Evaluating polymers and phosphonates for use as inhibitors for calcium, phosphate and iron in steam boilers

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Abstract

There are many commercial polymers and phosphonates available to the water treatment specialist today. It is no small task to determine which of these specialty chemicals will give the best performance for inhibition and stabilization of the impurities that plague the water consultants systems. Considerable work has been done in the evaluation of phosphonates and low molecular weight polymers for cooling water applications. Much less data is available for steam boiler applications. It is the purpose of this paper to investigate the use of polymers and phosphonates in steam boilers. Our goal is to research which polymers and phosphonates are available for use, the purpose of their use, how they are applied and how they are tested. We also want to present some ideas and results of in-house testing of these materials.

Introduction

In the process of making steam in a steam boiler, the steam which leaves the boiler to do its work is almost pure water. The water remaining in the boiler becomes more concentrated with the impurities which are introduced with the make-up water. After reaching a certain concentration and due to the inverse solubilities of some of these impurities they come out of solution and begin to adhere to the hot heat exchange surfaces such as the boiler tubes. This causes loss of efficiency, corrosion and mechanical failure. As a solution to this condition, some of the impurities can be removed mechanically before entering the boiler. In most cases a certain percentage of the impurities are removed mechanically followed by the addition of chemicals whose properties result in the elimination or reduction of deposits caused by the remaining impurities.

Two impurities that are main concerns in a steam boiler are hardness and iron. Hardness consists of the calcium and magnesium which enters the boiler via the make-up water as calcium and magnesium bicarbonate. These compounds are quite soluble. The problem begins as heat is added to the boiler and much of the calcium becomes calcium carbonate. Calcium carbonate is sparingly soluble and will precipitate. Magnesium will also form sparingly soluble compounds such as magnesium silicate and magnesium hydroxide. Iron entering the boiler as iron bicarbonate with the make-up water or as corrosion products from the condensate, feed water or boiler itself is especially troublesome. Because the iron compounds formed under boiler conditions are so insoluble it is imperative that they be dealt with. It is also speculated that iron hampers the dispersing ability of polymers by deactivating their functional groups.[1]

The two main chemical methods of dealing with hardness and iron in boilers are to intentionally precipitate the impurities in some form which is less troublesome than the untreated species or to keep the impurities in solution or dispersed so that precipitation and deposits are not formed. In fact, usually a dynamic combination of sequestration and dispersion takes place.

Precipitation Chemistry

Calcium Carbonate/Magnesium Hydroxide Precipitation

Calcium carbonate will precipitate. It will form faster with added heat and alkalinity. This is exactly how early boiler treatment programs worked. The calcium carbonate would form and attempts were made to remove it with bottom blowdown of the boiler. Sometimes this method even worked if the boiler pressure was not too high and the water was not too bad. Then it was discovered that natural products such as tannins, lignans and starches added to the boiler resulted in less deposits. These are natural polymers. Subsequently, synthetic polymers were produced which were much more temperature stable than the natural polymers. So, the first method of dealing with hardness and iron was their natural precipitation with the modification of adding a polymer to help disperse the precipitates and reduce deposition.

Calcium Phosphate (Hydroxyapatite)/ Magnesium Silicate (Serpentine) Precipitation

Calcium Phosphate compounds are even less soluble under boiler conditions than calcium carbonate. This can be good. Hydroxyapatite forms a less dense precipitate than calcium carbonate, is more easily dispersed, more easily removed by bottom blowdown and hence should form less adherent deposits. With this program a source of phosphate is added that will react stoichiometrically with the calcium. Hydroxide alkalinity such as sodium or potassium hydroxide and silicate are added if needed to complete the calcium and magnesium reactions. A good polymer for dispersion of calcium phosphate and iron is the final ingredient of this program.

Solubilizing Chemistry

Chelates

Chelation involves the bonding of the hardness and iron to a chelate such as EDTA to keep the hardness and iron completely in solution. This is a stoichiometric reaction. We will not deal with EDTA chelation in this paper other than to say it has been used as a very successful treatment method for steam boilers where the feed water is relatively soft (< 1 ppm of total hardness as Calcium Carbonate) and the control of the chelant feed is excellent.

Phosphonates

Phosphonates are used in almost all cooling water chemical treatment programs. Their successful use as threshold inhibition agents is well documented. Their use in boilers is not as prevalent due to the concern of reversion of the phosphonate to orthophosphate due to the temperatures and alkalinities encountered in steam boilers. Some investigators researching temperature stability data of phosphonates found that HEDP and ATMP had good temperature stability up to 400^{o} F.[2] The same investigation provided results of a study done to simulate boiler conditions at 250^{o}C, 600 psig. From this data, half lives of ATMP, HEDP and PBTC were 9.3 days, 4.5 days and 1 day respectively.[2] Data of this kind would lead one to believe that phosphonate in boilers should work to some degree, as long as their threshold inhibition capability is not lost despite their temperature stability. Other sources say phosphonates should only be considered as a source of orthophosphate in the boiler.[3] One of our goals is to investigate this ourselves using lab analysis. The use of phosphonate to solubilize hardness and iron should also incorporate polymers for added dispersancy and crystal distortion of any hardness or iron compounds which do form.

