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**Title: AN EVALUATION OF CORROSION CONTROL ADDITIVES FOR POTABLE RO
PERMEATE**

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AN EVALUATION OF CORROSION CONTROL ADDITIVES FOR POTABLE RO PERMEATE

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Abstract

Corrosion inhibitors are frequently used as post-treatment chemicals for potable RO plants around the country, but few are actually effective. In many cases, red water complaints are prevalent in counties spending millions of dollars annually on corrosion control chemicals. Multiple corrosion coupon studies were performed comparing various blends of polyphosphate/orthophosphate based products against zinc/orthophosphate based chemicals. It was found that products containing polyphosphates often had no effect on corrosion control of mild steel or lead, and sometimes actually increased the corrosion rates. By contrast, some zinc based inhibitors consistently reduced corrosion rates for steel to between 0.5 – 4 MPY, and almost completely suppressed lead corrosion at less than 0.02 MPY. The setback was that zinc based inhibitors tended to precipitate when permeate pH was adjusted above 8, a necessity for long term chloramines stability. This was remedied by the use of a product containing zinc stabilizers and chelated zinc compounds that were stable up to a pH of 8.5.

Introduction:

Most drinking water plants around the U.S. use corrosion inhibitors to prevent red water complaints due to corroding steel fittings, and more importantly, to comply with the EPA lead and copper rule. Some distribution systems contain ductile or cast iron piping, and in other cases, asbestos cement piping that can fail without proper corrosion treatment. It is estimated that 700 ductile iron and/or cast iron water main breaks occur each day in North America¹. Plants using conventional treatment on fresh water from lakes and rivers typically find high alkalinity and hardness in their finished water. This necessitates the use of products that contain polyphosphates to ensure adequate scale control.

On the other hand, plants that use Reverse Osmosis (RO), Nanofiltration (NF) or Lime Softening treatments tend to have very low hardness and alkalinity with absolutely no tendency for scale formation. Despite this, polyphosphate based products are widely used with water produced by these plants, with polyphosphate making up 60% - 75% of the total active phosphate content in most polyphosphate/orthophosphate blends.

Corrosion coupon studies were performed on the finished water of various plants on the East Coast of Florida. Of those plants, three produced finished water consisting of Reverse Osmosis (RO) permeate blended with filtered feedwater, one plant blended RO permeate with lime softened water, and one plant produced only lime softened water.

The purpose of the study was to compare polyphosphate containing corrosion inhibitors against zinc based inhibitors.

Background:

Corrosion of metals in aqueous solutions occurs by oxidation/reduction reactions. The metal is oxidized by dissolved oxygen in water, leading to the dissolution of the metal as an aqueous ion. The area where the metal is oxidized is known as the anode, whereas the area at which oxygen is reduced is known as the cathode.

Corrosion inhibitors protect metals by preventing reactions at the anode (anodic inhibitors) or the cathode (cathodic inhibitors). The best corrosion inhibitors are ones that provide both types of inhibition. The most commonly used anodic inhibitor for potable water systems is orthophosphate. Orthophosphate adsorbs to surfaces, forming a thin protective layer. When iron oxidizes to ferrous ions, the orthophosphate in solution reacts with the ions forming a ferrous phosphate barrier that prevents further metal dissolution into solution.

Polyphosphates are claimed to be cathodic inhibitors. However, while polyphosphates also tend to adsorb to surfaces, they have never been proven to effectively inhibit corrosion. They instead sequester dissolved metals and precipitating metal oxides². In the case of iron corrosion, this hides the appearance of red water, when in fact corrosion rates may be increasing due to the removal of protective oxide films³. Polyphosphates have also been found to increase copper corrosion⁴, most likely by inhibiting the formation of protective malachite scales ($\text{Cu}_2\text{CO}_3(\text{OH})_2$)⁵. A study by the American Water Works Research Foundation found that protective lead carbonate scales (cerussite)

became more soluble in water as a result of increased corrosion rates when polyphosphate based inhibitors were used⁶.

True cathodic inhibitors precipitate at the cathodic site, preventing contact of oxygenated water with metal. The precipitated barrier is also non-conductive, inhibiting the flow of current to the cathode and thereby inhibiting the reduction process. The most commonly used cathodic inhibitor is zinc which precipitates zinc hydroxide, and if there is sufficient alkalinity, precipitates as a more adherent zinc hydroxycarbonate.

