



## Project Summary

# Evaluation of Silicate and Phosphate Compounds for Corrosion Control

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Various dosages of selected silicate and phosphate compounds were evaluated for their ability to inhibit corrosion of cast iron, copper, lead, and galvanized steel specimens in drinking water. The compounds selected for study were zinc polyphosphate (Calgon C-39\*), zinc orthophosphate (Virchem V-931), sodium metasilicate, and glassy silicate. The effectiveness of these compounds for corrosion inhibition were studied under different water quality conditions using gravimetric and electrochemical corrosion tests.

Study results indicate that some corrosion inhibitors provide better protection for some metallic systems than others. Utilities should therefore use either a gravimetric or an electrochemical corrosion test to evaluate the corrosiveness of their water systems and the effectiveness of any corrosion-inhibiting compounds used.

*This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Corrosion in potable water distribution systems is a continuous problem faced by water utilities. The problems created as a result of corrosion can be grouped into three categories: economics, aesthetics, and health. Corrosion

may result in the deterioration of water quality and may significantly decrease the hydraulic capacity of water mains by promoting pipe wall pitting and the growth of tubercles. If corrosion is not inhibited, costly main replacements are inevitable. Excessive dissolution of iron and copper from plumbing and distribution systems can cause aesthetic problems with respect to taste, color, or staining characteristics. Furthermore, excessive lead levels can cause health problems.

Silicate and phosphate compounds have been used for corrosion control in numerous water systems, but their usefulness and effectiveness in various systems has not been well documented. Furthermore, the mechanisms by which these compounds prevent corrosion has not been clearly defined.

The general objectives of this research were to study the factors that influence the corrosion protection offered by selected silicate and phosphate compounds. Specifically, the research objectives were to examine the effectiveness of various dosages of selected silicate and phosphate compounds applied to test water for corrosion inhibition of cast iron, copper, lead, and galvanized steel coupons in a closed-pipe loop system. The study examined effectiveness of these compounds for corrosion inhibition under differing water quality conditions using gravimetric and electrochemical methods.

Chemical speciation studies were also performed for different silicate and phosphate compounds within the normal ranges of pH, alkalinity, chloride, sulfate, and hardness concentrations

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encountered in the water supply system. The corrosion products and coatings on the metal coupons were also characterized with and without the addition of corrosion-inhibiting compounds. The corrosion inhibitors tested were zinc polyphosphate (Calgon C-39), zinc phosphate (Virchem V-391), sodium metasilicate, and glassy silicate. The test water was University of Missouri tap water.

## Methods and Materials

Gravimetric corrosion experiments were conducted using a corrosion test apparatus with four parallel polyvinyl chloride (PVC) pipe loop systems of a recirculating type similar to that proposed in the Method B ASTM D2688-83. The loop system had five locations where duplicate metal coupons could be inserted into the test water flow path and selected coupons could be removed for examination after a set exposure period. The circulating test water in the loop system was treated with specific doses of the silicate or phosphate compound that was to be evaluated for corrosion control.

Batch experiments were conducted to evaluate the effectiveness of zinc polyphosphate (Calgon C-39) for controlling corrosion of cast iron in a galvanic cell configuration under different pH conditions. Cast iron and copper coupons were connected by a copper wire to form a galvanic cell and then immersed in the test water. The test system water quality parameters such as total iron, alkalinity, hardness, orthophosphate, total phosphate, and pH were measured at different times. At the end of the test period (28 days), the corrosion rates of the cast iron coupons were measured by the gravimetric procedure.

Electrochemical corrosion of metal samples was determined under different environmental and water quality conditions by measuring the polarization resistance of the sample.

Speciation studies for the phosphate systems were done initially by using equilibrium equations and constants from the literature. Simultaneous equations were solved by an iterative method on an Apple IIe microcomputer. A more sophisticated approach was later offered by REDEQLEPAK, an aqueous chemical equilibrium program. The program was set to allow for precipitation of solids, to balance both charge and mass, to keep the pH at 8.0, and to be open to the atmosphere with

respect to  $\text{CO}_2$ . Dilute aqueous solutions of silicic acid were studied with the interfaced calorimeter to look at enthalpies of protonation for various solutions. Computer modeling of these solutions was done using a program that solves simultaneous equations, SEQS, to determine the species present. All silica solutions were prepared upon dilution of a stock 0.1M  $\text{SiO}_2$  solution from solid hydrated metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ).

