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Carbon Steel Corrosion Control in the Past Twenty Years and in the New Millennium

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INTRODUCTION

Treatments for controlling carbon steel corrosion have changed greatly over the last 20 years and will continue to do so into the new millennium. The reasons for the changes include the increased awareness of product effects on health, safety and the environment, operation at higher cycles, the availability of improved treatments, and increasing economic pressures.

How awareness of chemical hazards has affected the evolution of water treatment is exemplified by the history of the use of chromate for corrosion control. In the 1960's and 1970's, chromate and zinc/chromate treatments were commonly used for controlling carbon steel and yellow metal corrosion. The chief reasons were the effectiveness and low cost of chromate treatments. The finding that chromate causes cancer, the liability associated with storing strong oxidants, and the negative impact of discharging chromate treated waters on the environment led to both the regulation and abandonment of chromate treatments. The liability of using chromate treatments created the need for water treatment companies to develop the replacement products that were developed in the last 20 years and are the subject of this paper.

Another example of the effect of concern over product safety is the trend to eliminate or reduce the use of sulfuric acid for pH control. While operation at more alkaline pH does reduce the corrosiveness of the cooling water, the elimination of the need to handle a highly acidic oxidant is a major factor in the trend over the last 20 years towards more alkaline operation.

The desire to operate at increasingly higher cycles has led to dramatic changes in water treatment, including the development of significantly more effective calcium phosphate and calcium carbonate inhibitors. There are several reasons for the desire to operate at higher cycles. One reason is the lack of water in regions such as the southwest, limiting the availability of make-up water. Another reason for higher cycles operation is to reduce the cost of make-up water, when costly municipal water is used. Also, limited budgets for water treatment encourage higher cycle operation, since treatment chemicals are cycled up, often reducing the level of treatment chemicals required in the make-up water. (For most make-up waters, however, the cost reduction becomes marginal after five cycles or so.) Lastly, higher levels of hardness and alkalinity will reduce the corrosiveness of the cooling water, if corresponding chloride and sulfate levels are not too high. In some cases, scale, such as calcium carbonate, rather than corrosion, becomes the primary concern, since corrosion is reduced in scaling waters.

With the maturation and globalization of water treatment, the effect of economic pressure is more pronounced than ever. End users have reacted to competitive pressures by demanding lower cost products with the same high standard of performance. Formulators/blenders have updated their product offerings by incorporating more cost-effective raw materials into their products. To make choices on product components, technical information is needed. This paper



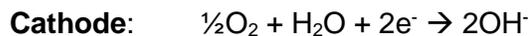
provides technical information on the components used in carbon steel corrosion inhibitor formulations.

DISCUSSION

How Inhibitors Function

Before evaluating the components in corrosion inhibitor formulations, an understanding of the corrosion process and how inhibitors work is needed. Corrosion is the deterioration of a metal because of a reaction with its environment. The breakdown of the metal can result from electrochemical reactions or physical forces. Here the focus is on electrochemical reactions.

For the corrosion process to occur, there must be an anode, where the oxidation reaction(s) occur, a cathode, where the reduction reaction(s) occur, an electronic path (the metal), and an electrolyte (the cooling water). In cooling waters, the anodic and cathodic reactions are as follows:



Inhibitors that function by depressing the anodic reaction are called anodic inhibitors, and inhibitors that function by depressing the cathodic reaction are called cathodic inhibitors. Inhibiting one reaction or the other works because the opposite reaction is then equally depressed to maintain the balance of electron flow.

Anodic Inhibitor Mechanism

At the anode, iron is oxidized to ferrous ion. Ferrous hydroxide, which is soluble, forms from the hydration of the ferrous ion. Ferrous hydroxide is in turn oxidized by dissolved oxygen to ferric hydroxide. Ferric hydroxide precipitates as an insoluble, non-protective iron corrosion product. Anodic inhibitors work by 1) promoting the formation of a protective gamma Fe_2O_3 film, instead of ferric hydroxide and/or 2) forming precipitates that become incorporated into voids in the protective Fe_2O_3 , enhancing the effectiveness of the film. The protective film inhibits the ability of the ferrous ion to form by interfering with electron transfer rates. [1] Electrochemically, this effect is measured as a movement to a more passive corrosion potential, hence anodic inhibitor films are often called passive films. [1]

Passive films are thin, only about 10^{-3} to 10^{-2} μm , and consequently, they have little effect on heat transfer. Passive films can be very effective, but pitting occurs when anodic inhibitors are under-dosed. When anodic inhibitors are underfed, the film is not completed and film breaks occur. The cathodic reaction occurs over the entire passive film surface, but the anodic reaction is confined to the film breaks. Corrosion in the form of pitting, therefore, occurs at the small, unprotected anodic sites. The corrosion current at the small anodic sites must be high to balance the cathodic current that is spread over a large area, thus resulting in the characteristic high corrosion rate at the pit sites.



