

CORROSION CONTROL PRINCIPLES AND STRATEGIES FOR REDUCING LEAD AND COPPER IN DRINKING WATER SYSTEMS

Michael R. Schock
and
Darren A. Lytle
Drinking Water Research Division
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

INTRODUCTION

The newly promulgated Lead and Copper Rule (CFR 141.82, May, 1991) will force substantial changes in the way water utilities of all sizes treat their water and control corrosion. The corrosion process is fascinating in that the more learned about it the more it is realized that there are very few generalities. This paper emphasizes concepts associated with sampling, and the trade-offs in water quality associated with various methods of corrosion control. The point-of-entry water treatment industry in general will have a substantial opportunity to grow in the area of corrosion control. There are things that central water treatment can't accomplish. Having an awareness of the complexities involved can put the water treatment industry in a good position to develop applications in the future that can be quite helpful.

There are two parts to this paper. First, an overview of the plumbing and corrosion issues for both building and domestic systems is presented. The United States Environmental Protection Agency (USEPA) is conducting research on building lead corrosion problems. The second part of this paper will discuss a joint project between the Water Quality Association (WQA) and USEPA, involving the impact of domestic-type water softeners on corrosivity. Naturally soft waters tend to be more corrosive than naturally hard waters; however, there are many exceptions. The soft water effect is probably more related to the pH of the water than the hardness. Most naturally soft waters tend to have a relatively low pH, for example, in the 5.5-7.0 range.

Suggested References

Several good general texts and discussions covering drinking water corrosion treatment considerations are available for more background on the subject. One such book: Internal Corrosion of Water Distribution Systems¹, was jointly produced by the American Water Works Association Research Foundation (AWWARF) and the Engler-Bunte Institute from Karlsruhe, Germany, and was published in 1985. The document will be revised this year by most of the original authors of the first edition, and the target publication time is the last half of the year. Hopefully, this revision will include much of the experience from Britain and the Scandinavian countries as well. The book contains chapters dealing with all types of drinking water and potable water corrosion, plus discussions of inhibitors, inhibitive mechanisms, and sampling and testing

protocols. A general overview of corrosion is also presented. Many case studies and references are included in the book.

Another book, Water Quality and Treatment, Fourth Edition², published by American Water Works Association (AWWA), deals predominantly with different types of water treatment and corrosion control. A third book available is an older publication particularly useful to the smaller water systems. It was originally developed by USEPA and was entitled Corrosion Manual for Internal Corrosion of Water and Distribution Systems.³ AWWA took the same document and published it under the name of Corrosion Control for Operators.⁴ The repackaged version, including color photographs, is still available from AWWA. Although parts of the book are outdated, a lot of practical information about chemical feed systems and alternatives associated with setting up small system corrosion control projects are presented. A fourth, more specific book is Lead Control Strategies⁵ which came out in 1989 and was published by AWWARF.

PART I. CORROSION CONTROL ISSUES AND STRATEGIES

Secondary Impacts of Corrosion Control

One issue that complicates the development of new regulations is that considerations of health effects and concern on the part of Congress are driving the EPA to regulate contaminants at levels that water treatment scientists and engineers sometimes doubt that central water treatment can control. When many simultaneous regulations are imposed, chances of chemical incompatibilities increase. Prioritizing regulatory choices then involves making a trade-off between one risk and another. For instance, attempting to enhance lead corrosion control through pH adjustment may adversely effect trihalomethane (THM) formation. THM's are potential carcinogens that are also being simultaneously controlled by another regulation. The ultimate result is that while trying to optimize treatment for one contaminant (lead levels), another situation may be made worse. States and utilities will have to deal with this problem in the future as more and more regulations are passed. Other water quality parameters that could be adversely affected by lead and copper control could be things like disinfectant effectiveness, formation of a variety of disinfection byproducts, and iron and manganese control. Another example is that many of the optimum conditions for sequestration of iron and manganese by treatment chemicals are precisely the conditions that would mobilize lead and copper.

Another secondary impact of corrosion control is wastewater discharge compliance for water containing phosphate and zinc. Many of the well-known corrosion inhibitors used to control lead and copper corrosion are based on phosphate compounds, and many of the inhibitors may also contain zinc. Several states are setting restrictions on zinc discharge into wastewaters, zinc in sludges, and phosphate

loading of treatment plants. Certainly there is a potential conflict between corrosion control in drinking water and the fields of water and solid waste management.

Corrosion control may also have an impact on industrial processes. Each industry has some particular new requirements for the water chemistry it has to process. Adding different chemicals, or manipulating the water quality for corrosion control, may force various industries to modify or completely change their current treatment process. One example is the fairly critical pH control on water required by textile industries. If a water utility is to suddenly implement corrosion control and raise their pH from 6.5 to 8.0, the textile industry needs to be informed of that so they have time to investigate potential impacts, and make allowances for modifying their process, if necessary. Major local industries should always be informed of potential municipal water treatment changes, so that they can make plans to adjust to the changes.

Water conservation in itself may increase corrosion problems. In areas where water usage is reduced by installation of low-flow and flow-restrictive devices, the stagnation time of water in contact with the pipe will be increased. The amount of water and the time required to flush that system of stagnated water will be increased. The problem may be worse for buildings with many lead-soldered joints or lead service lines. Flushing to clear unpreventable (through treatment) contamination will result in wasting water where water conservation is attempted.

Assessing and Locating Corrosion Problems

There are several different issues that are involved in assessing and locating domestic plumbing corrosion. One issue focuses on the characteristics and principles of corrosion control, and what corrosion control strategies utilities are going to have available to them. Another critical issue in this field is diagnostic sampling. Sampling is not only a science, but an art that can be used for many different purposes. One of the problems with sampling is that depending on how the sampling program is set up, sample bias can show almost any level of lead or copper desired. While trying to solve a metal contamination problem, both an accurate identification of what the problem was in the first place, and an assessment of how good any control measures are operating are critical. In one case study, a conscientious state agency thought there was a widespread lead problem in some school systems. The problem turned out to be primarily a sampling artifact. Once a very systematic and reproducible sampling program was applied, it was found that the high lead concentrations were seen to be an idiosyncrasy of when they chose to do the sampling, the size of the samples, and other related factors. There is a wide variety of materials in a distribution system and for each material there are water chemistry conditions that can be either corrosive or noncorrosive. Typically, older systems have some combination of lead pipe, lead goose necks, lead service lines, and copper pipe with plumbing having soldered joints. Until several years ago, normal solder used in drinking water systems was 50/50 or

60/40 Pb:Sn. Subsequently, in 1988, solder used in drinking water systems was restricted to 0.2% lead. Most brasses both used in the past and in the present contain 2 to 8% lead and various water chemistry conditions can cause leaching of this lead. Much of the application of brass materials are beyond the control of the utility (i.e. water fixtures). However, because the utility's compliance with parts of the new Lead and Copper Rule is going to be governed by tap water sampling, the brass plumbing fixtures enter into the picture. Copper is currently the material of choice now for most metallic plumbing systems. Other major materials currently in use are galvanized pipe, uncoated iron mains, cement-mortar lined pipe, asbestos/cement pipe, and plastic pipe. Many utilities have a major mix of all or many of the various pipe materials. These utilities will have a problem on their hands to come up with a compromise treatment that will help control contaminant levels from some pipe while simultaneously protect and prolong the lifetime of the other plumbing materials.

Principles of Corrosion

Source Materials

The principles of corrosion are based on several phenomena. One phenomenon is the oxidation of the metal which is the transformation of the metal from the base state to a chemical form where it can be mobilized. Metal solubility governs how much of the metal stays in the water and whether it forms a passivating film that will retard future corrosion. Speciation of the metal is important in governing the mobility of the metal, how it reacts to treatments and removal processes, and the relationship to the source of the material. For example, lead pipe will have the potential of producing or leaching lead indefinitely. However, lead leaching will follow a relatively uniform response to water quality after the initial films are built up on the surface of the pipe (normally five or ten years). Soldered joints on the other hand, are a inhomogeneous material and involve competing dissolution mechanisms. There is some passivation on the surface of the solder by chemical reaction with the water, but physical removal also takes place. Eventually, much of the surficial lead actually dissolves away.

Sometimes lead contamination is associated with the overuse of flux during soldering. The flux preferentially dissolves the lead, spreads it out over the pipe surface, and separates it from the rest of the solder. Eventually, the lead contained in the flux film will be partially removed. A similar reduction of leaching with time is observed for brass. Lead is disseminated fairly evenly throughout the brass. The lead is not really a part of the brass alloy, but is used for machinability purposes. After being exposed to water over time, the lead on the brass's external surface in contact with the water will be dissolved away. Lead is still present, but it is deep enough in the brass and some diffusion barriers exist on the brass surface to prevent further lead leaching. There is no universal guideline for the time frame these processes to work. The processes may take five months or they may take ten years. The reactions depend on the water quality, and there is no way of predicting it at this time. Predicting

contamination depends strongly on the nature of the source of the lead or other contaminant.

Electrochemical Oxidation

Base metal lead exposed to drinking water can react with oxygen to eventually form lead and hydroxyl ions in the water. These reactions will cause an increase in pH in water standing in lead pipe over an extended period of time (overnight to days). In a chlorinated drinking water, such as disinfected municipal drinking water, hypochlorous acid (HOCl°) and/or hypochlorite ion (OCl^-) are present, depending on pH. In drinking water systems, these species will become the dominant oxidants (more than oxygen) driving lead ion formation. Example reactions are shown in Figure 1 for dissolved oxygen and hypochlorous acid. These reactions are the initial driving forces that convert lead into a form it can be introduced into the water. Similar reactions can occur with copper. The copper reactions are slightly more complicated because copper can exist either as copper metal in the Cu(I) form (cuprous ion, Cu^+) or in the Cu(II) form (cupric ion, Cu^{2+}).

