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Strategies for assessing optimized corrosion control treatment of lead and copper

THREE STRATEGIES ARE
COMMONLY USED TO OPTIMIZE
CORROSION CONTROL:
ADJUSTING pH AND ALKALINITY,
DEVELOPING Pb(IV) SCALE BY
MAINTAINING FREE CHLORINE
RESIDUALS THROUGHOUT THE
DISTRIBUTION SYSTEM,
AND APPLYING
ORTHOPHOSPHATE-BASED
CORROSION INHIBITORS
AT APPROPRIATE DOSAGES
AND pH RANGES.

Optimized corrosion control treatment (OCCT) is a specific requirement of the Lead and Copper Rule (LCR). Methods for achieving OCCT continue to evolve over time. The authors collected information, reviewed literature, discussed current practices with state regulators, and interviewed corrosion control experts in order to create a summary of the current state of the science associated with OCCT implementation in the United States.

Researchers and practitioners who are generally acknowledged experts in corrosion control were interviewed with the objective of summarizing identified issues and outlining areas of consensus as well as opposing professional views. These findings, particularly the areas of commonality among experts in the corrosion control community, can be a useful guide to water providers who are evaluating their utility's OCCT status.

In this article, interviews are supplemented with references suggested by those interviewed in support of various positions. This article is not intended to be a complete literature review of all the complex issues surrounding treatment to reduce lead concentrations, and it does not deal with other issues that may be addressed in upcoming LCR modifications (e.g., partial replacement of lead components in distribution systems or sampling and analytical procedures) aside from OCCT.

This article begins with an evaluation of the improvement in lead monitoring data since the LCR was promulgated, followed by a summary of discussions with staff at 10 state regulatory agencies, and ending with a more detailed

discussion of OCCT issues, including treatment approaches and individual factors affecting corrosion control.

PROGRESS WITH REDUCING 90TH PERCENTILE LEAD CONCENTRATIONS

The LCR was originally promulgated in 1991 and required routine monitoring for lead and copper once every six months to once every nine years. Action levels (ALs) were established at 0.015 mg/L (15 µg/L) for lead and 1.3 mg/L for copper. Under this rule, if ≥ 10% of samples tested contain lead and copper concentrations above the ALs, the water system must increase monitoring, undertake additional corrosion control efforts, and implement training and public education for customers. Some details of the LCR were modified in 2000 and 2007, but this basic regulatory framework remains. The US Environmental Protection Agency (USEPA) is scheduled to propose the Long-Term LCR (LTLCR) revisions sometime in 2013, and the final LTLCR will likely be promulgated two years later—in 2015.

During initial LCR lead monitoring in 1992 and 1993, more than 800 utilities were serving populations of > 50,000 people. Of these, 177 had 90th percentile lead concentrations above the 15-µg/L AL during one or both of the first two rounds of sampling (USEPA, 2006). These data were generally collected before utilities formally implemented OCCT as defined by the LCR. Some utilities were already meeting the AL through their normal corrosion control practices or because of a lack of lead and copper in their water systems. A total of 166 of these original utilities were sampled between 2000 and 2005. The post-2000 samples were collected after mandated compliance with LCR OCCT requirements.

The authors compiled Figures 1 and 2 and Table 1 using data reported by USEPA (2006). The table and two figures summarize and compare 90th percentile lead concentra-

tions at utilities that exceeded the AL during 1992–93 versus 2000–05. Figure 1 shows the distribution of these three discrete groups of data (round 1 1992–93, round 2 1992–93, and 2000–05) relative to the 15-µg/L AL for lead. These utilities, all of which had difficulty meeting the AL before 2000, demonstrated such an improvement in post-2000 results that only about 10% (17 of 166 systems) continued to have 90th percentile lead concentrations ≥ 15 µg/L after 2000.

Treatment approaches encouraged by most drinking water experts and implemented by water systems basically involve three variations.

Figure 2 shows paired results for pre- and post-2000 sampling. In Figure 2, results from rounds 1 and 2 in 1992–93 are plotted separately on the vertical axis, and results from the same utility sampled since 2000 are plotted on the horizontal axis (round 1 results are depicted with x symbols and round 2 results with open squares).

Five labeled zones are shown in Figure 2 and described in Table 1. Zone A represents conditions in which 90th percentile lead concentrations increased from < 15 µg/L before 2000 to ≥ 15 µg/L after 2000, but no instances of this increase occurred at these utilities (Figure 2, Table 1). Zones B and C represent instances in which both pre- and post-2000 results were ≥ 15 µg/L, but in zone C lead concentrations improved (decreased) in post-2000 samples and in zone B lead concentrations increased in post-2000 samples. Most of the data shown in Figure 2 are in zone D, indicating conditions in which results were ≥ 15 µg/L before 2000 but improved to < 15 µg/L after 2000. Zone E represents instances in which both pre- and post-2000

results were < 15 µg/L (these instances occurred when results in round 1 were < 15 µg/L and round 2 were > 15 µg/L, or vice versa).

Figures 1 and 2 and Table 1 indicate that most facilities serving populations > 50,000 people that were having difficulty meeting the AL prior to 2000 were able to improve lead concentrations in later samples. The 90th percentile lead concentrations for 164 of the 166 paired results from round 1 (i.e., when both pre- and post-2000

samples were collected) were either < 15 µg/L or were lower under post-2000 conditions than under conditions during the 1992–93 sampling. Similarly, for round 2 it was 148 of 150 utilities. More important, at 146 of the round 1 locations and 132 of the round 2 locations, the result during post-2000 sampling was < 15 µg/L. Furthermore, the median value at these locations decreased from > 20 µg/L in 1992–93 to ~6 µg/L after 2000 (Figure 1). In fact, after 2000, > 44% of results at the locations that had previously had difficulty meeting the 15-µg/L AL in 1992–93 were < 5 µg/L.

QUESTIONS FOR STATE REGULATORY STAFF

Discussions with drinking water regulatory staff from 10 states (two in New England, two along the mid-Atlantic seaboard, one in the Southeast, four in the Midwest, and one in the West) were conducted to elucidate LCR implementation issues in these states. These conversations included questions about the threshold values that trigger violations, how states respond after such a triggering event, how states

implement requirements for OCCT and water quality parameters, and other issues. These inquiries and responses are summarized in the following paragraphs. USEPA has identified implementation of OCCT as one of the issues to be addressed in the proposed LTLCR revisions.

Question 1: Were all instances in which ALs were exceeded treated equally—e.g., copper versus lead, amounts of lead or copper detected, community water systems versus noncommunity systems?

Response: There were no differences, except as dictated by regulatory requirements (no public education requirements for copper—just for lead). All large systems had to institute OCCT, but smaller systems had to do so only after exceeding an AL.

Question 2: Which water quality parameters were monitored?

Response: Temperature, pH, alkalinity, calcium, conductivity, silica (if required), and orthophosphate (PO₄) (if required). Values for water quality parameters were set through a review of operating data. States set minimum or maximum values or ranges, depending on the water system. One state set

wide ranges because of changes in water quality over the course of the year. Another state tended to set maximum or minimum values for ease of monitoring. During a USEPA audit, one state with decentralized districts discovered that some of its districts didn't set water quality parameter values at all. At the time of the audit, data collection and reporting were not done electronically, so monitoring all of the systems was difficult.

