The Role of Corrosion Indices in Establishing Effective Corrosion Control Treatment

Christopher P. Hill

In November 2019, the U.S. Environmental Protection Agency (EPA) proposed revisions to the Lead and Copper Rule (LCR). It's anticipated that EPA will issue the final rule in late 2020. Among the provisions of the proposed rule are actions aimed at strengthening drinking water treatment requirements.

In addition to the current 15 µg/L action level (AL), the proposed rule establishes a threshold level (TL) of 10 µg/L for lead. Compliance status is based on the 90th percentile of lead samples compared to these levels. For those systems that previously established optimal corrosion control treatment (OCCT) with their primacy agency, an exceedance of the TL would require them to reoptimize corrosion control treatment (CCT). Systems that exceed the TL and have not established OCCT would be required to conduct a corrosion control study to determine OCCT.

Much emphasis has been placed on the value of standard "corrosion indices" in the control of lead and copper. In the years since the original LCR was implemented, corrosion indices have evolved from good rules of thumb for the prevention of internal corrosion to *de facto* guidelines for the control of lead and copper corrosion. As a result, a refresher is needed on the usefulness of these various indices and their value in controlling internal corrosion.

This article discusses several of these indices and how they should be used to establish an effective corrosion control program.

Christopher P. Hill, P.E., BCEE, ENV SP, is drinking water market sector leader—water with AECOM in Tampa.

Background

The LCR was originally published in 1991. Subsequent guidance from EPA identified three corrosion control treatment alternatives (EPA, 1992):

- *pH and alkalinity adjustment*, which refers to the modification of pH and/or alkalinity (as a surrogate for dissolved inorganic carbonate) to induce the formation of less-soluble compounds with the targeted pipe materials (hydroxyl-carbonate films). This method utilizes passivation as the mechanism of control.

- *Carbonate precipitation*, which refers to the adjustment of the pH, alkalinity, and/or calcium carbonate system equilibrium, such that calcium carbonate precipitation results. This method of corrosion control depends upon precipitation as the means of protecting piping systems.
- *Corrosion inhibitor addition*, which refers to the application of specially formulated chemicals characterized by their ability to form metal complexes and thereby reduce corrosion. This method promotes phosphate passivation of the metal surface as the means of corrosion control. The corrosion inhibitors utilized include various formulations of orthophosphates and blended ortho/polyphosphates.

In the years that followed, it was determined that carbonate precipitation is not an effective means of corrosion control because research has shown that calcium carbonate films only rarely form on lead and copper pipe and are not considered an effective form of corrosion control (Schock and Lytle, 2011; Hill and Cantor, 2011). As a result, EPA removed carbonate precipitation as an effective corrosion control treatment from updated corrosion control treatment guidance (EPA, 2016). Calcium hardness is important, however, in evaluating the amount of pH adjustment that can be made without causing calcium carbonate precipitation and resultant scaling problems in the distribution system.

It's important to note that each of the corrosion control strategies mentioned focuses on uniform corrosion; however, there are a number of different types of corrosion. When considering a corrosion control treatment method, the most appropriate corrosion control strategy will depend on the type of corrosion, as shown in Table 1.

Table 1. Types of Corrosion and Associated Corrosion Control Strategies

Corrosion Type	**Control Methods**
Uniform corrosion	• Carbonate passivation • Orthophosphate inhibitor addition
Pitting corrosion	• pH and dissolved inorganic carbonate (DIC) control
Microbially influenced corrosion (MIC)	• Limit nutrients • Maintain adequate residual • Reduce stagnation/water age
Galvanic corrosion	• Eliminate contact between dissimilar metals (e.g., lead and dissolved inorganic phosphorus [DIP])
Erosion corrosion	• Hydraulic controls
Other types: • Re-equilibration of scale • Adsorption and release	• Maintain stable distribution water quality • Enhanced treatment

Uniform Corrosion

Corrosion in drinking water systems refers to the electrochemical interaction between the