Cathodic Inhibitor Mechanism

At the cathode, water is hydrolyzed to form hydroxide ions in the presence of dissolved oxygen. The production of hydroxide ions results in a cathodic pH of about 10 at the metal/water interface. The localized high cathodic pH causes cathodic inhibitors to form protective precipitate films, sometimes called barrier films, which prevent dissolved oxygen from reaching the metal surface. Barrier films are macroscopic and often appear as a bluish, opalescent cast on the metal surface.

Anodic Inhibitors

In the presence of dissolved oxygen, the protective film that forms is gamma Fe_2O_3 . [2] Magnetite is sometimes found underneath the gamma Fe_2O_3 film, and is believed to be a partially oxidized intermediate layer. [2] The gamma Fe_2O_3 film is porous, with many voids and cavities. Orthophosphate works by forming ferric phosphate, dihydrate which fills the voids and cavities, eliminating unprotected sites where the anodic reaction could occur. [3] Orthophosphate is not effective in the absence of oxygen, since it cannot oxidize iron to gamma Fe_2O_3 and form the primary film. [2]

The mechanism for molybdate has not been clearly defined, but molybdate is believed to work by first forming a nonprotective complex with ferrous ions. In the presence of oxidizers, such as dissolved oxygen or nitrite, the ferrous complex is oxidized to a protective ferric molybdate film [4]. Because nitrite helps in the formation of the ferric molybdate film, combining nitrite with molybdate, reduces the molybdate requirement. Due to the conversion of nitrite to nitrate in the presence of oxygen, nitrite is not commonly used in open recirculating cooling towers.

In contrast, the anodic inhibitor, chromate, works by oxidizing ferrous hydroxide to gamma Fe_2O_3 . [5] Reduced chromate, Cr_2O_3 , is incorporated into the protective film and the film consists of 75% gamma Fe_2O_3 and 25% Cr_2O_3 . [6] In contrast to the use of chromate alone, the use of zinc/chromate provides cathodic inhibition. The combination is synergistic, requiring a far less inhibitor dose than chromate alone.

Like chromate, nitrite is an oxidizing inhibitor that promotes the formation of the gamma Fe_2O_3 film. [2] Nitrite is commonly used in closed systems, where oxygen levels are low. Since nitrite is a nutrient for some bacteria, the use of nitrite can result in problems with microbiological growth. Often biocides, such as isothiazoline, are used with nitrite based products. In the last five years, some operators have begun to switch from nitrite based programs to other programs. Where oxygen levels exceed 20 ppb, and where hardness, chloride, and sulfate levels are low, molybdate/borate products can be used effectively. (Borate is used primarily for pH buffering.) However, molybdate based programs can be pricey.

Anodic inhibitors have wide use in closed systems, where oxygen concentrations are low and waters tend to have low ionic strengths. Additionally, the high required doses of anodic inhibitors can be tolerated in closed systems, since make-up requirements are small. Historically,



chromate was fed at a maintenance dose of about 200 mg/L, at a pH of 8.0 to 9.0, whereas nitrite is fed at 600 to 1500 mg/L as NaNO_2 at a pH above 7.5. [4][7] Chloride ions and sulfate negatively impact the performance of chromate and nitrite, therefore the dose requirements increase with the concentration of these aggressive species.

Molybdate is fed at 200 to 300 mg/L as molybdate ion, at a pH of 7.0 to 9.0. [8] As with other anodic inhibitors, the effectiveness of molybdate is reduced by chloride ions. Consequently, the higher the chloride concentration, the higher the molybdate requirement. At a chloride concentration of 200 mg/L, 800 mg/L of molybdate ion is needed. [4] When the chloride concentration exceeds 500 mg/L, molybdate is not an effective treatment. [1] When combined with nitrite, the molybdate concentration can be reduced in water having a moderate chloride concentration, since nitrite enhances the performance of molybdate, as discussed earlier.