Example water quality parameters for specific situations at three facilities are as follows: facility A—pH 7.8–8.9 and alkalinity 20–125 mg/L as calcium carbonate (CaCO₃); facility B—minimum pH 7.5 and minimum alkalinity 68 mg/L as CaCO₃; facility C—pH 7.3–8.6 and alkalinity 20–60 mg/L as CaCO₃.

Question 3: How were OCCT requirements chosen?

Response: Most states developed OCCT requirements on the basis of recommendations in USEPA guidance manuals supplemented by state-specific refinements, including: (a) utility-specific engineering studies, (b) a modified Rothberg, Tamburini & Winsor model developed with USEPA

funding assistance, and (c) state-developed criteria based on engineering studies and computer models.

Question 4: What types of OCCT were chosen?

Response: Alternatives mentioned included silicates, pH and alkalinity adjustment, and orthophosphate. Silicates were rarely used. Several of the states surveyed used pH and alkalinity adjustment, including ~90% of systems in the New England states and ~50% in the western states. Orthophosphate was also commonly used, including by ~70–100% of systems in the Southeast, except for some groundwater systems that had no concerns about disinfection by-product (DBP) formation and used pH and alkalinity adjustment. Some states have had difficulty identifying a product suitable for a wide range of water quality conditions (e.g., seasonal and other variations in water quality).

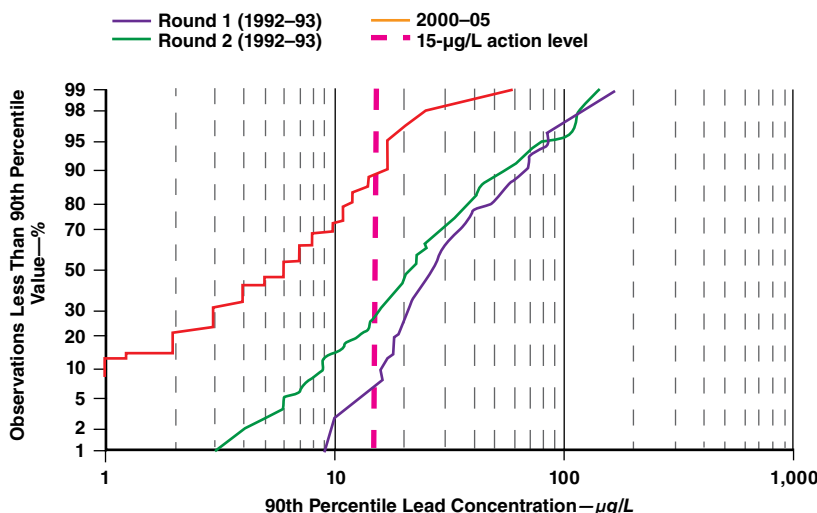
Question 5: Did systems exceed the ALs after instituting OCCT? What happened then?

Response: Some systems exceeded ALs after implementing OCCT—roughly 10% of systems in the states surveyed. State responses were situation-specific. Some state regulatory staff worked with systems to determine cause, encourage refinements (“tweaking”), or require additional study or different treatment. One state allowed utilities to exceed an AL one time before requiring additional study or lead service line (LSL) replacement. In a review of files from 10 states in 2006, USEPA found that about 75% of the time no action was taken after a system exceeded an AL (USEPA, 2006). Table 2 lists the number of times lead and copper ALs were exceeded in one state and what consequences were imposed.

Question 6: What other OCCT-related issues are regulators concerned about?

Response: Small and medium-size systems that install OCCT are not always required to report distribution system parameters that would

FIGURE 1 Distribution of 90th percentile lead values for utilities that served populations > 50,000 people and exceeded the lead action level during either round 1 or 2 sampling in 1992–93 and later results during sampling in 2000–05 at the same facilities



demonstrate that the treatment is, in fact, optimized.

- Many OCCT strategies were developed for a specific dosage of a specific corrosion control product, but utilities often obtained bids for alternative products with different formulations (e.g., orthopolyphosphate blends or zinc orthophosphate products with higher or lower zinc content) without converting the dosage of the new product to account for differences in orthophosphate content.

- Manual tracking of water quality parameters by district engineers could result in inconsistent enforcement.

- The ultimate decision process requiring LSL replacement varied from state to state.

- Some states allowed repeated tweaking of treatment, but one state allowed utilities only one chance to optimize treatment before beginning LSL replacement or conducting additional studies.

- One state determined that no LSLs were used in the state but required a “corrective action plan” if ALs were exceeded.

OCCT AND OTHER CORROSION CONTROL ISSUES

Although there was wide agreement among the experts consulted for this project regarding many corrosion control issues, there was some disagreement between one or more experts about certain issues. In these cases, this article describes the overall consensus and then includes a description of dissenting or conflicting viewpoints and interpretations.

Status of US drinking water corrosion control efforts. Most water systems have been successful at developing strategies to maintain lead concentrations below the AL. Conceivably, this could change if the need to achieve other treatment objectives (e.g., DBP control or removal of arsenic, perchlorate, or other contaminants) necessitates changes in treatment chemicals or processes that affect current corrosion control practices. Changes to

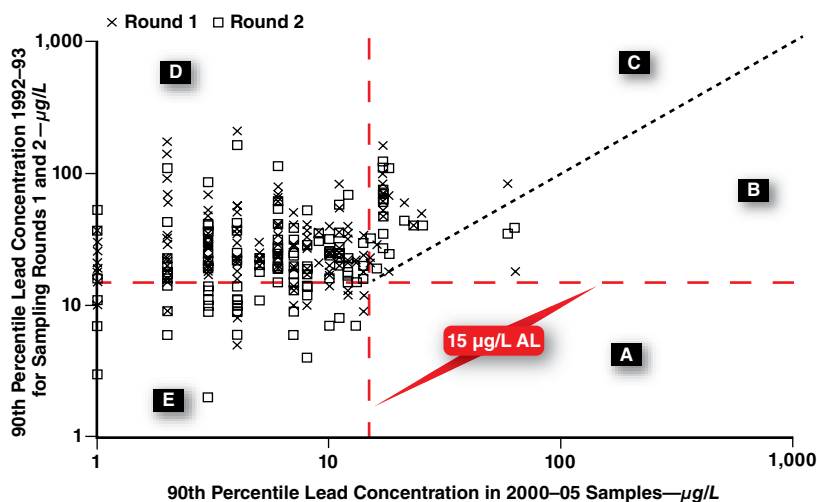
the LCR tap water sampling protocols or other potential LTLCR revisions might also cause some lead concentrations that are currently below the AL to be above the AL under the LTLCR. Also, the current LCR defines OCCT as achieving minimum lead concentrations (large systems), not just concentrations below the AL. However, the OCCT definition also recognized that in minimizing lead concentrations, utilities must exercise caution to maintain other water quality parameters. Consequently, many utilities did not minimize lead concentrations by increasing orthophosphate beyond the amount necessary to meet the AL in order to avoid unintended consequences.