Corrosion inhibitors are not effective without adequate pH and alkalinity, both of which are necessary to form a passive ferrous carbonate layer. The role of the corrosion inhibitor is to fill the gaps where ferrous carbonate and ferric oxide scales have not formed evenly. Otherwise, corrosion inhibitors would have to be dosed at excessively high dosages that would simply not be cost effective.

Experimental Setup

Three corrosion coupon racks receiving finished water were set up at each site. The first rack was a control, receiving no treatment other than pH adjustment applied by the plant. Water feeding the second rack was dosed with a blended polyphosphate/orthophosphate corrosion inhibitor currently used at the plant – the different facilities used different products from different manufacturers. The third rack was dosed with the Avalya A-751 stabilized zinc orthophosphate corrosion inhibitor. The racks each contained two sets of mild steel, copper, brass and lead coupons. The first set was collected after 30 days. The second set after 60 days.

At two of the plants, a second phase of testing was performed at full scale where the first set of coupons was collected after 3 months, while the second set was collected after 6 months.

Once the coupons were collected, they were sent to an independent lab where the corrosion rate was calculated in Mils per Year (MPY) based on weight loss.

For the purposes of this paper, only 60 day results are reported from the pilot scale coupon studies, and only 6 months results are reported from the full scale coupon studies.

Results and Discussion

The Avalya A-751 is a stabilized zinc orthophosphate (ZOP) that contains zinc stabilizers and chelated zinc compounds. While ZOP products typically lose effectiveness above pH 7.8 due to precipitation, the Avalya A-751 remains soluble up to a pH of 8.5. This higher pH is typically a necessity for plants that use chloramination.

During piloting and later when performing the full scale coupon testing, it was observed that there were significant increases in water turbidity while using the stabilized ZOP product. This was a serious concern while performing the full scale testing, as the turbidity of the water in the clearwell was beyond the acceptable criteria for drinking water. The increased turbidity coincided with a significantly reduced performance of the corrosion inhibitor. This was indicated by corrosion rates as high as those measured with the previous poly/ortho product.

The turbid water was collected and filtered through a 100 nm polycarbonate filter using a vacuum pump. A SEM/EDS analysis was performed and the precipitate was found to consist of zinc hydroxide, zinc phosphate and some calcium phosphate (Fig.1).

It became apparent that the cause of the problem was the chemical dosing system. Sodium hydroxide was being dosed for pH adjustment just a few inches upstream of the corrosion inhibitor and no static mixers were installed between the dosing points. The pH at the sodium hydroxide dosing point was well above 12, causing the zinc and phosphate salts to precipitate out prematurely. This was a design flaw that was found repeatedly in plants all over Florida. This problem was remedied by moving the corrosion inhibitor dosing point to the clearwell and thereby creating sufficient distance from the caustic dosing point. This allowed the pH to stabilize to its target range prior to introduction of the corrosion inhibitor.

