Sodium Silicate Corrosion Inhibitors: Issues of Effectiveness and Mechanism

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I. INTRODUCTION

According to the EPA’s 1991 Lead and Copper Rule (LCR), water distribution systems are required to have corrosion control measures completely installed by January 1997 for large systems (> 50,000 people), by January 1998 for medium systems, and by January 1999 for small systems (< 3300 people). The water systems are obligated to evaluate the methods listed below in order to find the optimal method for their particular system. They must ensure that the lead and copper concentrations at the consumers’ taps meet certain “action levels”; the 90th percentile of all sample measurements must not exceed 0.015 mg/L for lead and 1.3 mg/L for copper.

Possible treatment methods for corrosion control include:
1) Adjust pH and alkalinity to decrease corrosivity of water.
2) Saturation of calcium carbonate to promote precipitation of carbonate layer within pipes.
3) Add phosphate corrosion inhibitor.
4) Add silicate corrosion inhibitor.

Of these methods, the effectiveness and the mechanism by which silicates inhibit the corrosion of pipes are perhaps the least understood even though silicates have been used regularly for this purpose since the late 1920’s. There has been a confusing assortment of both positive and negative results, and consequently, many contradictory statements have been published concerning this method. For example, in the chapter on corrosion inhibitors in “Internal Corrosion of Water Distribution Systems” [1], the following statements can be found: “Silicates are generally not effective,” (p.570);
and, “Test applications... have shown a generally excellent protection with silicate inhibitors,” (p.553). The mechanism of corrosion inhibition by silicates is also in question. Again from the same reference: “The principal benefit of using silicates appears to be the increase in pH after dosage,” (p.552); and, “Surface analysis indicates that protection by the silicates occurs when a thin layer forms over a layer of corroded metal,” (p.552). Such contrary statements point to the need for a more definitive evaluation of the effectiveness of silicates to control corrosion in water distribution systems especially considering the requirements of the LCR.

In response to this need, this paper provides a review of various topics related to the use of soluble sodium silicates to inhibit corrosion of metal pipes. These topics include: metal corrosion and inhibition, characterization of silicate species in solution, known mechanisms of silicate film formation, review of experimental studies, and results of surface analysis of pipes. Some particular issues that are addressed include: effect on iron and manganese sequestration, the effectiveness of silicate treatment with and without pre-existing corrosion products, the effect of water quality on silicate film formation, and the pH effect of silicate treatment. It is hoped that this review will bring a measure of harmony to previous seemingly contradictory results and that a contribution can be made to the provision of safer drinking water.

II. BACKGROUND

Metal Corrosion and Corrosion Inhibition

Corrosion proceeds when all of the components of a “corrosion cell” are present. These include: 1) an anode, 2) a cathode, 3) an electrical connection between the anode and cathode, i.e., the metal itself, and 4) an electrolyte to serve as the transport medium for ions. The anode and cathode are areas on the metal surface whose difference in electrical potential spontaneously drives both the anodic oxidation reaction \( (M = M^+ + e^-) \) and the cathodic reduction reaction \( (A + e^- = A^-) \). In the case of a single metal, the electrical potential difference may result from inhomogeneities on the surface (such as defects, impurities, or different crystal structures) or from momentary or systematic differences in the concentrations of electrolyte, dissolved oxygen, or dissolved hydrogen [2]. In the case of two different metals or alloys, a galvanic cell forms, meaning that one metal or alloy, due to its more negative electrical potential, tends to be the anode and is oxidized while the other acts as the cathode. For example, copper is cathodic to iron, zinc, and lead. Generally speaking, the locations of the anode and the cathode may constantly change, resulting in a uniform corrosion across the pipe surface. On the other hand, the sites may be fixed, become large in area, and cause the formation of pits, crevices, or tubercles.

It is common in the literature to see terms like “plumbosolvency” or “cuprosolvency” to describe the solubility of a metal under various water conditions (e.g., pH, alkalinity, dissolved inorganic carbonate). Metals might not necessarily be thought of as being “soluble” in water; however, dissolution implies that ions are transferred from a solid into a solution. In the case of ionic compounds such as salts, the dissolving crystal decomposes. But in the case of metals, dissolution (also known as leaching) occurs electrochemically via reactions that are non-oxidative, oxidative, or reductive, all with or without complex formation. Therefore, “plumbosolvency” indicates the fact that lead
can get into solution to some extent, whereas “lead corrosion” denotes how lead gets into solution (i.e., by electrochemical process).

Besides anodic and cathodic reactions, a variety of other reactions can take place to form numerous types of corrosion products. For instance, in the iron system, any of the following species may form, disappear, and reform throughout the corrosion process: \( \text{Fe}^{2+}, \text{Fe}^{3+}, \text{FeOH}^{2+}, \text{Fe(OH)}_2^{+}, \text{FeOOH}_{(s)}, \text{Fe(OH)}_2^{(s)}, \text{Fe(OH)}_3^{(s)}, \text{Fe}_2\text{O}_3^{(s)}, \text{FeCO}_3^{(s)}. \) In the case of copper, which is not usually susceptible to galvanic corrosion because it is cathodic to most of the common plumbing metals, corrosion proceeds in the presence of oxidizers, e.g., \( 2 \text{Cu}(s) + \text{O}_2(g) + 4\text{H}^+ = 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \). And with bicarbonate, \( 2 \text{Cu}^{2+} + \text{HCO}_3^- + 2\text{H}_2\text{O} = \text{Cu}_2(\text{OH})_2\text{CO}_3^{(s)} \). Depending on the exact conditions, other corrosion products may include \( \text{CuO} \) and \( \text{Cu}_2\text{O} \) or a great variety of others: \( \text{Cu}_2\text{OH}_2\text{CO}_3, \text{CuCl}, \text{Cu}_2\text{CO}_3, \text{Cu}_2\text{SO}_4, \text{Cu}_2\text{S}, \text{Cu}_4(\text{OH})_6\text{SO}_4, \text{Cu}_3\text{OH}_4\text{SO}_4, \text{CuO•CuSO}_4, \text{Cu} (\text{OH})_2, \text{CuCO}_3•\text{Cu(OH)}_2, \text{Cu}_2\text{OH}_3\text{Cl}, \text{Cu}_2\text{OH}_3\text{NO}_3, \text{Cu}_5(\text{PO}_4)_2, \text{CuH}_2\text{SiO}_4 \). The specific water conditions will influence which of these phases occurs [3].

Corrosion is also influenced by the water quality. The concentrations of dissolved oxygen, chloride, sulfate, organics, and suspended solids plus the pH, alkalinity, and hardness may all have some effect on the corrosion process [2]. Theoretical predictions and experimental observations agree that plumbosolvency, for example, decreases with increasing pH [4-6].