Galvanic Corrosion

Another corrosion process is galvanic corrosion, which results from a coupling of dissimilar metals. Commonly observed examples of a potential for "galvanic corrosion" are metal screws in a dissimilar metal. The result is often a lot of rust, which is created because the two metals are electrochemically incompatible. In drinking water applications, galvanic corrosion is the principle behind the corrosion protection qualities of galvanized pipe. In the case of galvanizing, zinc is sacrificed or dissolves preferentially relative to the steel or iron. An empirical series often referred to as a "galvanic series" can be developed. The galvanic series places metals in order from most sacrificed to most protected metals. Figure 2 illustrates one galvanic series based on the work of Larson in the early 1970's.⁶ In the distribution system, lead-tin solders and brasses are typically coupled with copper. Based on the relative placement of lead, lead-tin solder, brass, and copper in Figure 2, electrochemically the solder and brass will dissolve preferentially to copper. This driving force helps mobilize the lead from the brass and soldered joints.

Water Quality

Distinguishing the difference between alkalinity and inorganic carbon is an important consideration in corrosion control. Alkalinity is normally measured in drinking water to control treatment processes, and to measure the water's ability to neutralize acids and bases. The amount of inorganic carbon is the fundamental variable of interest from a corrosion and metal solubility point. The form of carbonate present in the water will change with pH. At low pH, dissolved CO_2 or carbonic acid [$\text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3^\circ$] may be present. At intermediate pH, the bicarbonate ion (HCO_3^-),

is available and at high pH the carbonate ion (CO_3^{2-}) predominates. In a pure water containing carbonate as the only important weak acid species, total alkalinity (TALK) is defined as:

$$\text{TALK} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+]$$

where [] indicates concentrations in mol/L units, and TALK in eq/L. TALK can be converted to the conventional mg CaCO_3/L by multiplying by 50044. There is a theoretical linear relationship between alkalinity and the inorganic carbon content. Figure 3 shows this general relationship for a water at 25°C , with an ionic strength of 0.005. From the figure for example, if the alkalinity is 25 mg/L at pH 6, then there is 18.6 mg/L inorganic carbon (as C), but at a pH of 10 it represents 3.4 mg/L inorganic carbon. Many variables get confused because of the pH effect. Alkalinity and dissolved inorganic carbon (DIC) are related, but they are not identical. Figure 4 is a three dimensional projection of the effect of pH and alkalinity on lead solubility in water at 25°C . The solubility of lead is quite complicated. If there is very little alkalinity and essentially no inorganic carbon, the lead solubility is very high. Introducing a little inorganic carbon (producing a little more alkalinity) into the system will reduce the lead solubility. However, introducing too much inorganic carbon can cause an increase in lead solubility. The complexity of lead solubility was not fully understood until about 10 years ago. Preliminary work shows that copper behaves in a similar fashion.

The effectiveness of corrosion inhibitors, such as orthophosphate-based inhibitors to reduce metal levels, are dependent on several water quality parameters. Some of the more obvious parameters include: pH, dissolved inorganic carbon concentration, hardness, and temperature. Figure 5 illustrates the effect of orthophosphate addition on lead solubility at pH 7.5. Waters having a high alkalinity will require high levels of orthophosphate (PO_4) before a lead solubility decrease is observed. Whereas, in a water with a lower alkalinity and at the same pH, a great benefit from the first 0.5 or 1.0 mg/L of orthophosphate is achieved. The benefits taper off with increasing orthophosphate addition. The important concept to understand is that inhibitor dosages and general solubility controls, such as pH and alkalinity, are interrelated. Some utilities purchase an inhibitor and apply it without examining the entire water chemistry and are surprised when it doesn't work. An example is the widely reported failure of a "zinc orthophosphate" chemical to control lead when applied to the city of Boston's system in the late 1970's.⁷ The unadjusted pH was around 6.0-6.5, and the inhibitor formulation was acidic. Using the dosage applied in the 1970's, additional pH adjustments to around pH 7.5 would have been required for the inhibitor to work correctly. Because pH adjustment was not done, the failure of the treatment was assured from the start.

Figure 6 is a solubility diagram for zinc. The diagram shows the effect of carbonate on solubility is not as pronounced for zinc as for lead. A similar trend exists

where zinc solubility decreases as initial carbonate is added. However, higher levels of carbonate are required in the pH range normally encompassed by drinking waters to achieve a level where solubility is no longer reduced. In this case again, a little carbonate is good, but more is not necessarily better.

Figure 7 illustrates, for pH 7.5, two interesting points to be made about orthophosphate treatment chemicals containing zinc. First, there is a certain region at a particular pH, especially with lower carbonate concentrations, in which a large impact on zinc solubility can be made by a relatively small dosage of orthophosphate. However, under those conditions it is very possible to end up with a turbid water because the alkalinity and pH are too high to hold the zinc in solution. The phosphate might remain dissolved in the water, but zinc can precipitate as basic zinc carbonate, $Zn_5(CO_3)_2(OH)_6$. In many cases zinc is not essential to the performance of the inhibitor and in these cases it should not be used. Clearly, zinc solubility interrelates with lead control treatment. These differences in zinc and orthophosphate solubility, because of the interactions with other constituents in water, demonstrate that direct measurement of orthophosphate is the only viable way to monitor inhibitor dosages within the distribution system. Regardless of the ratio of zinc to orthophosphate in the treatment chemical at the time of dosage, the relationship between PO_4 and Zn concentration is not constant in the system itself. Similarly, when "blended" or polyphosphates are used, both orthophosphate and acid hydrolyzable (or "total") phosphate must be monitored.

Metal Speciation

The general simplified view of metal in water is that the metal is either dissolved in the water, such as Pb^{2+} , or it is as a base metal in the pipe. In actuality, lead in a water with inorganic carbon present is available in many forms, depending upon pH and temperature. Figure 8 shows the major lead forms present in water, at different pH's. In the intermediate pH range, lead is mostly present as $PbCO_3^0$ which is an uncharged, dissolved form (but it is not Pb^{2+} , which is what many tend to believe). As more carbonate is added to the water, the speciation is changed or driven away from the free metal and hydroxide forms into forms where lead is complexed to carbonate species instead. This illustrates that there are many aqueous chemical factors governing the performance and contamination potential of plumbing materials. Lead can exist as a negatively charged form at high pH's; it can exist neutrally in intermediate pH's; and, it can exist as a positively charged form at lower pH's. There is a lot of previously unexplained behavior that can be explained by the complexities of the chemistry. These characteristics are especially pertinent to adsorptive and ion-exchange metal removal systems.

Characteristics of Lead Sources

Plumbing Workmanship

Poor plumbing workmanship can be a contributor of lead in drinking water. Even well-made soldered joints by a professional plumber leave some exposed solder and lead. Ironically, one study showed that more lead was exposed in a solder joint by the experienced plumbers than by the inexperienced ones.⁵ The interesting characteristic about lead and lead/tin solder is that the lead is basically a diluent and allows solder to flow readily. In fact, the really doesn't bind with the copper. In actuality, copper forms an intermetallic alloy with the tin. If too much flux is used, or if an acid based flux is used, lead can preferentially run with the flux and spread out over the inside surface. This demonstrates how workmanship influences the availability of lead.

Faucet Characteristics

Lead, copper, and zinc from brass faucets present many problems caused by the lack of uniform flow through the faucet, unlike the flow in a distribution main in the middle of the city. A faucet is exposed to an intermittent flow pattern of pulsing turbulence in a variety of areas. It is difficult to build a firm, homogenous passivating film on the inside of faucet when there is vibration from the valve opening and closing. Physical examination of cut-open faucets confirm the absence of a uniform coating.

Lead Pipe Characteristics

The interior surface of used lead pipes look different depending on the type of water the pipe to which it was exposed. The pipe can be protected in different ways depending on water quality and water treatment practices. For example, a lead gooseneck from a midwest city using lime/soda softening to treat a hard water, was coated with a unique film. The film consisted primarily of a mixture of calcium carbonate, silica, and some basic lead carbonate $[(Pb_3(CO_3)_2(OH)_2)]$. In this case, the city had implemented a good corrosion control treatment. Pipe from a system that has been using a zinc orthophosphate compound for lead corrosion control will show a film that is much thinner and is different in color in different places. This film was composed of various layers with the outer surface composed primarily of lead orthophosphate $[Pb_5(PO)_3OH]$, hydroxypyromorphite. There is not any zinc compound in this coating. The nature of the protective film will differ from system to system and is important to understand.

Corrosion Treatment Strategies for Utilities

Selection Criteria

When utilities are trying to choose a lead control strategy, there are a variety of considerations they must take into account. The considerations may be briefly summarized as: 1) mix of materials, 2) initial water quality, 3) related requirements, 4) reliability in meeting compliance goals, and 5) cost.

The mix of materials involves understanding the materials that comprise the distribution system. If one type of pipe isn't present in the distribution system, any peculiar conditions that may pertain to the treatment of that material can be neglected. The initial water quality is an important consideration because it relates both to corrosion control and to what other treatment is needed to meet drinking water regulations. There also could be an engineering concern in that some plant process may affect the ability to alter treatment parameters or effects later on in the process train.

