are some of the most significant.

- 1. *The pH instrumentation and calibration.* Many pH-measuring devices do not allow for appropriate calibration. Calibration of the pH probe should be performed with 3 standards at pH = 4, pH =7, and pH= 10. Calibration should also be performed prior to each set of analyses.
- 2. *Aeration of the sample.* Loss or introduction of carbon dioxide can greatly affect the pH of the sample, almost immediately. The pH should be measured on-site (in the field) with extreme care being taken not to shake the sample, stir rapidly, or to expose the water to the atmosphere if it can be avoided. The use of small flasks and rubber stoppers bored out and fit around electrodes have been found to be very useful for minimizing the substantial errors that can result in pH from only a few minutes of contact of ground waters with excess carbon dioxide or pH adjusted waters with the air. (See: "Laboratory Techniques for Measurement of pH for Corrosion Control Studies and Water not in Equilibrium with the Atmosphere." Jour. AWWA, 72:5:304, 1980).

3. *Water Quality Variations.* pH may vary depending upon the time of day, the season, or in response to precipitation. For well supplies, the pH may vary depending on how long the pump has been running. It is critical to examine when the samples were collected and over what time period. If the water source varies seasonally as a function of precipitation or temperature it would be important to have data over the period of the entire seasonal cycle.

**Alkalinity** – The laboratory that performs the alkalinity analysis should report the data in the form mg/L as CaCO<sub>3</sub>".

**DIC Calculation** - DIC affects levels of lead and copper levels and plays an important role in stabilizing pH. The DIC is calculated by using Table 3, which was developed with good approximations for many water conditions. Determine the DIC by reading corresponding pH and alkalinity values measured by the water system.

Once the DIC has been determined, calculate the highest pH that can be achieved with your particular water given the hardness of the water.

**Hardness** – As pH is raised, calcium and magnesium compounds become less soluble and can scale. Determine the highest pH that can be achieved with your water using Figure 1 on page 18 by placing a horizontal line at your calcium level (i.e., hardness value divided by 2.5) and a vertical line at your DIC value. The point at which the two lines cross is the pH value at which scaling can occur. If the point is between two pH values, the lower pH value would be most conservative to use.

The treatment sheets begin on page 19. They are presented as described in the beginning of this section. The suggested treatment chemicals are listed in the order of most appropriate for most systems, with alternates or more complex options listed below. For example, in Sheet 1A, for systems that exceeded the lead action level and have DIC of <5 mg C/L, soda ash is the pH adjustment chemical that would be the most widely applicable treatment chemical, though all the other options should be reviewed to see which may be the most cost effective.

	Table 3: Dissolved Inorganic Carbonate Determination (DIC mg C/L)for Systems with pH of 4.6 to 7.4 and Alkalinities of 0 to 100For a Purely Carbonate+H <sub>2</sub> O Closed System at 10°C (50°F); Ionic Strength = 0.005 (TDS @ 200 or Cond. @ 312)														
Alpha H <sub>2</sub> CO <sub>3</sub> *	0.98	0.97	0.96	0.94	0.91	0.86	0.79	0.71	0.60	0.49	0.38	0.28	0.20	0.13	0.09
Alpha HCO <sub>3</sub> -	0.02	0.03	0.04	0.06	0.09	0.14	0.21	0.29	0.40	0.51	0.62	0.72	0.80	0.87	0.91
Alpha CO <sub>3</sub> =	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
рН	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	6.2	6.4	6.6	6.8	7.0	7.2	7.4
Alkalinit	y (as CaCC	D <sub>3</sub> )													
0	19	8	3	1	1	0	0	0	0	0	0	0	0	0	0
5	93	55	33	21	13	9	6	4	3	2	2	2	1	1	1
10	167	102	64	40	26	17	12	8	6	5	4	3	3	3	3
15	241	149	94	60	39	26	18	12	9	7	6	5	4	4	4
20	316	197	124	79	52	34	23	16	12	9	8	7	6	6	5
25	390	244	154	99	64	43	29	21	15	12	10	8	7	7	7
30	464	291	185	119	77	51	35	25	18	14	12	10	9	8	8
35	539	339	215	138	90	60	41	29	21	17	14	12	10	10	9
40	613	386	245	158	103	68	47	33	24	19	15	13	12	11	11
45	687	433	276	177	116	77	52	37	27	21	17	15	13	12	12
50	761	480	306	197	128	85	58	41	30	24	19	17	15	14	13
55	836	528	336	216	141	94	64	45	33	26	21	18	16	15	14
60	910	575	366	236	154	102	70	49	36	28	23	20	18	17	16
65	984	622	397	255	167	111	76	53	39	31	25	22	19	18	17
70	1058	670	427	275	179	119	81	58	43	33	27	23	21	19	18
75	1133	717	457	295	192	128	87	62	46	35	29	25	22	21	20
80	1207	764	488	314	205	136	93	66	49	38	31	27	24	22	21
85	1281	812	518	334	218	145	99	70	52	40	33	28	25	24	22
90	1355	859	548	353	231	153	105	74	55	42	35	30	27	25	24
95	1430	906	578	373	243	162	110	78	58	45	37	32	28	26	25
100	1504	953	609	392	256	170	116	82	61	47	39	33	30	28	26

