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The Influence of Water Clarification Chemicals on Deposit Control Polymer Performance in Cooling Water Applications

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Introduction

The major cause of performance deterioration in re-circulating cooling water systems is the deposition of undesirable materials on heat exchanger surfaces. The fouling of heat exchanger is a complex phenomenon involving the deposition of several different but related types of foulants on the heat exchanger surface. Industrial water system fouling problems are becoming more prevalent as the use of low quality feed water increases. In addition, surface water treated with cationic inorganic and organic flocculants poses very different and challenging problems. A brief discussion of five commonly encountered foulants (i.e., inorganic, particulate, microbial, corrosion, and organic) is presented below.

Biofouling

Fouling by microbiological slimes is a constant threat to the efficient operation of cooling water systems. Microorganisms, which cause the slime deposits, are living organisms capable of exceeding rapid reproduction. Biological fouling can occur when the feed and re-circulating waters contain sufficient nutrients to sustain rapid growth of organisms. Because microorganisms attach to the heat exchanger and other metal-based surfaces, especially in the low water flow areas, these are ideal conditions for optimum growth. In most re-circulating water systems, a thin biofilm is formed on the heat exchanger surface that does not interfere with short-term performance. However, during long periods of operation, biofilm accumulates thereby affecting heat transfer efficiency. Oil and other hydrocarbons are not usually present in significant quantities but can enter into cooling water system through leaks or spills. Even in low quantities, oil serves as a nutrient for accelerated microbiological growth, or can agglomerate other suspended particles into sticky mass. In many cases, microbiological fouling may influence under deposit corrosion. Biofouling is typically controlled by the addition of chemical agents (e.g., chlorine, bromochlorine, gluteraldehyde, quaternary ammonium compounds, etc.).

Colloidal Fouling

The fouling of heat exchanger surfaces by suspended matter is a critical concern to water technologists and plant operators. Certain feed waters, especially surface waters, require far more extensive pre-treatment than other sources such as deep wells. Changes in feed water composition can occur due to seasonal variations of the water supply. Feed waters containing suspended matter (e.g., clay, silt, organic debris, etc.) are typically treated with inorganic and organic clarification (coagulant and flocculating) agents. The effectiveness of surface water treatment to reduce suspended matter is dependent upon the proper selection and concentration of clarification agents (coagulants/flocculants), pH, mixing, and residence time. Commonly used water clarification agents include aluminum chloride, ferric chloride, and cationic polymers (e.g., diallyldimethyl ammonium chloride, copolymers of acrylic acid/acrylamide, and hydrolyzed polyacrylamide, etc.).

Corrosion Related Fouling

Corrosion is defined as the deterioration of metal by chemical or electrochemical reaction with its environment. In industrial water systems, corrosion of metal-based equipment if not properly controlled could lead to several operational challenges. Numerous factors such as metallurgy, water chemistry, temperature, pH, and water flow rate influence corrosion. Foulants resulting from the industrial water system corrosion include oxides of iron, copper, and zinc.

Over the last few decades, a variety of corrosion inhibitors were developed and are currently used to control corrosion in industrial water systems. These inhibitors generally are classified as anodic, cathodic, or both depending upon the corrosion control reaction mechanism(s). Examples of commonly used corrosion inhibitors include polyphosphates, silicates, molybdates, benzoates, nitrates, tannins and lignins, aromatic azoles, and phosphonates. Polyphosphates and phosphonates are effective inhibitors for carbon steel. However, under certain water hardness, pH and temperature conditions, both phosphonates and polyphospates are known to precipitate in the presence of calcium ion.[1,2]

Inorganic Fouling (Scaling)

The recirculation and concentration of sparingly soluble salts cause precipitation, deposition, and/or scaling on heat exchanger and other equipment surfaces. The major components of these precipitates include calcium carbonate, calcium sulfate, calcium phosphate, and calcium fluoride. Occasionally, sulfides of copper and iron are also encountered. The deposition of scale forming salts affects heat transfer efficiency, premature heat exchanger failure, and often results in increased operational costs. The inorganic scaling is generally controlled by the addition of low concentration of scale inhibitors (e.g., polyphosphates, phosphonates, acrylic acid/maleic acid based homo and co-polymers).

Organic Fouling

Organic fouling is a special case of recently recognized fouling caused by the interaction of deposit control agents with soluble and/or insoluble feedwater impurities. Currently, a variety of chemicals are used in water treatment formulations to manage corrosion and deposition of unwanted materials (e.g., mineral salts, suspended matter, microorganisms, etc.).