Reliability is an issue in the case where a treatment theoretically works very well, but, it is only possible to control the process or keep the hardware working 70% of the time. In this case, the process would not be a worthwhile procedure for compliance. For example, many small systems have trouble with lime feeders used to keep a constant pH in order to maintain stabilized film formation. However, the feeder can only be attended by an intermittent operator and there are many hardware problems with clogging of the valves, etc. The treatment system selected in this case is not a good way to perform pH adjustment and a different corrosion control strategy should be considered. There are many operational requirements that will help determine what a utility can and cannot do to address the corrosion issue.

Cost is also a factor when choosing a lead control strategy. In order to give comparable performance in regulatory compliance, the least expensive choice is preferred, if feasible. There are generally three broad approaches to control cost. One of these approaches is materials replacement. If the material of concern is replaced and thus not in the system, it won't create a problem. Point-of-use is another way to control costs. The point-of-use devices would provide an additional opportunity to assure protection where central water treatment could not meet the regulations adequately. The third cost control approach and the starting point for corrosion control, is the chemical water treatment strategies that can be used by utilities.

Control Strategies for Lead and Copper

There are two broad ways to accomplish lead and copper control by chemical treatment. The first way is to basically form a superficial coating consisting of either natural or induced diffusion barriers. A common example is pipe with a coating

consisting of some organic material (usually mixed with iron or manganese). This coating works very well with material such as asbestos-cement pipe. Lead and copper pipe can frequently have organic coatings (typically mixed with naturally-occurring silica) providing a barrier to corrosion.

Another way to develop a protective film is by forming calcium carbonate coatings. The calcium carbonate coating has been widely discussed in water treatment literature over the last 50 years. Although utilities and researchers have attempted to form these coatings, few have really been able to achieve it. Another way to put down a protective film would be to use sodium silicate or other types of silicate products. The mechanism with silicates is probably a surface film barrier formation, or converting an existing corrosion film to a less-permeable form, more so than reacting with the metal on the pipe itself.

Calcium carbonate stabilization is commonly mentioned and requires some focus. Many states and utilities strive to maintain a positive "Langelier Index" to prevent corrosion.^{1,2} However, there are many other complexities to consider. One consideration is that the bulk solution pH and alkalinity of the water are not necessarily exactly the same as at the pipe surface. The pH difference is seen when patches of calcium carbonate are deposited on the surface resulting in the pipe being unevenly coated. One reason for the uneven coating is that localized corrosion cells form, causing conditions at these sites to favor precipitation. Because the inside of the pipe is not covered by an even coating, this process would not be considered a good corrosion control measure. This uneven coating is also influenced by the pH, dissolved inorganic carbon, and alkalinity relationships previously discussed. Combine these parameters with the hardness of the water and the real issue becomes the available mass of CaCO_3 that can be precipitated. If the Langelier Index is positive, but there isn't enough calcium and carbonate in the water and the pH isn't favorable, the potential to form a coating does not exist. The Langelier Index dependency is a cause of problems in many water treatment plants. Water utilities try to control CaCO_3 deposition throughout the system, but find that the deposits in the mains exist for only a short distance from the plant. Plant filter clogging is also a problem. The further reaches of the distribution system stay undersaturated with CaCO_3 , resulting in no benefit from this corrosion control strategy.

There are two main computational approaches that can be employed when using calcium carbonate precipitation to control corrosion. The most common method is to calculate the Langelier Index. A more obscure but more accurate method is "calcium carbonate precipitation potential" (CCPP). CCPP is very amenable to calculation on personal computers and thus it should be usable by more workers in the future. The third way is an empirical test, like a "marble test". The marble test has gone out of fashion, but in many respects is still the most reliable method.

Many factors can confound the Langelier Index, or calcium carbonate precipitation potential. For example, anything that will inhibit precipitation and growth of calcium carbonate such as magnesium, zinc, or orthophosphate can be confounding compounds. These compounds will stick to the surface and distort the CaCO_3 crystal growth so that it can't continue to grow and nucleate correctly. The action of polyphosphates is a good example of this effect. The polyphosphates are generally added to the water to protect filters from post-deposition at the final phase of water softening in central water treatment plants. Polyphosphates can form calcium complexes, and can poison carbonate crystal growth by adsorbing on the surface of growing crystal nuclei. This action invalidates calculations of either the Langelier Index or the calcium carbonate precipitation potential by the conventional equations. In other words, if polyphosphates are being added to control post deposition, calculating the Langelier Index or CCPP would be totally futile. In this case, the only way to get an assessment of the conditions is to use an empirical procedure like the marble test.

Figure 9 is a comparison of the Langelier Index and the CCPP for a hard and a soft water. The Langelier Index is a thermodynamic driving force indicating if a water has a potential to form calcium carbonate based upon fundamental chemistry principles. The two waters have widely differing pH, hardness, alkalinity, and total dissolved solids (TDS) values, but have the same Langelier Index. However, one of them has a CCPP of 0.4 mg/L as CaCO_3 , and the other 15 mg/L as CaCO_3 . If a utility was trying to form a calcium carbonate film throughout their distribution system, the case where there is more mass of calcium carbonate (in this example, the hard water), would provide a much greater opportunity to deposit a film than the softened water. This is a good example of why the Langelier Index alone does not give an accurate picture of the potential to form a protective CaCO_3 film.

Another issue that complicates the whole picture is that cast iron mains and galvanized pipe frequently lack calcium carbonate films. The deposits that exist are often a combination of calcium and iron carbonate. Research has shown that there really is not a good correlation between any of the corrosion indices, the metal levels in the water, and the weight loss of the pipe materials in the absence of actually putting down a film.

Another type of barrier film is formed through silicate addition. Silicate addition is not understood very well, as it has not been studied systematically to any great extent. The actual silicate dosage probably depends upon the pH of the water and the hardness of the water. There is probably an interaction between the silica and the calcium in the water; however, it is presently hard to quantify and predict. The reactions that do occur would be slow, which is quite important. If tests are being conducted in a pilot plant or pipe loop setting and there is a deadline to have some corrosion control treatment be in place in 18 months, only about six months might be reserved for testing and evaluating treatments. Silicate addition may be a good

technique and 5 years down the road it may achieve excellent results, but benefits may not show up very well in a short time-frame.

Another silicate question is that they may require a preexisting film to work properly. Many researchers believe that the silicates bridge the gap between corrosion products already on the pipe. The existing films allow some diffusion of the oxidants into the pipes and migration of metals away from the pipe. Silicates might react with the existing film and "seal" it like grouting tile. If silicate chemicals are tested on brand-new plumbing, they may not work. If silicates require a preexisting film on the copper pipe, they will not work nearly as well in new homes as in older homes that have some scale built up in them.

The other general chemical treatment approach is to create a passivating film. A "passivating" film involves reacting the metal that is coming off of the pipe with some constituent in the water to form a film in place that helps to immobilize that metal. Undissolved particulate iron and manganese frequently cause a tremendous problem for consumers by forming "red" and "black" water, clogging filters, and creating other obnoxious aesthetic effects. Similarly, an insoluble phosphate or silicate compound can be formed by chemical treatment. However, if the compound will not adhere to the pipe surface and remain there, merely dispersing the compound into the water will not solve the problem. If a water sample is taken and measured for lead or copper, the colloidal forms of the metals are usually included in the analysis. What must really be done is to immobilize the metal. Solubility is not the only issue. Getting the film to stick uniformly to the pipe is also important. Generally, there are four specific chemical treatment approaches a utility can follow to achieve lead and copper control through the formation of a passivating film. The four approaches are: 1) pH adjustment; 2) pH/alkalinity/DIC adjustment; 3) orthophosphate addition, and 5) "blended" phosphate addition.

The issues involved in pH and DIC/ alkalinity adjustment are based on the sensitivity of the metal solubility. Figures 6-8 show that in certain ranges some solubility control can be achieved by controlling these parameters. Often, solubility can be reduced quite a bit by forming a passivating film. Solubility control is not equally sensitive to pH and alkalinity, or other inhibitive anions. Optimizing treatment involves considering these relative sensitivities.

Another factor to consider when adjusting pH and alkalinity is the buffer intensity of the water. The buffer intensity of the water is basically the resistance of the water to pH change. It is desirable to have a good buffering intensity at the surface of the pipe where it meets the water, as that will keep the conditions at the pipe surface as close to the bulk water conditions as possible. The uniform pH will prevent the formation of localized spots with really high pH that would tend to cause types of pitting corrosion. A particularly bad pH from this standpoint is about 8.3, which is the

buffer intensity minimum for the carbonate system.^{1,2} The buffer intensity is effected both by pH and DIC.

To control lead or copper by pH control, a pH of 8 to 9 and above is often necessary. However, calcium carbonate precipitation may limit the ability to get the pH high enough. One problem inherent here is that even though calcium carbonate precipitates, a protective film may not be formed.

Orthophosphate addition requires several considerations and does interrelate to pH and inorganic carbon. The orthophosphate dosage can also be limited by the calcium concentration. Octacalcium phosphate or other insoluble orthophosphate compounds may be formed, causing either turbid water or removing desirable phosphate from being available to form passivating films inside the pipe metal.

Zinc compounds are limited by both pH and DIC, so the ratio of zinc to phosphate in the chemical becomes important in many cases in preventing the previously mentioned turbid water or phosphate depletion. There is some data in the British literature suggesting that zinc compounds may be helpful for controlling brass corrosion, but this data is not definitive in all cases. Little is really known about beneficial effects of zinc in film formation with orthophosphate.