	Table 3: Dissolved Inorganic Carbonate Determination (DIC mg C/L)   for Systems with pH of 4.6 to 7.4 and Alkalinities of 110 to 400														
	For a Purely Carbonate+H <sub>2</sub> O Closed System at 10°C (50°F); Ionic Strength = 0.005 (TDS @ 200 or Cond. @ 312)														
Alpha H <sub>2</sub> CO <sub>3</sub> *	0.98	0.97	0.96	0.94	0.91	0.86	0.79	0.71	0.60	0.49	0.38	0.28	0.20	0.13	0.09
Alpha HCO <sub>3</sub> -	0.02	0.03	0.04	0.06	0.09	0.14	0.21	0.29	0.40	0.51	0.62	0.72	0.80	0.87	0.91
Alpha CO <sub>3</sub> =	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
рН	4.6	4.8	5	5.2	5.4	5.6	5.8	6	6.2	6.4	6.6	6.8	7.0	7.2	7.4
Alkalinity	y (as CaCC	<b>D</b> <sub>3</sub> )													
110	1652	1048	669	431	282	187	128	90	67	52	42	37	33	30	29
120	1801	1143	730	470	307	204	140	99	73	57	46	40	36	33	32
130	1949	1237	790	510	333	221	151	107	79	61	50	43	39	36	34
140	2098	1332	851	549	358	238	163	115	85	66	54	46	42	39	37
150	2247	1426	912	588	384	255	174	123	91	71	58	50	45	41	39
160	2395	1521	972	627	409	272	186	132	97	75	62	53	48	44	42
170	2544	1616	1033	666	435	289	198	140	103	80	66	56	51	47	45
180	2692	1710	1093	705	461	306	209	148	109	85	69	60	54	50	47
190	2841	1805	1154	744	486	323	221	156	115	90	73	63	57	53	50
200	2989	1899	1214	783	512	340	232	164	121	94	77	66	60	55	53
220	3319	2130	1323	881	587	377	264	185	135	108	85	73	66	61	58
240	3619	2312	1443	961	641	412	288	202	148	118	93	80	72	67	63
260	3919	2504	1563	1041	694	446	312	219	160	127	101	87	78	73	68
280	4219	2696	1683	1121	747	480	336	236	172	137	108	93	84	78	74
300	4519	2888	1803	1201	801	515	360	253	185	147	116	100	90	84	79
320	4819	3080	1923	1281	854	549	384	270	197	157	124	107	96	89	84
340	5119	3272	2043	1361	907	583	408	286	209	167	132	113	102	95	90
360	5419	3464	2163	1441	961	617	432	303	222	176	139	120	108	100	95
380	5719	3656	2283	1521	1014	652	456	320	234	186	147	127	114	106	100
400	6019	3848	2403	1601	1067	686	480	337	246	196	155	133	120	112	105

	Table 3: Dissolved Inorganic Carbonate Determination (DIC mg C/L) for Systems with pH of 7.6 to 10.4 and Alkalinities of 0 to 100For a Purely Carbonate+H2O Closed System at 10°C (50°F); Ionic Strength = 0.005 (TDS @ 200 or Cond. @ 312)														
Alpha H <sub>2</sub> CO <sub>3</sub> *	0.06	0.04	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alpha HCO <sub>3</sub> -	0.94	0.96	0.97	0.98	0.98	0.98	0.97	0.95	0.93	0.90	0.84	0.77	0.68	0.58	0.46
Alpha CO <sub>3</sub> =	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.04	0.07	0.10	0.16	0.23	0.32	0.42	0.54
pН	7.6	7.8	8	8.2	8.4	8.6	8.8	9	9.2	9.4	9.6	9.8	10	10.2	10.4
Alkalinity	(as CaCO	3)													
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1
5	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0
10	3	2	2	2	2	2	2	2	2	2	2	2	2	1	1
15	4	4	4	4	4	4	3	3	3	3	3	3	2	2	2
20	5	5	5	5	5	5	5	5	4	4	4	4	3	3	2
25	6	6	6	6	6	6	6	6	6	5	5	5	4	4	3
30	8	7	7	7	7	7	7	7	7	6	6	6	5	5	4
35	9	9	9	8	8	8	8	8	8	8	7	7	6	5	5
40	10	10	10	10	10	9	9	9	9	9	8	8	7	6	6
45	11	11	11	11	11	11	11	10	10	10	9	9	8	7	6
50	13	12	12	12	12	12	12	11	11	11	10	10	9	8	7
55	14	14	13	13	13	13	13	13	12	12	11	11	10	9	8
60	15	15	15	15	14	14	14	14	13	13	12	12	11	10	9
65	17	16	16	16	16	15	15	15	15	14	13	13	12	11	9
70	18	17	17	17	17	17	16	16	16	15	14	14	12	11	10
75	19	19	18	18	18	18	18	17	17	16	15	14	13	12	11
80	20	20	20	19	19	19	19	18	18	17	16	15	14	13	12
85	22	21	21	21	20	20	20	20	19	18	18	16	15	14	13
90	23	22	22	22	22	21	21	21	20	19	19	17	16	15	13
95	24	24	23	23	23	23	22	22	21	21	20	18	17	16	14
100	25	25	24	24	24	24	23	23	22	22	21	19	18	16	15