One way to inhibit corrosion in water distribution systems, then, is to make water less corrosive, for example, by increasing the pH. Another strategy is to eliminate one or more of the corrosion cell components. Arpaia [7] explains that the pipe surfaces may be modified by protective deposits which 1) act as a physical barrier between the surface and the electrolyte to inhibit the flow of electrons and/or the diffusion of reacting species; and/or 2) have an electrochemical effect by displacing reactive species from the surface and thereby changing the electrical potential difference. For instance, oxide, hydroxide, or carbonate passivation layers may form on pipe surfaces due to appropriate conditions in the system (e.g. high CaCO3 levels in the water), or the formation of protective layers may be induced by the addition of corrosion inhibitors such as phosphates or silicates. The corrosion of lead may be curbed by the formation of a protective layer of lead carbonate or basic lead carbonate (\( \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 \)) which serves as a physical barrier, limiting the uptake of lead [5, 8].

**Soluble Sodium Silicate Solutions**

Besides corrosion control in water distribution systems, soluble sodium silicates are utilized in a number of other applications. Some of these include the following: engine antifreeze (to inhibit corrosion), detergents (to inhibit corrosion, improve wetting, disperse oily soils, deflocculate inorganics, buffer wash water), paper adhesives, fire- and grease-proof films and coatings, ore beneficiation (to inhibit corrosion, disperse siliceous matter, aids in separation of minerals), textiles (buffer in bleaching and dying operations, remove oil and dust from cotton), binders for refractory materials, stabilization and solidification of hazardous waste, and concrete surface treatment to harden and improve acid-resistance. It is interesting to note that a number of these applications utilize the corrosion inhibiting properties of sodium silicate.
Liquid sodium silicate, also known as waterglass, is produced by melting high purity silica sand along with sodium carbonate at 1100-1200°C. The molten glass is combined with water resulting in a solution that may consist of 24-36 weight % SiO₂ with an SiO₂/Na₂O weight ratio between 1.60 and 3.22. For water treatment applications, the SiO₂/Na₂O ratio is usually 3.22; however a ratio of 2.00 may be used in the case of very acidic water. Manufacturer’s recommend a start-up dosage of about 24 mg/L SiO₂ for 30 to 60 days followed by an incremental decrease to a maintenance dosage of about 8-12 mg/L. A high startup dosage is critical to gaining control over corrosion. The protective layer should be formed as quickly as possible because if only parts of the pipe surfaces are protected while others are still exposed, the current density at the exposed parts will be magnified and corrosion may become worse before it gets better.

A sodium silicate solution consists of monomeric and polymeric species. The concentrations of monomer and polymer depend on the silica content and the SiO₂/Na₂O ratio of the solution. To illustrate, a concentrated solution having a SiO₂/Na₂O ratio of 1.0 or 0.5 mainly consists of SiO₃²⁻ and HSiO⁻;

n = degree of polymerization, depends on SiO₂/Na₂O
x = OH/Si in polymer (x decreases as n increases)

whereas solutions with higher SiO₂/Na₂O ratios are characterized by increasing polymer concentration and increasing polymer size (up to 30nm diameter). Furthermore, the polymer is in equilibrium with the soluble monomer Si(OH)₂ according to the following [9]:

\[ \text{Si}_n\text{O}_{(4n-nx)/2}\text{(OH)}_{nx} + [{(4n-nx)/2}]\text{H}_2\text{O} = n\text{Si(OH)}_4 \]

The polymers are equiaxed and approximately uniform in size. In larger polymers, the interior Si are linked by bridging oxygen while exterior Si may be bonded to at least one OH⁻. In addition, the polymeric particles may be ionized [9]:

\[ \text{Si}_n\text{O}_{(4n-nx)/2}\text{(OH)}_{nx} + z\text{OH}^- = \text{Si}_n\text{O}_{(4n-nx)/2}\text{(OH)}_{nx-z}\text{O}^{2-z} + z\text{H}_2\text{O} \]

So, the polymeric particles are in equilibrium with Si(OH)₄, as stated above, and the Si(OH)₄, in turn, is in equilibrium with monomeric silicate ions, for example [9]:

\[ \text{OH}^- + \text{Si(OH)}_4 = (\text{HO})_3\text{SiO}^- + \text{H}_2\text{O} \]
\[ \text{OH}^- + (\text{HO})_2\text{SiO}^- = (\text{HO})_2\text{SiO}_{2}^- + \text{H}_2\text{O} \]

Therefore, an equilibrium exists between ionic silica and colloidal, or polymerized, silica. Arpaia expresses it this way:

\[ n\text{SiO}_{3}^- + 3n\text{H}_2\text{O} = (\text{H}_2\text{SiO}_3)_{n}\text{nH}_2\text{O} + 2n\text{OH}^- \]

In general, as concentrated alkali metal silicate solutions are diluted (to a lower limit of ~330 ppm), the pH and [OH⁻] are reduced, and silicate ions hydrolyze to form larger polymeric species along with a lower SiO₂/Na₂O ratio silicate [9]. As stated by Iler [10](pg.20): “When a solution of soluble silicate, which is always highly alkaline, is neutralized by acid to a pH below about 10.7, the silicate ions decompose to silicic acid [Si(OH)₄], which then polymerizes to silica.”

However, for very dilute solutions (< 300 ppm SiO₂) as in the case of drinking water applications (4-25 ppm SiO₂), essentially complete depolymerization occurs and monomer (i.e., Si(OH)₄ and HSiO₃⁻ [9]) is the dominant
species. For example, upon adding a sodium silicate solution \((\text{SiO}_2/\text{Na}_2\text{O} = 3.22, \sim 400,000 \text{ ppm SiO}_2)\) to water, Lehrman and Shuldener [11, 12] observed that for dilutions of 14, 70, 140, and 350 ppm SiO\(_2\), only a few percent of the silica at most was in colloidal form whereas the majority was molybdate-reactive (i.e., monomer). According to the authors, these equilibria were reached very rapidly, “probably instantaneously.” For dilutions of 700 and 1400 ppm SiO\(_2\), the percent colloidal silica increased over the seven days of the experiment up to 21 and 29%, respectively.