An effective cooling water treatment program must control scale, corrosion, particulate matter, and microbiological growth. Over the years, a variety of water treatment chemicals, both polymer and non-polymeric, have been developed and are being currently used to treat industrial water systems. The performance of these chemicals as scale inhibitors, dispersants, metal ion stabilizers, corrosion inhibitors, and biocides under cooling water conditions have been well documented.[2] It has also been reported that various water soluble impurities such as Fe (III), Zn (II), Mn (II), scale inhibitors (i.e., polyphosphates, phosphonates), cationic flocculant and coagulant, and cationic biocides have antagonistic effects on the performance of scale and deposit control polymers.[3,4,5]

Much work has been published on scale, deposit, and microbiological control. However, the interactions of cationic polymeric chemicals (i.e., biocides, coagulants, flocculants) with anionic scale and deposit control polymers have been mostly overlooked. This paper focuses on cationic polymer-anionic polymer salt formation under cooling water conditions (i.e., hardness, pH, and temperature). The influence of cationic polymer architecture (i.e., polymer molecular weight [MW], polymer type and composition, cationic charge) on the performance of scale and deposit control polymers has been investigated. In addition, Fourier Transform Infra-Red (FTIR) technique has been employed to characterize the polymer-polymer salt. Hopefully, the new data presented herein will enable water technologists to consider various factors (i.e., water treatment chemical types, molecular architecture, interactions between various chemicals, etc.) prior to selecting water treatment chemicals for new high performance formulations.

The cationic polymers (flocculant, coagulant, biocide) and anionic polymers (antiscalant, dispersant) and non-polymeric antiscalants tested in this study are shown in Tables 1, 2, 3, and 4, respectively. As illustrated in Tables 1, 2, and 3 the polymers (cationic, anionic, and non-ionic) vary significantly in terms of molecular weight, ionic charge, and composition.

The aqueous solutions of polymeric and non-polymeric additives, biocides, and flocculants/coagulants used include both commercial and experimental products. All additives evaluated are tested and reported on an active solid basis. All other chemicals used in this study were of reagent grade. Stock solutions of chemicals were prepared using distilled water.

Experimental

Interactions of Cationic Polymers with Anionic Polymers

The composition of the synthetic water used in the polymer-polymer salt precipitation experiments includes 100 mg/L Ca, 100 mg/L Mg, 110 mg/L Na, 470 mg/L Cl, 150 mg/L SO_4, 100 mg/L HCO_3, and pH 8.0 (unless specified otherwise). A known amount (ranging from 1.5 to 20 ppm) of antiscalant or dispersant solution (see Table 2) was added to the synthetic water containing known amount of cationic polymeric or non-polymeric material (flocculant/coagulant or biocide). The development of turbidity (% transmittance) as a function of time was recorded at 420 nm using a PC-1000 colorimeter (Brinkmann Instrument, Westbury, New York). Unless otherwise noted all precipitation experiments were done with 5-ppm cationic polymer and 5-ppm anionic polymer in synthetic water. During the experiment pH of the experimental solution was maintained constant by the addition of dilute hydrochloric acid or dilute sodium hydroxide. System water chemistry variables evaluated to study polymer-polymer salt precipitation include pH (3.0 to 9.0), ionic strength (5,800 to 24,000 ppm, NaCl) and temperature (22 to 55ºC). During the precipitation experiments, the solutions were stirred continuously at constant stirring speed (approximately 350 revolutions per minute) with a Teflon® coated magnetic stirring bar. Unless noted otherwise, all polymer-polymer salt precipitation experiments were conducted at room temperature (~22ºC) and duplicate/triplicate experiments were made to check the reproducibility of the turbidity data. Turbidity readings were taken 30 minutes after mixing. Extreme care was taken to eliminate air bubbles in the solutions, especially in the vicinity of the turbidity probe in order to avoid faulty signals. Turbidity values were reported as “100 - %T,” which is linearly proportional to the absolute turbidity in the range 80 to 100 %T. Figure 1 illustrates the experimental set up used to study polymer-polymer interaction.

Calcium Phosphate Inhibition

The procedure described by Amjad and coworkers[5] was used and is briefly described below. The sub-saturated calcium phosphate solution was made by the slow addition of the phosphate solution to the desired volume of water. The calcium phosphate inhibitor and other ionic constituents (e.g., cationic biocide, flocculant, and coagulant) were added to the phosphate solution. After a 30-minute equilibration period, the calcium stock solution was added, making up the total volume to 600 mL. For all experiments, the reaction period was fixed at 20 hours. During each experiment, the test solution was maintained at pH 8.50 ± 0.01 using a Metrohm pH stat instrument. Unless specified, the standard test conditions for calcium phosphate inhibition were 140 mg/L Ca, 9.0 mg/L phosphate, pH 8.50, 50ºC, 20 hr, and 10-ppm polymer.