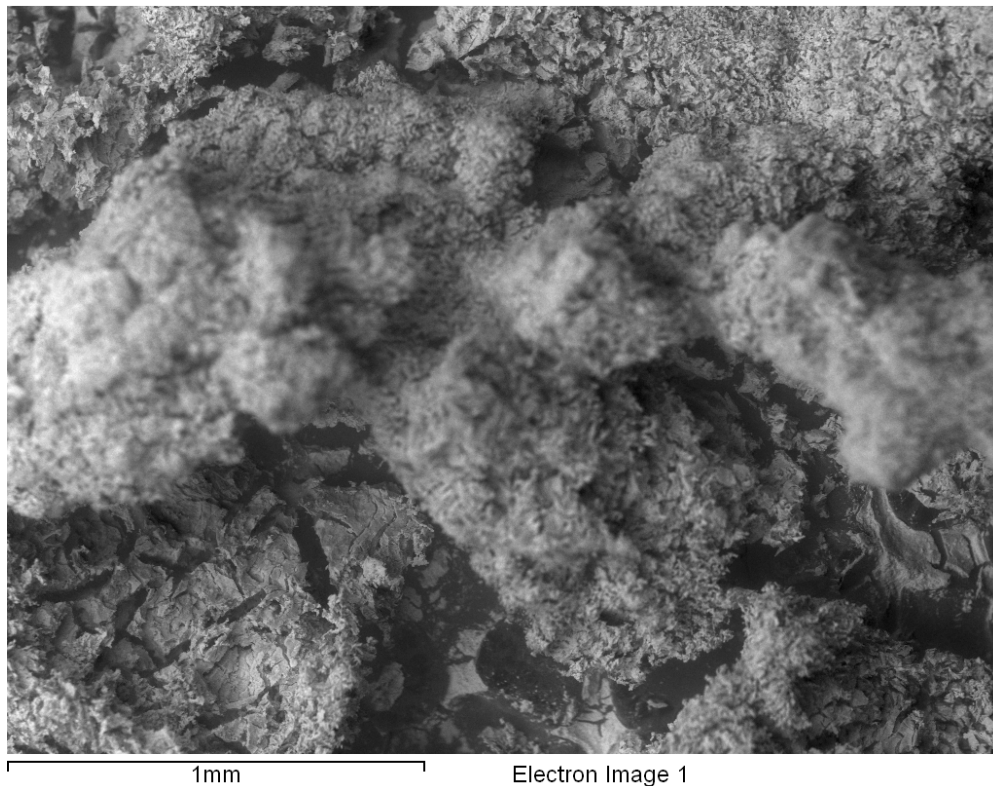


Figure 1: SEM Image of Precipitated Material when Corrosion Inhibitor was Dosed Immediately after Sodium Hydroxide without Static Mixer or Sufficient Distance between the Dosing Points

Quantitative results

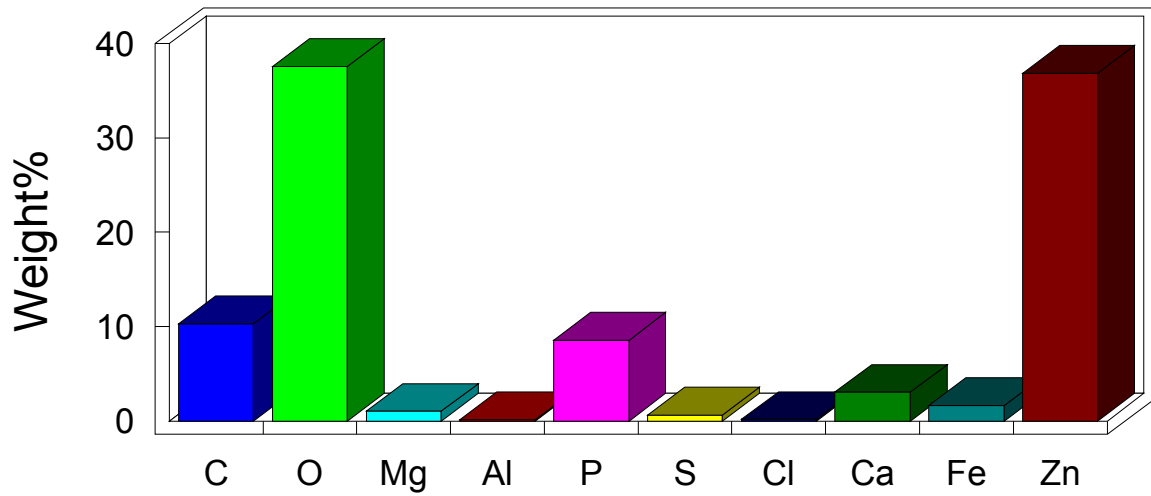


Figure 2: Chart Showing Elemental Analysis Results from Figure 1

Element	Weight%	Atomic%
C K	10.29	20.28
O K	37.59	55.61
Mg K	1.02	0.99
Al K	0.14	0.12
P K	8.58	6.56
S K	0.65	0.48
Cl K	0.17	0.11
Ca K	3.05	1.80
Fe K	1.65	0.70
Zn L	36.86	13.34
Totals	100.00	

Table 1: EDS Analysis of Image in Figure 1 shows deposit to be composed mainly of zinc hydroxy carbonate, zinc hydroxide, zinc phosphate and calcium phosphate