Dispersing Chemistry

All Polymer

Another treatment method would incorporate only polymers to keep the iron and hardness stabilized via threshold inhibition, crystal modification and dispersancy. This involves a three pronged approach. The first line of defense is to keep as much of the iron and hardness in solution as possible using the threshold inhibition capability of the polymer. The second line of defense is crystal modification. This assumes that the polymer has the capability to distort the calcium, magnesium and iron compounds in such a way that the resulting crystal structure is much less adherant. The final line of defense is dispersancy of the polymer so that wholesale precipitation of the polymer/impurity is prevented. The key to polymers in steam boiler treatment is to choose polymers whose functionality supports threshold inhibition, crystal modification and dispersancy at boiler conditions.

Mechanisms of Deposit Prevention

Threshold Inhibition

This mechanism results from a chemical agent when added to a supersaturated solution of a potentially scale forming metal cation at substoichemetric levels will retard or inhibit precipitation. It is thought that the threshold agent is adsorbed on the growth sites of the scalant crystallite during the process of crystallization. The resultant scalant crystals are formed more slowly. Well known threshold agents are the polyphosphates and phosphonates. Certain polymeric carboxylates (polyacryalates and polymaleates) also act as threshold agents.

Sequestration

This mechanism is defined as the ability of a water soluble chelant to form a complex which remains in solution despite the presence of a precipitating agent. Well known chelants which are sequestering agents are EDTA, NTA, gluconates, glucoheptonates, citric and acetic acid. These chelants are fed at stoichemetric levels and have little or no threshold inhibition properties. On the other hand, phosphonates when fed at high enough dosages can act as sequestering agents.

Crystal modification

This mechanism is the continuation of the adsorption process of the chemical agent on the crystal growth. The crystals although growing, become highly distorted, have much less regular surface area and become less adherant to surfaces. Many phosphonates and polymers provide for crystal modification.

Dispersancy

This is the ability of a chemical additive to keep the precipitating compounds dispersed via charge neutralization and defloculation so that they do not deposit on the hot metal heat exchange surfaces such as boiler tubes. Polymers are used for this purpose.

Adhesion/Cohesion Modification[5]

The mechanism by which the total sum of all the additives properties prevent the adherence of the precipitate to the systems surfaces. It is what keeps the precipitate which is not dispersed from depositing.

Functional Groups

Phosphates- These are the backbone of many useful scale inhibitors. They are good complexing agents but their reaction products have limited solubility. They are used for calcium precipitation and contain a single phosphorus atom.

Polyphosphates- These inorganic molecules contain two or more phosphorus atoms linked by oxygen atoms. They are good water soluble complexing agents, sequestering agents and display threshold inhibition for calcium carbonate and iron oxide. They have the tendency to revert to orthophosphate with high temperature, high pH and metal oxides.

Phosphonates- These are organic phosphorous compounds and are good for threshold inhibition and crystal modification. They have sequestration capabilities at higher feed rates. Reversion to phosphate is much less than the polyphosphates. PBTC and POCA contain phosphonate and carboxylate functionality.

Phosphinates- This is another organic phosphorous compound. Their C-P-C bond is reported to have better stability than the C-P-O bond of the phosphonates and the C-C-C bond of the carboxylates.[4] PCA (Belsperse 161 and Belclene 500) contain both phosphinate and carboxylate functionality.

Carboxylates- These are weak acids. Acrylates and maleates fall into this category. They are good for threshold inhibition and crystal modification.

Sulfonates- Being a strong acid they are excellent dispersants using electronic repulsion.

Non Ionic- Acrylamide, Terbutylacrylamide, etc. They reportedly enhance dispersancy by increased sterric hindrance between particles.[1]

Application and Testing of Polymers in boilers

Application

Application rates for polymers in boilers have not been well defined. One method of control is to feed polymer on an active basis at 3 to 10 ppm per ppm of total hardness as $CaCo_3$ plus 3 to 10 ppm per ppm of total iron in the feed water. Usually a maximum of 1 ppm of hardness in the feed water is stipulated. This would be applied to a solubilizing program approach. Other recommendations that this author has heard or read are anywhere from 2 to 50 ppm active polymer in the boiler and no mention is made of the boiler water quality or boiler pressure.

The Association of Water Technologies has published reasonable suggestions for polymer feed in boilers.[6] An all polymer approach is to feed 15 to 90 ppm of active polymer in the boiler depending on boiler pressure and total hardness plus iron demand in the system. Where phosphate is fed to precipitate the calcium then a feed of 10 to 240 ppm of active polymer in the boiler is recommended depending on boiler hardness and conductivity.

Testing

Testing of boiler polymer is another area that has not been thoroughly addressed. Polyacryalate test kits are available but these usually only test the carboxylates.[7] Rohm & Haas has added a tag based on an immunoassay reaction to some of their polymers for testing in the field.[8] BioLab has a test for their Polymaleic Acid based on immunoassay technology reported to be free of common interferences.[9] Another test exists that relies on breaking the polymer bond with EDTA after filtration and then adding a cationic reagent to form turbidity.[10] The resultant turbidity is directly proportional to the amount of polymer in the sample. The accuracy of this test has not been well established. It usually requires laboratory construction of a calibration curve for each boiler product in your line based on the polymers used and their concentration in the blend.

Application and Testing of Phosphonates in boilers

Application

Phosphonate feed rates in cooling towers for threshold inhibition are usually in the range of 3 to 10 ppm as active phosphonate. Three to five ppm is usually preferred to prevent calcium phosphonate precipitation and deposition.[11] There can be a range of phosphonate dosage where calcium phosphonate precipitate is formed due to calcium ion intolerance especially at elevated temperatures and alkalinities. This usually takes place in the range between phosphonate threshold inhibition and chelation at higher feed rates.[12] This condition of calcium phosphonate precipitation is to be avoided in cooling towers since the solution then becomes the problem. Furthermore, the high dosages needed for chelation in a cooling tower is usually cost prohibitive. With careful control of phosphonate feed and addition of calcium phosphate and calcium phosphonate polymer inhibitors this becomes less of a problem.