Many utility laboratory or pilot studies were not set up to find a method to minimize lead concentrations but were designed solely to meet the AL. Furthermore, interviews with utility staff indicated that pipe-loop and other OCCT studies often were not predictive because changing conditions within a distribution system could not be adequately replicated at this scale. Consequently, field experience and

field trial and error enabled these utilities to establish target treatment conditions (chemical dosage, target pH, and so on) (Brown et al, 2012). The LTLCR may re-emphasize the requirement for optimizing corrosion control rather than simply meeting the AL, and this could require utilities to conduct a new evaluation of corrosion control and lead minimization techniques while meeting other water quality requirements. In any case, there may be instances in which a water system that is in compliance may need to refine its current practices or adopt completely new approaches as a result of future changes in treatment processes or LTLCR revisions.

Treatment approaches for corrosion control. Treatment approaches encouraged by most drinking water experts and implemented by water systems basically involve three variations: (1) controlling pH and alkalinity, (2) developing an insoluble scale of lead in the +4 oxidation state [Pb(IV) scale] formed under oxidized conditions by maintaining a free chlorine (Cl₂) residual, and (3) adding orthophosphate-based

FIGURE 2 Comparison of 90th percentile lead values from sampling rounds 1 and 2 in 1992–93 versus values from samples collected at the same utility in 2000–05



AL—action level
Letters in figure indicate zones

corrosion control inhibitors. Controlling pH and alkalinity and adding orthophosphate are common corrosion control practices. However, maintenance of oxidized conditions (item 2) is not normally considered primarily a corrosion control strategy. Although lead solubility can be controlled by the formation of corrosion-resistant Pb(IV) scale under oxidized conditions, the oxidized conditions (i.e., the free chlorine residual) must be maintained in order to keep the Pb(IV) from being reduced to more soluble lead in the +2 oxidation state [Pb(II)].

Various water utilities have successfully used each of these approaches, but an approach that is suitable for one water system's conditions may not be suitable for a system with different characteristics or for the same system if conditions change (e.g., use of a new source water supply or treatment technique). Each of these corrosion control approaches has advantages and disadvantages, and the experts do not always agree about the best conditions for each one.

In general, any kind of change in treatment or raw water quality complicates corrosion control efforts.

These changes require either robust treatment solutions or diligent and rapid adaptation to the changing conditions, including seasonal changes in water quality. Conversely, corrosion control efforts are simplified and a larger suite of alternatives is available when raw water quality and treatment performance are more stable.

Adjustment of pH and alkalinity can provide suitable corrosion control for conditions involving a single water source that changes little as a result of seasonal or storm events. However, maintaining required pH and alkalinity conditions can be difficult with water sources that change seasonally or in response to other events. This is particularly true when a utility blends more than one water source (e.g., multiple combinations of surface water and groundwater that vary spatially and temporally within a distribution system).

Analogous to these issues in systems using pH and alkalinity to control lead solubility, the preservation of oxidized conditions to control lead solubility by means of maintaining Pb(IV) deposits can be compromised by small changes in the distribution system's oxidation state, which can prove difficult to reliably monitor and control. This situation can cause intermittent problems with exceeding the lead AL (Schock & Lytle, 2012). Furthermore, utilities that have difficulty controlling DBPs may not be able to develop a high enough free chlorine residual in all parts of the distribution system for Pb(IV) scale to form. In addition, utilities that currently use or later convert to using monochloramine as a secondary disinfectant cannot develop conditions suitable for formation or maintenance of Pb(IV) scale (Schock et al, 1996), so use of chloramination eliminates the reliance on Pb(IV) scale as a corrosion control method. Use of orthophosphate should normally be more robust than the other two approaches, but some circum-

TABLE 1 Improvement in 90th percentile lead concentrations at utilities whose lead values exceeded the action level during monitoring rounds 1 and 2 in 1992–93 compared with samples collected during 2000–05*

Zone in Figure 2	Monitoring Results	1992–93 Data Versus 2000–05 Data	
		Round 1	Round 2
A	< 15 µg/L before 2000 but later increased to ≥ 15 µg/L	0	0
B	≥ 15 µg/L before 2000 and increased after 2000	2	2
C	≥ 15 µg/L before and after 2000 but decreased after 2000	17	16
D	≥ 15 µg/L before 2000 but < 15 µg/L after 2000	134	92
E	< 15 µg/L before and after 2000	12	40
Number of systems sampled before 2000 but not after 2000		11	5
Number of samples collected before 2000		176	155

*See also Figure 2.

TABLE 2 Data for one state in which lead and copper ALs were exceeded

Lead	Copper
Since July 2010, 27 utilities have exceeded the AL 31 times.	Since July 2010, 16 systems have exceeded the AL 18 times.
12 CWSs, 15 NCWSs	6 CWSs, 10 NCWSs
Some situations are chronic, but some involve new systems.	Some situations are chronic—e.g., the school that has exceeded the AL 13 times over a 10-year period.
Cases were referred to the district engineer.	Since 1993, the copper AL has been exceeded 444 times.
Since 1992, 45 systems have been required to replace lead pipelines.	

AL—action level, CWS—community water system, NCWS—noncommunity water system

stances limit its use (e.g., its effect on galvanic corrosion, microbiological growth, or downstream wastewater discharges).

Each of these three corrosion control approaches is discussed in more detail in the following paragraphs.

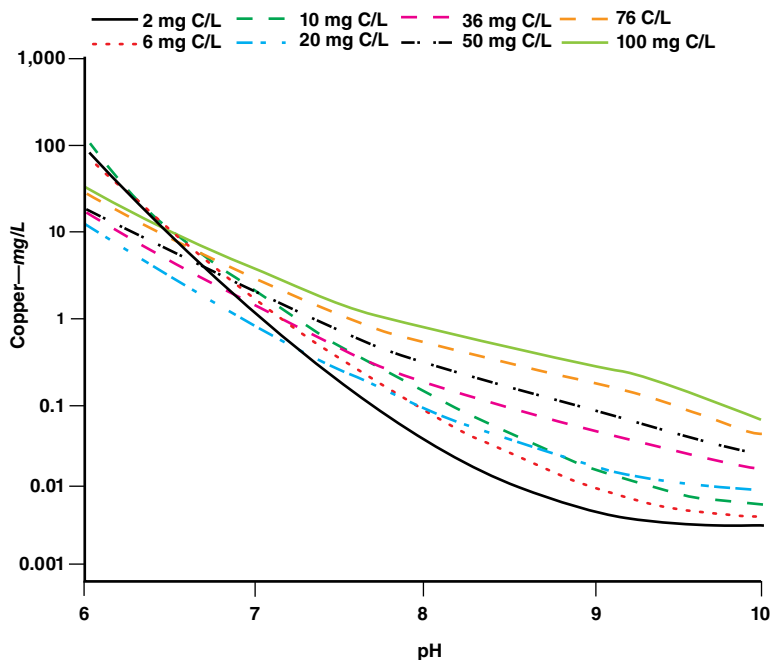
Control of pH and alkalinity.

High pH and adjustment of alkalinity to appropriate levels can reduce lead and copper solubility. As shown in Figure 3, at all pH values displayed, copper corrosion decreases as dissolved inorganic carbon (DIC) decreases. However, as shown in Figure 4, the optimal DIC for lead control depends on pH. At high pH values (~8.2 or higher), lower DIC reduces lead corrosion, as it does with copper at all pH values. However, at lower pH values (~8.2 or lower), lead corrosion diminishes with increasing DIC, although soluble lead concentrations are predicted to be too high for low pH and high alkalinity to be an effective means of controlling corrosion. Because these diagrams describe theoretical systems at equilibrium, they can be used to show general trends with increasing or decreasing pH and DIC at equilibrium, but they should not be interpreted as predicting lead or copper solubility for any specific source water.