The reaction progression was determined by spectrophotometric analysis of filtered (0.45 micron) aliquots of the test solution for phosphate ion. Polymer efficacy as a calcium phosphate inhibitor was calculated using the following equation:

$$\%\ \text{Inhibition} = \frac{[PO_4]_{\text{sample}} - [PO_4]_{\text{control}}}{[PO_4]_{\text{initial}} - [PO_4]_{\text{control}}} \times 100$$

Where the terms above are as follows:

Inhibition (%) = %I
$[PO_4]_{\text{sample}}$ = PO_4 concentration in the presence of inhibitor at the end of the test
$[PO_4]_{\text{control}}$ = PO_4 concentration in the absence of inhibitor at the end of the test
$[PO_4]_{\text{initial}}$ = PO_4 concentration at the beginning of the test

Results and Discussion

It is reported that pairs of oppositely charged polymers typically form complexes (soluble and insoluble) from aqueous solution.[6] Depending primarily on the molecular weights and charge densities, these complexes may be amorphous solid[7] or soluble (colloidal) aggregates.[8] The forces driving the formation of these complexes are primarily electrostatic. Hence, electrostatic parameters such as polymer surface and linear charge densities, solution pH, and ionic strength are particularly important. The behaviors of various cationic polymer - anionic polymer systems studied are analyzed in the following sections.

Cationic–Anionic Polymer Interactions

- ***Effect of Time on Turbidity Titration***

Figure 2 shows titration curves as a function of time for F-3 (polydiallyldimethyl ammonium chloride), a commonly used flocculant with three different anionic polymeric dispersants. As illustrated, 5 ppm concentrations of all three dispersants [namely SLS (sodium lignosulfonate), P-AA2 (polyacrylic acid), and terpolymer (P-AA/SA/SS)] in synthetic water exhibit varying degrees of incompatibility with 5 ppm F-3. It is evident from Figure 2, that the terpolymer compared to SLS and P-AA2 showed the highest turbidity. The trend observed between F-3 and three different anionic dispersants may be due to differences in ionic charge, molecular weight, and types of functional groups (e.g., carboxyl, sulfonic, phenolic) present in the polymers. The data in Figure 2 further indicate that solution turbidity gradually increases in the first 30 minutes and then levels off (no significant turbidity reading increases) from 30 to 90 minutes.

For the experiments shown in Figures 3 to 12, all turbidity readings were taken at 30 minutes.

- ***Effect of Dispersant Dosage***

Figure 3 presents the data for a series of compatibility experiments using a synthetic water containing 5 ppm F-9 (P-EPI/DMA) and varying concentrations of polyacrylic acids with weight average MW (M_W) values ranging from 1,500 to 5,000. These results provide concentration-compatibility profiles for a cationic polymer (F-9) and three (3) anionic polymers. As Figure 3 illustrates for a fixed F-9 concentration, the P-AA3----F-9 salt formation (or turbidity) strongly depends upon P-AA3 concentration in solution. For example, given a 0 to 2.0 ppm P-AA3 concentration, the solution is essentially clear (100 %T or no [0] turbidity). However, increasing the P-AA3 concentration above 2.0 ppm to 3.75, 5.0, and 10 ppm, results in a gradual increase in turbidity readings, from 12.5, 15.1, and 16.8, respectively. Furthermore, doubling P-AA concentration from 10 to 20 ppm (data not shown) does not significantly change turbidity readings. This suggests that the precipitation of polymer-polymer salt is essentially complete at 10 ppm P-AA3.

Figure 3 also shows titration curves for P-AA1 (M_W 1,500) and PAA-2 (M_W 2,100). As illustrated, under similar experimental conditions, P-AA1 compared to P-AA2 and P-AA3 is relatively more compatible with F-9. For example, the turbidity readings obtained with 10 ppm of three anionic polymers (i.e., PAA1, P-AA2, and P-AA3) are 8, 12, and 16.8, respectively. It should be noted that a solution exhibiting 97% transmittance (or a turbidity reading of 3) is visually turbid.