Cathodic Inhibitors

In contrast to anodic inhibitors, cathodic inhibitors work by forming barrier films that inhibit the hydrolysis of water in the presence of dissolved oxygen. The barrier films prevent dissolved oxygen from reaching the metal surface and receiving electrons. The barrier films are formed by the precipitation of the cathodic inhibitors as a result of the localized, high pH at the cathode. Examples include zinc, which forms zinc hydroxide, zinc phosphate and zinc phosphonate precipitates; polyphosphate, which forms calcium polyphosphate precipitate; phosphonates, which form calcium phosphonate precipitate; and calcium carbonate, which can be used as a protective film at high calcite saturations. The key to the success of cathodic inhibitors is the formation of a protective film at the metal surface while at the same time preventing bulk precipitation of scale, usually with the use of polymers.

In open cooling systems, effective formulations are based upon cathodic inhibitors and a polymer, but often contain an anodic inhibitor as well. The anodic inhibitor is generally orthophosphate, which can be incorporated into a product formulation, be supplied from the make-up water, or be supplied in the treated water as a result of the breakdown of cathodic inhibitors, such as polyphosphate and phosphonates. The cathodic inhibitors are generally polyphosphate, phosphonate, and/or zinc. Zinc is a very effective cathodic inhibitor, at low dose. However, environmental restrictions on zinc discharge have begun to limit the use of zinc.

Stabilized Phosphate Products

The evolution of modern, open system corrosion inhibitor treatments began in the 1940's with the introduction of glassy polyphosphates by Calgon Corporation. [9] (Table 1 is a timetable of the introduction of various inhibitor formulation components.) The glassy polyphosphates are commonly called sodium hexametaphosphate, but generally are not exactly 6 units in length, but rather 6 to 12 units in length, depending on the production process variables. Other polyphosphates used for controlling corrosion include sodium triphosphate, and sodium or



potassium pyrophosphate. Additional glassy phosphates, some of which incorporated zinc, were subsequently introduced in the 1950's and 1960's. [10]

In the 1970's interest arose in phosphate esters as an alternative to glassy polyphosphates. [11] [12] [13] In addition to providing corrosion inhibition, polyphosphoric acid esters reduce the viscosity of polyphosphoric acid, making it a more suitable product offering. Polyphosphoric acid esters are liquids and are therefore easier to formulate than solid polyphosphates. They contain phosphate ester and various polyphosphate chain lengths. Some believe that the variety of chain lengths improves corrosion inhibition versus phosphate glass. In any case, both polyphosphates and phosphoric acid esters have been shown to be effective over many years of use.

Inorganic phosphate based products are effective, but in the 1960's, 1970's, and early 1980's, prior to the introduction of effective polymer technology, the pH had to be maintained near neutral to prevent calcium phosphate precipitation. The need to maintain a near neutral pH necessitated the addition of sulfuric acid. Cycles then had to be limited, to prevent calcium sulfate precipitation, due to the build-up of sulfate ions from the addition of sulfuric acid.

Early attempts at controlling calcium phosphate precipitation, and thus improve treatment with inorganic phosphates, were with the use of polymaleic acid (PMA) and maleic acid/sulfonated styrene copolymers (MA/SS). [14] [15] The use of these polymers was marginally successful. Then, in the 1979, the introduction of the Betz stabilized phosphate product line (Dianodic II) changed water treatment. [8] The Betz program combined the use of orthophosphate for corrosion control with the use of an acrylic acid/hydroxypropylester copolymer (AA/HPE) for calcium phosphate inhibition. The National Starch Company commercialized the copolymer as Natrol 42 (now Alco Narlex LD-42), and Betz patented its use for calcium phosphate inhibition. [16]

Unlike later stabilized phosphate programs, the Dianodic II program is based upon the formation of a passive, protective film, rather than a cathodic barrier type film. To maintain the passive film, an orthophosphate dose of 10 to 25 mg/L is required. The pH ranges from 6.8 to 7.8, so the Dianodic program is not really an alkaline program, but rather a much-improved neutral pH program. [8]

In the early 1980's, Calgon Corporation followed with the introduction of the first successful alkaline stabilized phosphate product line (pHreeGUARD), which combined the use orthophosphate/polyphosphate with their copolymer of 60/40 acrylic acid/acrylamidomethylpropylsulfonic acid (AA/AMPS). [17] Early on, Nalco based its stabilized product line on acrylic acid/acrylamide copolymers (AA/AM). [18] Later, the Nalco acrylic acid/sulfonated acrylamide (AA/SAM) line of polymers was introduced to better compete with other sulfonated copolymers. [19] Likewise, in the late 1980's, Betz developed their copolymer of acrylic acid/allylhydroxypropylsulfonic ether (AA/AHPSE) to allow higher pH operation, than with