Although these diagrams show that adjusting pH and alkalinity to appropriate conditions can control lead or copper corrosion, they also illustrate that a change in raw water conditions (e.g., a change in a given source or a change caused by blending one or more new sources) can bring about a new set of pH and alkalinity conditions that can result in different metal solubility. In these cases, the altered pH and alkalinity must be adjusted through treatment such as blending practices or chemical addition in order to maintain target pH and alkalinity ranges.

Development and maintenance of insoluble Pb(IV) scale under oxidized conditions. Under oxidized conditions—a free chlorine residual that is maintained throughout the

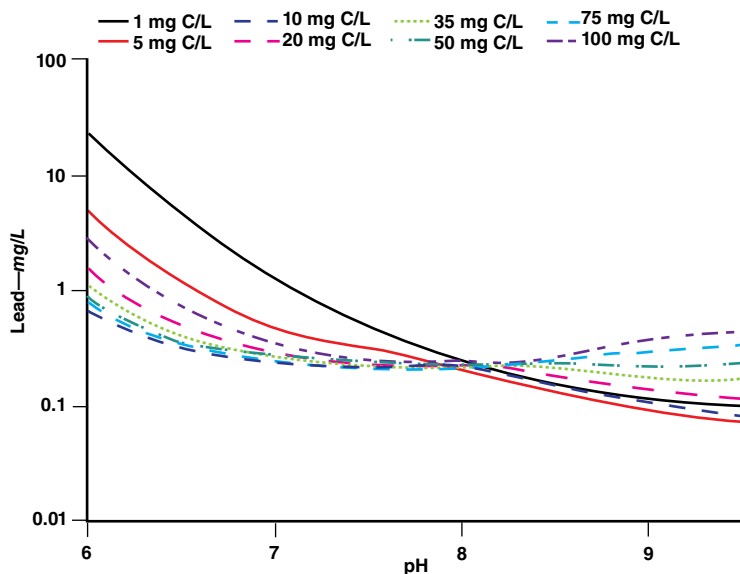
FIGURE 3 Theoretical effect of pH and DIC on copper solubility in drinking water under ideal equilibrium conditions assuming the presence of Cu(II) and no orthophosphate*



Cu(II)—copper in the +2 oxidation states, DIC—dissolved inorganic carbon

*Schock & Lytle, 2012

FIGURE 4 Theoretical effects of pH and DIC on lead solubility in drinking water under ideal equilibrium conditions, assuming the presence of Pb(II) and no orthophosphate



DIC—dissolved inorganic carbon, Pb(II)—lead in the +2 oxidation state

*Schock & Lytle, 2012; based on Schock & Lytle, 2011

distribution system all the way to the homeowner's tap—stable Pb(IV) scale [e.g., PbO_2 (s)] can form, although other deposits (Giammar, 2012; Lytle & Schock, 2005) can form at the same time [e.g., Pb(II) hydroxycarbonates]. The Pb(IV) scale can be established and maintained at measurable free chlorine residuals, although this scale will form more readily in the presence of higher free chlorine residuals, at higher pH values, and in water with low oxidant demand (Giammar, 2012; Lytle & Schock, 2005). However, if the free chlorine residual is consumed, insoluble Pb(IV) will be reduced to more soluble Pb(II) and consequently will go into solution. Fortunately, once free chlorine is re-introduced (Giammar, 2012), the solubilized Pb(II) can be oxidized back to insoluble Pb(IV). Therefore, although high free chlorine residuals can lead to the development of highly desirable, corrosion-resistant scales, this approach may not protect consumers who drink water that has been stagnant for prolonged periods. Likewise, water quality, temperature, or treatment changes that reduce the chlorine residual can decrease the stability of Pb(IV) deposits (Schock & Lytle, 2011; Lytle & Schock, 2005).

Factors that can affect the development of Pb(IV) scales include:

- Free chlorine residual—Without free chlorine, the formation of Pb(IV) scale is thermodynamically impossible (Edwards, 2012; Schock & Lytle, 2011; Switzer et al, 2006). Furthermore, as discussed subsequently, the galvanic current between lead and copper is reversed under oxidized conditions when Pb(IV) scale is present (Arnold & Edwards, 2012).

- Orthophosphate—When Pb(II) is oxidized to Pb(IV), insoluble Pb(IV) scales form. Typically, however, not all of the Pb(II) is oxidized. Consequently, orthophosphate can stabilize Pb(II) that is co-deposited with the Pb(IV) scale. If orthophosphate is present before Pb(IV) scale is formed, however, the orthophos-

phate can inhibit formation of new Pb(IV) scale (Giammar, 2012; Lytle & Schock, 2005).

- DIC—Higher concentrations of DIC increase the dissolution of Pb(IV) scale, though pH buffering capability may offset the detrimental effects of dissolution (Giammar, 2012). See the discussion of pH in the next paragraph.

- The pH value—Pb(IV) scale formation kinetics are faster at high pH values (Schock & Lytle, 2011). At $\text{pH} < 7$ dissolution of Pb(IV) scale increases drastically (Schock & Lytle 2011).

- Dissolved natural organic matter—The presence of these compounds promotes microbiological activity and, more important, consumes free chlorine residual (Giammar, 2012).

- Polyphosphate sequestering agents—These chemicals have a negative effect on Pb(IV) stability because polyphosphate increases lead (and copper) solubility (Schock & Lytle, 2011; Schock, 1989).

- Conversion to chloramines—Monochloramine is not a strong enough oxidant to convert Pb(II) to Pb(IV), according to basic electrochemical research by Pourbaix (1966) and reported in more recent publications by Valentine and Lin (2009), Rajasekharan et al (2007), Switzer et al (2006), James et al (2004), and Schock et al (2001, 1996). If a distribution system with a free chlorine residual is in equilibrium with Pb(IV) and then the utility switches to chloramines as a secondary disinfectant, the Pb(IV) will be reduced to more soluble Pb(II).

Use of orthophosphate-based corrosion inhibitors and polyphosphate sequestering agents. The theoretical copper and lead solubility relationships shown in Figures 3 and 4 depict the effects of pH and DIC, assuming no orthophosphate is present. Orthophosphate use can allow more neutral pH values and can produce comparable or better lead and copper control than DIC and pH control without orthophosphate. The

optimal pH for corrosion control with orthophosphate is about 7.4, though it does well over a wider range of pH values (7.2–7.8), so long as the orthophosphate dosage is adjusted appropriately for a given source water. Many utilities that use chloramination also use orthophosphate. The optimal pH for chloramination (about 8.0–9.0) is slightly higher than the optimal pH for orthophosphate, but because monochloramine is the predominant chloramine species present at $\text{pH} > 7$ —with little dichloramine formation at chlorine-to-ammonia ratios $< 10:1$ (Kirmeyer et al, 2004)—many utilities that use chloramines are able to control pH, the ratio of chlorine to ammonia, DIC, and orthophosphate dosage to maintain corrosion control under these conditions.