The kinetics of depolymerization of soluble sodium silicates in very dilute solutions has been studied by Dietzel and Usdowski [13]. They obtained an empirical pseudo second-order law to describe the depolymerization:

\[
\frac{[T]}{[P]_t} = \frac{[T]}{[P]_0} + \frac{[T]}{[P]_0} k_D t
\]

\([T] = \text{Total silica concentration}
\]

\([P]_t = \text{concentration of polymer at time } t
\]

\(k_D = \text{reaction rate constant for depolymerization}
\]

For the case of a waterglass WG 37/40 \((\text{SiO}_2/\text{Na}_2\text{O} = 3.15, 25.2 \text{ wt. }\% \text{ SiO}_2)\) diluted to 23 mg/L SiO\(_2\) at 20°C and a constant pH of 5.74, they found \(k_D = 0.3428 \text{ L/mol•sec}\) and, by extrapolating to \(t = 0\), \([T]/[P]_0 = 1.123\). They also observed that the depolymerization rate increased with pH and decreased with increasing final concentrations of silica (over 3.8 to 23 mg/L SiO\(_2\)). For 23mg/L SiO\(_2\), \(k_D\) varies with pH according to: \(k_D = \text{pH}^{11.61}(5.662 \times 10^{-10})\). So for a pH of 8.0, \(k_D = 17.29 \text{ L/mol•sec}\). Substituting this into the above equation and assuming a similar \([T]/[P]_0 = \) [13], it will take about 22.4 min. for the 23 mg/L SiO\(_2\) solution to depolymerize to 90% monomer, and about 4.2 hours to attain 99% monomer. Such values agree with the previous statements that depolymerization in very dilute sodium silicate solutions occurs rapidly.

The fact that negatively charged monomeric silicate species are present in very dilute solutions of sodium silicates is significant, especially considering the charged nature of pipe surfaces due to the presence of anodes, cathodes, or other ionic corrosion products. No doubt, the possibility and reality of silicate film formation on pipe surfaces within water distribution systems is linked to these characteristics.

Iron and Manganese Sequestration

One of the challenges facing water systems is having to control a variety of water quality parameters. For instance, compliance with the LCR requires a pH of 7-10; however, the polyphosphates that are commonly used to control red and black water problems are less effective with increasing pH [14]. Therefore, chemicals that serve in more than one capacity of water treatment are desirable. In fact, silicate, in combination with chlorine, is effective for Fe and Mn sequestration [15, 16]. As a result, silicate treatment may simultaneously provide corrosion inhibition and Fe and Mn sequestration.

III. THE ROLE OF SILICATE IN THE FORMATION OF PROTECTIVE FILMS

Silicate Usage and Observations up to 1945

The formation of protective silicate layers was observed as early as 1920 by Speller who, based on experiment, suggested that the natural silica present
in water precipitated onto pipe surfaces via reaction with colloidal ferric hydrate. Speller further suggested that water could be purposefully endowed with the properties that promote the formation of such corrosion inhibiting films [17]. Perhaps the first occasion of adding sodium silicate to a water supply was reported by Thresh in 1922. In this attempt to prevent further occurrences of lead poisoning in an English moorland community, the silicate treatment not only controlled the dissolution of lead but also solved the red water problems by inhibiting iron corrosion. The treatment also was used successfully in other English communities having similar water problems. Besides water distribution systems, sodium silicates were added to water systems in small apartment buildings, office buildings, and laundries in New York, Boston, and Pittsburgh in the early 1920's. This water treatment served as an alternative to mechanically or chemically deaerating corrosive waters. In 1923 Texter [18] reported that a "self-healing" protective film formed in hot water systems upon additions of soluble sodium silicates.

Stericker [17] summarized in 1945 what was known at that time about utilization of sodium silicates as a corrosion inhibitor. The selected items in the following list are taken from his summary:

1. Large amounts of silicate speed up the formation of the protective film but increase the chances of removing accumulated products of corrosion from old piping.
2. The preferred silicate for waters in which the pH is > 6.0 is 3.22 SiO₂/Na₂O.
3. Larger amounts of silica are required when the water contains considerable amounts of chlorides.
4. Because of the negative charge on silica, it will migrate to anodic areas where at least a part of the charge will be neutralized.
5. The silicate films are electric insulators.
6. In stagnant water, the supply of silica is soon exhausted.
7. If only part of the area is protected, the remainder takes all the attack of the corrosive medium. Therefore it is important to use enough inhibitor.

**The Mechanism of Film Formation in Galvanized Iron and Brass**

The mechanism of silicate film formation in Zn-containing metal pipes, specifically yellow brass and galvanized iron, was determined by Lehrman and Shuldener [11, 12]. These authors showed that after a year of continuous addition of sodium silicate (8-12 ppm SiO₂) to hot water, a thin gelatinous film formed on the pipe surfaces. The film consisted of two layers. The layer adjacent to the pipe was white and mainly composed of zinc hydroxide and/or zinc silicate with trace amounts of carbonate, and the layer adjacent to the water was darker in color and contained silica gel along with precipitates of Fe₂O₃ and organic material. By chemical analysis, the overall compositions of the films that formed in each kind of pipe were as follows:

- **Brass:** 67% silica and organic matter, 4%Cu, trace Bi, 9%Fe, 6% Zn, 1% Ca, <1% Mg, and 13%Na. (Metals were present as hydroxides and/or silicates.)
- **Galvanized iron:** 63% silica and organic matter, trace Cu, 10% Fe, 20% Zn, 1% Ca, <1% Mg., and 6% Na. (Metals were present as hydroxides and/or silicates.)
Although the overall compositions of the layers were different for the two different pipes, Lehrman and Shuldener indicated that the compositions of the white layers adjacent to the metal were very similar. In fact, the layers were similar even for the different kinds of pipes that had carried silicate treated (8-12ppm SiO₂) hot and cold waters over 7 months to 20 years.

In brass pipe, the film was described as being evenly distributed, tan-colored, and adherent; whereas in galvanized iron pipe, the film was evenly distributed, loose, rust-colored, and included white blobs which were determined to be Zn(OH)₂. For both types of pipe, analysis by X-ray diffraction (XRD) revealed that the predominant crystalline phases present in the films were βFe₂O₃·H₂O and quartz. (Quartz deposits were common for that particular water even without silicate treatment.) In order to crystallize the amorphous material in the films, they were heated at 1000°C for 30 min. This resulted in the crystallization of α-cristobalite (SiO₂) plus either copper oxide in the film from brass pipe or zinc oxide in the film from galvanized iron pipe.

Based on the above results and additional experiments, the authors determined that the mechanism of film formation consisted of two steps. First, positively charged corrosion products, namely zinc hydroxide, developed on the pipe surface to become the bottom layer of the total film. Secondly, negatively charged silica species were adsorbed, specifically by chemisorption, and formed the gelatinous, upper layer. This silica gel then “mechanically enmeshes particles” such as iron and hardness precipitates and organic matter.