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pipe wall and the water with which it’s in contact. To occur, the interaction requires the following (Cantor, 2011):

- Negative terminal called the “anode”
- Positive terminal called the “cathode”
- Medium to carry electrons from the anode to the cathode
- Chemical that can accept the electrons at the cathode
- Chemical that can pair with the metal ion released at the anode

In uniform corrosion, the anode and cathode occur dynamically at random sites on the pipe wall (Figure 1). The electrons flow from the anodes to the cathodes through the pipe wall. The water in contact with the cathode provides the chemicals to accept the electrons; for instance, oxygen in the water solution can accept an electron (a reduction reaction). In the meantime, metal atoms from the solid metal at the anode, having given up electrons, undergo an oxidation reaction. The oxidized metal is now soluble in the water, and this oxidation of the metal is termed “corrosion.”

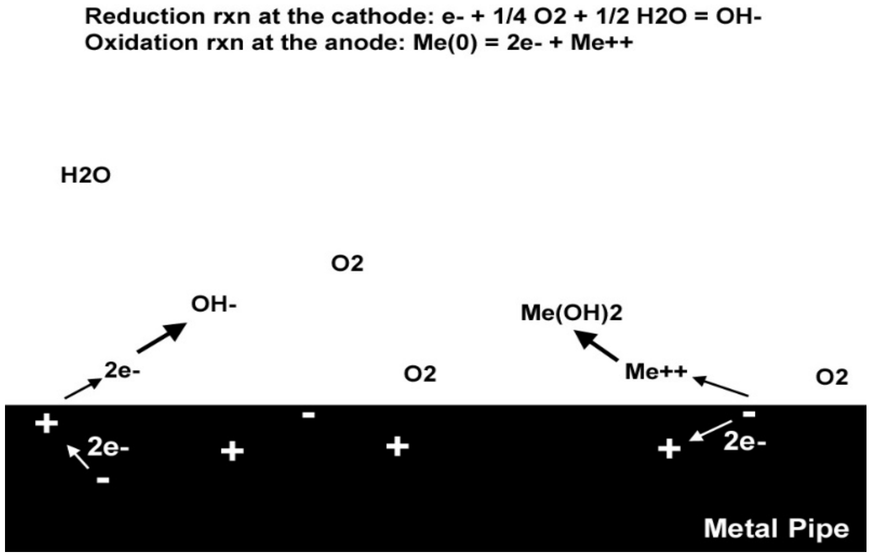

Figure 1. Uniform Corrosion Process *(Cantor, 2011)*

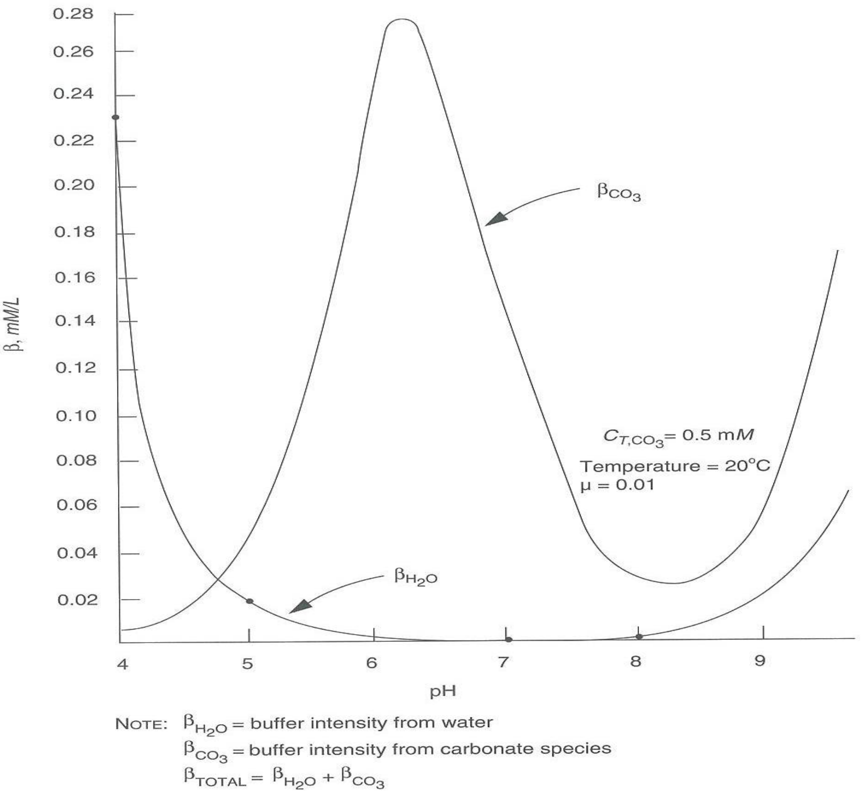

Figure 2. Variation of Buffer Intensity WIth pH *(Snoeyink and Wagner, 1996)*

Based on Figure 1, it’s conceivable that, if a protective layer could be formed between the pipe wall and the water, then it would be possible to control corrosion; however, to be effective the film must be an insoluble, uniform, nonporous layer. It has also been reported that significant calcium carbonate scales do not form on lead, galvanized, or copper cold water pipes. When they do form, carbonate scales are coarse, nonuniform, and subject to dissolution under varying water quality conditions. It’s for these reasons that calcium carbonate is not an effective means of corrosion control (AwwaRF and DVGW, 1996).

Corrosion Indices

Despite its unsuitability as a corrosion control method, calcium carbonate scale formation is still regularly used as an indicator of corrosion potential. A number of corrosion indices are frequently used as a measure of the corrosivity of a particular water toward lead, copper, or other distribution system material, but the majority are not related to corrosion at all and are instead based on calcium carbonate saturation. The two most commonly cited when discussing corrosion control are the calcium carbonate precipitation potential (CCPP) and the Langlier Saturation Index (LSI).

The CCPP denotes the quantity of calcium carbonate that can theoretically be precipitated from oversaturated waters or dissolved by undersaturated waters in units of mg/L. A CCPP value of 4 to 10 mg/L is typically cited as protective without contributing to the excessive deposition within the distribution system.

Another frequently utilized saturation index is the LSI, which can be determined based on the following equation:

$$Langlier\ Saturation\ Index\ (LSI) = pH - pH_s$$

A negative LSI value indicates undersaturation and a positive LSI indicates oversaturation with regard to calcium carbonate. A slightly positive LSI (i.e., greater than 0 but less than 1) is typically cited as protective without contributing to the excessive deposition within the distribution system.

A lesser known and lesser utilized carbonate saturation index is the Ryznar Stability Index (RI). The RI can be determined based on the following equation:

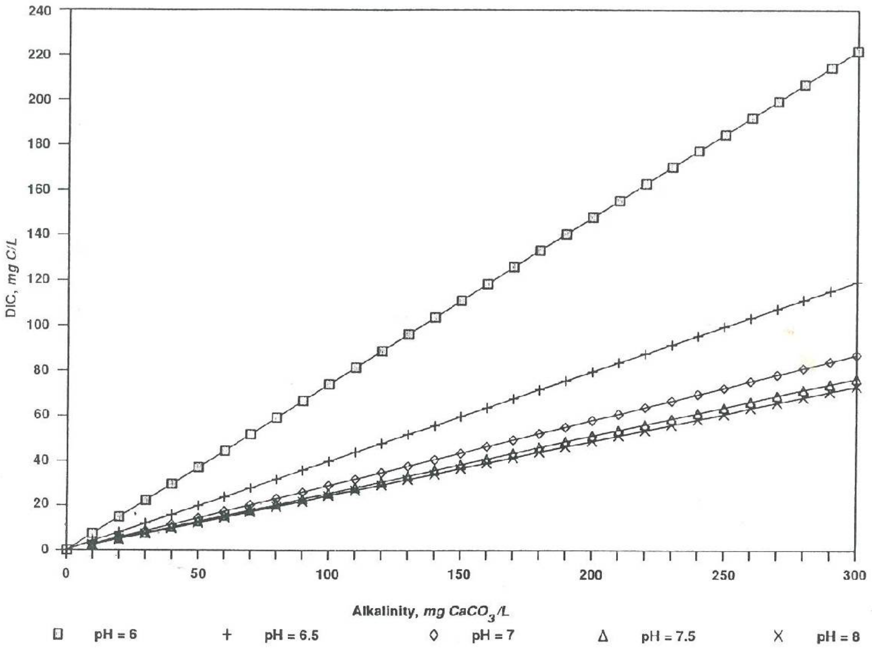

Figure 3. Relationship Between Akalinity and Dissolved Inorganic Carbonate for Various pH Levels (pH = 6-8, I = 0.005, T = 25 ° C) *(Economic and Engineering Services, 1990)*

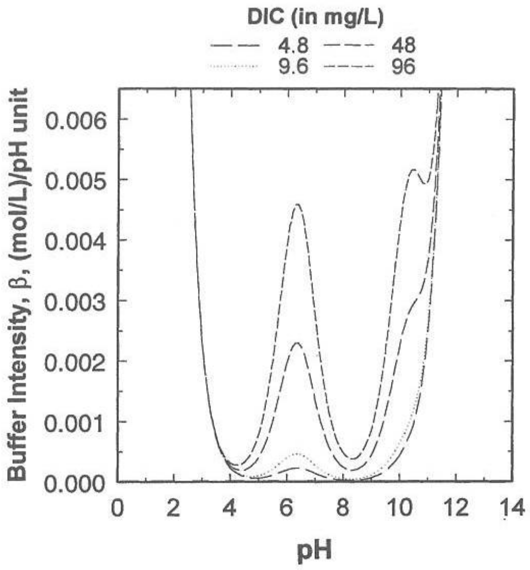

Figure 4. Effect of Dissolved Inorganic Carbonate (Measured as C) on Buffer Intensity *(Schock, 1999)*

$$Ryznar\ Stability\ Index\ (RI) = 2 \times pH_s - pH$$

Where pH is the actual pH and pH_s is the pH at saturation for the actual calcium carbonate concentration.

There are a number of recommendations relative to the RI and recommended ranges. Generally, however, the potential for calcium carbonate precipitation increases as the RI decreases, and the following ranges are generally accepted:

- RI < 6 are considered scale-forming.
- 6 < RI < 7 are thought to be in equilibrium.
- RI > 7 are undersaturated and mildly aggressive to steel (Awatif, et al., 2014).

Another regularly cited corrosion index is the Larson-Skold Index (LI), which can be calculated according to the following equation:

$$Larson - Skold\ Index\ (LI) = \frac{[Cl^-] + [SO_4^{2-}]}{[HCO_3^-] + [CO_3^{2-}]}$$

Where each of the terms in the index is in units of eqivalents per mil (epm) of the respective ion.

The LI results are typically interpreted as follows:

- LI < 0.8: Chlorides and sulfate probably will not interfere with natural film formation.
- 0.8 < LI < 1.2: Chlorides and sulfates may interfere with natural film formation. Higher-than-desired corrosion rates might be anticipated.
- LI > 1.2: Tendency toward high corrosion rates of a local type should be expected as the index increases.

Unlike the other indices mentioned, which are based solely on calcium carbonate saturation, the LI is truly a corrosion index rooted in carbonate film formation. It's based on evaluation of in-situ corrosion of mild steel lines transporting Great Lakes waters. Extrapolation to waters other than the Great Lakes, such as those of low alkalinity or extreme alkalinity, goes beyond the range of the original data (Larson and Skold, 1958). Further, the applicability to other metals, such as lead and copper, should be considered with caution.