Key issues associated with the use of orthophosphate and other phosphate chemicals for corrosion control include

- Orthophosphate dose and residual—Typical orthophosphate dosages in the United States are 0.5–3.0 mg/L as PO_4 or 0.2–1.0 mg/L as phosphorus (P). The distribution system should be monitored and the appropriate residual maintained, as can be demonstrated by the OCCT program. In the United Kingdom, the recommended target residual is higher than in the United States (0.5–2.0 mg/L as P), and the use of orthophosphate is required unless an equivalent approach can be demonstrated (Hayes, 2010). It is possible that US applications should be moving toward the higher dosages recommended in the United Kingdom, although some experts consulted for this project were reluctant to recommend dosages higher than 1.0 mg/L as P. In any event, optimal pH, DIC, and orthophosphate values should be established on the basis of site-specific conditions.

- The pH value—Optimal pH is about 7.4 and typically is best between 7.2 and 7.8. Balancing pH for the use of both orthophosphate and chloramines can be challenging

(because optimal pH for chloramination is slightly higher than optimal pH for orthophosphate), but maintenance of appropriate chlorine-to-ammonia ratio, DIC, orthophosphate dosage, and pH between 7 and 8 typically produces the most favorable conditions for corrosion control with orthophosphate while also ensuring suitable chloramination conditions (Schock et al, 2008).

- Orthophosphate with and without zinc—Studies have demonstrated that orthophosphate helps control lead release by forming a passivation layer but that zinc content has little if any effect on lead (Schneider et al, 2011; Atassi et al, 2009; Edwards & Holm, 2001). However, the zinc content may be useful in controlling corrosion of cement-based pipe and linings and may potentially improve corrosion control in iron, steel, and galvanized pipe (Schock & Lytle, 2011).

- Effect of orthophosphate-based corrosion inhibitors on wastewater—The necessity of controlling nutrient discharges from wastewater facilities has limited the use of orthophosphate-based corrosion inhibitors in some localities. Zinc-based orthophosphate corrosion inhibitors have the additional disadvantage of affecting zinc discharges from wastewater facilities, limiting the applicability of these agents for drinking water applications. No comprehensive assessment of the relative importance (or lack of importance) of orthophosphate-based corrosion inhibitors added to drinking water versus phosphorus from other sources in wastewater was identified during the interviews for this study. To put the situation in perspective, the median inorganic phosphorus concentration in wastewater treatment plant influent is about 5 mg/L as P (Metcalf & Eddy, 2003). When phosphorus removal is required during wastewater treatment, the required effluent targets are usually lower than 2 mg/L as P. Therefore, water utility use of orthophosphate-based corrosion inhibitors probably will not drive a

wastewater system that currently does not require removal of total phosphorus to implement phosphorus removal. However, if total phosphorus removal is required for a wastewater system receiving water that has been supplemented with orthophosphate-based corrosion inhibitors at concentrations of 1–2 mg/L as P, the phosphorus added for corrosion control would affect wastewater treatment costs.

- Effect of orthophosphate on copper control—Although most of the discussion in this article concerns the control of lead, information published by Schock and Sandvig (2009) points out that in parts of a water system with new household copper pipe (i.e., new construction), orthophosphate will initially control copper release better than it was controlled without orthophosphate. However, copper concentrations in distribution systems without orthophosphate will decrease as copper aging produces copper hydroxide scales, which eventually (in years or decades) may produce lower soluble copper concentrations than in systems that continuously apply orthophosphate throughout the same period.

- Polyphosphate sequestering agents—Polyphosphate is widely used as a sequestering agent for iron, manganese, and calcium in finished water. However, these agents also solubilize lead and copper, negatively affecting their control (Hayes, 2010; Schock et al, 1996; Schock, 1989).

Other factors affecting lead and copper corrosion. Particulates. OCCT and other corrosion control approaches typically target conditions that inhibit solubility and release of soluble lead and copper. However, lead deposits can be released intermittently by flow fluctuations and other disturbances in the water and the pipe. Furthermore, soluble lead can sorb onto the surfaces of particulates (Schock & Lytle, 2011). After they dislodge from the pipe surface, these lead-containing particles can be trans-

ported to the customer's tap. The amount of lead contained in or sorbed onto these particulates can be significantly higher than the AL for soluble lead. Some experts suggested that the intermittent (i.e., uncontrolled and unpredictable) nature of releases of particulate lead, and the magnitude of lead concentrations associated with these releases, necessitates industrywide efforts to evaluate and control particulate lead concentrations, but these experts also emphasized the need to control the original release of soluble lead.

Some experts suggested that it may be beneficial to focus on controlling iron corrosion and iron and manganese postprecipitation rather than simply targeting lead control. If water providers focused first on limiting the production and release of iron and manganese deposits, particulate releases in distribution systems would be limited, and thus the release of lead accumulated on these deposits would be limited. For example, particulate releases can occur in old galvanized plumbing that has lost its galvanization layer and has developed heavy iron scaling and associated accumulated lead (Reiber, 2012; McFadden et al, 2011, 2009). Iron corrosion scales accumulate throughout the distribution system, including household plumbing, and can accumulate significant amounts of lead (Friedman et al, 2010). Consequently, efforts to control sources of iron and manganese particulates may also enhance lead control.

Galvanic corrosion. The galvanic current produced when two dissimilar metals are in contact will result in galvanic corrosion of the metal that is lower in the galvanic series (the less noble metal), referred to as the anode. The metal that is higher in the galvanic series (the more noble metal) is called the cathode, and its rate of corrosion will be reduced. When copper and lead pipes are connected electrically (Larson, 1975), for example after a section of lead pipe is replaced with a piece of copper pipe or when lead and copper are

connected in the home, the resulting galvanic current will produce corrosion of the less noble lead. Other possible galvanic connections occur between lead anodes and brass or lead-tin solder cathodes.

The importance of galvanic corrosion has been the subject of some disagreement among experts. Galvanic corrosion is a recognized phenomenon, and there is general agreement that it occurs in household plumbing throughout drinking water systems because of the presence of numerous copper-to-lead and similar connections. The phenomenon occurs not only at direct lead and copper connections but also at various sites of deposition corrosion. Deposition corrosion can occur when copper in solution is deposited as a solid on a lead surface, creating a new lead-copper galvanic couple (Britton & Richards, 1981). The disagreement among researchers centers on the significance of galvanic corrosion in both experimental studies and field observations. One school of thought contends that galvanic corrosion stops after a short period of time and may not be a long-term issue. In contrast, others cite studies demonstrating the continuation of galvanic corrosion for months or years (Cartier et al, 2012; Edwards, 2012).

Evidence on both sides of this issue has been listed and discussed in USEPA's Sept. 28, 2011, Science Advisory Board report dealing with issues related to partial LSL replacements, including the potential effect of galvanic corrosion (USEPA, 2011). On the basis of the board's review of the information cited, the report asserts that galvanic corrosion does pose a risk of increasing lead concentrations at customer taps, especially taps that are close to lead-copper galvanic connections and particularly shortly after creation of a lead-copper connection, including direct connections and deposition corrosion locations. Since the USEPA report was published, a literature review and critique of previous Water Research Foundation research

efforts dealing with galvanic corrosion has been published (Giammar et al, 2012).