the original Dianodic II program. [20] In the 1990's, manufacturers, such as Rohm and Haas, introduced terpolymers. [21] [22] [23] The Rohm & Haas terpolymer contains acrylic acid, acrylamidomethylpropylsulfonic acid, and tertbutylacrylamide (AA/AMPS/TBAM). [21] Another terpolymer, Goodrite K-798, contains sulfonated styrene in addition to acrylic acid and acrylamidomethylpropylsulfonic acid (AA/AMPS/SS). [22] Claims have been made that the performance of the terpolymers is better than that of sulfonated copolymers for controlling calcium phosphate, etc., but the comparisons were made with the less effective 75/25 AA/AMPS, rather than the more effective 60/40 AA/AMPS. [24] [25] Today, 60/40 AA/AMPS copolymer, 75/25 AA/AMPS copolymer, terpolymers, etc. are readily available from several suppliers on the open market.

How do the polymers compare? To answer this question, several polymers were compared in a calcium phosphate inhibition study. In this study, untreated and treated supersaturated solutions of calcium phosphate were incubated for 24 hours at 60 oC. The supersaturated solutions contained 200 mg/L Ca^{+2} , 9.0 mg/L PO_4^{-3} , and 100 mg/L total alkalinity expressed as HCO_3^- for buffering pH. Without treatment, less than or equal to 0.1 mg/L phosphate remained in solution, but with a sufficient inhibitor dose, 8.5 to 9.0 mg/L of phosphate remained in solution. Based upon the remaining concentration of phosphate, the percent inhibition for each inhibitor level was determined. For each polymer, the minimum effective dose, that is the dose required for 90% or greater inhibition was determined and is listed in Table 2. As shown in Table 2, polymer technology has come a long way. Early copolymers, MA/SS and AA/HPE were not very efficient, requiring doses of 17 mg/L for over 90% inhibition. PMA and AA/AM polymers were not effective in this test, even at high doses. In contrast, 60/40 AA/AMPS, and the terpolymers, were effective at only 7 to 8 mg/L. Several other polymers, including 75/25 AA/AMPS, were effective at 9 to 10 mg/L.

In moderately scaling applications, 75/25 AA/AMPS copolymer is often used because of its lower cost per pound. For the choice of 75/25 AA/AMPS to be a good one, the 15% additional dose must be compensated by the reduction in cost per pound. Under more stressful conditions, the 60/40 AA/AMPS or terpolymers should be used because of their increased effectiveness. Generally, 60/40 AA/AMPS is less costly, than the terpolymers, and would be a more cost-effective choice. Naturally customer preference can enter into the selection of a polymer. In many cases, to meet a customer request, an adjustment in polymer concentration can be made, based upon the relative performance of the polymers.

Today, because of the development of effective polymers for controlling calcium phosphate precipitation, stabilized phosphate programs are run at pH 6.8 to 8.4. Inorganic and organic phosphates are sometimes both used. Phosphonates are usually added to stabilized phosphate programs to bolster calcium carbonate inhibition, and are occasionally added at



sufficient levels for bolstering corrosion control as well. Total phosphate levels (expressed as orthophosphate ion) range from 5 to 20 mg/L, with typical programs running at 7 to 10 mg/L. Polymer levels range from 3 mg/L to 20 mg/L. The phosphate concentration is determined by the corrosiveness of the water, and correspondingly, the phosphate requirement increases with decreasing pH and calcium concentration, and increasing temperature and chloride/sulfate saturation. The polymer requirement is determined by the calcium phosphate supersaturation. In general, more phosphate and less polymer is needed at lower pH and more polymer and less phosphate is needed at higher pH.

What should the ratio of orthophosphate to total phosphate be? Studies have shown that good corrosion control can be obtained with ratios ranging from 1:4 to 4:1, with 1:1 being optimal.²⁶ [26] In systems having a long half-life and/or high temperature, polyphosphate reversion rates can reach 80%, therefore feeding straight polyphosphate is a good choice. Where residence time is short and/or temperatures are low, and reversion rates are then low, feeding a blend at about a 1:1 ratio is desirable.