The Role of Carbonate in Corrosion Control

It has been established that calcium carbonate precipitation is not an effective means of corrosion control (EPA, 2016; Schock and Lytle, 2011; Hill and Cantor, 2011); however, carbonate and bicarbonate still play an important role in corrosion control. For example, the most common compounds found on lead pipe walls are cerussite ($PbCO_3$) and hydrocerussite ($Pb_3[CO_3]_2[OH]_2$) (Colling, Whincup, & Hayes, 1987). Therefore, a thorough understanding of the factors that influence the presence of carbonate and bicarbonate species in water, called the "carbonate balance," is necessary to developing an effective corrosion control program.

pH. Maintaining a consistent target pH throughout the distribution system is always critical to minimizing lead and copper levels at the tap, even if other corrosion control methods are employed. The pH also plays a significant role in the carbonate balance in that it impacts buffer capacity and DIC concentrations.

Alkalinity. Alkalinity is the sum of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and hydroxide (OH^-) anions, and is typically reported as mg/L as calcium carbonate (mg/L as $CaCO_3$). Waters with high alkalinities tend to have high buffering capacities, or a strong ability to resist changes in pH. Low alkalinity waters are less able to neutralize acids or resist changes in pH.

Buffer intensity or buffer capacity. Buffer

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Table 2. Source Water Quality Characteristics

Source	Description	Alkalinity (mg $CaCO_3$/L)	pH	CCPP	LSI
A	Blended shallow groundwater and surface water	210	7.4	4.6	0.1
B	Deep groundwater	170	8.3	4.4	0.3
C	Surface water	50	7.0	-3.3	-0.1

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intensity is a measure of the resistance of water to upward or downward changes in pH, and is a function of pH and alkalinity. Bicarbonate and carbonate ions are the most important buffering species in most drinking water supplies. Buffering intensity from carbonate species is normally greatest at approximately pH 6.3 and above 9, and lowest in the range of pH 8 to 8.5 (Figure 2).

Dissolved inorganic carbonate. The DIC is the sum of all dissolved inorganic carbonate-containing species and is one of the most critical parameters to controlling internal corrosion. It includes dissolved aqueous carbon dioxide gas (CO_2 or H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}) in a particular water, and is usually expressed as mg of carbon per liter (mg/L as C) or mg of calcium carbonate per liter (mg/L as $CaCO_3$). Although DIC and alkalinity are similar, they are not the same water quality parameter.

The DIC varies according to water temperature, pH, ionic strength, and alkalinity. An example of this relationship is provided in Figure 3.

The DIC also significantly impacts the buffer intensity of water. Figure 4 shows that, as the DIC concentration increases, the buffer capacity of the water also increases. Since DIC controls the buffer capacity in most water systems, sufficient DIC is required to maintain a stable pH throughout the distribution system for control of lead and copper (Schock and Lytle, 1995).

Hardness. Hardness is a characteristic that primarily represents the presence of dissolved calcium and magnesium in water, and is reported as an equivalent quantity of calcium carbonate (mg/L as $CaCO_3$). When sufficient calcium and alkalinity are present in waters with pH greater than the saturation pH, calcium carbonate may precipitate distribution piping. As previously discussed, there are a number of saturation indices that can be used to predict calcium carbonate precipitation.

It's important to note that the formation of carbonate scale can interfere with corrosion control when other methods, such as phosphate passivation, are employed. Hardness must also be taken into consideration when corrosion control is selected and implemented because it can create scaling problems within the treatment plant and distribution system infrastructure. In this regard, hardness is an important parameter to be considered in developing a corrosion control program, but it's not a stand-alone indicator of the corrosive nature of a particular water.

Case Studies

Case Study 1

Population growth in a community in the southwestern United States resulted in an increase in service population to more than 50,000 people. As a result, that community was required to conduct a corrosion control study to determine if changes to its current corrosion control strategy (carbonate passivation) were warranted.