Blended phosphates have all the same considerations of zinc orthophosphate because orthophosphate is critical in achieving the control of the metal pipe corrosion. One of the reasons blended phosphates were developed was to attempt to enable a utility to address more than one problem at the same time. For example, blended phosphates may be used to inhibit tuberculation in iron mains or to inhibit red water caused by iron in the source water, while at the same time attempting to provide some control of lead, copper, zinc or some other metals in the system. One important parameter that must be considered when using blended phosphates is the polyphosphate to orthophosphate ratio. The amount of orthophosphate available for forming the passivating films will govern the metal solubility. The speciation of the polyphosphate component is also important, because the different kinds of polyphosphates (eg. tripolyphosphate, pyrophosphate, hexametaphosphate, etc.) have different affinities for metals. Some polyphosphate species favor complexing calcium very strongly and iron only weakly, while others complex iron and manganese more strongly than calcium. There are many intricacies in polyphosphate chemistry, and little has been published in the objective scientific literature. Depending on what the background water quality is and to what extent the lead or copper must be controlled, the particular polyphosphate can be important. A good corrosion control situation would be when a polyphosphate blend is found that adequately sequesters or stabilizes iron and manganese, but does not have a residual complexing capacity to attack copper and lead. An orthophosphate could then be used to control the lead and possibly the copper corrosion. If a utility uses a type of polyphosphate that complexes trace metals very strongly and it isn't

otherwise occupied with hardness ions or iron and manganese, the polyphosphate will increase the lead and copper corrosion. There are many combinations that need to be tested and considered, and no single product or blend is even remotely universally applicable.

Diagnostic Sampling

An important issue that is often highly overlooked is sampling. There is a high level of normal variability in sampling.^{9,10} Every time a sample is taken, the sample is going to be somewhat different from those taken before and after it. Therefore, there is no such thing as "the lead level" of a house. A question exists as to how different are each of the water samples. One possible scenario exists where water probably flowed through a sequence of materials. Prior to the distribution system, the water contains no lead. The distribution system may be comprised of iron mains or cement-mortar lined mains, for example. Possibly, there could be joints in the mains that were filled in with a lead-containing compound which used to be a common practice. Later on, the water then arrives at the service line containing lead pipe. The household plumbing could be galvanized steel, copper, or even all lead. In some cases there is no lead at all in contact with the water until it reaches the faucet. The isolation of these potential sources through sampling is important, because the best treatment for corrosion may be dependent on the source of metal. For example, brass corrosion control may not be the same best treatment as for controlling copper pipe corrosion, or lead pipe corrosion. It is necessary, and possible to a great degree, to be able to precisely sample so that the source of the problem can be identified.

The determination of "baseline" metal levels is another task that is very important. Many investigators take a couple of samples, decide they have a problem, and immediately implement some kind of control program. This strategy does two things, one of which is that they can never then really be sure there was a general problem. Even if the "problem" goes away, it's not clear how much of the problem has been addressed, since it wasn't correctly quantified in the first place. Because of the variability in normal sampling, it is difficult (if not statistically impossible) to tell whether or not there is any difference between implemented treatment practices, whether evaluated by pipe rig tests, or directly in field studies. It is very important to determine a baseline metal level because a utility embarking on a corrosion control program is going to be regulated based on its effectiveness as reflected in tap water sampling.

Variability obscures and complicates detection of treatment trends. If a pipe loop or pilot plant system is used to evaluate five or six different kinds of treatments side by side, one or two of them will not always *consistently* be lower than the others. There is a lot of variability in metal level concentrations created by corrosion and

corrosion controls. Sometimes curves connecting the points for a treatment will cross over due to natural variability, making it very hard to tell one treatment from the other.

The new regulations will require "optimization" of corrosion control for lead and copper. It may be very difficult to determine a one true "optimization" for any system. To illustrate this point, Figure 10 shows a test run at the Illinois Water Survey.⁵ In this test run, there were three identical lead loops (3 equal lengths cut from a 100 foot section of pipe), from the same manufacturer, running simultaneously in the same rig. At the beginning of the run, the lead levels were fairly consistent. However, as time went on, discrepancies (30 to 40 $\mu\text{g/L}$) arose among them. If a comparison of relative treatment effectiveness is the goal of rig studies, simultaneous replication is absolutely necessary regardless of the metal involved. If only one pipe is present for each treatment, one treatment may appear to be better than another treatment, but this relationship may be an artifact of the behavior of that particular pipe. Enough replication and sampling over time must be done to ensure a basis for taking into account this type of variability.

Figure 11 shows flushed sample data taken from pipe loop experiments conducted at the USEPA¹ under an identical sampling protocol. Some of scatter can be attributed to minute invisible colloidal particles, and some due to dissolved lead. The essential point is that there is a lot of scatter under very reproducible and controlled experimental conditions. This scatter would be more out of control when sampling is done at a consumer's house. Figure 12 displays pipe loop data for lead samples after different standing times.¹ After the first few hours, under the same sampling conditions and with the same length of standing time, there is still 50 percent or more variability in the lead concentrations. The scatter decreases as the standing times used approach what is needed for chemical equilibrium. Once again, under reproducible experimental conditions there is still considerable variability in the data. A final example is shown in Figure 13, where a set of standing samples are taken from three lead-soldered copper loops.⁵ Three copper loops with lead soldered joints (as identically made as possible), have a relative standing water lead level variability by at least a factor of 2. The lead levels in this case are near the quantification and detection limits of the measuring instrument. Here, there is much analytical variability factored in with actual physical variability of the operation of the system. It is difficult to make any important interpolations with pipe loops having soldered joints, because the whole workmanship issue is built into it. From statistical considerations well beyond the scope of this paper, it follows that the more accurate small differences that need to be detected, the number of samples to be taken becomes quite large.⁵ Practically speaking, differences in real systems can only be determined imprecisely. Very expensive treatment and design decisions may be made based on this kind of test data, so careful effort and consideration to understand the limits of data interpretation must be made.

Isolation of Sources

Some logic and common sense will serve investigators well in isolating the source of contamination. A "first-draw" water sample can also be thought of in terms of the feet of pipe represented. For example, a liter of water represents approximately 25 feet of lead pipe, with 0.5 inch inside diameter (ID). In other words, one foot of pipe will hold 40 mL of water. Galvanized and copper pipe are slightly different than lead pipe because of the definition of ID. For "half inch" ID copper pipe, the internal diameter is not exactly one-half inch, but the volume of water available can easily be calculated from the correct ID.

Knowing the length of pipe or fixture represented by a water sample becomes important when trying to determine if a problem is coming from the brass faucet, the soldered joints, or some inner section of the building or distribution system. For example, there may be a feed line and a tee coming off into a building wing with a concentration of soldered joints. This area may be 15 or 16 feet prior to the sampling point. If a 125 mL sample is taken, it represents essentially the faucet. With a 250 mL first draw sample, the faucet and about 3 feet of pipe (0.5-inch ID) are represented. A 1 L sample represents the faucet and 20 feet or more of the pipe. In a consumer's house, a first draw 1 L sample may not reach the service line. To illustrate this point, Figure 14 shows data from a field study that tried to assess the impact of some water quality parameters and water quality adjustments on tap water lead levels from houses that had lead service lines. Schematically, this shows that 1 L of water was in contact with some of the internal plumbing, plus the faucet. To obtain samples in contact with the service lines, water was wasted so that samples would "intercept" water coming from the desired source, the lead service lines. The trouble with remote sampling is that there is turbulent flow and mixing in the system. If there are not high lead levels, or if the water isn't very corrosive, the ability to intercept and detect that lead becomes very difficult. From a consumer's standpoint, that is very good because it means that in a fairly noncorrosive water, a lead service line will not cause any adverse effects at the tap. When examining and comparing studies of corrosion control and the sampling schemes are not consistent, the data is not necessarily equivalent in terms of conditions and sources.

Britton and Richards did an interesting study in Scotland¹¹ where they were taking samples from the same tap and varied the flow rate. They found that when the flow rate was very slow, there is relatively more contact time with the brass material and was more lead. As the flow was increased, there was relatively less lead pickup. However, when the flow went beyond a certain point, turbulence resulted and erosion from the flow was created and higher lead levels appeared again. This is another factor contingent upon the variability and reproducibility of sampling and the meaning of measured lead levels. It has been shown that mixing during flow reduces the concentration at the end of the water parcel in contact with the pipe. More information is given in reference 5.

PART 2: THE WQA/USEPA JOINT STUDY

A WQA/USEPA joint project was an outgrowth of a new program under the Federal Technology Transfer Act. The program allows the government to accept money from "private industry" under terms that are agreed upon by mutual consent. All components of the project including how the data is disseminated and a work plan must be agreed upon by both parties. The focus of the study is to obtain some initial information on whether or not there are impacts from water softeners on corrosivity. The Water Quality Association donated \$50,000 to USEPA to help begin this investigation. There has been much speculation, but little systematically generated data about the effects of water softeners. The reason the softening issue is complex and somewhat controversial, is that whether or not softening will have any effect at all depends very much on the water quality.

Possible Impacts of Softening

Why might softeners impact corrosion, and why might they not? There are many issues to be considered here. One possibility is that softening could reduce the water scaling tendency. If the pipes of a system are protected by surface films (for example mixed calcium- and magnesium- based films), removal of the calcium and magnesium from the water by softening will have an adverse impact on that film. Some utilities that have a high pH and very low hardness, typically produce films composed of basic copper carbonate, copper oxide, zinc hydroxy carbonate, basic lead carbonate, etc. Here, the calcium and magnesium don't play an integral role in scale formation. Therefore, the softening really shouldn't have an impact on corrosivity.