Under reducing conditions, at lead-copper couples the lead is the anode and corrodes. However, under oxidized conditions (e.g., in the presence of a free chlorine residual), the polarity is reversed, and lead becomes the cathode and is protected (Arnold & Edwards, 2012; DeSantis et al, 2009). Therefore, another benefit of increasing the oxidation of lead by maintaining free chlorine residuals is the possibility of reversing the galvanic effect, thus protecting lead instead of releasing it through galvanic activity.

Except for reversing the galvanic relationship of lead and copper under oxidized conditions when Pb(IV) scale is present, there are really no established methods to remediate galvanic corrosion. Reversal would require every direct copper-to-lead connection to be identified and disconnected. This would mean removing one of the two dissimilar metals or adding a nonconductive (dielectric) material to break the copper-to-lead or lead solder-alloy connection at each valve, coupling, and other fitting throughout the system.

There is evidence that when conditions are conducive to galvanic corrosion of lead, adding orthophosphate can actually increase galvanically induced lead release (Edwards, 2012; Cartier et al, 2012). Furthermore, as noted in Schock and Lytle (2011), the effect of a galvanic cell in water that has low conductivity is generally limited to the vicinity of the galvanic connection, though the effect can spread to more of the surface area of the anode if the conductivity of the water is higher. There is also evidence that changes in the relative amounts of chloride and sulfate in water (caused by a change in coagulant) can affect galvanic corrosion (Triantafyllidou & Edwards, 2010). Therefore, any change in corrosion control

practices, including the addition of orthophosphate, or other changes in treatment need to be carefully evaluated for site-specific conditions before full implementation.

Microbiological activity. Microorganisms require carbon (C), nitrogen (N), and phosphorus to grow, typically at molar ratios of about 100:10:1 (LeChevallier et al, 2011). For situations that are phosphorus-limited, addition of orthophosphate for corrosion control could result in large increases in microbiological growth that, once established, would be difficult to bring back under control. For systems that are switching to chloramination and that also have added or will add orthophosphate, the potential effect could be even greater as a result of the application of two potentially growth-limiting constituents. Consequently, though most water systems in the United States are not phosphorus-limited, water providers who are contemplating conversion to orthophosphate for corrosion control should at least quantify or estimate C:N:P ratios for their proposed finished water supplies and perhaps conduct experiments investigating microbiological growth, if feasible.

One potential issue for chloraminated systems using orthophosphate for corrosion control in water with low DIC concentrations is that nitrification could reduce the pH to a value that is below optimal for proper corrosion control with orthophosphate (Schock & Lytle, 2011).

Silicate. Silicate-based corrosion inhibitors can act as anodic inhibitors that inhibit oxidation and release of metals, including lead and copper. Orthophosphate has been demonstrated to be more effective than silicates at controlling lead and copper releases in laboratory studies using new pipe or coupons. However, one field study investigating the combined long-term effects of replacing polyphosphate with silicate and maintaining high pH and free chlorine residuals resulted in

improved iron and manganese sequestration while also controlling lead and copper corrosion (Schock et al, 2005). With the use of silicates, however, it is unclear whether lead and copper control is achieved by silicate or high pH.

Chloramination. Controlling corrosion by adjusting pH and alkalinity (without adding orthophosphate) generally requires an optimal pH of > 9. Chloramination can be used successfully at a pH above 9. At this pH value, essentially all the chloramines are monochloramine, which is the desired chloramine species. Because the reaction rate between chlorine and ammonia is slow at pH 9, the reaction should be carried out at a lower pH (the reaction is fastest around pH 8.3), and the pH should be increased afterward. If the chlorine–ammonia reaction is carried out at pH > 9, sufficient mixing time needs to be provided. The chlorine–ammonia reaction time at pH 9 requires minutes instead of seconds required at pH 8 (White, 1986). At the higher pH, a reaction chamber may be needed for the ammonia addition.

Chloramines can also be used in combination with orthophosphate at a pH of 7.2–7.8 for corrosion control. Challenges are involved in balancing pH to get the best corrosion control with the combination of orthophosphate (pH 7.2–7.8) and chloramination (a pH of 8.0–9.0 is optimal but it can be adjusted to 8 or lower), even though the best pH for the combined treatment process may not be optimal for either disinfection or corrosion control individually.

SUMMARY

The information reported in this article indicates that most water systems serving populations > 50,000 people meet the 90th percentile lead AL required by the LCR. Most utilities that exceeded the AL before 2000 have refined their corrosion control approaches to the extent that lead concentrations in their finished water

supplies are now below the 90th percentile AL. However, there are a few systems that continue to exceed the 90th percentile AL.

The information about issues affecting corrosion control efforts at drinking water utilities is based on consultations with several engineers, chemists, and microbiologists from drinking water systems, academic institutions, federal and state regulatory agencies, and other areas of the profession. Although there is still much to learn about lead control,

improve their existing OCCT approach or, as a last resort, can re-evaluate the other available OCCT strategies shown in Figure 5. Although other corrosion control alternatives are possible (e.g., silicate), these figures focus on the three major options.

Site-specific conditions typically dictate that water utilities assess and implement these corrosion control strategies while balancing other factors such as cost, compliance with other drinking water regulations (e.g.,

Although there is still much to learn about lead control, there are large areas of agreement among those consulted about the state of science on OCCT.

there are large areas of agreement among those consulted about the state of science on OCCT. There are various paths to reducing the release of lead from plumbing into drinking water, and many, sometimes complicated, flow diagrams have been developed for water providers to use in selecting an appropriate corrosion control method on the basis of water quality characteristics and other considerations. However, the current consensus is that three principal methods exist for controlling lead corrosion: (1) adjustment of pH and alkalinity, (2) development of Pb(IV) scale through maintenance of free chlorine residuals (highly oxidized conditions) throughout the distribution system, and (3) application of orthophosphate-based corrosion inhibitors at appropriate dosages and pH ranges.

The decision tree in Figure 5 illustrates the use of these three corrosion control strategies and summarizes current thinking about OCCT alternatives. Figure 6 addresses evaluations needed by water utilities that have an OCCT program in place but want or need to improve corrosion control. Water providers in this situation can evaluate methods to

those governing DBPs), and wastewater implications (limits on phosphorus and zinc discharges). Consequently, it is inappropriate to develop a generic, one-size-fits-all, sectorwide generalization as to how corrosion control should be implemented. Figure 5 represents the authors' overview of the findings gleaned from discussions with industry experts during this study, but it is not intended to apply to every specific site.

When a utility begins to evaluate different OCCT strategies, a possible starting point is to address whether orthophosphate will be used (Figure 5). Orthophosphate is most effective for corrosion control when the water's pH is within the range of 7.2–7.8. Some experience in the United Kingdom indicates that a pH as high as 8.5 could be used, but to date US data do not support this finding. The required orthophosphate dosage rises with increasing DIC, but an exact relationship or a simple chart for estimating dosage is not available. General practice in the United Kingdom is to use a higher phosphate dosage than in the United States, and some experts believe the dosages used in the United States

should be higher in order to minimize lead concentrations. Typical orthophosphate dosages in the United States are within the range of 0.2–1.0 mg/L as P, whereas dosages in the United Kingdom are in the range of 0.5–2.0 mg/L as P.