In addition to identifying the mechanism of film formation, other experiments in this work revealed the importance of having corrosion products present in order for silica to adhere to pipe surfaces. In saturated solutions of hydroxides of Fe, Zn, and Cu (with no solid precipitate present), the concentration of silica did not decrease over eight weeks indicating that the silica species were not reacting with any of the metal hydroxides in solution. However, when solid hydroxide was present in the saturated solutions, the silica concentrations did decrease. The decrease was greatest for zinc hydroxide followed by ferric hydroxide and then cupric hydroxide. In addition, it was observed that the original hydroxide solids became stickier, adhering strongly to the bottom of the bottle. Furthermore, pieces of black iron and galvanized iron removed silica from sodium silicate solutions (initially 10 and 292 ppm SiO₂) over six and eight weeks, respectively. (In 1952 they reported [12], “Magnetite Fe₂O₃ removes silica from very dilute sodium silicate solutions (8.5 and 290 ppm SiO₂) to a larger extent than zinc hydroxide at room temperature. However, the work has not progressed far enough to indicate the mechanism.”) A yellow brass sample did not remove silica, however neither did this sample corrode over the course of the experiment. All of the above results indicate that the presence of solid corrosion products is another variable to be considered when designing experiments or interpreting results.

In a subsequent paper [19], Shuldener and Lehrman investigated the role of the bicarbonate ion on corrosion in the presence of silicate for waters at 160°F (71°C). Again they showed that silica was removed from water by iron and zinc corrosion products and was deposited on the specimens’ sur-
faces. This process occurred more quickly for zinc than for iron. But in addition, they observed that the bicarbonate ion (HCO₃⁻) reversed the potential from zinc being anodic to cathodic. Silicate, however, has the opposite effect, making the zinc more anodic, and therefore counteracts the bicarbonate ion. The final potential, then, is determined by the relative amount of each species in solution. For lower concentrations of silica and in the presence of bicarbonate, they deduced that the potential was moved toward iron being anodic, and because iron corrosion products are slower to remove silica, rust formed. They concluded that bicarbonate ion reversed the potential between zinc and iron to cause the formation of rust, but that in the presence of silicate, the corrosion rate decreased. (E.g., 2.0 ppm SiO₂, 4 ppm HCO₃⁻, at pH 7.1 proved to be a more corrosive water than 8.5 ppm SiO₂, 14 ppm HCO₃⁻, at pH 7.1.)

IV. CORROSION CONTROL STUDIES USING SODIUM SILICATES

In 1945 Stericker noted that there was a history of laboratory tests not matching field experience for sodium silicate treatment [17]. He believed that perhaps some factors had not been considered when the experiments were designed. This section reviews several studies that have utilized sodium silicate and evaluates the experimental design, the experimental procedure, and the resulting conclusions.

A. York Water District, York, Maine [20]

Data was collected over 1991 on this system consisting of 40% 50-100 year old unlined cast-iron pipes and 60% cement-lined cast and ductile iron pipes. The average flow rate varies from 5MLD in the winter to 11MLD in the summer. The source of water is a surface water supply characterized as soft (Ca < 1 mg/L), low alkalinity (8-10 mg/L CaCO₃), pH 8.3-8.8, with low turbidity (<0.10 NTU), low color (<10CU), temperature of 13°C (range 4-24°C), 0.03 mg/L Fe, 0.06 mg/L Mn, and 0.05 mg/L Al. The water also has a natural silica content of approximately 4 mg/L SiO₂, which was monitored during the study. Regular treatment includes additions of aluminum sulfate and NaOH for coagulation; chlorination for disinfection; and additions of NaOH to raise the pH back to 8.3-8.8 (after chlorination) and ammonia gas to promote the formation of monochloramine. Consumers had red water complaints due to an iron content in the range 0.40-1.9 mg/L. For example, there were 15 complaints from 6/90-12/90.

Over 12/90 to the first week of 1/91, the average metal concentrations were 83 ± 145 µg/L Pb, 0.33 ± 0.55 mg/L Fe, and 0.15 ± 0.13 mg/L Cu. Sodium silicate (SiO₂/Na₂O = 3.22) was added at 15-16 mg/L SiO₂ for the first two months followed by a dosage of 9-14 mg/L SiO₂. The pH, alkalinity, Ca, Pb, Cu, and Fe were measured at twelve points throughout the distribution system. First-draw samples were taken after a 6-12 hour stagnation period. After a five min. flush, second- and third-draw samples were taken. The flow rate over the course of the experiment was 130-280 million liters per month.

For the period 5/91-12/91, average metal contents for the first-draw samples showed reductions compared to the previous measurements: 16 ± 9 microgram/L Pb, 0.10-1.37 mg/L Fe (compared to the range 0.10-1.9 mg/L Fe
measured previously), and “slight” reductions in Cu. According to the report, some sites consistently had reductions in Pb content while others remained relatively constant or increased. In general the iron contents decreased but then increased over the course of the study. The authors suggested that this increase was due to decreasing flow rate, although it appears to be better correlated with increasing water temperature. Red water complaints, however, were eliminated. It was observed that the pH was lower at dead ends (7.52 ± 0.38) compared to central points (8.17 ± 0.05). Also there were lower silica concentrations (16.0 ± 1.2 vs. 17.8 ± 0.53 mg/L SiO₂, includes natural silica) and lower alkalinity (5 mg/L vs. 10 mg/L CaCO₃) at dead ends. Consequently, the highest concentrations of lead were found at dead-end locations. In addition, the average silica content was lower for unlined cast-iron mains (15.6 ± 1.5) than for other types of pipes (17.5 ± 0.71), and second-draw silica was being taken out of solution (e.g., by being adsorbed onto pipe surfaces) by home plumbing systems. The authors also noted that it was very difficult to maintain constant pH and silica content of the finished water because of the low buffering capacity and variations in the coagulation process. It was also evident that the problems of low silica content and low pH at the dead-ends were of some concern. They suggested monitoring silicate treatment for two or three years in order to gain a better understanding of any fluctuations that occur with a particular season.

B. City of Rochester Water Bureau [21]

Both a pipe loop and a field study were reported by the City of Rochester Water Bureau. In this case, zinc orthophosphate and KOH treatments were analyzed along with sodium silicate and a control. The initial water had an alkalinity of 60 mg/L CaCO₃, pH 7.5-8.5, and hardness 80 mg/L CaCO₃.

**Loop Study:** The pipe loop study, performed on AWWARF test racks, consisted of three different phases. In the first five weeks (4/22-6/7/92), no chemicals were added, and the four test racks were studied to see if their corrosion characteristics were similar. Only the soldered Cu loop Cu results were significantly lower in the rack that was to be treated with KOH. In phase II (6/8-12/10/92), treatment began: 1) KOH, pH to 8.5; 2) zinc orthophosphate, 1 mg/L as PO₄ for two weeks and then 0.4 mg/L PO₄ for the remainder; 3) sodium silicate (3.22 SiO₂/Na₂O), 20 mg/L SiO₂ for two weeks followed by 22 weeks at 12 mg/L SiO₂. In phase III (12/11-2/25/93), the silicate dose was changed to 8 mg/L SiO₂ while the others were treated as in phase II.