The community receives water from three sources: a blend of groundwater and surface water, shallow groundwater, and surface water. Table 2 provides a summary of water quality and corrosion indices for each of the sources.

As previously mentioned, the original LCR guidance manual identifies three potential corrosion control treatment methods: calcium adjustment, carbonate passivation through pH/alkalinity adjustment, and corrosion inhibitor addition. Coupon studies were conducted using lead solder and copper coupons to determine the most-effective corrosion control treatment for this system. The state regulatory agency did not require testing of calcium adjustment and pH/alkalinity adjustment for sources A and B because the CCPP and LSI were already in the recommended ranges. All three methods were tested for source C. Table 3 compares average lead and copper concentrations for each source and corrosion control method for the duration of the coupon studies.

The results in Table 3 show that the average lead concentrations for all three sources were similar without any additional treatment, despite the fact that source C did not meet the traditional CCPP and LSI guidelines. On the other hand, copper concentrations for source A were significantly higher without treatment compared to sources B and C, though it too fell within recommended ranges for CCPP and LSI. This is also consistent with traditional copper corrosion theory, in that high alkalinity (> 200 mg/L as $CaCO_3$) and low pH (< 7.5) waters can be aggressive to copper.

Table 3. Corrosion Control Study Results

Treatment Option	Source A		Source B		Source C	
	Pb (mg/L)	Cu (mg/L)	Pb (mg/L)	Cu (mg/L)	Pb (mg/L)	Cu (mg/L)
No treatment	143	698	208	301	154	461
Inhibitor A (1.5 mg/L)	30	248	674	681	--	--
Inhibitor A (3 mg/L)	22	293	1,653	1,600	--	--
Inhibitor B (1.5 mg/L)	41	194	383	489	--	--
Inhibitor B (3 mg/L)	29	160	514	790	--	--
Phosphoric acid (1.5 mg/L)	--	--	--	--	39	156
Phosphoric acid (3 mg/L)	--	--	--	--	29	125
pH adjustment[1]	--	--	--	--	118	396
Calcium adjustment[2]	--	--	--	--	136	433

Inhibitor A, 1:3 orthophosphate to polyphosphate ratio
Inhibitor B, 3:1 orthophosphate to polyphosphate ratio

Table 4. Corrosion Control Study Test Conditions

Loop	pH	Alkalinity	Local GW	Brackish GW	NF Permeate	Inhibitor Dose	Calcite Contactor
1	7.8	56.8	10%	20%	70%		
2	8.0	81.7	50%	20%	30%		
3	8.0	82.0	10%			2 mg/L	90%
4	8.0	83.7	50%			2 mg/L	50%
5	8.2	87.1	10%				90%
6	8.2	70.4	50%				50%

There are a couple of other interesting items regarding the effectiveness of treatment. For both source A and B, inhibitor A (which had a higher percentage of polyphosphate) was less effective than inhibitor B (low polyphosphate) for copper. In fact, in both cases copper corrosion increased as the inhibitor A dose increased. Similar results were seen for source B (lower alkalinity) lead concentrations, but there was little difference in inhibitor performance for source A regardless of polyphosphate percentage or dose, suggesting that perhaps carbonate passivation was able to minimize some of the impact of the polyphosphate at higher alkalinity conditions.

Case Study 2

Another community in the southwestern U.S. is considering addition of a new source (potable reuse) to its current water supply portfolio, which consists of groundwater, brackish groundwater, and surface water. As a result, the community conducted an extensive pilot-scale evaluation of treatment alternatives, which included harvested pipe loop studies to determine what, if any, impact this new source might have on its current corrosion control treatment.

Seven harvested pipe loops, each with two galvanized service lines and one copper service line, were constructed. This community does not have lead service lines. Testing was conducted in three phases:

- Acclimation period, during which the loops were allowed to stabilize using plant tap water (blended groundwater and surface water).
- Phase 1, with water from the advanced purified water treatment plant (APWTP) pilot using different corrosion control treatment methods to see which performed best (pH/alkalinity adjustment, plus two different inhibitors at two different pH and alkalinity conditions).
- Phase 2, during which different blends of groundwater, brackish groundwater, and water from the APWTP were treated using the corrosion control methods that performed best during Phase 1.