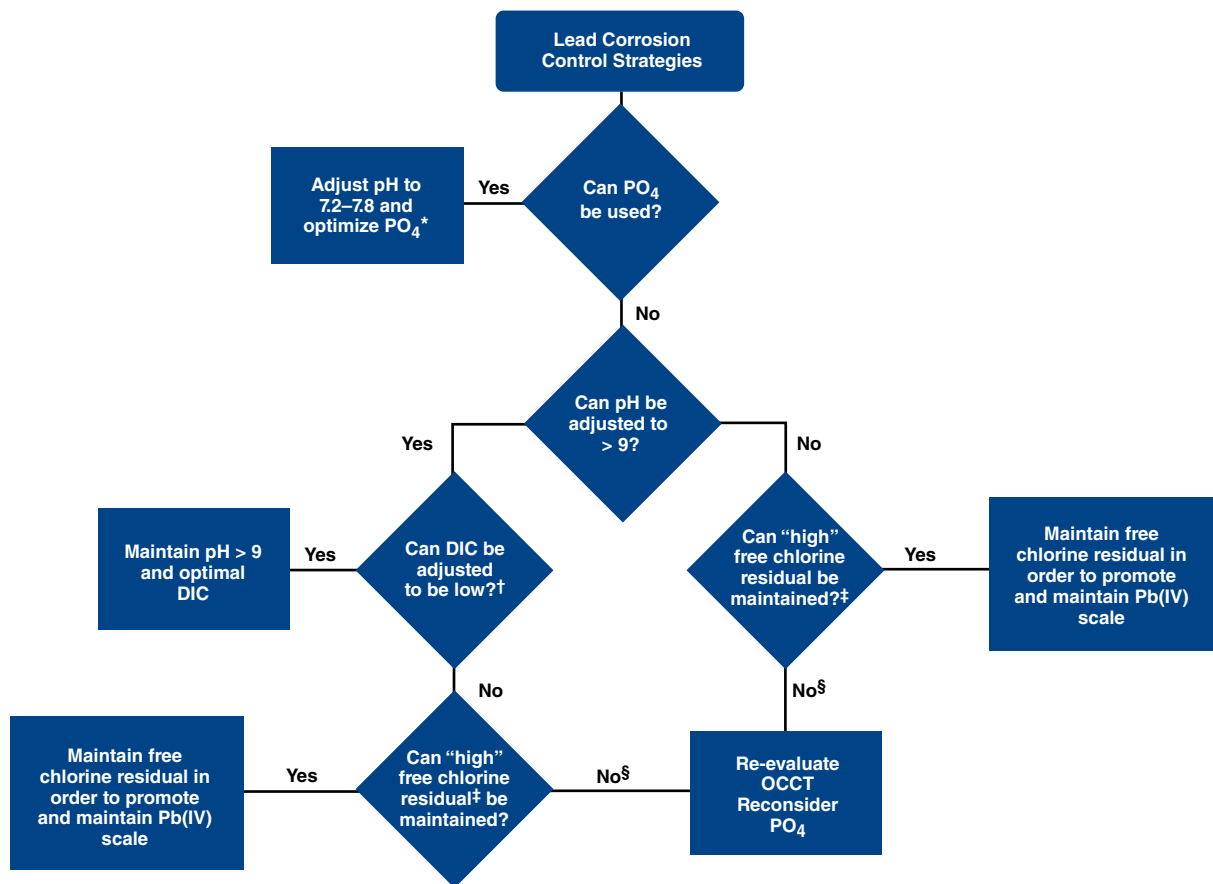
Many large utilities have conducted pilot pipe-loop studies in an effort to establish target pH values, chemical dosages (e.g., for orthophosphate), and other conditions needed to meet ALs or to minimize lead concentrations. However, utility personnel who have used loop stud-

ies indicated that only field experience and field trial and error enabled them to establish a chemical dosage or other treatment condition. The loop studies often were not predictive because the actual conditions that exist in a distribution system over time could not be adequately replicated at bench or pilot scale with sufficient certainty to ensure effective corrosion control without unacceptable unintended effects (Brown et al, 2012).

Orthophosphate can be used with free chlorine or chloramines. The

only caution with using chloramines is the operating pH range. There are potential drawbacks to using orthophosphate, including effects on (1) discharges to wastewater and wastewater treatment (phosphorus can be an issue with all orthophosphate products, plus zinc, for zinc orthophosphate products), (2) galvanic corrosion, (3) biofilm growth (phosphorus is often the limiting nutrient), and (4) cost. A substantial regulatory effort under the Clean Water Act also limits the acceptability of high phosphate dosages in some US communi-

FIGURE 5 A potential decision tree illustrating OCCT strategies as discussed in this report



C—carbon, DIC—dissolved inorganic carbon, OCCT—optimized corrosion control treatment, PO₄—orthophosphate, Pb(IV)—lead in the +4 oxidation state

*Higher pH may be acceptable.

†Typically < 10–20 mg/L as C, but depends on site-specific conditions

‡A high free chlorine (Cl₂) residual may require a concentration of 1 mg/L as Cl₂ or higher throughout the distribution system, depending on local conditions (e.g., water quality, type and age of pipe, and water age in certain parts of system).

§For example, in a chloraminated system

ties, whether there is a significant effect on actual phosphorus concentrations in wastewater or not.

If utility personnel decide that orthophosphate is not an option or not the preferred option, there appears to be one other option for systems using chloramines and two other options for systems using free chlorine as the secondary disinfectant. Chloramine systems can use high-pH values and low-DIC concentrations to reduce lead concentrations, whereas free chlorine systems can use that method as well as maintaining high free chlorine residuals throughout the distribution system. Without orthophosphate and depending on the free chlorine concentration, lead corrosion can be controlled either by lead hydroxycarbonate [Pb(II) scale] when chloramines or low free chlorine residuals are present or by PbO₂ solids [Pb(IV) scale] when high free chlorine residuals are present.