For the phase II lead and copper results (i.e., Pb loop Pb results, solder Cu loop Cu and Pb results, and Cu loop Cu results), the phosphate was most effective, followed by silicate, for reducing lead contents, while silicate was best, followed by phosphate, for reducing copper contents (based on median measurements). Both the phosphate and the silicate were better than the control for Pb and Cu uptake. The KOH also showed improvement over the control except for the case of the soldered Cu loop Pb results. Based on the mean corrosion rates of the steel coupons, the KOH loop was the best followed by the control, silicate, and phosphate loops. The pH of each of the loops during this phase generally ranged as
follows: 8.5-9.25 for silicate; 8.25-8.75, KOH; 7.75-8.5, control; 7.5-8.25, phosphate.

In phase III which used a smaller silicate dosage, the silicate treatment did not perform well. Although it still resulted in significantly lower Pb levels than the control for Pb loop Pb results, it was not significantly different for the soldered copper loop Pb results. (No copper results were reported for phase III.)

The pipe loop studies showed that all of the treatments were effective at reducing lead levels from lead pipes, with zinc orthophosphate being the best followed by sodium silicate. In addition, these two treatments were the only ones to significantly reduce lead from soldered copper pipes.

Samples of copper pipe from this experiment were sent to The Pennsylvania State University to be analyzed by x-ray photoelectron spectroscopy (XPS), a method especially suited for studying thin films. (Please refer to the paper, “XPS Characterization of Films Formed on Distribution Systems Using Additives to Control Pb/Cu Levels in Drinking Water,” for details of the analysis.) The analysis revealed that Si had been incorporated into the film on the pipe treated with silicate; thus confirming the theory that silicate forms some kind of layer on the pipe surface.

Field Test: Two hydraulically isolated sections of the city’s distribution system were selected for the field study. Measurements were taken at 20 different sites within each section, all of which had lead service lines to single family residences. Every two weeks, lead levels were measured from first-draw samples. Before treatment began, the two sections were monitored (5/4-7/27/93). The mean lead concentration in the test area was 24ppb which was statistically higher than that of the control (21ppb). From 7/29 to 11/12/93, a silicate dose of 7-10 mg/L SiO₂ was added to the test area. During this time there was no statistical difference in lead levels between the test and control areas. (Although this may be considered an improvement over the pretreatment results.) The mean lead levels dropped in both cases to 11.3 ppb for the control and 9.7 ppb for the silicate. However, the lead action level was exceeded in both cases. From 11/13/93 to 1/26/94, the silicate dosage was raised to 12 mg/L SiO₂. For this period, only the silicate test area met the lead action level, and it was statistically less than the control area having an average lead concentration of 7.3 ppb compared to 10.9 ppb. For two months the silicate treatment was stopped, and, as expected, there was a small increase in lead uptake in the test area. The average was 8.6 ppb which was not statistically different from the control average of 9.7 ppb.

Although the lead levels decreased in the control area over the course of the experiments, the lead action level was exceeded in every set of measurements. The same test area was then treated with KOH. (The zinc orthophosphate was not used in the field study because zinc would cause a sludge disposal problem and phosphate could stimulate algae growth in the system’s reservoirs.) Because of control problems, the pH varied from about 8.4-9.1 throughout the approximately 10 weeks of the treatment. During this time, the lead concentrations between the test (7.2 ppb) and the control (9.1 ppb) areas were not statistically different.
In general, the City of Rochester Water Bureau concluded that a 7-12 mg/L silicate treatment reduced lead levels at the consumers’ taps with a dose of 12 mg/L SiO$_2$ being the most effective. However, they planned to continue investigating pH adjustment to 8.5 with KOH since it also seemed effective and could be less expensive.

C. University of South Carolina, Dept. of Civil Eng. [22]

The water used in this study was a ground water, low in alkalinity (0-2 mg/L CaCO$_3$), acidic (pH 5.2-6.3), soft (1-3 mg/L CaCO$_3$), conductivity 13.0-19.0 $\mu$mhos/cm, < 0.05 $\mu$g/L Pb, 0.4-1.4 mg/L nitrate, < 0.05 mg/L fluoride, < 0.05 mg/L Zn, 0.03 mg/L Cu, 0.1 mg/L Mn, 0.05 mg/L Fe, 2.1-3.2 mg/L Cl, 22-23$^\circ$C. This water also had a natural silica content of 6.3-7.1 mg/L SiO$_2$. Each of the seven lines in this batch-mode, fill and draw type, system consisted of a 4L polyethylene solution tank from which water flowed into an acrylic sleeve that housed ten copper couplings. These couplings had been partially coated with a 50:50 Pb:Sn solder and were electrically insulated from each other. For the first five weeks (4/28-5/17/93), all lines were treated with a high test hypochlorite to maintain a 0.5 mg/L chlorine content. This was done to accelerate corrosion of the coupons so that corrosion products would be present when sodium silicate (SiO$_2$/Na$_2$O = 3.22) and NaOH treatments began. From 5/18 to 10/6/93, lines 1-3 were adjusted to 15, 20, and 25 mg/L SiO$_2$, respectively. (These concentrations included the background silica.) Line 4 received chlorinated water and served as the control. The pH of lines 5-7 was adjusted with NaOH so that the pH of line 5 matched that of line 1 (pH 6.6), line 6 matched line 2 (pH 7.0), and line 7 matched line 3 (pH 7.6). From 10/7 to 12/1/93, the silicate concentration in line 1 was increased to 30 mg/L SiO$_2$, and the pH in line 5 was raised correspondingly (pH 8.6). There were no changes in the treatments of the other lines during this time.

Every week, copper and lead concentrations were measured in 125 ml samples that were drawn from the columns after 8 and 68 hr. stagnation periods. On other days, the columns were gently flushed with at least two through-put volumes of treated water. The pH and silica contents were analyzed daily. Water samples from the solution tanks were analyzed twice/week to monitor alkalinity, total dissolved solids, conductivity, dissolved oxygen, and temperature. The effects of stagnation were observed by monitoring the water quality in the tanks and in the coupon assemblies. The corrosion rates were determined by coupon weight loss after they had been removed at the end of the study.

The copper up-take was minimal in all cases. The lead up-take was reduced by 75, 81, and 87% over the control in the 20, 25, and 30 mg/L SiO$_2$ lines, respectively, somewhat better than the corresponding NaOH lines by 12, 8, and 0%. However, for the last (i.e., seventh) month of treatment, the improvement over NaOH increased to 18, 11, and 7%, respectively. These results suggest that silicate offers some benefit besides that of raising the pH. Also, with increasing silicate dose, there is less difference between silicate treatment and the corresponding NaOH treatment; though with time, silicate provides increasing protection relative to NaOH. It may be that because of the higher pH resulting from the higher silicate dosage, the formation of lead corrosion products is slowed. However, with
time, they do form, and the silicate can interact with the corrosion products (adsorb onto them) and provide additional protection. To verify this, the rate of lead corrosion product formation must be known at different pH’s.