All-Organic Products

With higher pH operation, where pH's can approach and exceed 8.5, and the use of stabilized phosphate programs, calcium phosphate saturations become high. Consequently, polymer requirements become high and calcium carbonate control becomes more difficult. In order to reduce the polymer requirements and improve calcium carbonate control, all-organic, phosphonate based programs were developed. The interest in all-organic programs spurred the development of new phosphonates, such as phosphonobutanetricarboxylic acid, (PBTC) and hydroxypropylacetic acid (HPA). [27] [28] All-organic programs usually contain combinations of phosphonates, since combinations were found to work better than individual phosphonates, perhaps due to better surface coverage with varying size molecules. In the absence of oxidizing biocides, phosphonates decompose to orthophosphate far less readily than inorganic phosphates, thus reducing the driving force for calcium phosphate precipitation. Polymer use helps to control calcium phosphate formation and to keep in check calcium phosphonate precipitation. Calgon patented AMP/HEDP in 1980; Nalco patented HEDP/PBTC in 1985; and Grace/Dearborn patented HEDP/HPA in 1987. [29] [30] [31] [32]

While phosphonates do not decompose readily in the absence of oxidizing biocides, most do in the presence of chlorine or bromine. In response to this problem, chlorine stabilizers such as cyanuric acid, sulfamic acid, methylenesulfonic acid, toluenesulfonic acid, and monoethanolamine were developed with moderate success. [33] [34] [35] [36] Also, more chlorine tolerant phosphonates, such as Bayer's PBTC and Albright and Wilson's Bricorr 288 (less than 5 unit polymaleic acid endcapped with a phosphonate group, termed PMAP in this paper) were developed and are growing in popularity. [37] [38]



Combinations of phosphonate and orthophosphate are often used. While not truly “all-organic,” these combinations are often categorized as all-organic formulations. Betz patented the combination of phosphonate and orthophosphate in 1974, but in reality, with the breakdown of phosphonates in the presence of oxidizing biocides, orthophosphate was present, anyhow. [39] Today, with the availability of chlorine tolerant phosphonates, such as PBTC and PMAP, orthophosphate is sometimes purposely added for anodic inhibition and/or as a low cost replacement for phosphonates, such as HEDP, that would decompose to orthophosphate in the presence of oxidizing biocides.

Zinc Products

Another area of development that occurred in the 1980’s was the development of alkaline zinc chemistries. The same polymers that disperse calcium phosphate, are also effective for zinc dispersion, thus allowing zinc formulations to be used at alkaline pH. The pursuit of zinc formulations was largely driven by the desire to replace zinc/chromate products with zinc/phosphate products, due to the toxic nature of chromate. Interestingly, zinc/polyphosphate glasses were patented in the 1950’s and 1960’s, followed by zinc/phosphates and zinc/phosphonates in the 1960’s and 1970’s. [10] [11] [40] [41] [42] [43] [44] However, it was not until the desire to abandon zinc/chromate products grew, that zinc/phosphate products gained wider use. For most applications, zinc programs are run at a pH of 6.8 to 8.3, with zinc concentrations of less than or equal to 2 mg/L, and total phosphate concentrations range from 5 to 10 mg/L. Polymer levels range from 5 to 15 mg/L, with polymer levels increasing with pH.

Zinc/phosphate products are very effective in general application and considered by some to be the products of choice in soft water, when zinc discharge limitations do not preclude their use. The reason for using zinc products in soft water is that zinc hydroxide and zinc phosphate/phosphonate can form and provide cathodic inhibition in the absence of calcium ion. Phosphate based programs require calcium for the formation of calcium salt formation, and therefore are not effective at very low calcium concentrations. Pyrophosphate products, the best polyphosphate products for soft water, can work at as low as 20 mg/L calcium (as calcium ion), however, below 20 mg/L, zinc is needed.

To augment phosphate programs in the absence of zinc, molybdate is sometimes used, especially in soft water. [45]45 Due to the high cost of molybdate, the concentration of molybdate ion is kept below 20 mg/L. In the past five years, non-zinc products based on PMAP have shown surprising success in soft water, as well as in more typical cooling waters. [38] Another non-zinc approach is to replace zinc with manganese, but this approach has not gained wide use. [46] [47]

High Calcite Saturation Products

In the mid 1990’s, the desire to operate at more alkaline, higher cycle conditions gave rise to the idea of controlling carbon steel corrosion by operating at a 150 to 200X calcium carbonate saturation. To do so, a very effective calcium carbonate inhibitor is needed, since typical calcium