Phosphonates in boilers could be used in three ways. They could be used as a source of PO_4 in a precipitation program if one is willing to pay the cost for an expensive source of PO_4 and if one believes that all or most of the phosphonate would revert to orthophosphate because of high temperature and alkaline conditions. This program has been used and works. Another program would be to feed phosphonate at substoichemetric levels for threshold inhibition as in a cooling tower. Some investigators report that the phosphonates may remain stable up to 450^o F depending on which phosphonate but that their threshold inhibition capabilities can drop off dramatically at boiler temperatures and alkalinities.[2] If this is true this would be an unsuccessful method of phosphonate application in boilers. There are reports however that addition of an appropriate polymer may significantly stabilize the phosphonate so that its' threshold capabilities remain active.[13] We try to investigate this phenomena in our testing. A third method of application would be to add the phosphonates stoichiometrically based on feed water hardness and iron. What would this stoichiometry be? According to one good technical source[14] the theoretical chelation values of 60% HEDP for hardness (as $CaCO_3$)

and iron (as ion) are 3.43 ppm and 6.15 ppm respectively. The total 60% HEDP demand for a system with 1 ppm of hardness and .1 ppm of iron in the feed water is 3.43 + .615 = 4 ppm of 60% HEDP in the feed water. Adding additional polymer for dispersancy and hardness upsets may be a viable option for this solubilizing all organic program. As a side note, if the boiler were operating at 30 cycles of concentration with the aforementioned water and all of the 60% HEDP reverted to orthophosphate, you would find about 50 ppm of PO_4 in the boiler water. As with an all polymer program, this all organic program would necessitate good control in minimizing hardness leakage to the system. The all polymer and all organic programs theoretically provide for less residual PO_4 in the boiler, less sludge to deal with and cleaner boilers. In the search for " green chemistries" and the potential need to reduce phosphate use[17] these alternatives become more attractive.

Testing

Phosphonate testing is well documented. The preferred method for accuracy is reversion to orthophosphate using UV with an appropriate conversion factor depending on the number of Phosphorous atoms in the particular phosphonate molecule analyzed. One must be aware of the amount of orthophosphate or poly-phosphate in the feed water that is naturally there as it arrives from city water sources. The total phosphate is the sum of the orthophosphate, poly-phosphate and organic phosphate when testing. Boiler programs these days usually have polymers added along with any phosphonate so polymer testing is an option to trace product levels.

Types of Phosphonates

Name	Example	PO_4 Content	% Active	PO_4 (Delivered)
ATMP	Dequest 2000	95.4	50	47.7
HEDP	Mayoquest 1500	92.2	60	55.3
PBTC	Bayhibit AM	35.2	50	17.6
HPA	Belcor 575	67.1	50	33.6
PMAP	Bricor 288	36.7	30	11.0
DTMPA/MDTP	BPS 319	----	---	40.0
HEMPA	Mayoquest 1352	77.3	60	46.4
MAPA	Versenex CSI	----	28	----
POCA	Belclene 494	2.45	50	1.23
PCA	Belsperse 161	5.75	48	2.8

Types of Polymers

Name	Example	% Active
PAA	K-732	49.5
PMA	Belclene 200	48.0
MA/SS	Versa TL-4	20.0
AA/AM	Cyanamer P-35	50.0
AA/AMPS	TRC-233 HS	45.0
AA/MA/NI	Aquatreat AR-980	41.0
AA/SPME/NI	Aquatreat AR-540	40.0
AA/SPME/NI	Aquatreat AR-550	33.0
AA/AMPS/TBAM	Accumer 3100	39.5
AA/AMPS/SS	K-798	48.0
MA/EA/VA	Belclene 283	45.0

Evaluation of Phosphonates and Polymers

Important considerations when selecting a phosphonate or polymer are their percent activity and cost. Another important consideration for steam boiler use are FDA and USDA clearances. The only phosphonate which is cleared for use in an FDA plant where the steam may contact food is HEDP. The polymers which are cleared for use under CFR Title 21 173.310 are Sodium Polyacrylates, Sodium Polymethacrylates, Polymaleic Acid, Sodium Acrylate/Acrylamide, Acrylic Acid/2-acrylamido-2-methyl propane sulfonic acid copolymer and Poly(acrylic acid-co-hypophosphite). Other considerations are thermal stability, hydrolytic stability, threshold inhibition capability and phosphorous content. Still other considerations are its corrosion potential, blending and neutralization requirements, pH stability and calcium tolerance, foaming tendencies, half life and aquatic toxicity. Finally, the polymer or phosphonate must be able to perform as intended. We try to evaluate this performance through are testing.

Product Validation Methods

Laboratory Screening Tests

These tests usually consist of methods to evaluate the threshold inhibition, dispersancy or adhesion/cohesion modification capabilities of a chosen phosphonate or polymer. Protocols for these tests are sometimes available from the vendors providing the additives.[15] These tests involve evaluating an analyte at supersatured conditions at a specified temperature, pH and induction time guaranteed to form precipitate species. The procedure may or may not involve agitation. Sometimes a NACE standard test is used. The samples are dosed with chosen polymers or phosphonates and the treated sample(s) are compared with an initial condition, sample and/or control. Typical tests for cooling systems will be calcium carbonate, calcium sulfate, calcium phosphate and calcium phosphonate inhibition. Also tested may be iron, manganese or zinc stabilization. Finally, silt (kaolin clay), iron oxide, calcium carbonate or calcium phosphate dispersancy might be evaluated. For RO treatments, barium and strontium sulfate inhibition could also be added. Our retort or boiler treatment product validation methods will be described later in the paper. The laboratory screening tests are usually the cheapest to establish and can yield valuable results if done properly.