The corrosion products on the cast iron coupons were analyzed by X-ray diffraction and scanning electron microscope (SEM) analysis. A nuclear magnetic resonance (NMR) spectrometer was used to determine the extent of pyrophosphate hydrolysis in the test water.

## Results and Conclusions

### Gravimetric Corrosion Evaluation

1. At doses  $\geq 4.36$  mg/L as P in test water, zinc polyphosphate (Calgon C-39) effectively controlled the corrosion rate of cast iron after 21 days of exposure, at a temperature of  $30^\circ \pm 2.5^\circ\text{C}$  and a flow rate of 19.5 cm/sec. At lower temperatures ( $20^\circ \pm 2.5^\circ\text{C}$ ) and flow rates (9.5 cm/sec), it was also effective in controlling the corrosion of cast iron at 4.36 mg/L as P. The system with 13.09 mg/L as P had a higher corrosion rate compared with the control after 26 days of exposure. Zinc polyphosphate was more effective in controlling the corrosion of cast iron at pH 5.0 than at higher pH values.

2. At 2.18 mg/L as P in test water, zinc orthophosphate (Virchem V-391) was marginally more effective than the control in inhibiting the corrosion of cast iron after 38 days of exposure time. Higher doses of zinc orthophosphate did not effectively control the corrosion of cast iron.

3. At a dose of 30 mg/L as  $\text{SiO}_2$  in tap water, sodium metasilicate was most effective in controlling the corrosion of cast iron compared with other doses tested.

4. At a dose of 15 mg/L as  $\text{SiO}_2$  in test water, glassy silicate controlled the corrosion of cast iron more effectively than other doses tested.

5. Among the four corrosion inhibitors tested, zinc polyphosphate was the most effective in controlling the corrosion of cast iron at comparable temperatures and flow velocities.

6. At doses of 4.36 mg/L and 13.09 mg/L as P in test water, zinc polyphosphate effectively controlled the corrosion of copper.

7. At 13.09 mg/L as P, zinc polyphosphate had the lowest lead corrosion rate, but the difference between lead corrosion rates at 4.36 and 8.72 mg/L as P was not much higher than at 13.09 mg/L as P after 28 days of exposure.

8. At the doses tested (4.36 to 13.09 mg/L as P), zinc polyphosphate did not effectively control the corrosion of galvanized steel.

9. The alkalinity and hardness decreased with time in all the systems tested. The largest decrease was observed in the blank systems. A good correlation generally existed between the alkalinity and hardness decreases in the different systems. This result indicates some precipitation of  $\text{CaCO}_3$  and/or calcium silicate or calcium phosphate, depending on the system. Decreases in alkalinity and hardness in the zinc-polyphosphate-dosed systems were higher with cast iron than with copper, lead, or galvanized steel systems. Precipitation of  $\text{CaCO}_3$  in the blank systems did not sufficiently inhibit corrosion compared with systems having inhibitors. A positive saturation index did not protect the metal from corrosion. Generally, little correlation existed between corrosion rate and saturation index.

### Electrochemical Corrosion Testing

1. The corrosion rate of cast iron was significantly lower in the absence of oxygen. Systems with zinc salts provided better corrosion protection for cast iron than did zinc salt combined with pyrophosphate in oxygenated systems in distilled water experiments.

2. Up to a point, orthophosphate increased the effectiveness of the sodium hexametaphosphate corrosion inhibitor for cast iron in test water systems; but larger doses of these chemicals raised the corrosion rate.

3. The presence of zinc salt increased the effectiveness of sodium pyrophosphate corrosion inhibitor for cast iron in test water. Adding more zinc salt improved the inhibitor's effectiveness more than adding a corresponding amount of pyrophosphate.

4. Systems with a zinc polyphosphate (Calgon C-39) dose of 13.09 mg/L as P in test water produced the lowest cast iron corrosion rate.

5. Zinc orthophosphate (Virchem V-931) at comparable doses did not control the corrosion rate of cast iron in test water as effectively as zinc polyphosphate (Calgon C-39).

6. At nominal doses of sodium metasilicate (up to 50 mg/L as  $\text{SiO}_2$ ), the cast iron corrosion rate in test water was not measurably affected compared with the blank system. At doses up to 30 mg/L as  $\text{SiO}_2$ , glassy silicate did not effectively inhibit the cast iron corrosion rate.

7. A low dose of zinc polyphosphate (2.18 mg/L as P) effectively controlled the corrosion rate of copper, but sodium silicate was not as effective at comparable doses.

8. Zinc polyphosphate controlled the corrosion of lead and galvanized steel more effectively than sodium silicate, but the overall corrosion rates were quite low, and meaningful conclusions were difficult to obtain.