	Table 3: Dissolved Inorganic Carbonate Determination (DIC mg C/L)   for Systems with pH of 7.6 to 10.4 and Alkalinities of 110 to 400														
	For a Purely Carbonate+H <sub>2</sub> O Closed System at 10°C (50°F); Ionic Strength = $0.005$ (TDS @ 200 or Cond. @ 312)														
Alpha H <sub>2</sub> CO <sub>3</sub> *	0.06	0.04	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alpha HCO <sub>3</sub> -	0.94	0.96	0.97	0.98	0.98	0.98	0.97	0.95	0.93	0.90	0.84	0.77	0.68	0.58	0.46
Alpha CO <sub>3</sub> =	0.00	0.00	0.00	0.01	0.01	0.02	0.03	0.04	0.07	0.10	0.16	0.23	0.32	0.42	0.54
рН	7.6	7.8	8	8.2	8.4	8.6	8.8	9	9.2	9.4	9.6	9.8	10	10.2	10.4
Alkalinit	y (as CaCO	D <sub>3</sub> )													
110	28	27	27	27	26	26	26	25	25	24	23	21	20	18	16
120	30	30	29	29	29	28	28	28	27	26	25	23	22	20	18
130	33	32	32	31	31	31	30	30	29	28	27	25	23	21	20
140	36	35	34	34	34	33	33	32	31	30	29	27	25	23	21
150	38	37	37	36	36	36	35	35	34	33	31	29	27	25	23
160	41	40	39	39	38	38	37	37	36	35	33	31	29	27	24
170	43	42	42	41	41	40	40	39	38	37	35	33	31	28	26
180	46	45	44	44	43	43	42	41	40	39	37	35	33	30	27
190	48	47	46	46	46	45	44	44	43	41	39	37	34	32	29
200	51	50	49	48	48	47	47	46	45	43	41	39	36	33	31
220	55	54	54	53	53	52	51	51	49	48	45	43	40	37	34
240	60	59	59	58	58	56	56	56	54	52	50	47	43	40	37
260	65	64	63	63	62	61	61	61	58	57	54	51	47	43	40
280	70	69	68	68	67	66	65	65	63	61	58	54	51	47	43
300	75	74	73	73	72	71	70	70	67	65	62	58	54	50	46
320	81	79	78	77	77	75	75	75	72	70	66	62	58	54	49
340	86	84	83	82	82	80	79	79	76	74	70	66	62	57	52
360	91	89	88	87	86	85	84	84	81	78	74	70	65	60	55
380	96	93	93	92	91	89	89	89	85	83	78	74	69	64	59
400	101	98	98	97	96	94	93	93	90	87	83	78	72	67	62

#### Table 3 Footnotes

Constants For DIC Calculations at 10°C

	TEMP Farenheight	49.986
	TEMP Centigrade	10.0
	TEMP Kelvin	283.15
	TDS mg/L	200.0
	CONDUCT	312.0
	ION STRENGTH	0.0050
"A"-Davies' Single Ion Activity Constant		0.4976
Activity Correct Factors	log f0- undissoc./no charge	0.0005
	log fm-monovalent	-0.0392
	log fd-divalent	-0.1522
Equilibrium Constants	log Kw (Temp. Corrected)	-14.5332
	log K'w (Ion Strength Corrected)	-14.4548
	log K1 (Temp. Corrected)	-6.4633
	log K'1 (Ion Strength Corrected)	-6.3845
	log K2 (Temp. Corrected)	-10.4879
	log K'2 (Ion Strength Corrected)	-10.3357
DIC (mg/L as C) =	[(ALK(mg/L CaCO3)/50044(mg CaCO3/equiv.) - K'w /{ x [1/(alpha HCO3 + Z(alpha CO3))]	H} + {H})]
	x 12011 (mg C/mole)	



Figure 1: Saturation pH for Calcium Carbonate Precipitation



Sheet 1A: Exceeded Lead and Copper Action Levels





\* Initial dose should be > 0.5 mg/L orthophosphate as P either orthophosphate or blend.



Sheet 1B: Exceeded Lead Action Level Only







\* Initial dose should be > 0.5 mg/L orthophosphate as P either orthophosphate or blend.







Sheet 2C: Exceeded Copper Action Level Only

\* Initial dose should be > 0.5 mg/L orthophosphate as P either orthophosphate or blend.



\* Initial dose should be > 0.5 mg/L orthophosphate as P either orthophosphate or blend.



### Sheet 1D: Exceeded Lead and/or Copper Action Levels and Have Raw Water Iron or Manganese

#### Sheet 2D: Exceeded Lead and/or Copper Action Levels and Have Raw Water Iron or Manganese



\*The blend should provide a minimum of 0.5 mg/L orthophosphate as P.





\*The blend should provide a minimum of 0.5 mg/L orthophosphate as P.



#### Sheet 2E: Exceeded Lead and/or Copper Action Levels and Have Raw Water Iron or Manganese

\*The blend should provide a minimum of 0.5 mg/L orthophosphate as P.

#### Section 2 - Water Treatment Considerations

For some water systems, more than one corrosion control treatment option may be chemically viable. The purpose of this section is to provide information regarding specific treatment criteria, operation, and secondary impacts associated with each treatment option which may further influence which final treatment option should be chosen for your water system.

After identifying possible appropriate treatment strategies using the flow charts in Section 1, Water Treatment Considerations should be reviewed to obtain more information about potential strategies. The increases in pH, orthophosphate, or silicate concentration necessary for lead and copper control may sometimes result in scaling in distribution system valves, in hot water heaters, or in some industrial chemical processes, thus the need to determine the maximum pH feasible for the water to be treated. The criteria listed under each specific treatment method must be met in order for that treatment to be selected.

**pH Adjustment Systems -** Caustic (sodium or potassium hydroxide), soda ash, limestone contactors (calcite filters) and aeration (air stripping) are the principal methods for increasing the pH. Soda ash, potash, and limestone contactors also increase DIC while aeration decreases DIC in the process of increasing pH.