Non Evaporative Dynamic Test Rigs

These product validation configurations may be quite simple or complex and are intended to more closely duplicate actual field conditions. They provide for circulation of the test water and may have a make-up water source which equals the blowdown. A fouling and /or corrosion coupon test specimen may be included. The water quality, chemical levels, pH, temperatures, heat fluxes, flow rates, dissolved oxygen and carbon dioxide may be controlled automatically or manually. Test measurements versus time may be documented via electronic monitors or via manual testing. In addition to having the advantage of taking into account many dynamic variables, this method also maximizes the ability to measure the capabilities of additives to prevent the phenomena of adhesion/cohesion on heat exchange surfaces. This method may be expensive but usually yields considerable data for the time spent testing.

Evaporative Pilot Scale Models

These units attempt to duplicate actual field equipment only on a smaller scale. It incorporates the final variable of system evaporation to the product validation method. Again, these units may be quite simple or may be very complex. For open recirculating cooling towers, this method results in steady state concentrations of dissolved oxygen and carbon dioxide near equilibrium conditions. This is important for calcium carbonate precipitation studies since the system pH will be a function of the carbon dioxide mass transport.[16] This method is probably the most expensive and time consuming for the data collected.

Field Testing

This method involves validating products at a customer or prospect site on a trial basis. It is a method whose results may depend to a large degree on the competency of site personnel. It may be time consuming and a poor method of validation. It should be reserved for specific applications, unique situations where both the client and supplier will benefit by such an evaluation. The client must be well aware of the product trial status yet understand that if successful a real benefit may be realized.

Experimental

Purpose

Our purpose is to establish some in-house tests using commonly available equipment to validate the use of polymers and phosphonates in steam boilers. In addition we want to have the ability from our test results to differentiate between the polymers and phosphonates as to which one(s) are preferred under our test conditions for a given impurity. With the data we also try to validate our choices for use at higher temperatures and pressures.

Test Water

We can either develop a synthetic water by seeding DI water with reagent grade impurities, use existing or blended water supplies on site from hard city water, softened city water and DI or use water from off site from a customer or prospect. We chose to use on site waters with the addition of caustic to simulate boiler conditions. Sometimes we added additional iron (as $FeCl_{2*}4H_20$) to simulate higher iron conditions or phosphate (as $Na_3PO_{4*}12H_2O$) for forced precipitation of calcium as Hydroxyapatite.

Apparatus

Our “boiler” consisted of an autoclave (some might call it a sterilizer or pressure cooker) with automatic temperature control. The samples were contained in regular canning mason jars. The autoclave can reach maximum temperatures of 250^o F and 20 psi. Sample size was usually 250 ml in the 473 ml jars. Hardness, iron, phosphate, phosphonate and turbidity were done using a HACH DR 890 Colorimeter. Alkalinities and pH’s if needed were done via a HACH digital titrator and ORION model 310 pH meter respectively. Filtration was done using a .45 micron Supor-450 Hydrophilic polyethersulfone filter from PALL Gelman Laboratory with a hand operated Nalgene filter apparatus. Samples could be centrifuged to decrease precipitation time if needed.

Procedure

The temperature of our autoclave is not as high as most boilers operate, yet we felt we could get significant data at the lower temperature and pressure. The metal capped canning jars did not add a significant amount of metals to our analysis. Any metals and phosphates from the lids were accounted for in the controls. We had a control and an initial water sample for each run. Final analysis (as opposed to practice) runs were done using new jars to eliminate poor results due to deposits left from poor cleaning. We tailored our tests to mimic boiler programs of phosphate precipitation of calcium, all organic and all polymer.

Initial Tests

A) Phosphonate Thermal Stability in DI water with added NaOH to pH 11.5
B) Iron stabilization in DI water with added NaOH to pH 11.5 and addition of various phosphonate and/or polymer.

Orthophosphate precipitation plus Polymer

Enough PO_4 (as TSP) and OH (as NaOH) is added to precipitate all hardness. Polymer is added based on the AWT Technical Manual specifications. The pH is brought to11.5 Additional iron is added if needed to stress the system.

Test: (Hydroxyapatite + Iron) Dispersancy with Various Polymers

All Organic Phosphonate plus Polymer

Enough phosphonate is added to theoretically chelate the hardness and iron. Polymer is added as if all the phosphonate reverts to orthophosphate. The pH is brought to 11.5 Additional iron is added if needed to stress the system.

Test: (Hardness + Iron) Stabilization and Dispersancy with HEDP plus Various Polymers

All Polymer

Enough polymer is added to stabilize, modify the crystal structure and disperse hardness and iron compounds. Polymer is added based on AWT Technical Manual specifications. The pH is brought to 11.5. Additional iron is added if needed to stress the system.