### **Comparison of Gravimetric and Electrochemical Corrosion Testing**

1. The electrochemical corrosion rates were generally higher than the gravimetric corrosion rates measured on the same metal under similar test conditions. Note, however, that the electrochemical corrosion test measures the corrosion rate on a clean metal surface, whereas the gravimetric method measures the average corrosion rate for the exposure period during which the metal surface is subjected to corrosion and deposition of compounds produced from inhibitor reactions.

2. In many instances, similar corrosion inhibition trends were measured by the two methods in the presence of various corrosion inhibitors for different metals (e.g., cast iron, lead, and galvanized steel in the presence of zinc polyphosphate). However, the corrosion rate data produced by the two methods did not correlate well for some systems (e.g., cast iron in the presence of sodium silicate, and copper in the presence of zinc polyphosphate). Selection of the corrosion rate measurement method will therefore depend on the type of system being studied.

### **SEM and X-Ray Diffraction Studies**

1. Application of scanning electron microscopy (SEM) to the cast iron corrosion products showed the presence of iron, silica, phosphorus, aluminum, and

zinc. Phosphorus was found in samples from tests that had used phosphate inhibitors for corrosion control. A sample of corrosion products from a blank system (test water, cast iron, and no inhibitor) showed significant amounts of calcium; otherwise, the calcium content of the corrosion product was quite small. The SEM data on cast iron coupons (from which corrosion products had been removed) indicated the presence of zinc, phosphorus, and calcium on the protected areas of the coupon compared with the unprotected part.

2. The X-ray diffraction data on the cast iron corrosion product showed the presence of zinc phosphate and calcium phosphate when zinc orthophosphate inhibitor was used. In the presence of sodium metasilicate inhibitor, the corrosion products contained iron silicate compounds. After removal of corrosion products, X-ray diffraction of the cast iron coupon surface that had been inhibited with phosphate compounds showed very little residual phosphate. But systems using sodium metasilicate inhibitor indicated the presence of various silicate compounds on the coupon surface.

### **Speciation Studies**

1. A model solution of test water containing zinc and pyrophosphate indicated that 20 mg/L  $\text{Na}_4\text{P}_2\text{O}_7$  reduced the corrosion of cast iron significantly. Addition of 10 mg/L  $\text{ZnSO}_4$  in the presence of 20 mg/L  $\text{Na}_4\text{P}_2\text{O}_7$  further reduced the corrosion rate. This additional corrosion reduction was due to the formation of zinc silicate (silicates are present naturally in the test waters). At doses of  $\text{ZnSO}_4 > 30$  mg/L, the corrosion rate drop was due to the formation of zinc pyrophosphate.

2. In the experiments with sodium metasilicate as an inhibitor (<60 mg/L as  $\text{SiO}_2$  and pH 8), the occurrence of calcium and magnesium silicate should theoretically be negligible, since most of the silicate will occur as  $\text{Si}(\text{OH})_4$ . The extent of silicate polymerization should be negligible. The silicate solid phase compounds are very difficult to identify because of the large number of possibilities. More kinetic and thermodynamic data are needed to define the compounds formed.

### **NMR Studies**

At pH 10, there was no hydrolysis of the pyrophosphate compound tested. At pH 8.0, which is nearer that of the test water, pyrophosphate hydrolysis was

negligible during the electrochemical corrosion tests. Some hydrolysis could probably occur during the course of the gravimetric studies, which can last a month or more.

### **Recommendations**

1. Study results indicate that some corrosion inhibitors provide better protection for some metallic systems than others. To evaluate the corrosion inhibition effectiveness of an inhibitor compound or to evaluate the corrosiveness of a water system, one must perform either a gravimetric or an electrochemical corrosion test. In most cases, the two tests give parallel results. Utilities should use such corrosion-testing procedures to validate their use of corrosion-inhibiting compounds.

2. The saturation index is of minimal value in monitoring the corrosivity of water to various metals. Even a system with a positive saturation index and  $\text{CaCO}_3$  precipitation does not prevent corrosion of the metal under consideration. A better corrosion-monitoring index is needed for the utilities to evaluate their water supplies.

3. More research needs to be done to determine the kinetic and thermodynamic data for the solid phase and complexed silicate systems.

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*The complete report entitled "Evaluation of Silicate and Phosphate Compounds for Corrosion Control," (Order No. PB 87-180 972/AS; Cost: \$18.95, subject to change) will be available only from:*

*National Technical Information Service  
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