According to a visual inspection of the samples, a “non-uniform, fibrous film” developed on most of the coupons. It was more prevalent on the solder surface but did “extend” to the copper surface as well. Consequent XPS analysis at Penn State University on samples from Loops 3 and 7 revealed that, as with the Rochester sample, Si was prevalent in the film from the silicate treated pipe. A smaller amount of Si was also found in the NaOH treated pipe, presumably from the natural silica.

Although the stagnant feature of this experimental set-up is unique compared to other studies which utilize the AWWARF pipe racks, it was suggested that further investigation be performed under flowing conditions. Flow tends to enhance the performance of silicates because, apparently, more silica is likely to come in contact with the pipe surfaces compared to stagnant conditions which rely solely on diffusion.

D. City of Portland, Bureau of Water Works [23]

This water is low in alkalinity (6.0 mg/L CaCO₃), soft (7.2 mg/L CaCO₃), with a pH of ~ 6.8, and a natural silica content ~ 9 mg/L SiO₂. The AWWARF test racks included galvanized pipes and Pb-Sn soldered copper pipes. Copper and steel coupons were also incorporated. From 7/1 to 8/8/93, water flowed 23hr/day during a pretreatment phase. After this (through 2/14/94), flow was restricted to 3.5hr/day, and the following treatments were administered:

1) pH9 (lime), alk. 20mg/L CaCO₃ (actual pH was ~9.2)
2) pH8 (lime), alk. 25mg/L CaCO₃
3) Trisodium phosphate, 0.5 mg/L as P, lime to adjust pH to ~7.5
4) Sodium silicate, 10mg/L SiO₂ (pH ranged from 8-9 from 8/23-10/25, then it was usually ~9.2 for 11/3/93 to 2/14/94)
5) Control

Every week a 1L sample was drawn after an 8 hr. stagnation period, and metals uptake was analyzed. Of the five treatments, #1 and #4 performed the best and are described below:

<table>
<thead>
<tr>
<th>Source Metal</th>
<th>Metal Uptake</th>
<th>#4 % reduction over #5</th>
<th>#1 % reduction over #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb solder</td>
<td>Pb</td>
<td>75</td>
<td>68</td>
</tr>
<tr>
<td>Brass</td>
<td>Pb</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>Cu pipe</td>
<td>Cu</td>
<td>95</td>
<td>87</td>
</tr>
<tr>
<td>Brass</td>
<td>Cu</td>
<td>90</td>
<td>87</td>
</tr>
<tr>
<td>Brass</td>
<td>Zn</td>
<td>96</td>
<td>93</td>
</tr>
<tr>
<td>Galvanized steel</td>
<td>Zn</td>
<td>78</td>
<td>80</td>
</tr>
</tbody>
</table>

E. Las Vegas Valley Water District, Southern Nevada Water System [24]

This water was characterized by: alkalinity 125 mg/L CaCO₃, pH 7.8, hardness 90 mg/L CaCO₃, total dissolved solids 680 mg/L, 9 mg/L Si, 248-259 mg/L SO₄, 0.0017-0.0067 mg/L PO₄, 16°C. Copper test loops were given the treatments listed below for six months and compared to a control. In
each case, there was 8 hr. of flow per day. Also shown are copper and lead reductions over the control. (The source of lead is not clear from this report.)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Dosage (mg/L)</th>
<th>% Pb Reduction</th>
<th>% Cu Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Sodium polyphosphate</td>
<td>3.74</td>
<td>72</td>
<td>23</td>
</tr>
<tr>
<td>2) Silicate polyphosphate</td>
<td>4.44</td>
<td>-55</td>
<td>27</td>
</tr>
<tr>
<td>3) Zinc orthophosphate</td>
<td>0.93</td>
<td>67</td>
<td>-61</td>
</tr>
<tr>
<td>4) Sodium silicate</td>
<td>3.99</td>
<td>59</td>
<td>14</td>
</tr>
<tr>
<td>5) Blended orthophosphate</td>
<td>4.00</td>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>6) NaOH</td>
<td>7.65</td>
<td>22</td>
<td>36</td>
</tr>
</tbody>
</table>

The conclusions of this study were to continue testing only the three best—sodium polyphosphate, blended orthophosphate, and zinc orthophosphate—although it was admitted that silicate may have performed better if a higher start-up dosage had been used. For the final 3 months, the silicate reduced Pb uptake by 64%. Had higher start-up and maintenance dosages been used, and if a pretreatment phase had allowed some corrosion product to form before silicate was added, the silicate treatment would have probably provided additional reductions in metal uptake.

F. City of Newark, NJ, Division of Water/Sewer Utility [25]

The City of Newark Water Utility employed a two-cell corrosion test device and AWWARF test racks to investigate treatments of lime, orthophosphate, ortho-poly blended phosphate, and silicate. The water quality was described as: alkalinity 22-35 mg/L as CaCO₃, pH 6.2-6.9, hardness 24-45 mg/L as CaCO₃, turbidity 1.0-2.5 NTU, color 10-25 CU, 0.1-0.3 mg/L Fe, 5-25 mg/L sulfate, 4.0 mg/L SiO₂, 0.01-0.06 mg/L Mn, DIC 48-49 as CaCO₃, 6-32 mg/L chloride, 1-20°C.

In the two-cell device, steel coupons were placed in each of the cells. Raw water flowed through the first cell and then was mixed with the inhibitor. The treated water then flowed through the second cell. The % reduction of Pb leaching for each of the inhibitors was as follows:
1) 15% for lime, pH 8.5-9.0
2) 50% for zinc orthophosphate (dose not specified)
3) 40% for ortho-poly blended phosphate (dose not specified)
4) 45% for silicate (1 month 20 mg/L, 1 month 9 mg/L)