Another question is the effect softening has on chlorine, chloramines, and dissolved oxygen. These are oxidants that greatly effect the ability to mobilize the metals, and especially corrode copper. The fate of these species in water passed through domestic water softeners has not been documented. One of the objectives of this project will be to measure small changes in concentration of potentially important chemical parameters.

It is not known whether or not there is an interaction between the softeners and corrosion inhibitors. If a utility doses a zinc orthophosphate and there is a case where the zinc does play a role in the formation of the protective film, removal of the zinc by the softener will change the nature of the film formed on the pipe after the water softener.

The effects of changes in scaling potential on corrosivity may depend upon the temperature. Larson did some work where he pointed out that calcium carbonate becomes less soluble as temperature goes up.⁶ Scaling is often observed in hot water systems. However, this increase in scaling only takes place in certain ranges of hardness and alkalinity. A water that is not very hard and has a low alkalinity may

become less scale-forming at higher temperatures.² What happens is that as the water is heated, the intrinsic pH of the water goes down as the temperature goes up. In a closed system, like a household plumbing system, the water is still under pressure in the pipe, and the pH will go down by itself just because of the carbonate chemistry involved.^{2,5} In harder waters, and in waters with more alkalinity, that effect does not occur very much because the water is buffered.

Formation of Mixed Solids

As mentioned previously, metals can participate in the scale formation. In hard waters, calcium exists in many forms other than in just Ca^{2+} . Often 10 to 20 percent of the calcium can be in the form of either bicarbonate or carbonate ion complexes (called "ion-pairs). If the water quality is drastically changed by removing calcium and magnesium by substituting sodium, the carbonate equilibrium could become slightly perturbed because the sodium and potassium forms of these complexes are much weaker. That is real subtle and probably doesn't have much of an effect, but it is something that should be considered.

Other Indirect Effects

Another indirect effect of softening is lack of binding of ligands. Ligands, such as polyphosphate, tie up and bind metals. If for example, assume iron or manganese is being controlled in the source water, or post deposition of calcium is being controlled with a polyphosphate, the polyphosphate's complexing ability is filled. However, if a home water softener is used, the metal is stripped from the polyphosphate ligand, and the polyphosphate passes through. In this case a greater potential to dissolve the lead and the copper may be created because now an aggressive chemical is present that wasn't aggressive in its previous state because it was chemically associated with other metals. There have been no studies that show the exact chemistry of these indirect effects of softeners along with the other effects mentioned earlier, such as the ion pairing difference and the fate of chlorine and chloramines. These studies should be done.

Experimental and System Design

A set of test loops much like the ones used and produced for the AWWA's Lead Control Strategies manual⁵ has been designed for the joint project. These loops are also very similar to the ones used for the corrosion inhibitor studies currently being conducted at the USEPA research facility, Cincinnati, OH. The loops basically consist of five materials including lead/tin solder, copper pipe, copper tubing (unjoined copper tubing), galvanized pipe, and lead pipe. Lead pipe was included because the Cincinnati Water Works is interested in seeing softening effects on the worse case scenario. Two brass faucets were also included to see if there is impact on the lead and copper contributions to the water from the faucets.

The basic design of the system is a uniform pipe diameter of 1/2" ID and uniform flow rate of one gallon per minute, which is comparable to domestic systems. Each of the loops will be 50 ft in length. There will be an intermittent flow and an 8 hour stagnation time during the day to simulate domestic use. One hundred gallons of water per day will be used for each loop, which is less than what most typical houses probably use. But, because water quantity must be conserved, a balance must be struck. All of the materials to support the system will be lead and copper free plastics. The system will be set up at Cincinnati's Bolton Water Treatment Plant, which utilizes a ground water source. The Bolton Plant treats the ground water by lime softening, with a low level of polyphosphate addition (to protect the filters), chlorination, and fluoridation before distribution.

The Bolton plant offers a location in which the raw, untreated water, and the finished, treated water can be used. The raw and treated water quality is shown in Figure 15. In Ohio and most of the Midwest, the kind of water Cincinnati normally distributes is considered hard enough by many consumers to justify using water softeners. The water coming off the main line will be split, one side feeding an ion exchange softener and then the pipe loops. The other side feeds a set of identical loops directly. There will be duplicate loops, two of each, used because triplicate loops (although desirable) would require too many samples and too much water. Operating in duplicate will improve statistics on differentiating trends over single loop studies. Sampling ports will be placed immediately before and after the softener to evaluate the chemistry effects of the softener. Each loop will have a flow control and sampling port at the end of it so standing and running samples can be taken from each loop. Figure 16 represents a schematic of the pipe loop system.

After six months, the input water lines are going to be crossed. That is, the loops in contact with softened water will be switched to unsoftened water, and vice versa. Total chemical analysis will be done on the samples of the water immediately before and after the softeners. In the loops themselves, metal levels will be monitored.

In summary, several short term results will come from this study. Statistical differences between softened and unsoftened waters will be determined, taking into account the appropriate comparison statistics will be applied. An understanding of the chemical characteristics in metal leaching, and the chemistry of the corrosion process will be gained. If these results show some intriguing information and trends, it would be valuable to eventually evaluate systems operating in the field. It may be possible to locate homes that have had softeners, and have comparable temperatures to those of the lab pilot study, and collect data from them. The field data could then be compared to the data acquired from the lab and pilot study to see if there is any correspondence.

REFERENCES

1. American Water Works Association Research Foundation and DVGW Forschungsstelle. Internal Corrosion of Water Distribution Systems. Denver, AWWA Research Foundation, 1985.
2. American Water Works Association. Water Quality and Treatment. 4th edition. New York, McGraw Hill, 1990.
3. USEPA. Corrosion Manual for Internal Corrosion of Water and Distribution Systems. EPA 570/9-84-001, Washington, D.C., April. 1984.
4. American Water Works Association. Corrosion Control for Operators. Denver, AWWA, 1986.
5. American Water Works Association Research Foundation. Lead Control Strategies. Denver, AWWA Research Foundation, 1990.
6. Larson, T.E. Corrosion by Domestic Waters, Bulletin 59, Illinois State Water Survey, Urbana, IL (1975).
7. Karalekas, P. C., Jr. "Control of Lead, Copper and Iron Pipe Corrosion in Boston", Jour AWWA, 75:2:92 (1983).
8. APHA-AWWA-WPCF Standard Methods for the Examination of Water and Wastewater, 17th Ed. (1989).
9. Schock, M. R., Levin, R., & Cox, D. "The Significance of Sources of Temporal Variability of Lead in Corrosion Evaluation and Monitoring Program Design", Proc. AWWA Water Quality Technology and Conference, St. Louis, MO. (1988).
10. Schock, M. R. "Causes of Temporal Variability in Lead in Domestic Plumbing Systems, Environmental Monit. & Assessment.
11. Britton, A. & Richards, W. N. "Factors Influencing Plumbosolvency in Scotland". Jour. Inst. Water Engr. and Scientists, 35:4:349 (1981).

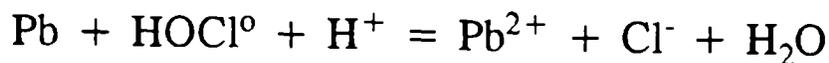


Figure 1. Oxidation reactions for lead in water.

Abbreviated Empirical Galvanic Series

Corroded End (Anodic)

Zinc

Steel or Iron

Cast Iron

Chromium-iron

Lead/Tin Solders

Lead

Tin

Brass

Copper

Silver Solder

Silver

After Larson (1975), ISWS Bulletin 59

Figure 2. Galvanic series for common plumbing materials used in the drinking water distribution system.

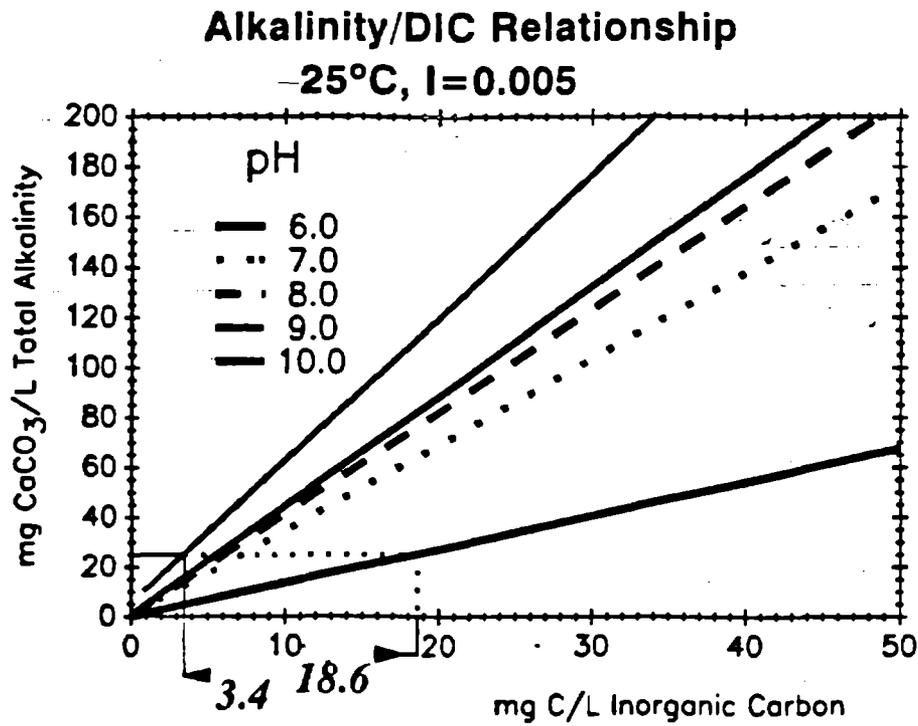


Figure 3. Alkalinity /DIC relationship for various values at 25°C.