<u>Caustic (Sodium or Potassium Hydroxide)</u> - Caustic, a liquid chemical, is very hazardous if not handled carefully. It can cause severe burns and damage the eyes. Caustic feed systems at a minimum should include an eye washing system, full shower, eye goggles, protective gloves, boots, aprons, easy-to-handle barrels and chemical containment areas. For very small systems (e.g., schools, trailer parks), a safer option such as soda ash should be used if possible. While caustic traditionally means "sodium hydroxide" solution, potassium hydroxide can always be substituted for sodium hydroxide if a water system prefers, and dosages adjusted accordingly. Sodium hydroxide may be obtained as 25% or 50% solutions while potassium hydroxide is available as a 45% solution.

To use this treatment, a water system should have: Raw water DIC > 5 mg C/L or the potential for severe pH swing or overfeed is great. Note: A small change ( $\pm 1 \text{ mg/L}$ ) in caustic dosage can result in pH variations of up to 2 pH units, a 100-fold change in hydrogen ion concentration. Effective corrosion control requires stable pH values so, for water systems with low DICs, an alternate means of pH adjustment should be used.

<u>Soda Ash/Potash</u> - Soda ash, or sodium carbonate, and potassium carbonate ("potash") are dry compounds which are relatively safe to handle compared to caustic. These carbonate chemicals will not cause skin irritation. When soda ash or potassium carbonate is added to a water, there is an increase in DIC as well as pH. Because soda ash and potassium carbonate are safe to handle, they are strongly recommended as the pH adjustment chemical for schools, condominiums, or any facility where technical resources are limited. They dissolve more easily than lime. Potassium carbonate is more expensive than soda ash but is more soluble and easier to handle, so many very small water systems have found it the best choice for pH/alkalinity adjustment.

To use this treatment, a water system should have: Raw Water DIC levels that are higher than 2 mg C/L but lower than 25 mg C/L.

<u>Aeration Systems</u> - Aeration systems can increase the pH of groundwater systems or stratified surface water systems by removing over-saturated carbon dioxide. A stratified surface water is one that creates different density and water quality layers as a result of temperature changes over the summer season. The bottom layers often lose dissolved oxygen and have elevated levels of carbon dioxide, iron, and manganese because the stratification prevents diffusion of dissolved oxygen from the upper water to the lower. Aeration is the only pH adjustment method that does not add a chemical to the water and the only one that can <u>reduce</u> excess DIC. Many groundwater systems have low to moderate levels of alkalinity but low pH and high DIC values due to the presence of carbon dioxide at levels exceeding saturation values. A water system can test for excess carbon dioxide by testing for pH carefully at the source, collecting a sample and letting it sit in open air while stirring to allow the carbon dioxide to escape and then, after 10 - 15 minutes of mixing, re-testing the pH. There are a wide variety of pH adjustment systems including diffused bubble systems, packed or tray tower, and venturi systems. Any aeration system selected for pH adjustment should be capable of removing at least 80 - 90% of the carbon dioxide. Larger amounts of pH adjustment will require the use of designs that produce higher percentages of carbon dioxide removal. One of the disadvantages associated with aeration is that re-pumping of the water is required. Some water systems can configure their well, plant, and storage locations to maximize the use of gravity in the hydraulics of their distribution networks. Some State regulatory agencies require systems to disinfect the water after aeration so that any microbes introduced during aeration will not grow out in the distribution system.

To use this treatment, a water system should have: Groundwater source or stratified surface water source. See aeration feasibility tree – Sheets 4A and 4B located on pages 34 and 35.

<u>Limestone Contactors</u> - A limestone contactor is usually an enclosed filter containing crushed highpurity limestone (CaCO<sub>3</sub>). As the water passes through the limestone, the limestone dissolves, raising the pH, calcium, alkalinity, and DIC of the water. Since the system does not require any pumps or continuous addition of limestone, it is very simple and requires very little maintenance. Occasionally the limestone must be replaced. The limestone is not a hazardous material. When obtaining a design for a limestone contactor, it is important to ensure that it is adequately sized to produce sufficiently high pHs for the range of flow rates and temperatures encountered during plant operation.

In Europe and the Middle East, limestone contactors have been designed to assist in iron removal from groundwater as well as pH and alkalinity adjustment. These contactors have bypasses and the capability for backwash to help remove some of the iron that accumulates on the limestone. The most successful are operated in an up-flow rather than a down-flow mode. Flow rates for successful iron removal with a limestone contactor are generally lower than typical flow rates for limestone contactors used for pH and alkalinity adjustment only.

To use this treatment, a water system should have pH < 7.2, calcium < 60 mg/L, and alkalinity < 100. See Limestone Contactor Feasibility Tree -- Sheet 5A located on page 36.



Sheet 4A: Aeration Feasibility Tree

Revised Guidance Manual for Selecting Lead and Copper Control Strategies

March 2003



#### Limits of Aeration Sheet 4B



**Secondary Water Quality Impacts from pH/alkalinity adjustment** - When the pH and alkalinity of a water supply is increased, several unwanted side effects may occur. Water systems with a low pH (~7), elevated levels of iron and manganese, and no process for iron and/or manganese removal at the source may notice a significant increase in black and red water complaints when the pH is increased. Elevated pH enhances the oxidation of both iron and manganese which is of benefit if the system removes these metals but can be problematic if the system relies on sequestration to prevent red/black water incidents.