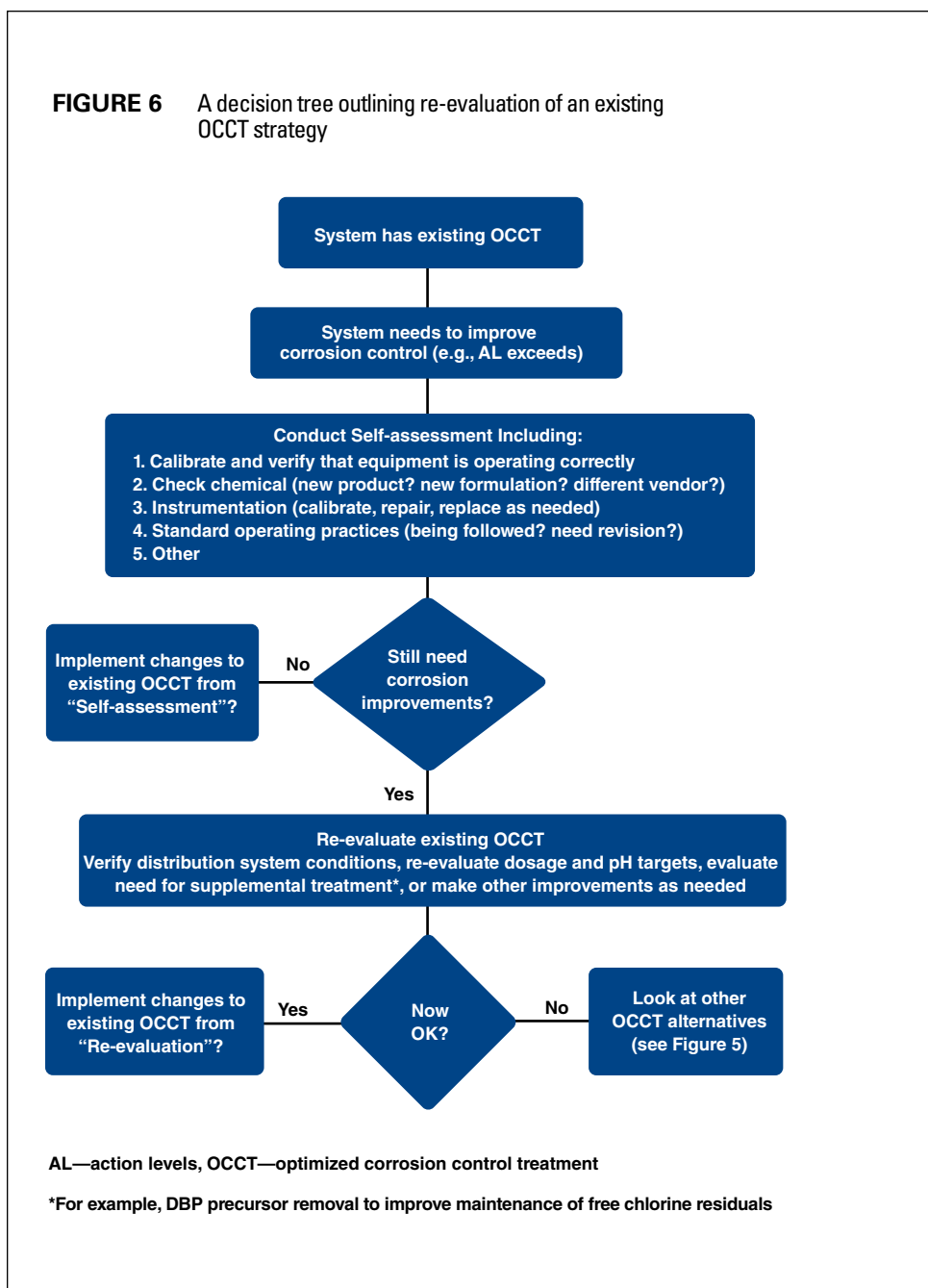
Lead hydroxycarbonate passivation requires that the pH be maintained above 9 and the DIC concentration be maintained at < 10–20 mg/L as C. The DIC concentration could vary from these guidelines at specific locations, but this is a generally accepted range. Lead hydroxycarbonate will predominate if the free chlorine residual is low or if chloramines are used. Under these high-pH and low-DIC conditions, deposits of both lead hydroxycarbonate and PbO₂ solids will form if a high enough chlorine residual is maintained at the lead source (pipe, solder, fittings, and so on). Maintaining a high chlorine residual may require a concentration of 1 mg/L as Cl₂ or higher throughout the system, depending on local conditions (water quality, type and age of pipe, water age in certain parts of the system, and so on). One advantage of passivating the system with Pb(IV) scale (high chlorine residual) is that its formation is independent of pH and DIC in the normal ranges found in water distribution systems, and therefore a pH > 9 and a low DIC

concentration are not required in this situation as they are for protection by lead hydroxycarbonate. Maintaining high free chlorine residuals throughout the distribution system and at the source of lead while also avoiding the formation of DBPs may require water with a low concentration of natural organic matter. In general, it is likely that the lead concentrations achievable by lead hydroxycarbonate will be higher than those achiev-

able by either the PbO₂ solids or an effective Pb(II) orthophosphate film.

Figure 5 shows the re-evaluation of OCCT and the use of orthophosphate as a final contingency in case no other solutions are deemed effective. Even in cases in which system personnel do not desire to use orthophosphate, if the finished water's pH cannot be adjusted to > 9 and high free chlorine residuals cannot be maintained (for example, in a chloraminated system), the utility may

FIGURE 6 A decision tree outlining re-evaluation of an existing OCCT strategy



need to revisit the orthophosphate option. If orthophosphate still is not considered a viable alternative, then other aspects of treatment need to be revisited. For example, if chloramines are used because the potential for DBP formation is too high, perhaps some method for improving DBP precursor removal could be used to produce acceptable DBP concentrations so that free chlorine could replace chloramines.

Another concern arises when the secondary disinfectant is changed from free chlorine to chloramine. Again, there were some areas of agreement among the experts regarding this situation. In a distribution system that has developed Pb(IV) scale (high free chlorine residuals, no orthophosphate), the Pb(IV) will reduce to soluble Pb(II) after the change to chloramines is made. In the short term following this change, lead concentrations in the water will increase. If the system has a pH > 9 and a DIC concentration less than about 20 mg/L as C and if the change is made from free chlorine to chloramines without orthophosphate addition, the system should eventually be passivated with a lead hydroxycarbonate scale. However, at lower pH or higher DIC values, lead hydroxycarbonate scale will not form, and the only viable method for controlling lead corrosion after switching to chloramines is to add orthophosphate.

Figure 5 and the accompanying discussion relate to the overall selection of an OCCT method. However, most utilities already have an OCCT program approved and in place. The need to re-evaluate an existing OCCT approach may arise when an AL is exceeded after a history of compliance or there is a desire to reduce lead concentrations below the current AL for an additional margin of safety or as the result of a regulatory requirement. Figure 6 is designed to help with the decision process in this situation.

The first step recommended for a utility that unexpectedly exceeds an

AL or wants to reduce lead concentrations is to conduct a self-assessment. During this self-assessment, the water system's equipment, treatment chemicals, and water chemistry should be checked. Assessments would be conducted for the functioning of chemical feed pumps, the functioning and calibration of on-line instrumentation, the operation of chemical weighing scales or feed-monitoring devices, changes in chemical products (different product or different vendor), and maintenance of water quality parameters. This self-assessment will indicate program corrections as appropriate. If changes to OCCT are needed, Figure 6 can lead a utility through that process. If the current OCCT includes orthophosphate, then possible interferences such as the effects of biofilm and galvanic corrosion could be checked. Increasing the orthophosphate dosage should also be considered. If the OCCT relies on a high free chlorine residual, system personnel should make sure the residual is being maintained all the way to customer taps or consider taking action to better maintain the residual, including raising the chlorine dosage. In systems that rely on high pH and low DIC values, not much can be done to lower lead concentrations if all water quality parameters are being maintained. In all cases, if further lead reduction is needed, all OCCT alternatives should be revisited.

USEPA is scheduled to propose LTLCR revisions in 2013 and will likely finalize the new rule within another two years (in 2015). Water system personnel have the opportunity to begin evaluating current OCCT practices and to gather data to inform future OCCT decisions that might be necessary as a result of operational changes or new regulatory requirements. It is possible that the LTLCR will cause more water systems to exceed the lead action level and thus require them to reexamine their OCCT practices.

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