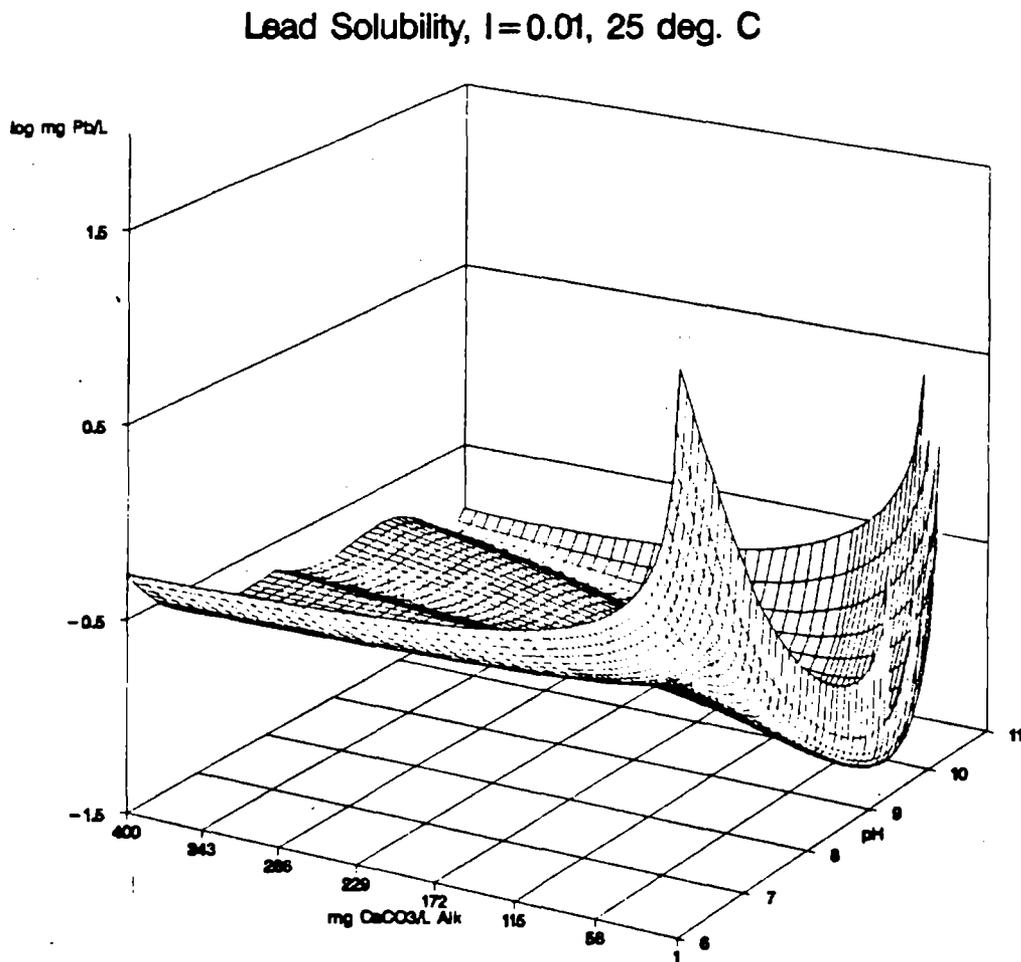


Figure 4. Lead solubility as a function of alkalinity and pH at 25°C.

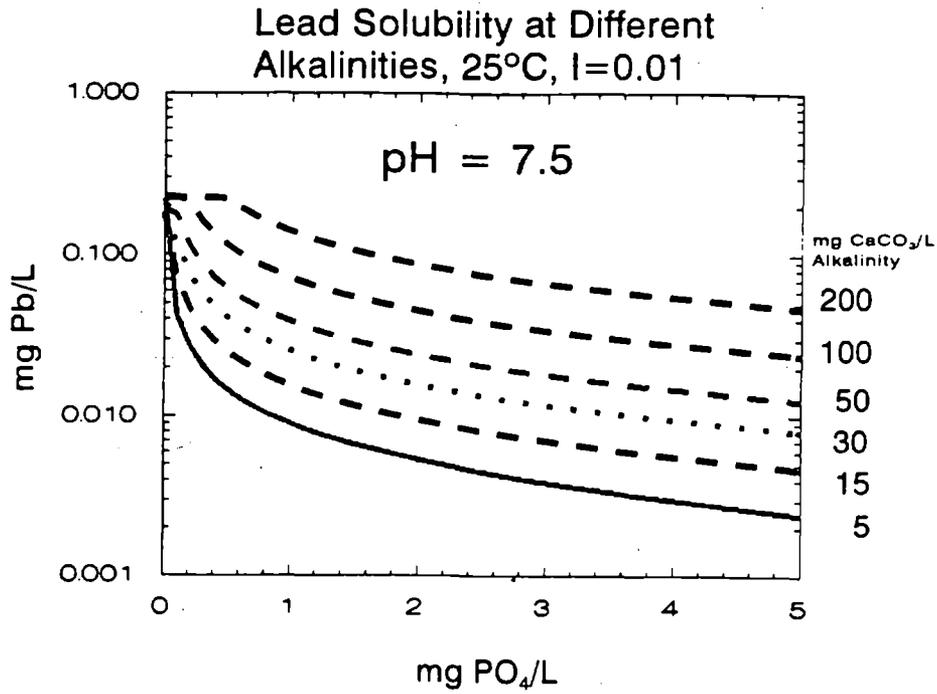


Figure 5. Lead solubility as a function of phosphate concentration at different alkalinities and pH 7.5.

Zinc Solubility

I = 0.01, 25°C

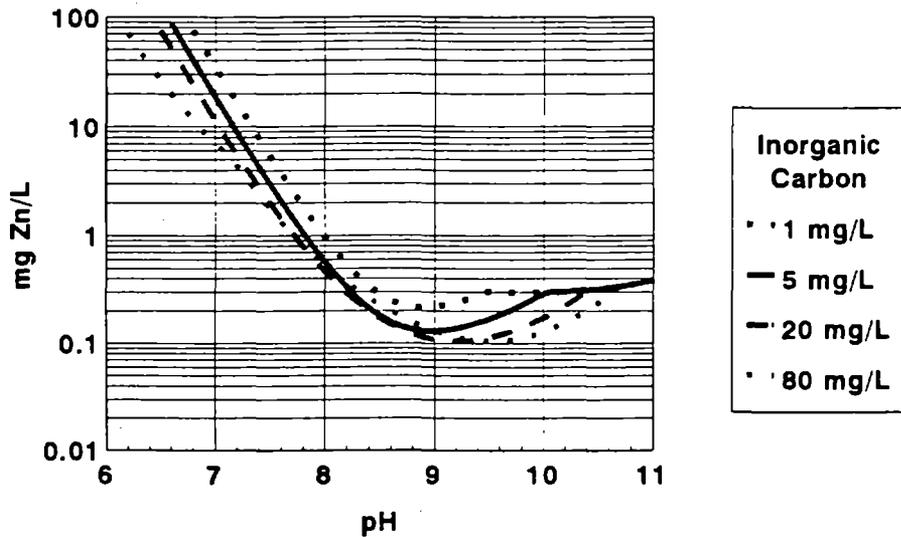


Figure 6. Zinc solubility as a function of pH at 25°C.

Zn Solubility, pH = 7.5, I = 0.01, 25°C

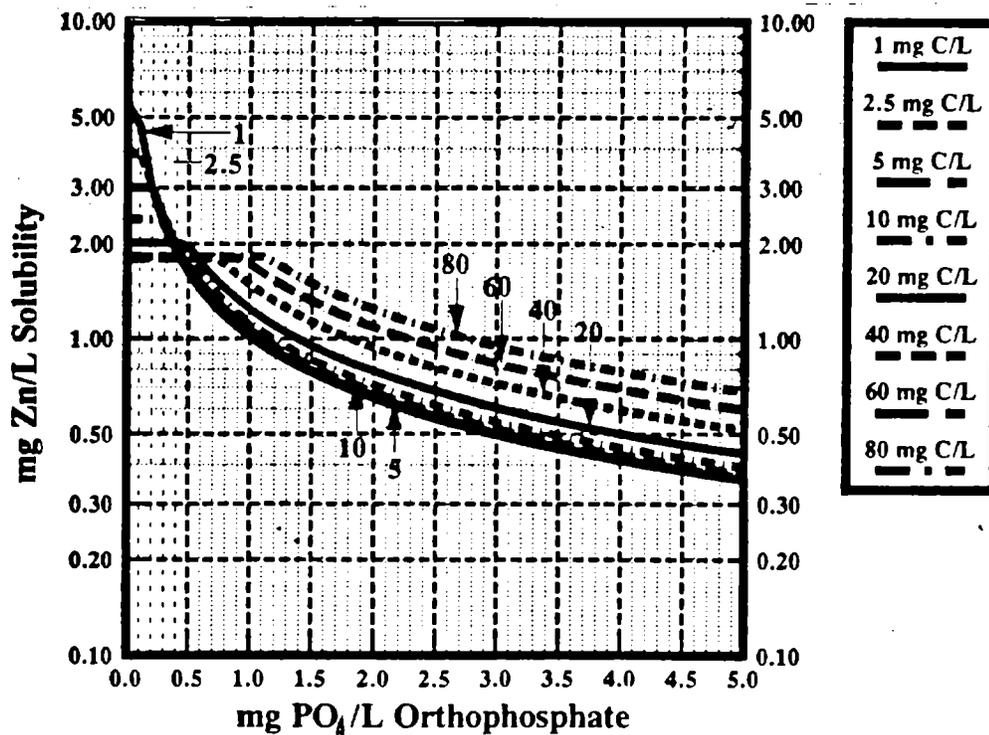


Figure 7. Zinc solubility as a function of orthophosphate concentration at 25°C.