Table 4 summarizes phase 2 test conditions, including the percent of each source in the blended supply. The nanofiltration (NF) permeate refers to permeate from the APWTP pilot study without any alkalinity adjustment, and the calcite contactor refers to permeate from the APWTP after it's passed through a calcite contactor for stabilization.

In preparation of the testing plan, this community consulted with its state regulatory agency, which recommended that the treated water (phase 2) meet tradition corrosion control indices to prevent lead and copper corrosion and meet the requirements of LCR. Table 5 summarizes these recommendations.

Table 6 summarizes the results of the loop testing and presents average metals concentrations for each of the test loops over the duration of phase 2 of the study. The results show that loops 1 and 2, which were simply blends of the different sources without any alkalinity adjustment or inhibitor addition, had the lowest average metals concentrations of any of the test conditions, despite being the only test conditions that failed to meet any of the recommended corrosion indices guidelines. Loops 3 and 5, which came the closest to meeting the recommended guidelines, were actually the worst-performing loops with respect to both lead and iron. Again, this highlights the importance of not putting too much credence in traditional corrosion indices when it comes to predicting metals release and the efficacy of corrosion control treatment.

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Conclusions and Recommendations

The forthcoming revisions to the LCR will result in a number of public water systems having to re-evaluate their existing CCT. Historically, systems have attempted to provide water that is slightly, but not too, saturated, with respect to calcium carbonate. Such water is considered "stable" and nonaggressive to metals in the distribution system. Water with these characteristics is thought to "form just a little, but not too much" calcium carbonate to create scale-related issues in the system.

At the same time, these waters may help to preserve cement mortar lining and concrete pipe walls, so while it's good operational practice to provide finished water with such a characteristic, there should not be a false sense of security that such water is not, or cannot, be aggressive to lead or copper.

Calcium carbonate saturation indices are not effective indicators of the corrosivity of a water toward lead and copper pipe, yet the carbonate balance plays a very important role in corrosion control. In fact, is it probable in systems that are utilizing "carbonate precipitation" as a corrosion control method that the actual inhibition of corrosion is a result of high pH, alkalinity, DIC, and other factors, but not a result of a protective scale of $CaCO_3$ forming on the interior of pipe walls?

Thus, a good understanding of the carbonate balance and the role of carbonate and bicarbonate in scale formation and corrosion control is needed, but calcium carbonate precipitation is not an indicator of corrosion control effectiveness. An understanding of traditional lead solubility models and the role of other water quality parameters, such as oxidation-reduction potential, is truly needed to establish effective corrosion control treatment.

Table 5. Recommended Corrosion Control Indices Values

Corrosion Index	Target Value
CCPP (mg/L)	4-10
LSI	>0
RI	5-7
Larson Ratio*	<0.3

*Compared to a typical recommended value of <0.8

Table 6. Corrosion Control Study Test Results

Loop	Avg Pb (µg/L)	Avg Cu (mg/L)	Avg Fe (mg/L)	CCPP (mg/L)	LSI	Ryznar Index	Larson Ratio
1	3.8	50.6	0.040	-4.32	-0.65	9.09	3.33
2	1.0	75.8	0.024	-0.55	-0.05	8.1	3.42
3	6.4	52.7	0.051	1.05	0.12	7.81	0.73
4	4.1	49.0	0.040	1.35	0.15	7.73	2.26
5	4.3	65.6	0.063	3.45	0.35	7.45	0.82
6	3.6	67.4	0.061	1.95	0.27	7.65	2.32

1,2 – no inhibitor, no alkalinity adjustment
3,4 – inhibitor and alkalinity adjustment
5,6 – alkalinity adjustment only

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