Further, increasing the pH of a water that contains calcium may promote the precipitation of calcium carbonate. In some circumstances, precipitation of calcium carbonate can clog hot water heaters and produce cloudy water. To limit the problems associated with calcium precipitation, the pH at which calcium is likely to precipitate can be estimated by use of Figure 1. The pH of calcium precipitation is estimated by finding the point on the figure that corresponds to the DIC and calcium level. The calcium needs to be expressed as calcium (Ca) and not calcium carbonate (CaCO<sub>3</sub>). Note that maintaining the pH below the level estimated on the chart should minimize, not eliminate the potential for precipitating calcium carbonate. In many cases, it will be possible to exceed the estimated pH levels without having a calcium precipitation problem because the precipitation of calcium is affected by many factors, such as temperature and other dissolved metals.

Water systems using surface water are subject to a series of regulations under a broad heading of the Microbial and Disinfection Byproducts Rules (MDPR). These systems must meet certain disinfection criteria. This includes maintaining an adequate contact time with chlorine at a specific pH and temperature, by meeting certain "CT" criteria, and other disinfection credits through filtration. A corrosion control strategy that causes an increase in pH may affect your ability to maintain adequate chlorine contact. Increases in finished water pH for surface water supplies should be performed after the chlorine contact chamber.

Disinfection byproduct (DBP) formation also varies with pH. There is a tendency for trihalomethanes (THMs) to increase with prolonged exposure to higher pHs, whereas haloacetic acids tend to form or persist at lower pH values. Depending on the points of chlorination and the DBP precursor material concentration remaining after initial treatment, corrosion control strategies may be limited by concerns of violating regulatory levels for DBPs in the distribution system.

**DIC Adjustment Systems -** The adjustment systems for DIC include aeration and soda ash/potash (described above), and sodium bicarbonate (baking soda).

<u>Sodium Bicarbonate</u> - Sodium bicarbonate is a dry chemical that substantially increases the alkalinity and DIC, while providing a very minimal increase in pH. This chemical is typically applied to waters with very minimal DIC ( $\leq 5 \text{ mg C/L}$ ). Because it is a dry chemical, it must be dissolved in a tank of water for feeding. It is very safe to handle and will not increase the pH above 8.3. Some utilities use both soda ash or caustic and sodium bicarbonate together if a significant increase in pH and alkalinity are needed.

To use this treatment, a water system should have: DIC < 5 mg C/L.

**Phosphate Addition** - The addition of orthophosphate to a water supply can be achieved by adding any one of several different formulations. These include zinc orthophosphate, potassium or sodium orthophosphate,

and phosphoric acid. Various chemical suppliers can furnish orthophosphate chemicals in liquid or dry chemical forms. The goal is to ensure that an adequate dosage of orthophosphate is maintained throughout the distribution system. Phosphoric acid is not recommended for small systems because it is a strong acid that can be difficult to handle, as it is both a skin contact and inhalation hazard requiring stringent safety procedures. Orthophosphate may also be added by dosing poly/orthophosphate blends, so the ratio of orthophosphate to polyphosphate is very important to assure sufficient orthophosphate residual to control the lead or copper release. Too much polyphosphate will cause instability of protective scales. The addition of orthophosphate or blended phosphates may cause the temporary release of particles (turbidity) from the inside surfaces of pipes. Over time, the conditions will stabilize and turbidity and color levels should return to existing levels.

<u>Orthophosphate</u> - Orthophosphate formulations are available as phosphoric acid, sodium phosphate compounds, or proprietary compounds that contain zinc or other special ingredients. The compounds that contain zinc may promote problems with receiving wastewater treatment plants. Orthophosphate is a nutrient, so many wastewater treatment plants are limited in the amount of orthophosphate they can discharge to the receiving stream. It is important to check with the wastewater treatment plant to establish proper limits for the phosphate dosage. If zinc is a problem, either a non-zinc based orthophosphate or a high orthophosphate/low zinc product should be used. However, water systems with soft water may find zinc as a very important additive to reduce the pH increases caused by contact with cement and cement-lined pipes.

To use this treatment, a water system should have: pH in the range of 7.2-7.8 and DIC > 5 mg C/L. Note: When substantial cement-lined or asbestos-cement pipe is present, formulations containing zinc are beneficial.

<u>Blended Phosphates</u> – Blended phosphates contain some proportion of orthophosphate with the remainder being a long-chain polyphosphate. The orthophosphate portion is most beneficial for corrosion control while the polyphosphate sequesters hardness, iron, or manganese. As there are many formulations, it is important to find what proportion of orthophosphate to polyphosphate works for your water and specify a product that contains the correct proportion when it is delivered. Over time, polyphosphates change to become orthophosphates so long term storage of the blended product, particularly if it is a liquid, is not recommended.

To use this treatment, a water system should have: 1) pH 7.2-7.8; 2) DIC > 5 mg C/L; and 3) either iron or manganese over secondary limits of 0.20 mg/L for iron and 0.05 mg/L for manganese or creating water quality problems (red or black water), or hard water precipitation is a problem or a potential problem.

**Secondary Water Quality Impacts from Phosphate Addition -** When phosphates are added to a water supply, several unwanted side effects may occur. There can be increased clogging of evaporative or injection humidifiers; increased sludge buildup in hot water heaters; less clarity of ice cubes; and increased scaling or algae growth in aquaria, fountains, and ornamental water bodies.