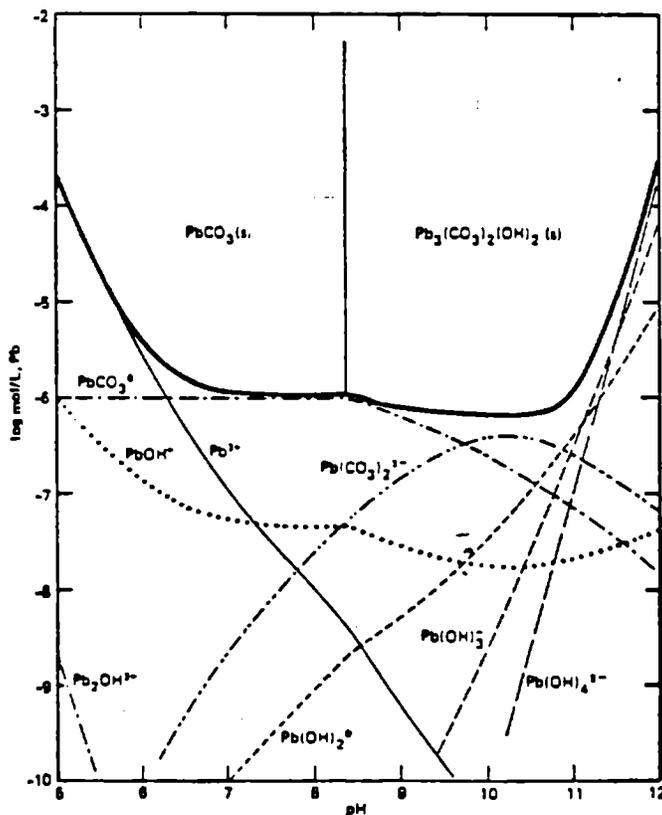


Figure 8. Lead speciation as a function of pH at 25°C.

LI versus CCPP Same Langelier Index

Concentration mg/L	Soft Water High pH	Hard Water Low pH
Temp (°C)	15	15
Alkalinity (mg/L as CaCO ₃)	25	350
Calcium (mg/L)	17	130
TDS (mg/L)	75	750
pH (units)	8.90	7.03
LI (units)	0.10	0.10
CCPP (mg/L)	0.40	15

Figure 9. Comparison of the Langelier Index versus the Calcium Carbonate Precipitation Potential for two waters.

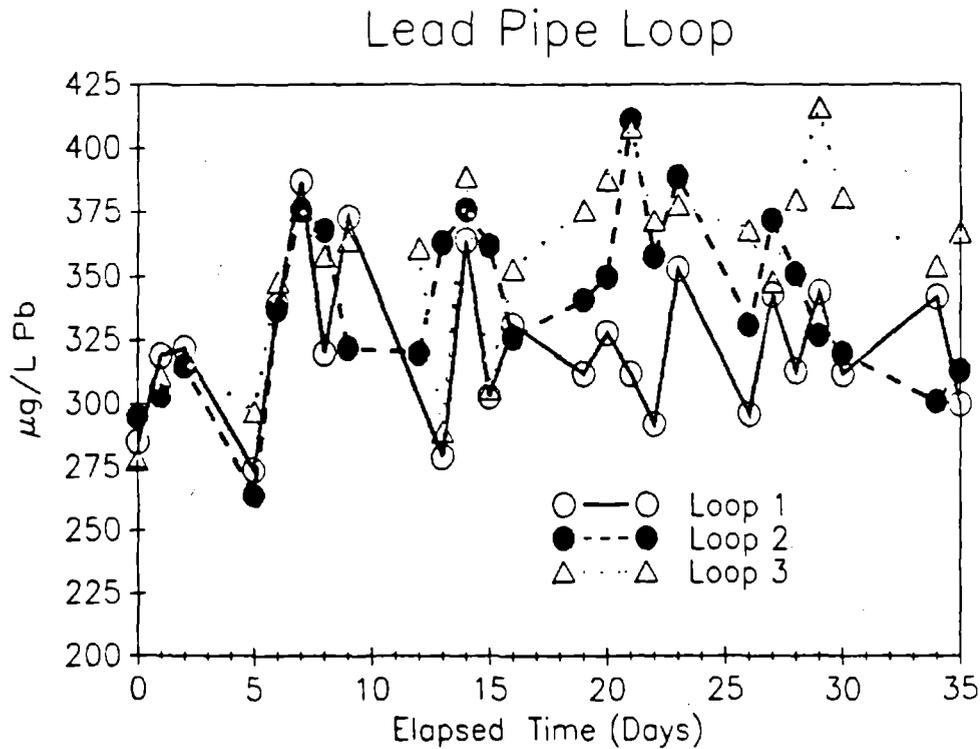


Figure 10. Lead pipe leaching data from a study conducted at the Illinois State Water Survey.⁵

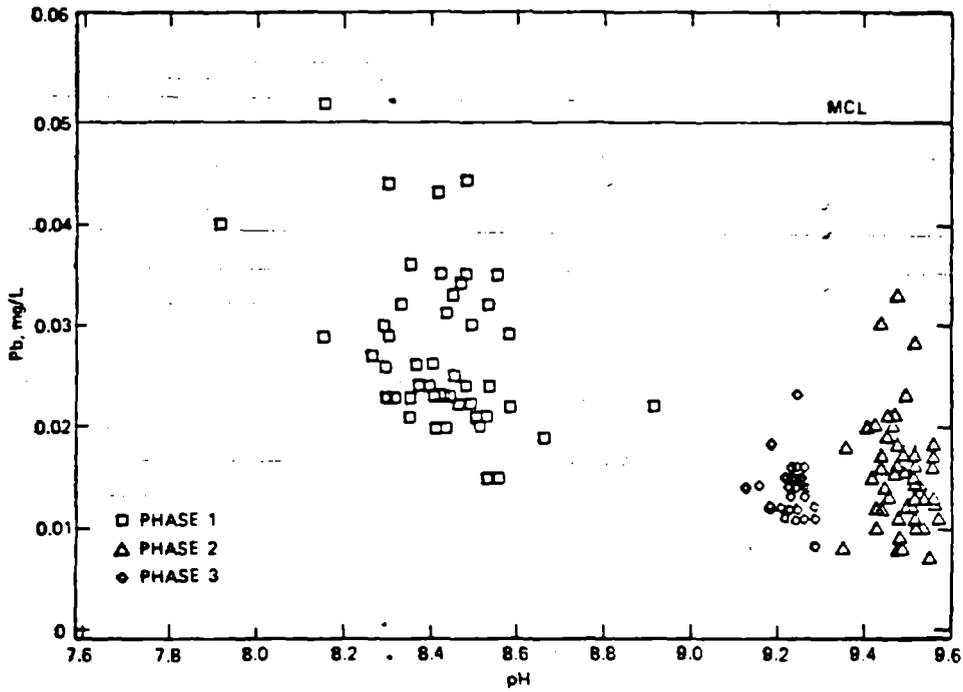


Figure 11. Lead concentrations of flushed samples taken from pipe loop experiments conducted at USEPA.

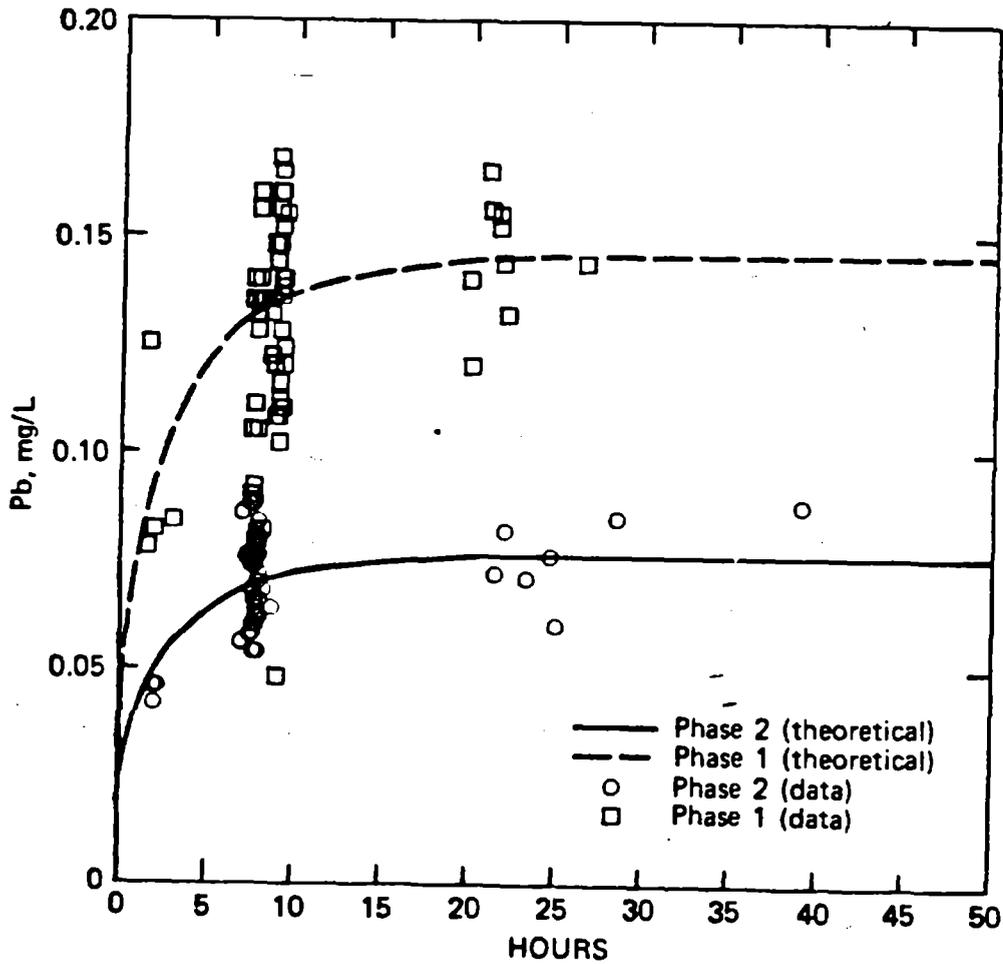


Figure 12. Lead concentrations of samples taken from pipe loop experiments at various standing times.