These tests were followed by AWWARF pipe loop experiments. For six weeks three racks were run with no treatment in order to flush them, to allow corrosion to begin, and to allow the water quality and metal content to stabilize. By the end of this period, the water had an alkalinity 19.2 mg/L CaCO₃, pH 7.3, and Ca hardness 23.0 mg/L CaCO₃. After some initial fluctuations from pipe to pipe and rack to rack, the lead and copper concentrations leveled off to the following: soldered copper pipe Pb was 47.5-47.9 ppb, soldered copper pipe Cu was 0.31 ppm, and lead pipe Pb was 428.5-437.0 ppb. The flow rate was one gal./min., and 1 L samples were drawn every week following an 8 hr. stagnation period. The following treatments were applied after the stabilization period:
1) Non-zinc orthophosphate: 1 mg/L, weeks 7-25 of the study
2) Sodium silicate: 24 mg/L SiO₃ for weeks 7-9; 18 mg/L for wks. 10-13; 12 mg/L for wks. 14-21, 9 mg/L for wks. 22-33, 8 mg/L for wks. 34-38
3) Control: weeks 7-40
After the first 25 weeks of the study, the orthophosphate treatment was stopped. That rack was cleaned, and then water with no treatment was run through from weeks 26 to 29. After this, ortho-poly blended phosphate was fed at a dose of 1 mg/L (as ortho) from weeks 30 to 42. The average water quality during the course of treatment was: alkalinity 31.0 mg/L (all racks), Ca hardness 37.0 mg/L (all racks), and pH of 7.4 for the phosphate treatments, 8.4 for 8 mg/L SiO2 dose, and 9.0 for the 24 mg/L SiO2 dose.

The blended phosphate did not provide effective corrosion control, and although the orthophosphate was considerably better, the water utility decided against phosphate treatment because of anticipated problems with algae growth in its open reservoirs. The silicate treatment proved to be very effective. It reduced the Pb content from lead pipe 65% over the control and Pb from soldered copper pipe 60% over control. With respect to lead control, it was described as being more effective and more consistent than the orthophosphate treatment. All three treatments reduced copper concentrations. In the end, the water utility recommended sodium silicate to control corrosion starting with a dosage of 18-20 mg/L and then decreasing to an 8 mg/L maintenance dose.

G. Greater Vancouver Water District [26]

The combination of acid rain and the absence of lime in Canadian lakes result in acidic surface water. Greater Vancouver is no exception. Its water has a pH of 6.0-6.3 which drops to 5.4-5.9 after chlorination. The alkalinity of 1.5-3.7mg/L CaCO3 also drops to 0.5-2.0 mg/L after chlorination. In addition, the dissolved oxygen content is near to saturation levels. All these factors contribute to produce a rather corrosive water.

The following treatments were administered in this pilot plant study which was conducted over 12 months, 3/91-3/92:

1) Control, raw water
2) Treated control; pH 8, alk. 20 mg/L
3) Silicate/orthophosphate blend, 5 mg/L (0.18 mg/L as P, 0.83 mg/L as SiO2 ); pH 8, alk. 20 mg/L
4) Sodium silicate, 12 mg/L; pH 8, alk. 20 mg/L
5) Zinc orthophosphate 1.5 mg/L (0.13 mg/L as P, 0.13 mg/L as Zn); pH 8, alk. 20 mg/L
6) Zinc orthophosphate, 4.5 mg/L (0.37 mg/L as P,0.37 mg/L as Zn); pH 8, alk. 20 mg/L
7) Zinc orthophosphate, 4.5 mg/L (0.37 mg/L as P,0.37mg/L as Zn);
   pH7.5, alk. 10-12 mg/L

Loops 2-7 were disinfected with chloramine (2.5 mg/L). The alkalinity was adjusted with NaHCO3. For loops 2, 3, and 5-7, the pH was raised with Ca(OH)2. And, although the report does not say so, MacQuerrie’s thesis clearly says that the pH of loop 4, the silicate loop, was lowered from a value >9 to 8 with addition of HCl [27].

Each loop consisted of the following: cast iron and copper pipe coupon inserts (4” long, 1” ID), copper and mild steel corrosometer probes, 84’ of lead soldered copper plumbing coils downstream of the coupon inserts.
PQ CORPORATION
CORPORATE HEADQUARTERS
PO Box 840
Valley Forge, PA 19482-0840
Phone: 800-944-7411

IN CANADA
National Silicates
Phone: 416-255-7771

IN MEXICO
Silicates y Derivados, S.A.
Phone: 52-555-227-6801

IN EUROPE
PQ Europe
Phone: 31-33-450-9030

IN AUSTRALIA
PQ Australia Pty. Ltd.
Phone: 61-3-9708-9200

IN TAIWAN
PQ Silicates Ltd.
Phone: 886-2-2383-0515

(50:50 Pb:Sn solder every 4’, velocity 2.6'/sec., metal content from this section was measured from 24 hr. standing water), 500g 50:50 Pb:Sn solder coils contained in plastic canisters downstream from the plumbing coils, and brass faucets. Each loop had a total flow of 6 hr./day. The water temperature varied with the season. Any fluctuations that may have occurred in the water quality were not reported.

The silicate treatment (#4) provided comparatively good protection in several categories. The 12 month average copper coupon corrosion rate was lowest for treatments #6 and #7 (~0.0024 mm/yr) followed by #4 and #5 (0.0047 mm/yr). The 12 month average cast iron corrosion rate was lowest for #4 (0.1350 mm/yr) followed by #6 (0.1510 mm/yr) and #7 (0.1600 mm/yr). The copper corrosometer probe corrosion rates were lowest for #6 (0.0014 mm/yr) followed by #7 (0.0023 mm/yr) and #4 (0.0035 mm/yr). The mild steel corrosometer probe corrosion rates were lowest for #6 (0.217 mm/yr) followed by #7 (0.265 mm/yr) and #4 (0.308 mm/yr). The copper uptake from the plumbing coils and the faucets was generally lowest for #2 followed by #4, and #6 followed by #4, respectively. The uptake of lead from the plumbing coils was generally lowest for #2 followed by #1 and #4. In the case of zinc uptake, only #2, 3, and 4 reduced the Zn level below that of #1, the raw water case.

One interesting note is that there were several coincidental spikes in the data for different metals and different loops. Coincidental spikes occurred for copper from solder coils (loops 5, 6, and 7 only), zinc from solder coils, lead from solder coils (except loop 4), copper from plumbing coils, and lead from plumbing coils. This phenomenon, however, may be generated by the open nature of the different test coupons (i.e., corroding copper coupons upstream from lead and zinc).

At this point, it must be clear that silicate treatment performs best when there has been 1) a pretreatment phase to allow the formation of some corrosion products and 2) a higher start-up dosage to facilitate a speedier transition from pipe surfaces being partially protected (i.e., highly susceptible to corrosion) to fully protected. Neither of these conditions were provided in this study. Furthermore, the addition of HCl to a water distribution system is, to state it mildly, unrealistic, and undoubtedly this detracted from the performance of the silicate. In spite of these shortcomings, the silicate treatment performed better than many or most of the other treatments especially for the cases of reducing the corrosion rate of cast iron pipe coupons, reducing copper uptake from the plumbing coils and faucets, and reducing lead uptake from the plumbing coils.