The fact that many of the phosphate-based products are proprietary makes it more difficult than with commodity chemicals such as sodium hypochlorite or caustic, to evaluate the composition and amount of phosphate in a particular product. Comparisons between products are not always clear from product information sheets; often the Material Safety Data Sheets must be reviewed to determine phosphate type and concentration.

Silicates – Silicates are mixtures of soda ash and silicon dioxide. Silicates can raise pH and have sequestering capabilities, thus have been used by some utilities with low pH, low alkalinity water for corrosion control for lead, copper and iron. The predominant mechanism is the rise in pH and DIC though the role of the silicate hasn't been completely elucidated. Silicate has ability to sequester raw water iron and manganese if the levels of these metals are not too high (> 1 mg/L combined). At least one system reported that, while the silicates sequestered iron and manganese adequately, customers reported development of a tenacious white film on glass shower doors and other glass surfaces in contact with hot water.

To use this treatment, a water system should have pH < 7.2, DIC < 10 mg C/L, and iron or manganese over secondary limits or iron release in distribution system is a problem.

#### Section 3 – Optimizing Treatment

Once the best treatment strategy has been identified using the Flow Charts in Section 1, Water Treatment Considerations in Section 2 and the appropriate operating pH has been determined, treatment can be optimized. In addition, if orthophosphate is added, an appropriate distribution system orthophosphate concentration needs to be maintained. No matter what the intended corrosion control strategy is, a comprehensive flushing program should be started at least a few months before initiation of treatment changes to remove sediment and loose scale material that could be easily re-suspended or destabilized by the new treatment. Disinfection and microbial quality should be carefully monitored during the flushing period. It is also important to continue the frequent and comprehensive flushing while the new treatment program is stabilizing. The flushing will also aid in assuring delivery of the corrosion inhibitor or water of proper pH and DIC levels to the surface of the pipes, which will help promote more rapid and more stable protective film development on the pipes.

**pH Adjustments** - When using treatment chemicals including caustic (sodium or potassium hydroxide) or soda ash (sodium or potassium carbonate), adjustments of pH should be made in 0.3 or 0.5 unit increments as outlined on the sheets in Section 1. The pH should never be increased beyond 10. At a minimum, for systems with a pH of less than 7.0, the pH should be increased to at least 7.0. For other pH increasing systems, either aeration or limestone contactors, the final pH will be established by the specifics of the water chemistry and design of the contactor or aerator.

Systems with unlined cast-iron pipe or large amounts of galvanized pipe need to consider the impacts of pH adjustment on iron corrosion. Although, the water quality impacts that affect iron corrosion are poorly understood, it appears that lower buffer intensity may accelerate iron corrosion. Water's minimal buffering intensity occurs approximately in the pH range of 8.0 - 8.5. Water systems that move their pH into this range may experience iron corrosion and red water. Lead and copper levels should be monitored at representative homes or buildings four to six months after the pH has been adjusted. The State should then be consulted to determine if another pH increase is needed. A decision to increase the pH should not be made before this time because it usually takes at least four to six months and often longer in larger systems for lead and copper levels to stabilize after a pH adjustment.

Orthophosphate Addition - The addition of orthophosphate should be performed by incremental increases in the dosage. Orthophosphate should only be added when the pH is in the range of 7.2-7.8. Initially a system selecting orthophosphate should add enough of the orthophosphate-based chemical to establish at least a 1 mg PO<sub>4</sub>/L residual in the system. A close approximation is that 1 mg/L of orthophosphate expressed as P corresponds to 3 mg/L expressed as PO<sub>4</sub>. Systems with high DIC and considerable new copper piping may need to start with 3 mg  $PO_4/L$  (1 mg/L as P) if possible. To establish this residual, the amount of orthophosphate added will need to be higher than what is measured in the system since some of the orthophosphate will be depleted. After establishing a residual of 1 mg  $PO_4/L$  for 6 months, samples from selected homes and buildings should be analyzed for lead and copper. The results should be discussed with the State to determine if increasing the dosage is necessary to satisfy the "orthophosphate demand" of the distribution system. If the local wastewater system can handle higher levels of phosphate, the dosage should be increased in 1 mg PO<sub>4</sub>/L increments, with lead and copper monitoring following after 6 months with the same dosage. The increases should continue until the desired metals levels are achieved. Even when lead and copper levels are substantially reduced, dosages should not be lowered until the orthophosphate residual throughout the distribution system is constant and is nearly equal to the concentration leaving the treatment plant.

#### Section 4 – Example Treatment Determinations

#### Water System 1 – A typical New England Water System

Population:	2,000
Supply:	single well
Status:	system exceeded both lead and copper action level
pH Data:	6.7, 6.9, 6.4, 6.4, 6.7
Alkalinity:	56 and 45 mg $CaCO_3/L$
Hardness:	$45 \text{ mg/L}$ as $CaCO_3$
Calcium:	18 and 20 mg Ca/L

Step 1. Determine the DIC in mg C/L -- The median (mid-value pH) is 6.7 and the average alkalinity is 50.

Go to Table 3 and determine the DIC. Because there are no DIC values for a pH 6.7, determine the DIC at a pH of 6.6 and a pH of 6.8 for an alkalinity value of 50, and average the two DIC results to determine the DIC at pH 6.7.

- For a pH of 6.6 and alkalinity of 50 the DIC is 19.
- For a pH of 6.8 and alkalinity of 50 the DIC is 17.
- For a pH of 6.7, the DIC would be approximately 18.

*Step 2. Determine the maximum pH to minimize calcium precipitation --* Using Figure 1 with an average calcium concentration of 19 mg/L and a DIC of 18, the maximum pH is about 8.3.