Test: (Hardness + Iron) Stabilization and Dispersancy with PAA plus Various Polymers

Results and Discussion

Phosphonate Stability

Three well known phosphonates were tested for thermal stability. HEDP was also tested with the addition of a terpolymer to see if polymers might help stabilize the phosphonate. As shown in (Fig. 1), the order of thermal stability under our test conditions were:

ATMP > PBTC > HEDP/TPOLY-A > HEDP

The terpolymer seemed to add about 13% thermal stability to HEDP. All phosphonates retained greater than 80% thermal stability with ATMP retaining 100% stability under our conditions.

As shown by (Fig. 10) , the phosphonates also retained greater than 80% stability under much harsher conditions of added hardness and iron. Iron stabilization was also good as shown by (Fig. 11). We could not quantify the hardness inhibition (all results showed greater than 100% inhibition) due to interference of the phosphonate with our method of testing. However, (Fig. 12) would indicate excellent solubilization of the hardness as well.

Iron Stabilization

Various polymers and phosphonate were tested to assess their iron stabilizing capability. The samples were analyzed for iron after filtration with a .45 micron filter. This test does not measure dispersancy but a picture of the suspended or precipitated particulate can be seen in (Fig. 3). As shown in (Fig. 2), the order of iron stabilization under our test conditions were:

HEDP > HEDP/TPOLY-A > PCA = AA/AM > TPOLY-A

The apparent 12% reduction of stabilization using a combination of HEDP and polymer versus just HEDP is evident in (Fig. 2). This may indicate competition between the polymer as dispersant and the phosphonate as sequestrant. Further study would be needed to verify this.

Hydroxyapatite/Iron Dispersion

Various polymers were compared for their hydroxyapatite and iron dispersion capability to imitate a boiler phosphate precipitation program. The turbidity of sample supernatent is measured after 2 Hrs. The greater the turbidity value, the greater the expected dispersancy of the polymer. This test does not quantify percent dispersion but is a comparative test between polymers under one set of conditions. (Fig. 6) shows the reduction in dispersancy due to the addition of iron to an alkaline phosphate system. (Fig. 4) and (Fig. 5) show examples of dispersancy with and without added iron to a simulated boiler phosphate precipitation program. In all cases the order of hydroxyapatite and iron dispersion under our test conditions was:

TPOLY-A > PAA-5100 > TPOLY-B > AA/AMPS

Hardness and Iron Stabilization in an All Polymer Program

Polyacrylate (2100 MW) plus various polymers were tested to determine their hardness and iron stabilization capabilities. We did dispersancy testing on the samples by taking their supernatent turbidity after two hours. These values were much less than the turbidities when evaluating hydroxyapatite. This may indicate it is harder to disperse calcium carbonate than hydroxyapatite. We felt further refinement of our method was necessary before making determinations on dispersancy in an all organic program test. We tested hardness after filtration with a .45 micron filter. As shown in (Fig. 7), the order of hardness inhibition was:

PAA + AA/AMPS > PAA + PMA > PAA + TPOLY-B > PAA + TPOLY-A

We also tested iron after filtration with a .45 micron filter. As shown in (Fig. 8), the order of iron inhibition was:

PAA + TPOLY-B > PAA + AA/AMPS > PAA + TPOLY-B >> PAA + PMA

It is evident that PAA + PMA is a much better hardness inhibitor than iron inhibitor. (Fig. 9) shows a picture of the various suspended or precipitated particulate after filtration.

Hardness and Iron Stabilization in an All Organic Program

HEDP plus various polymers were tested to determine their hardness and iron stabilization capabilities. The HEDP was added at theoretical chelation levels for hardness and iron. We did not measure dispersancy because the samples (except the control) were not turbid. After filtration through a .45 micron filter we measured hardness, iron and phosphonate. As mentioned before, all hardness values were about the same and were higher than the control. Interference of our test method by phosphonate probably lead to inaccurate values. Testing of hardness by another method such as Atomic Absorption is necessary to prevent interference. It seems by looking at (Fig. 10), (Fig. 11) and (Fig. 12) that hardness and iron are chelated well under our test conditions.

Conclusions

The following conclusion were drawn from our investigation:

A) The phosphonates we studied retained > 80% stability at our test conditions.

B) HEDP retains its chelation ability of hardness and iron at our test conditions.

C) Inhibition of iron and hardness is greater with phosphonate than with polymer.

D) Hydroxyapatite dispersion with polymer is easier without iron contamination.

E) Phosphonates in steam boilers warrant further study.

F) In- house testing of polymers and phosphonates can be used for comparison and quality control.

G) In- house testing can be used as a training aid.

H) Some of the data obtained may be applicable to cooling towers, retort systems and steam boiler systems operating over 250^{o} F.