V. DISCUSSION

With respect to the studies A through G given above, sodium silicate was proven to be very effective at reducing metal uptake in all cases except E and G. In E a very low dosage of 4 mg/L SiO₂ was used for the duration of the six month experiment. In addition, there was no pretreatment phase to allow for the formation of corrosion products which appear to be necessary for silicate film formation. Study G not only lacked a pretreatment phase, but HCl and NaHCO₃ were both added to the silicate loop and undoubtedly reduced its effectiveness. (Recall the article by
Shuldener and Lehrman [19] which discussed the adverse effect of the bicarbonate ion with silicate treatment.)

In many of the studies reported above, references were given indicating that silicate was not an effective corrosion inhibitor. The three references that were usually cited included Sheiham and Jackson [28], Boffardi [29], and Schock and Wagner [30]. Sheiham and Jackson analyzed the deposits in lead pipes, studied the theoretical solubility of lead for different water conditions, and performed experiments to measure the lead uptake from lead pipes with different water conditions. The lead pipes were 4-6.5" long, 1/2" diameter. Water was fed continuously through them, and the "mean residence time" of water in the pipe was about 30 min. In one case, sodium metasilicate (SiO$_2$/Na$_2$O weight ratio = 1) was added continuously at a level of 10 mg/L SiO$_2$ at a location immediately before water entered the pipe. As a variation, the silicate treated water was first fed through tubing for two days and then entered the lead pipe. These two tests were run on new pipes at pH 6.5 and on older pipes, which had been removed from service, at pH 7.5. A low alkalinity moorland water with a pH of 7.5 was used. Addition of sodium silicate raises water pH anywhere from 1-2 units depending on the dose and soda content. Considering the original pH of the water, it is apparent that after silicate treatment the pH was adjusted down to 6.5 and 7.5 thereby losing any benefit that the silicate would have provided in raising the pH. (Details of the procedure indicate that the pH was lowered by adding CO$_2$(g).) In comparing the results that they obtained for silicate treatment vs. phosphate treatment, Sheiham and Jackson concluded that, compared to the control, the silicate had little effect but phosphate was "much more attractive." Since these tests were conducted under conditions that misrepresent real service, one cannot conclude by extrapolation that silicate treatment is ineffective in the field.

Boffardi [29] is another reference that portrays silicates as ineffective: “Their effectiveness has not matched that of phosphate-based treatments for protecting iron and steel. Silicate treatments are not recommended for control of lead solubility in distribution systems.” Boffardi, however, provides neither experimental evidence nor reference citation to support these statements. Since Sheiham and Jackson is one of three references listed at the end of the paper, it may be supposed that their report was influential in forming Boffardi’s opinion.

Schock and Wagner [30] report on experiments performed by the Drinking Water Research Div. of the USEPA in 1979 and 1980. In these experiments, sodium silicate was added at 10 and 20 mg/L SiO$_2$ to a soft, low alkalinity (20 mg/L CaCO$_3$) water. The pH for both silicate treatments and a control was 8.2. Obviously for the three to be the same, the pH was lowered for the silicate treated water. Three recirculating systems were used with new pipes. The lead levels in the control rose to about 0.175 mg/L Pb after 60 days and then fell to about 0.140 mg/L Pb by the end of 75 days. The 10 and 20 mg/L SiO$_2$ cases exhibited slightly better results. The lead levels at 75 days were about 0.105 mg/L Pb and 0.095 mg/L Pb, respectively, with peaks at 0.110 and 0.105. By the end of 90 days, the levels were about 0.095 mg/L Pb for both. After the first runs, the water was emptied from the system and water of the same quality was added. For the second run, the control peaked at about 0.125 mg/L Pb and then
decreased to about 0.065 mg/L Pb by 105 days. At 105 days, the lead levels for 10 and 20 mg/L SiO₂ were about 0.060 and 0.072 mg/L Pb after having peaked at 0.063 and 0.095, respectively. The last measurement for the 10 mg/L SiO₂ was about 0.050 at 115 days, and that of the 20 mg/L SiO₂ was about 0.040 mg/L Pb at almost 260 days. The authors concluded that in order to achieve significant control, a treatment of 20 mg/L SiO₂ would have to be administered.

Of those studying corrosion in water distribution systems, some believe that sodium silicate inhibits corrosion by raising the pH of the water; others hold the opinion that silicates form a protective layer against corrosion. The former implies a neutralization approach to corrosion control, and the latter, a passivation approach [27]. If raising the pH is the only benefit to adding silicate, then its effectiveness is limited to suppressing those reactions in which H⁺ is a reactant and to changing the solubilities of metal, corrosion products, etc. However, if silicate forms a thin protective layer, then there should be additional benefits. This was the case in an experiment reported by Wehle [31] in which a dose of 7 ppm SiO₂ reduced the corrosion rate of galvanized steel significantly more than a NaOH treatment at the same pH. The work of Duffek and McKinney [32] also directly compared the effects of silicate treatment with NaOH treatment adjusted to the same pH. For a range of 3 mg/L SiO₂ (pH 7.9) to 500 mg/L (pH 9.3), the NaOH treatments were comparatively ineffective at preventing corrosion. In the study by the University of S. Carolina (described above) in which silicate treatments were analyzed alongside companion treatments of the same pH, the silicate performed more effectively for lead uptake although to a lesser degree with increasing silicate dosage and pH. However, with time, the differences between the corresponding treatments increased. Considering the fact that corrosion products must be present in order for silica to adsorb onto the surface of iron, copper, and zinc-containing metal pipes, perhaps the same is true for lead. In that case, the results are consistent with the idea that at higher silicate concentrations, the pH is raised causing the corrosion of lead to slow. Since the corrosion products that are needed for a silicate film to form are slow to appear, the benefits of a silicate passivation layer are not experienced until later. Since the silicate layer depends on the presence of corrosion products, once these products are covered, the layer will cease to accumulate.

VI. CONCLUSIONS

Historically, silicate’s role as a corrosion inhibitor has received mixed reviews. This is due, in part, to the mystery surrounding how it works and also because of the wide range of experimental findings. However, new evidence provided by XPS analysis indicates that a silicate film does form on the interior of pipes. This film may help to inhibit corrosion as indicated by experiments in which silicate treatments were compared to NaOH of the same pH - silicate always provided superior corrosion control. In addition, silicate’s poor or mediocre performance in some studies must be reconsidered because of misconceptions about how silicate functions. In some cases, the pH of silicate treated water was actually lowered and then compared to other treatments. Also, it is apparent that silicate films require the presence of corrosion products in order to form on pipes.
Some experiments, then, had a negative influence on the effectiveness of silicate because of their design. In order to clarify silicate’s efficacy, further study is warranted especially considering its potential to simultaneously control corrosion and red and black water problems.

VII. REFERENCES