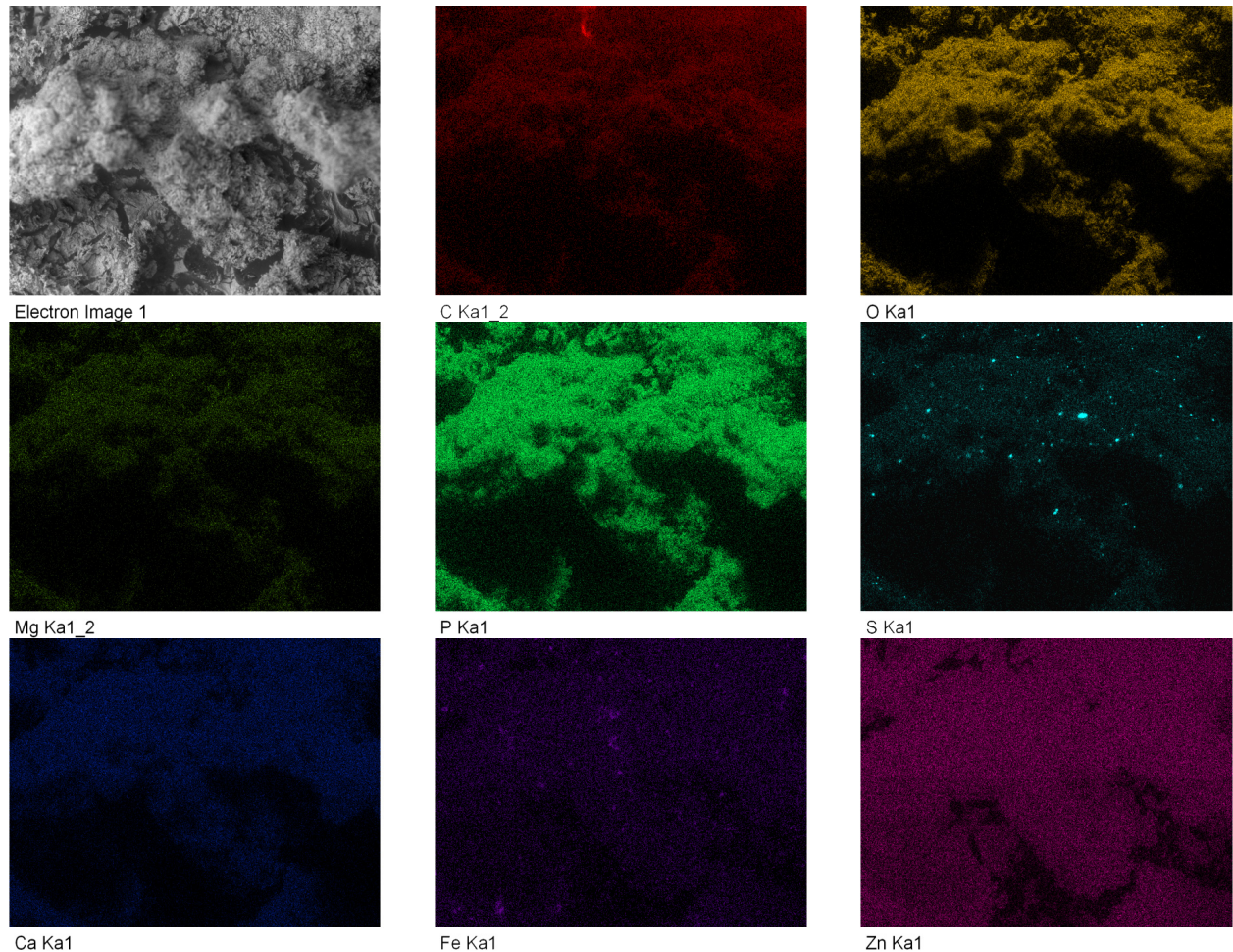


Figure 3: Elemental Mapping of SEM image in Figure 1 – In Addition to the Calcium Phosphate, Zinc Phosphate and Zinc Hydroxide and Hydroxycarbonate Precipitates, Elemental Sulfur Deposits are Clearly Visible.

Once this problem was resolved, corrosion coupon testing was repeated and the results were outstanding. In Port St. Lucie, the first full scale corrosion tests were performed at the James E Anderson (JEA) Plant which blended RO permeate with filtered raw feed. The plant was initially operated at pH 9.1 and excellent corrosion inhibition was achieved despite some minor zinc precipitation. When the pH was reduced to 8.9, there was only a slight impact on the corrosion rates for steel, and no impact on lead corrosion rates. The JEA plant had always maintained a pH of 9.2 to minimize lead corrosion, but since completion of the studies outlined in this paper, they have reduced their operating pH to 8.5 with a corrosion inhibitor dosage of only 2 ppm. In addition to the cost savings from reducing sodium hydroxide and cutting the corrosion inhibitor dosage in half, point of use (POU) tap analysis showed a significant improvement in dissolved lead and copper levels. The 90th percentile values for lead were actually reduced from 0.01 mg/L using the Poly/Ortho product to 0.0031 mg/L using the stabilized ZOP product – a 69% reduction despite the lower pH and dosage. The 90th percentile values for copper were reduced by 33% from 0.0647 mg/L using the Poly/Ortho product to 0.052 mg/L using the stabilized ZOP product.