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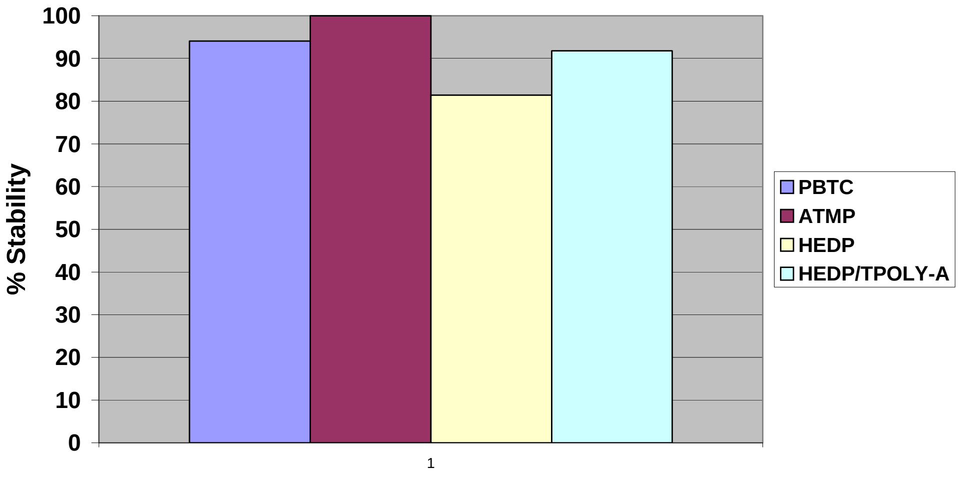
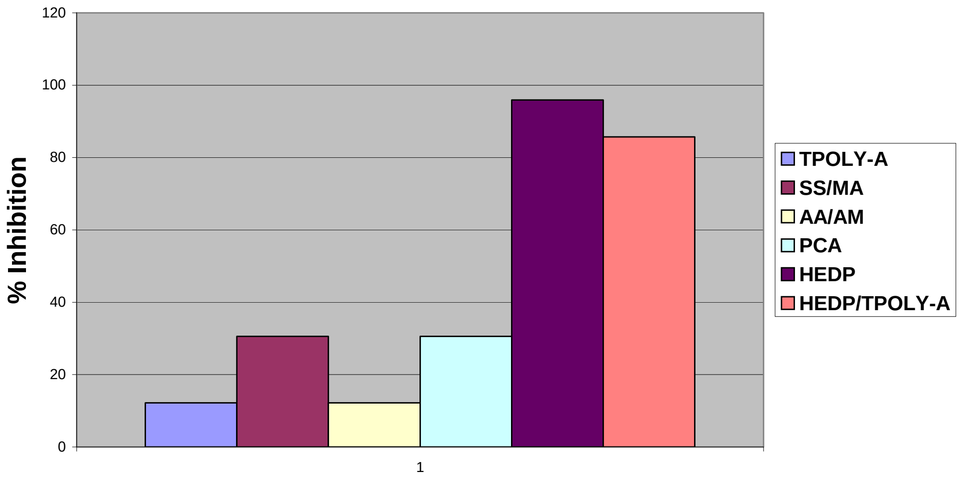


Phosphonate Thermal Stability (Fig. 1)

pH= 11.5, 250 F for 5 Hrs., DI Water with NaOH added, Phosphonate = 10 ppm

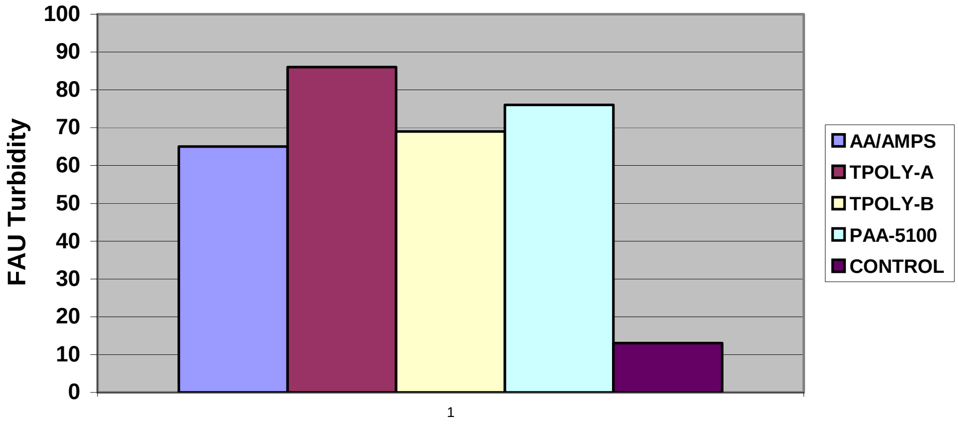


Iron Stabilization (Fig. 2)

pH= 11.5, 250 F for 5 Hrs., Fe= 4.9 ppm, DI Water with NaOH, 20 ppm Active Additive

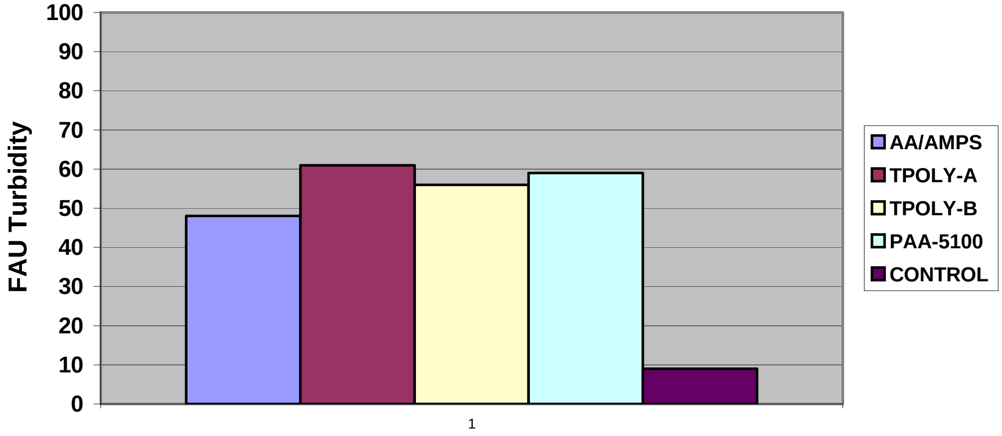
Iron Filtration
(Fig. 3)

Hydroxyapatite Dispersion (Fig. 4)