carbonate inhibitors are not effective at saturations exceeding 150X, due to the limited calcium tolerance of most inhibitors. To determine which commercially available inhibitors could be used for this purpose, various inhibitors were evaluated in a 240X (L.S.I. of 2.8) calcium carbonate inhibition study. In this study, untreated and treated, pH 9.0, supersaturated solutions of calcium carbonate were incubated for 20 hours at 60°C. The solutions contained 150 mg/L calcium (expressed as calcium) and 600 mg/L alkalinity (expressed as calcium carbonate). After 20 hours, the solutions were filtered, analyzed for total hardness, and then the percent inhibition of calcium carbonate was calculated for each inhibitor dose. As shown in Table 3, Natcolene polyether phosphonate (PEP) was the only inhibitor giving over 90% inhibition at any dose, and therefore is the inhibitor of choice for high calcite saturation. PBTC was the only other inhibitor giving greater than 70% inhibition. PEP can be used at saturations as high as 300X, but the recommended maximum saturation is 250X (L.S.I. of about 2.8), since tower fill fouling is more likely at saturations exceeding 250X. PEP can be blended with other phosphonates and acrylic acid based polymers, to enhance corrosion inhibition performance. PEP is not chlorine tolerant, but low concentrations (0.2 mg/L free halogen residual) of bromine can be tolerated. If control guidelines are followed, experience has showed that excellent carbon steel corrosion control can be maintained at high calcite saturations, by controlling calcium carbonate precipitation from solution and using calcium carbonate as a cathodic inhibitor at the carbon steel surface. [48] [49] [50]

Green Chemistries

In recent years, interest in “green chemistries” has developed. Green chemistries include products that are safe to handle, nontoxic, biodegradable, and safe for the environment. Polyaminoacids, which meet these requirements, are being evaluated as antiscalents. [51] [52] [53]

For this paper, polyaspartic acid was evaluated in both the calcium phosphate and calcium carbonate inhibition tests. (See Tables 2 and 3.) In both cases, it was not found to be effective, and therefore, is not useful in carbon steel inhibitor formulations. Other studies have shown that polyaspartic acid is, however, effective for controlling calcium carbonate precipitation at more moderate saturations. [53]

In search of greener chemistries, some investigators have focused on eliminating or reducing zinc and phosphate in corrosion formulations, since zinc and phosphate have a negative effect on the environment. Success in reducing the total phosphate requirement for effective treatment has been made with the use of PMAP, since active PMAP contains a low 36.7% total phosphate, and works well at low dose. [38] [54] In fact, the low total phosphate requirement has enabled PMAP based formulations to be used to treat tower supply water, and then in turn treat the tower water, without exceeding total phosphate limits in the tower, as the tower water cycles up. With growing restrictions on zinc and phosphate use, further study is needed in this area.



CONCLUSIONS

1. The most important development in the last 20 years was the development of polymer chemistries, which enable alkaline operation with stabilized phosphate, all-organic, and zinc products.
2. Based on the results of the calcium phosphate inhibition study, 60/40 AA/AMPS is the polymer of choice for inclusion in stabilized phosphate products. Some sulfonated terpolymers are as effective, but tend to be more costly.
3. Based on the results of the calcium carbonate inhibition study, Natcolene PEP is the inhibitor of choice for controlling corrosion by operating at high calcite saturation.
4. Additional studies are needed to develop green chemistries for controlling carbon steel corrosion.



APPENDIX A

TABLE 1
Water Treatment in the Last 20 years
 (When Possible, Dates Are Patent Issue Dates)

Company	Inorganic Phosphate/Esters	Polymer	All Organic	Heavy Metal	Chlorine Tolerant	High Saturation/ Green
Rhodia/ Albright & Wilson					PMAP, 1997	
Bayer			PBTC, 1990		PBTC, 1990	
Betz		MA/SS, 1981 AA/HPE, 1981 AA/AHPSE, 1987	Phosphonate/Ortho, 1974			
Calgon/Hercules	Polyphosphate, 1943 Pentaerythritol Phosphate Ester, 1977	PMA, 1981 60/40 AA/AMPS, 1975	HEDP/AMP, 1980	Zn Glass, 1952 Zn/Ortho, 1977 Zn/Phosphonate, 1969 Zn/HEDP, 1970	MSA, 1995 TSA, 1995	Polyether Phosphonate, 1994
FMC/Ciba Geigy			HPA, 1987	Zn/HPA, 1986	MEA, 1994	
Dow				Mn/X, 1987 Mn/X/HPA, 1991		
Goodrich		AA/AMPS/SS, 1990				
Grace/Dearborn			HEDP/HPA, 1987			
Nalco	Glycerin Phosphate Ester, 1975	AA/AM, 1984 AA/SAM, 1989	HEDP/PBTC, 1985	Zn/Glycerin Phosphate Ester, 1975 Zn/Pyro, 1978	SA/CA, 1987	Polyamino Acids, 1997, 1998
Alco/ National Starch		AA/SPME, 1990				
Rohm&Haas	Phosphated Polyol Esters, 1971	AA/AMPS/TBAM, 1987				

Legend:

AA	Acrylic Acid	MA	Maleic Acid	SAM	Sulfonated C-1 to C-3 AM
AHPSE	Allyl Hydroxy Propyl Sulfonic Ether	MEA	Monoethanolamine	SPME	Sulfonated Phenol Methacrylic Ether
AM	Acrylamide	MSA	Methylenesulfonic Acid	SS	Sulfonated Styrene
AMP	Aminotrimethylenephosphonic Acid	Ortho	Orthophosphate	TBAM	Tertbutylacrylamide
AMPS	Acrylamido Methyl Propyl Sulfonate	PBTC	Phosphono Butane Tricarboxylic Acid	TSA	Toluene Sulfonic Acid
CA	Cyanuric Acid	PMA	Polymaleic Acid	X	Large Amino Methylene Phosphonates
HEDP	Hydroxy Ethylidene Diphosphonic Acid	PMAP	Poly MAX, where X<5, phosphonate endcap		
HPA	Hydroxy Phosphono Acetic Acid	Pyro	Pyrophosphate		
HPE	Hydroxypropylester (of AA)	SA	Sulfamic Acid		



FIGURE 1
Water Treatment Timeline

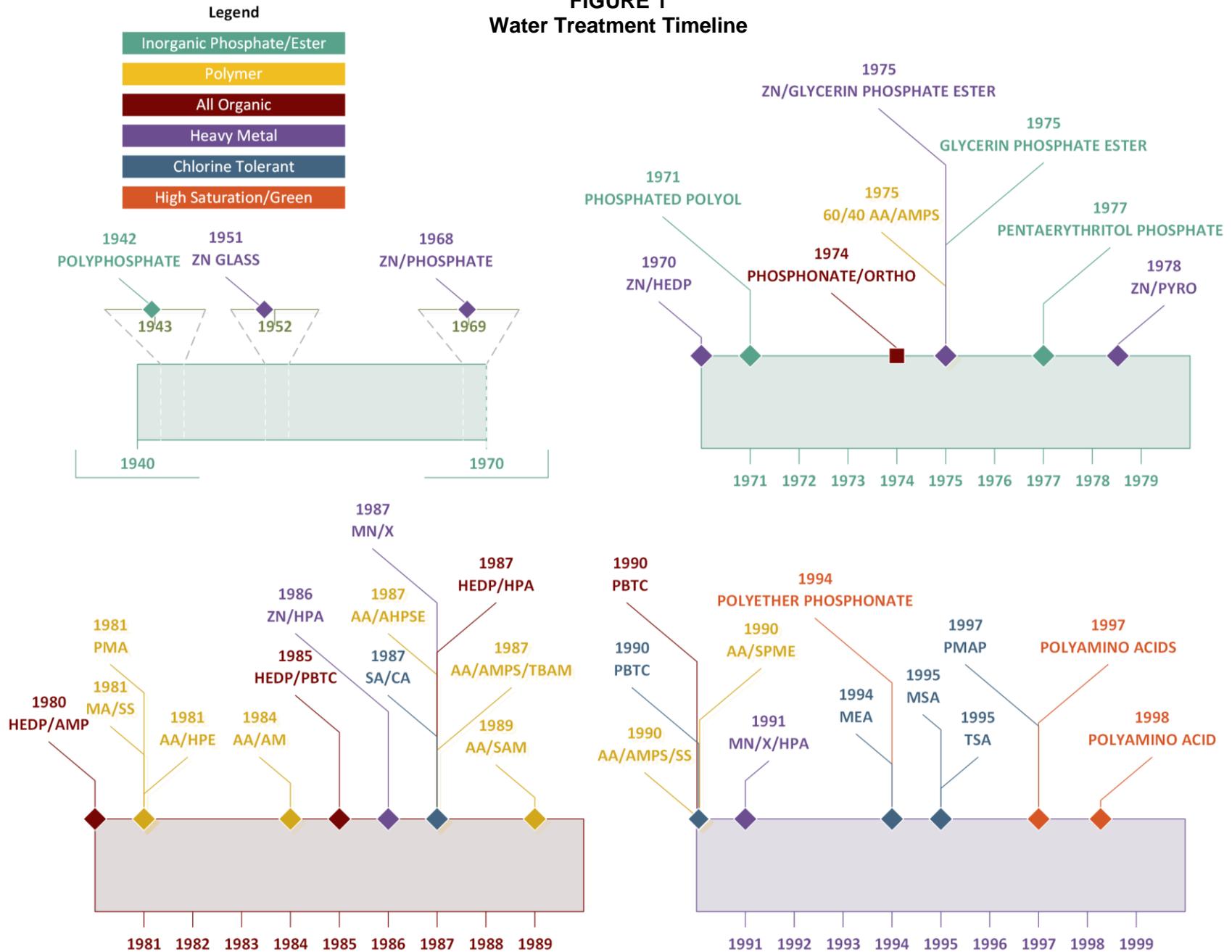


TABLE 2
The Minimum Effect Dose* of Polymers for Controlling Calcium Phosphate

Polymer	Company/ Trade Name	Active Dose (mg/L)
60/40 AA/AMPS (Acrylic Acid/Acrylamidomethylpropylsulfonic Acid)	Calgon/TRC-233HS	7-8
AA/AMPS/TBAM (Acrylic Acid/Acrylamidomethylpropylsulfonic Acid/ Tertbutylacrylamide)	Rohm & Haas/ Acumer 3100	7-8
AA/AMPS/SS (Acrylic Acid/Acrylamidomethylpropylsulfonic Acid/ Sulfonated Styrene)	Goodrich/ Goodrite K-798	7-8
43/57 AA/AHPSE (Acrylic Acid/Allylhydroxypropylsulfonicether)	Lab Synthesized	8**
Sulfonated Acrylic Polymer	Alco/Aquatreat AR-540	8
75/25 AA/AMPS (Acrylic Acid/Acrylamidomethylpropylsulfonic Acid)	Calgon/TRC-233I Alco/Aquatreat AR-545	9-10
AA/SPME (Acrylic Acid/Sulfonatedphenolmethacrylicether)	Alco/ Aquatreat MPS	9-10
70/30 AA/AM Copolymer (Acrylic Acid/Acrylamide)	Buckman/ BSI-82	<25% Inhibition @ 50 mg/L
AA/HPE (Acrylic Acid/Hydroxypropylester of Acrylic Acid)	Alco/Narlex LD-42 (formerly Natrol 42)	17**
1:1 MA/SS Copolymer (Maleic Acid/Sulfonated Styrene)	Alco/ Versa TL-7	17