The Prineville plant, which blended RO permeate with lime softened water, was the second plant in Port St. Lucie where full scale corrosion studies were performed. This plant also showed drastically improved corrosion results for all metals when compared to the coupon results of the Poly/Ortho product. As a matter of fact, the Poly/Ortho product was doing no better than the control in inhibiting steel corrosion and seemed to be increasing the rate of lead corrosion.

Alkalinity in the finished water for both plants was relatively low, ranging from 15 – 30 ppm. This was due to loss of CO₂ at the degasifier during H₂S removal.

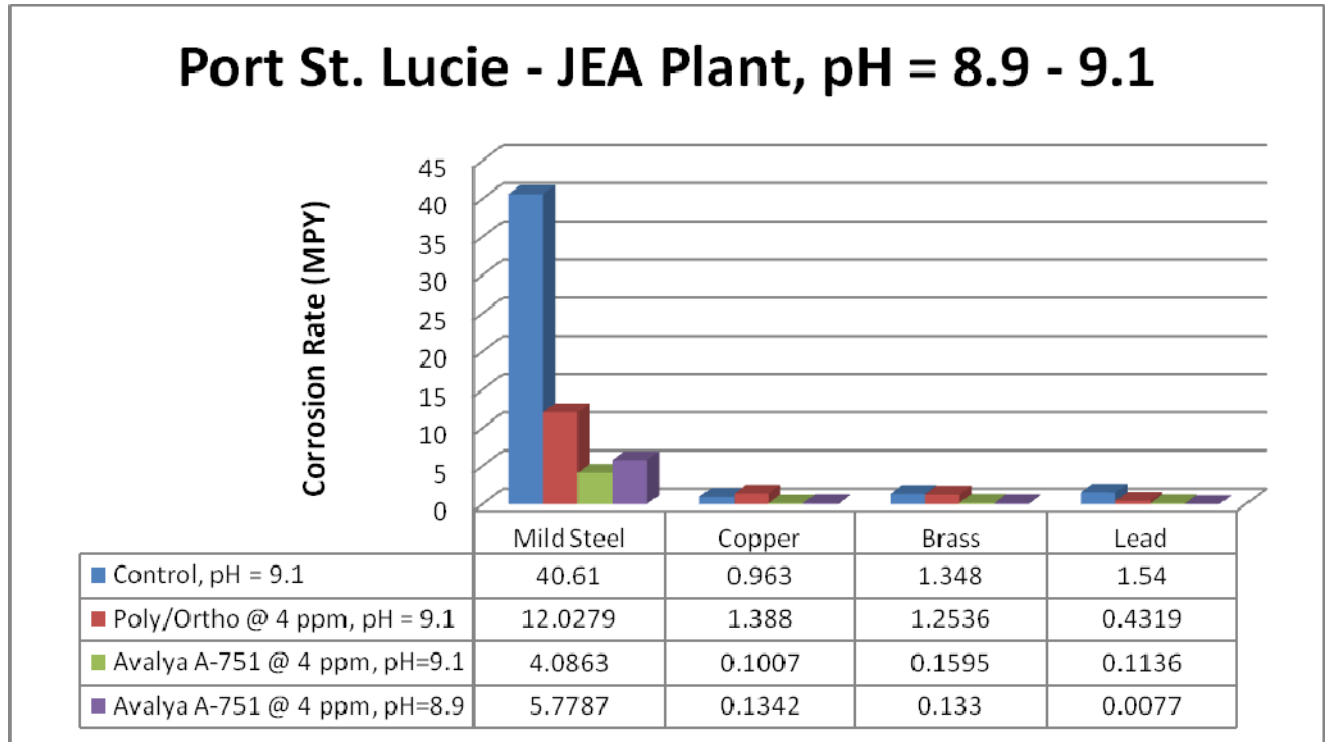


Figure 4: Port St. Lucie JEA Plant, Corrosion Coupon Results at 6 Months

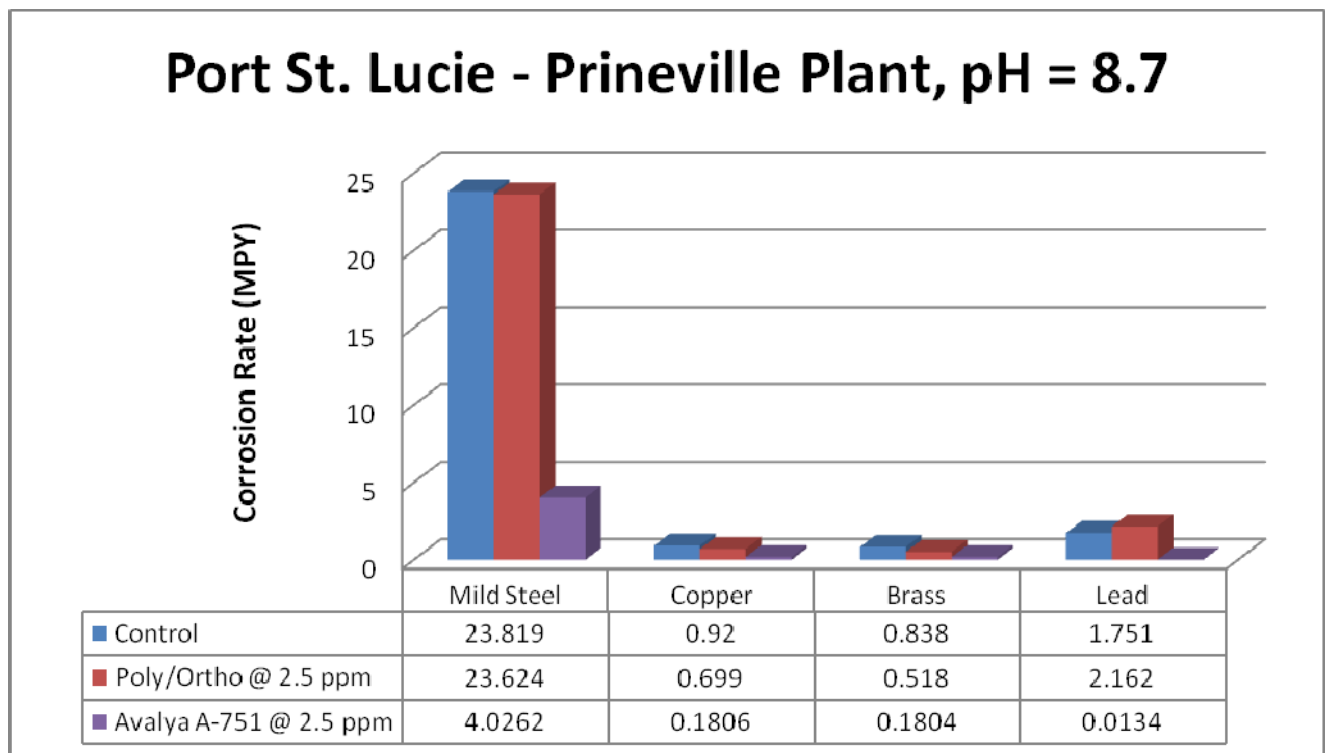


Figure 5: Port St. Lucie Prineville Plant, Corrosion Coupon Results at 6 Months

The tests performed at Palm Coast compared the Poly/Ortho product that was being dosed at the full scale, to the control and Avalya A-751 on a sidestream corrosion rack. The results here were significant because the results from Plant #1, a limesoftening plant, showed that the poly/ortho product had almost double the mild steel corrosion rate as that of the control, and about 38 times the corrosion rate of the Avalya A-751. Similar results were seen at Plants #2 and #3, even when the dosage of the stabilized ZOP was significantly lowered. Results for copper and brass were consistently better using the stabilized ZOP compared to the Poly/Ortho product. Lead corrosion at Plant #1 was very similar for the Poly/Ortho and the stabilized ZOP, but at Plants #2 and #3, lead corrosion rates were up to 4 times higher when comparing the Poly/Ortho product to the stabilized ZOP.

The alkalinity at Plant #1 was in the range of 85 – 95 ppm, while alkalinities at Plants #2 and #3 were consistently in the range of 70 – 80 ppm.