*Step 3. Use flow charts* -- The sheets for systems that exceeded both the lead and copper (set 1A) action levels are used. The first sheet is used since the pH is less than 7.2. The DIC is greater than 12 mg C/L, therefore the viable treatment options are: aeration, caustic, or soda ash or potash.

*Step 4. Use the Water Treatment Considerations* -- Check the requirements for each of the viable treatment options. Because all the criteria listed under the three treatment options have been met, any of the three treatment options may be selected. A study of the costs/benefits of each of the three methods should then be undertaken to see which treatment is the least expensive and most able to meet other regulations (e.g., MDBP rules, Arsenic Rule, wastewater discharge requirements).

#### Water System 2 – A Midwestern Water System

Population:	100
Supply:	single well
Status:	system exceeded copper action level
pH Data:	6.9, 7.2, 7.1, 7.0, 7.0
Alkalinity:	$300 \text{ and } 330 \text{ mg/L} \text{ as } \text{CaCO}_3$
Hardness:	280  mg/L as CaCO <sub>3</sub>
Calcium:	estimated at 112 mg Ca/L ( $280/2.5 = 112$ )

*Step 1. Determine the DIC in mg C/L --* The median (mid-value pH) is 7.0 and the average alkalinity is 315. Go to Table 3 and determine the DIC. For a pH of 7.0 and alkalinity of 315, the DIC is 96 mg C/L.

*Step 2. Determine the maximum pH to minimize calcium precipitation --* Using Figure 1 with a calcium concentration of 112 mg/L and a DIC of 96 the maximum pH is about 6.95 so this water has tendencies to scale at the ambient pH.

*Step 3. Use flow charts* -- The sheets for systems that exceeded the copper action level (set 1C) are to be used. The first sheet is used since the pH is less than 7.2. The DIC is > 25 mg C/L, therefore the viable treatment option is addition of blended phosphate to control scaling and help control copper corrosion along with the minor addition of caustic to raise the pH to 7.2.

*Step 4. Use the Water Treatment Considerations* -- Check the requirements for the viable treatment option. Because all the criteria listed under the treatment option has been met, with the exception of the presence of iron and/or manganese, the next step is the selection of the most appropriate blended phosphate. Often the State Lead and Copper Coordinator can provide some information about products that have worked for systems with similar water quality. The product needs enough orthophosphate (0.5 mg/L minimum) to provide corrosion control but enough polyphosphate to minimize scaling of the hardness in the system.

#### Water System 3 – A Western Water System

Population:	2,900
Supply:	surface water and groundwater
Status:	system exceeded both lead and copper action level

<u>GROUNDWATER DATA</u> 20 % of supply		<u>SURFACE WATER DATA</u> 80% of Supply - 140,000 GPD		
Alkalinity:	60 to $75$ mg CaCO <sub>3</sub> /L	Alkalinity:	17 to 37 mg/L	
Hardness:	90 to 95 mg/L as $CaCO_3$			
Calcium:	30 to $38$ mg Ca/L	Calcium:	10  mg Ca/L	
Iron:	0.35 mg/L			

#### Multiple Source System

Several factors must be examined when determining treatment for a water system with multiple sources.

- 1. *Amount of Water.* The surface water in this case is where most of the water is derived. It is of greater importance on that basis.
- 2. *Corrosiveness:* The primary factors here are the pH and alkalinity. The groundwater, having higher pH and alkalinity values, is less corrosive.

Based on these factors, the approach should be to determine a treatment recommendation for the surface water supply.

*Step 1. Determine the DIC in mg C/L* -- For the surface water source, the median (mid-value) pH is 6.8 and the average alkalinity is 27. Go to Table 3 and determine the DIC. For a pH of 6.8 and alkalinity of 30 (closest value to 27), the DIC is 10 mg C/L.

For the groundwater source, the median (mid-value) pH is 7.6, the average alkalinity is 68. From Table 3, the DIC is 17 mg C/L.

*Step 2. Determine the maximum pH to minimize calcium precipitation --* Using Figure 1 with a calcium concentration of 10 mg/L and a DIC of 10, the maximum pH is about 9.25.

*Step 3. Use flow charts* -- The sheets for systems that exceeded both the lead and copper action levels (Sheets A) are to be used. Sheet 1A is used since the pH is less than 7.2. The DIC is 10 mg C/L, therefore the viable treatment options for the surface water are: soda ash, potash, caustic, or limestone contactor. Aeration is rejected because stratification is not a major observation for the surface water supply. A treatment compatible with the groundwater quality would be beneficial so Sheet 2E is reviewed. This sheet is for a groundwater source that exceeded lead and/or copper, have elevated iron with no iron removal, and have an average pH greater than 7. Flowchart 2E lists blended phosphate addition as the best option. The surface water pH and alkalinity would have to be raised in order to be in the correct range for blended phosphate addition and to more closely match the pH and alkalinity of the groundwater.

*Step 4. Use the Water Treatment Considerations* -- Check the requirements for each of the viable treatment options. Soda ash or potash can be used because surface water system DIC falls within the required range of 2 - 25 mg C/L as outlined in the Water Treatment Considerations. Caustic is an option but should be looked at carefully as the surface water alkalinity is quite variable and an overfeed could result in very high distribution system pH values. A limestone contactor is an option. A cost-benefit study should be conducted with the awareness that a higher pH water in the distribution system may affect iron oxidation within the boundary area where the surface water meets the groundwater. Matching the pH and alkalinity of the groundwater source may reduce adverse iron reactions.