PMA (Polymaleic Acid)	Buckman/ BSI-97	<20% Inhibition @ 50 mg/L
Polyaspartic Acid	Bayer/ Polyaspartic Acid	<20% Inhibition @ 50 mg/L

Note:

* The dose required for greater than 90% inhibition of calcium phosphate

** Calgon Screening Studies, 1980's

*** Where dose ranges are listed, multiple lots were tested. Where a single point is given, one lot was tested.

Conditions:

200 mg/L Ca⁺²

9.0 mg/L PO₄⁻³

100 mg/L HCO₃⁻

pH 8.5

24 hr at 60°C

1-3 micron filter



TABLE 3
Performance of Inhibitors for Controlling Calcium Carbonate at High Saturation

Inhibitor	Company/ Trade Name	15 mg/L Active	20 mg/L Active	30 mg/L Active
Polyetherphosphonic Acid	T.N.C.C. Natcolene PEP	82	91	100
PBTC (Phosphonobutanetricarboxylic Acid)	Buckman Phos 9	-	72	76
HEDP (Hydroxyethylidenediphosphonic Acid)	Buckman Phos 6	-	58	53
AMP (Aminotrimethylenephosphonic Acid)	Buckman Phos 2	-	-	51
HPA (Hydroxyphosphonoacetic Acid)	F.M.C. Belcor 575	-	-	44
PMAP (PolyMAx, x<5, phosphonate ends)	Rhodia Bricorr 288	-	46	39
PMA (Polymaleic Acid)	Buckman BSI-97	-	-	51
Maleic Copolymer	ALCO AR-980	-	-	35
50/50 MA/SS (Maleic Acid/Sulfonated Styrene)	ALCO Vera TL-7	-	34	26
Phosphinocarboxylic Polymer*	F.M.C. Belsperse 161	-	-	50
Acrylic Copolymer	ALCO AR-540	-	-	29
80/20 AA/AMPS**	Chemtall CT-20	-	55	50
AA/IA/AMPS***	Polyacryl C36-50A	-	-	30
90/10 AA/AM (Acrylic Acid/Acrylamide)	Buckman BSI-75	-	55	53
Polyaspartic Acid	Bayer Polyaspartic Acid	-	-	39

* $[PAA]_N-PO_2Na-[PAA]_M$, where $N + M = 16$

** Acrylic Acid/Acrylamidomethylpropylsulfonic Acid

*** Acrylic Acid/Itaconic Acid/Acrylamidomethylpropylsulfonic Acid)

Conditions:

150 mg/L Calcium Ion as Calcium Ion (374 as $CaCO_3$)

600 mg/L Alkalinity as $CaCO_3$

pH 9.0, 60°C, 20 hr



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