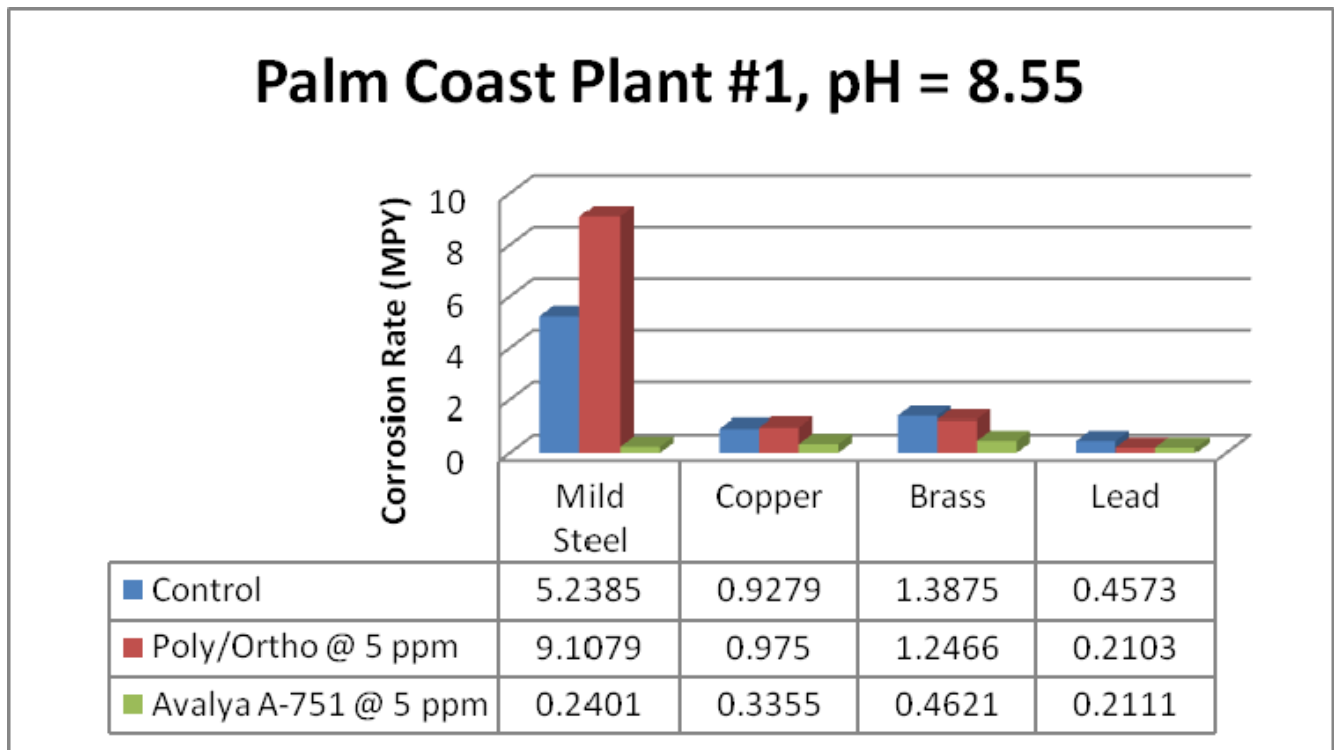


Figure 6: Palm Coast Plant #1, Corrosion Coupon Results at 60 days

Palm Coast Plant #2, pH = 8.7

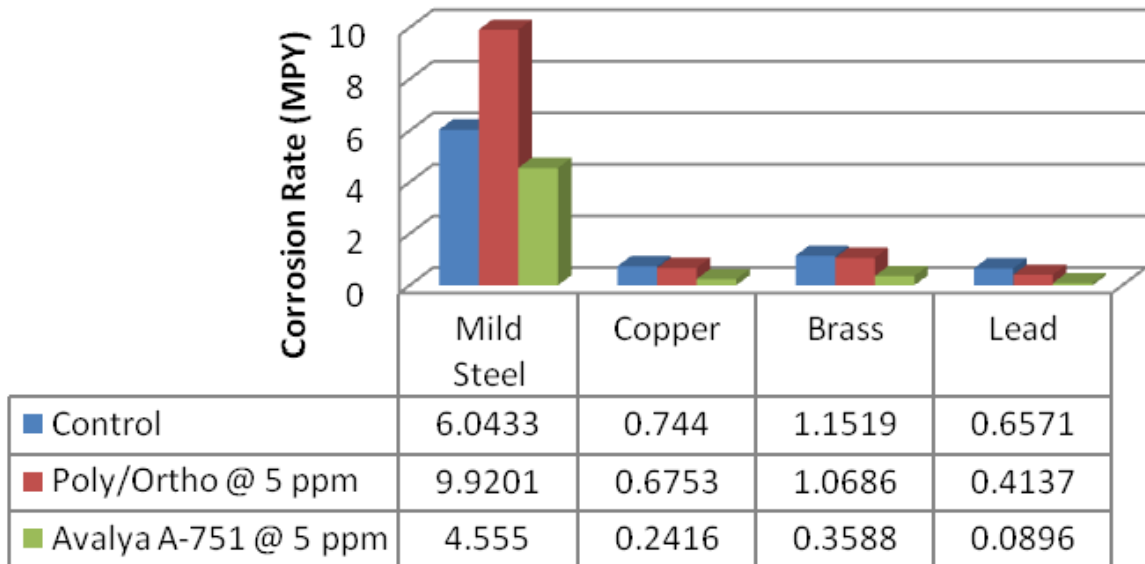


Figure 7: Palm Coast Plant #2, Corrosion Coupon Results at 60 days

Palm Coast Plant #3, pH = 8.41

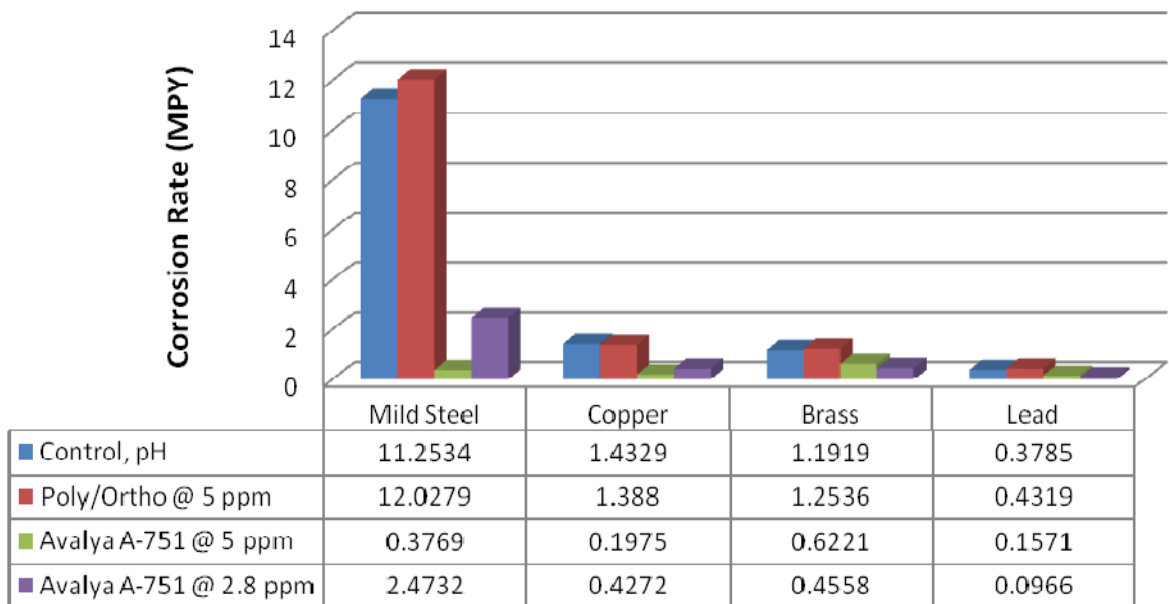


Figure 8: Palm Coast Plant #3, Corrosion Coupon Results at 60 days

Conclusion:

It is very evident from the corrosion studies performed herein that stabilized ZOP is a far superior to Poly/Ortho for inhibition of corrosion in systems carrying low alkalinity, low hardness water. It seems counterintuitive that most Reverse Osmosis, Nanofiltration and Lime Softening plants around the US still use Poly/Ortho based products in their distribution systems.

The main hurdle in the use of the stabilized ZOP product is its sensitivity to being dosed in the same area as strong caustic solutions such as concentrated sodium hydroxide. This issue can easily be resolved by installing a static mixer after the caustic dosing point, but prior to the corrosion inhibitor injection point in new installations. In existing plants, the problem can be minimized by moving the corrosion inhibitor injection point away from the caustic dosing point. This would allow the sodium hydroxide to mix sufficiently and the pH to stabilize, preventing the corrosion inhibitor from being exposed to highly concentrated caustic solutions and excessively high pH levels.

In reviewing literature, although most studies find that ZOP based products are better at protecting metals from corrosion, a few studies have found Poly/Ortho products to perform better with copper, and sometimes steel. The authors of this paper believe that the chemical injection points may have been overlooked in those cases and that the zinc may have been precipitating due to inadequate mixing of the pH adjustment chemicals.

The Avalya A-751, a proprietary stabilized ZOP, outperformed different Poly/Ortho products even at pH levels as high as 9.1 where slight zinc precipitation occurred. At pH 8.5, the zinc was completely soluble due to the proprietary stabilizers in the Avalya A-751.

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