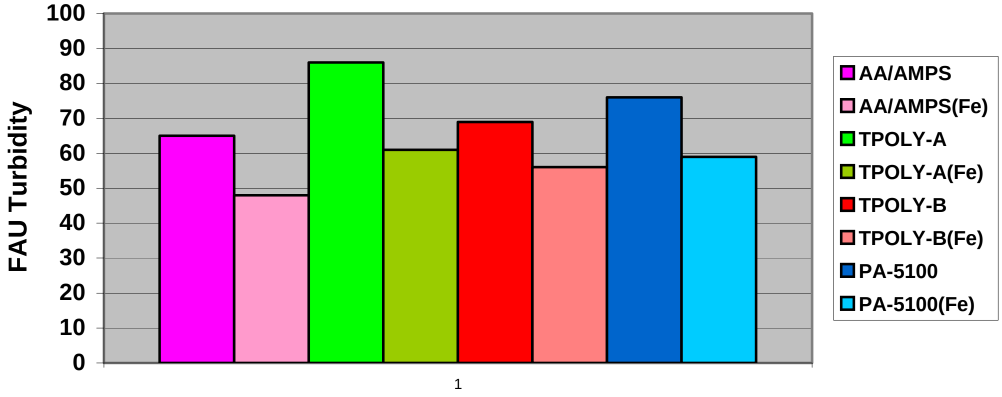
pH= 11.5, 250 F for 5 Hrs., TH= 60 ppm, PO4= 66 ppm,
Polymer= 50 ppm

Hydroxyapatite/Iron Dispersion (Fig. 5)

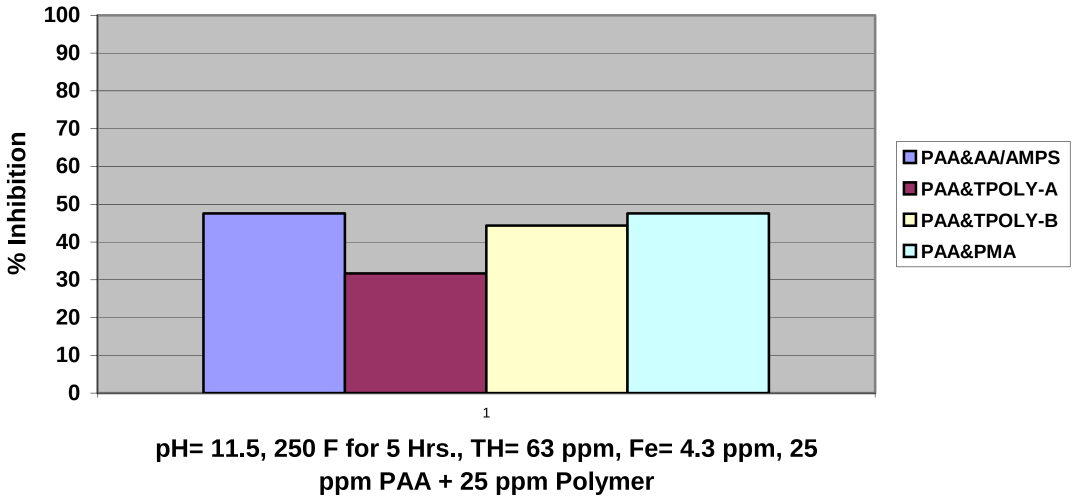


pH= 11.5, 250 F for 5 Hrs., TH= 60 ppm, Fe= 4.5 ppm, PO4= 66 ppm, Polymer= 50 ppm

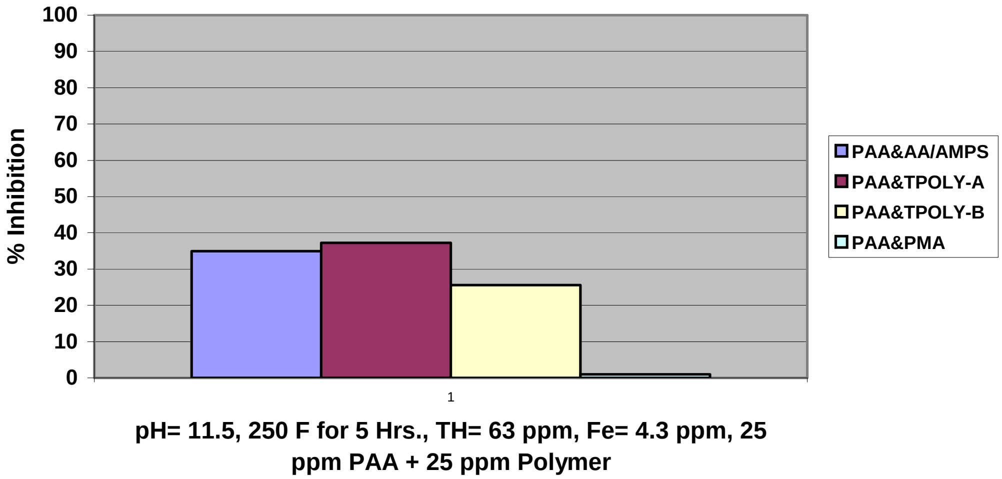
Effect of 4.5 ppm Iron on Hydroxyapatite Dispersion (Fig. 6)