#### Section 5 – Some Additional Sources of Information

Anderson, D.R., Row, D.D., and Sindelar, G.E., 1973. Iron and Manganese Studies of Nebraska Water Supplies, *Jour. AWWA*, 65:10:635.

AWWA (American Water Works Association), 1999. *Water Quality and Treatment*. R.D. Letterman (ed.). McGraw-Hill, New York, NY.

AWWARF (American Water Works Association Research Foundation), 1990. *Lead Control Strategies*. AWWA Research Foundation and AWWA, Denver, CO.

AWWARF (American Water Works Association Research Foundation), 1997. *A General Framework for Corrosion Control Based on Utility Experience*. AWWA Research Foundation, Denver, CO.

AWWARF-TZW, 1996 (Second ed.). *Internal Corrosion of Water Distribution Systems*. AWWA Research Foundation/DVGW Forschungsstelle-TZW, Denver, CO.

Cantor, A.F., Denig-Chakoff, D., Vela, R.R., Oleinik, M.G., Lynch, D.L., 2000. Use of Polyphosphate in Corrosion Control. *Jour. AWWA*, 92:2:95.

Dodrill, D.M. & Edwards, M., 1995. Corrosion Control on the Basis of Utility Experience. *Jour. AWWA*, 87:7:74.

Kettunen, R., and Keskitalo, P., 2000, Combination of membrane technology and limestone filtration to control drinking water quality. *Desalination* 131 (2000) 271-283

Letterman, R.D., Driscoll, C.T., Haddad, M., and Hsu, H.A., 1986. Limestone Bed Contactors for Control of Corrosion at Small Water Utilities, USEPA 600/S2-86/099

Letterman, R.D., Haddad, M. & Driscoll, C.T., Jr., 1991. Limestone Contactors: Steady State Design Relationships. Jour. Envir. Engrg. Div.--ASCE, 117:3:339.

Letterman, R.D., 1995. Calcium Carbonate Dissolution Rate in Limestone Contactors, Research and Development Report, EPA/600/SR-95/068, Risk Reduction Engineering Laboratory, Cincinnati, OH.

Letterman, R.D. & Kathari, S., 1996. A Computer Program for the Design of Limestone Contactors. Jour. NEWWA, 110:1:42.

Lytle, D.A., Schock, M.R., Clement, J.A., and Spencer, C.M., 1998. Using Aeration for Corrosion Control. *Jour. AWWA*, 90:3:74; Erratum. *Jour. AWWA*, 90:5:4 & *Jour. AWWA*, 90:9:4

New England Water Works Association and USEPA Region 1, 1993. *Basic Chemistry and Corrosion Control Water Treatment to Meet the SDWA Lead and Copper Rule: Reference Notes for Small Systems.* New England Water Works Association.

Rezania, Lih-In W., and Anderl, W.H. Copper Corrosion and Iron Removal Plants Proc. National Conference on Integrating Corrosion Control and Other Water Quality Goals, Cambridge, MA (1996)

Rezania, Lih-In W., and Anderl, W.H. Corrosion Control for High DIC Groundwater: Phosphate or Bust. *Proc. AWWA Annual Conference*, Atlanta, GA (1997)

Rooklidge, S.J. and Ketchum Jr., L.H., 2002. Corrosion control enhancement from a dolomite-amended slow sand filter. *Water Research*, 36(2002)2689-2694

Schock, M.R., 1999. Reasons for Corrosion Control other than the Lead and Copper Rule. *Jour. NEWWA*, 113:2:128.

Schock, M.R. & Clement, J.A., 1998. Control of Lead and Copper with Non-zinc Orthophosphate. *Jour.* NEWWA, 112:1:20.

Schock, M.R., Clement, J.A., Lytle, D.A., Sandvig, A.M., and Harmon, S.M., 1998. Replacing Polyphosphate with Silicate to Solve Problems with Lead, Copper and Source Water Iron, *Proc. AWWA Water Quality Technology Conference*, Nov. 1-4, San Diego, CA.

Schock, M.R., Edwards, M., Powers, K., Hidmi, L., and Lytle, D.A., 2000. The Chemistry of New Copper Plumbing, *Proc. AWWA Water Quality Technology Conference*, November 5-9, Salt Lake City, UT.

Schock, M.R., Lovejoy, T.R., Holldber, J., Lowry, J., and Egan, J., 1999. California's First Aeration Plants for Corrosion Control, *Proc. AWWA Water Quality Technology Conference*, Oct. 31-Nov. 3, Tampa, FL.

Schock, M.R. & Fox, J.C., 2001. Solving Copper Corrosion Problems while Maintaining Lead Control in a High Alkalinity Water Using Orthophosphate, *Proc. American Water Works Association Annual Conference, June 3-7, Washington, DC.* 

Smith, P.G., and Gaber, A., 1995. The Use of Limestone Bed Filtration for the Treatment of Ferruginous Groundwater, Jour. CIWEM, 9, April, 192

Spencer, C.M. & Brown, W.E., 1997. pH Monitoring to Determine Aeration Effectiveness for Carbon Dioxide and Radon Removal, *Proc. AWWA Water Quality Technology Conference*, November 9-13, Denver, CO.

Spencer, C.M., 1998. Aeration and Limestone Contact for Radon Removal and Corrosion Control. Jour. NEWWA, 112:1:60.

USEPA Guide to the Part 503 Rule. 1994