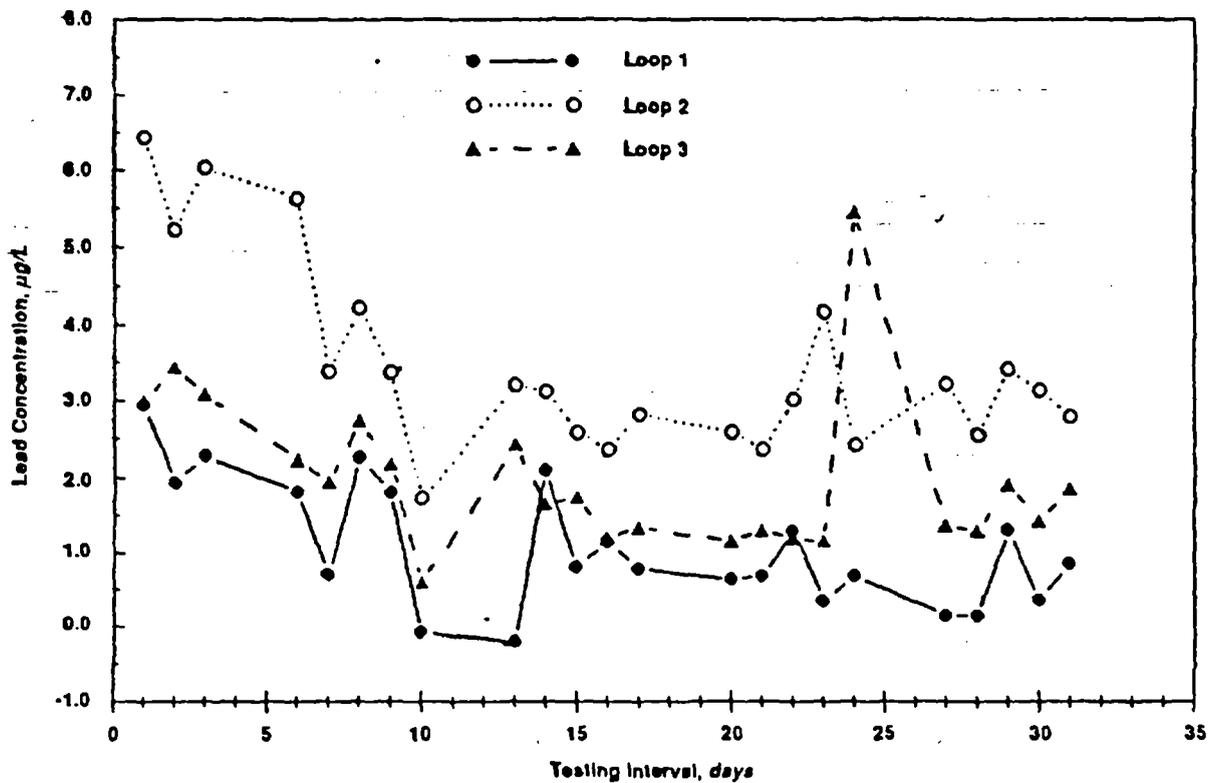


Figure 13. Lead concentrations of standing samples taken from three identical as can be made lead solder/copper tube sections.

PLUMBING REPRESENTED BY SAMPLES

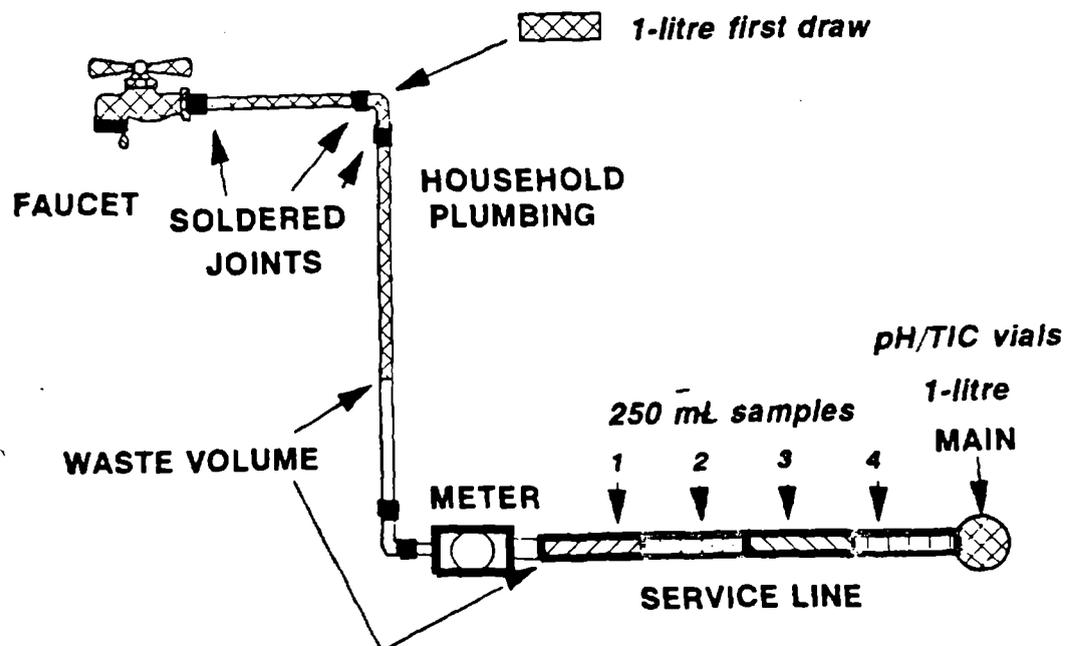


Figure 14. Household plumbing represented by samples.

Water Quality

Bolton Plant

Constituent mg/L	Raw	Treated
pH	7.4	9.2
Calcium	90	25
Magnesium	25	23
Sodium	19	19
Alkalinity	254	82
Sulfate	58	60
Chloride	35	36
Nitrate	3	4
Total-PO ₄	<0.3	>0.5
Silica	9	10

Figure 15. Raw and treated ground water quality from Cincinnati's Bolton Treatment Plant.

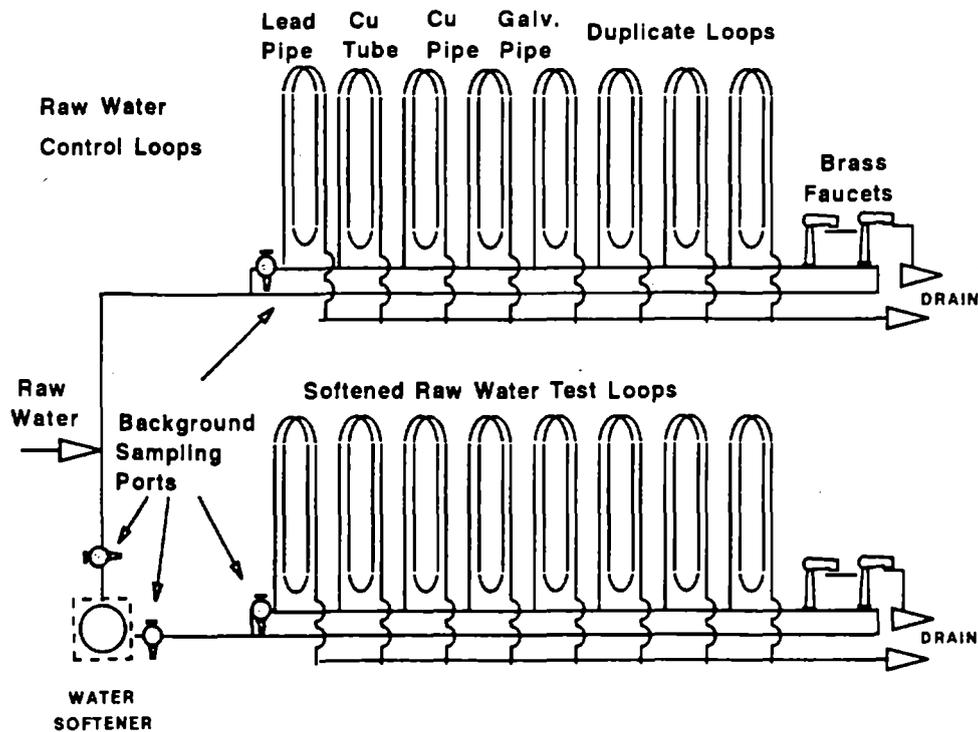


Figure 16. Schematic of pipe loop system to be used in WQA/EPA Joint Corrosion Study.