pH= 11.5, 250 F for 5 Hrs., TH= 60 ppm, PO4= 66 ppm, Polymer= 50 ppm

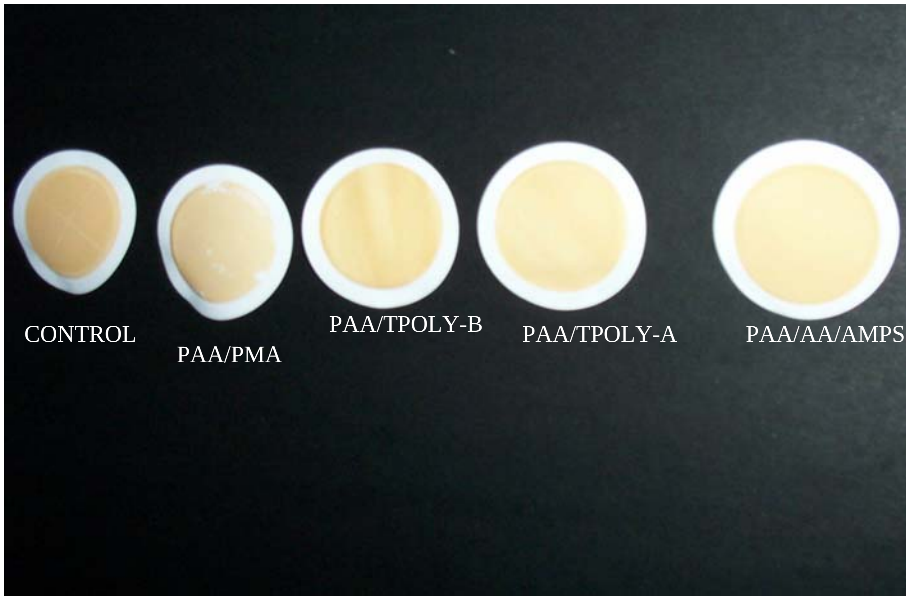


Hardness Stabilization in All Polymer Program (Fig. 7)

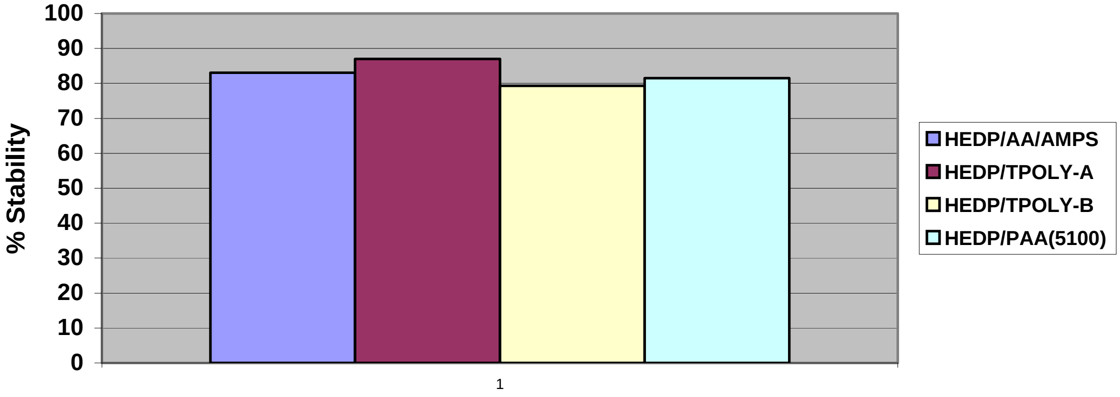


Iron Stabilization in All Polymer Program (Fig. 8)

All polymer program filtration (Fig. 9)

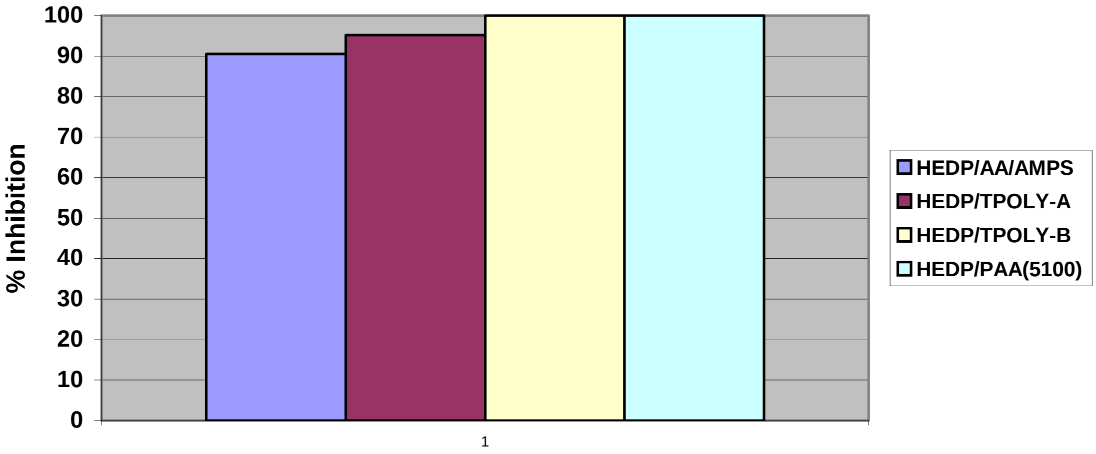


Phosphonate Stability in All Organic Program (Fig. 10)



pH= 11.5, 250 F for 5 Hrs., TH= 20 ppm, Fe= 2.1 ppm, 36 ppm HEDP + 30 ppm Polymer

Iron Stabilization in All Organic Program (Fig. 11)



pH= 11.5, 250 F for 5 Hrs., TH= 20 ppm, Fe= 2.1 ppm,
36 ppm HEDP + 30 ppm Polymer

All Organic Program Filtration (Fig. 12)