- ***Effect of Cationic Polymer Architecture***

Polymer Composition: The effect of cationic polymer composition with P-AA/SA/SS was investigated by conducting a series of turbidity experiments under standard test conditions. Figure 4 presents the turbidity data for these experiments. Figure 4 suggests that the compatibility of P-AA/SA/SS strongly depends on cationic polymer composition. It is interesting to note among the two homopolymers (i.e., P-EI and P-DADMAC), that P-EI shows the poorest compatibility with P-AA/SA/SS. This observed difference between P-EI and P-DADMAC may be attributed to the higher cationic charge present on P-EI. The turbidity data for the two copolymers presented in Figure 4 indicate that P-Am/AETAC compared to P-EPI/DA is more compatible with P-AA/SA/SS. It should be noted that the improved compatibility of P-Am/AETAC over P-EPI/DMA might be attributed to decreased cationic charge due to the presence of neutral acrylamide (Am) component.

Cationic Charge: The role of ionic charge in influencing the formation of cationic-anionic polymer salt was studied under standard test conditions. The turbidity data on various flocculants carrying different ionic charge (from 0 to 100%) are presented in Figure 5. It is evident from Figure 5 that compatibility of P-AA/SA/SS with various flocculants strongly depends upon the amount of cationic charge present in the flocculant. For example, the turbidity reading obtained for P-Am/AETAC (10% cationic charge, F-6) is 2 compared to 13 for P-Am/AETAC (50% cationic charge, F-7) and 14.2 for P-DADMAC (100% cationic charge, F-2). As pointed out earlier, solutions containing 5 ppm each of cationic and anionic polymer with turbidity reading of <3 are visually clear or cationic-anionic polymer salts are soluble under the test conditions evaluated. Figure 5 also shows turbidity data for two flocculants containing zero charge (P-Am) and partially anionic charge (hydrolyzed acrylamide). As expected both these polymers are compatible with P-AA/SA/SS as indicated by turbidity values <1.

Molecular Weight: In recent years, the influence of molecular weight (MW) on the performance of polymers as scale inhibitors, dispersants, and flocculants has been the subject of numerous investigations. Amjad [9,10,11] in studies on the evaluation of PAA in controlling the precipitation of $BaSO_4$, $CaSO_4 \bullet 2H_2O$, CaF_2, and calcium phosphates from aqueous solutions reported that polymer MW polymer plays a key role in the inhibition of scale forming salts. These studies indicate that the optimum performance for PAA is obtained with polymers having a weight-average MW (or M_W) approximately 2,000. Wales[12] in his study on the flocculation of colloidal particles by cationic flocculants, postulated that an optimum polymer M_W exists that is dependent upon the surface area of the colloidal system being investigated.

If the M_W is too high, the bridging may be hindered by steric stabilization. If the M_W is too low, the bridging will be ineffective because the extended segments will be too short.

Excellent examples of the M_W dependence are provided by P-DADMAC. In Figure 6, the turbidity data collected for P-AA/SA/SS with P-DADMAC of varying M_W clearly show that P-DADMAC in the M_W range 300,000 to 1,400,000 is more incompatible than low M_W (100,000) P-DADMAC. For example, turbidity readings obtained with low M_W flocculant was 4 compared to >12 obtained for polymers of higher M_W (>300,000).

- ***Effect of Biocides***

The use of biocides to control microorganisms in cooling water systems is well documented.[13,14] The type and selection of biocide(s) are dependent on system design, loading, and desired results. The treatment program may require one or more biological control agents and the application of these agents may be continuous or intermittent. Biodispersants are used to improve the effectiveness of biocides. Recent recommendations[15] on the control of Legionella pneumophila suggest the use of non-oxidizing biocides in combination with either continuous or intermittent halogen addition. Biocides are commonly applied in the presence of deposit and corrosion control agents. Therefore, the interaction of biocides on the other components of the water treatment program is of interest.

Figure 7 presents the results of our testing of the interactions of cationic biocides (Table 2) with P-AA/SA/SS. The turbidity data clearly show that non-polymeric cationic biocides [e.g., tetrakishydroxyphosphonium chloride (B-2), dialkyldimethyl ammonium chloride (B-3), and n-alkyldimethyl benzyl ammonium chloride (B-4)] compared to polyquaternium biocide (B-1) are relatively more compatible with the anionic terpolymer. For example, turbidity values obtained with B-2, B-3, and B-4 are less than one (<1) compared to a turbidity of five (5) with B-1. Increasing the biocide concentration from 5 to 10 ppm at fixed anionic terpolymer concentration causes more pronounced incompatibility effects with nitrogen containing biocides (e.g., B-1, B-3, and B-4) than observed with the phosphorous containing biocide (B-2). For example, increasing the biocide concentration by two fold results in an approximately 400% increase in turbidity values for nitrogen containing biocides compared to an approximately 30% increase for the phosphorous containing biocide. The observed difference in compatibility between nitrogen and phosphorous containing biocides may be attributed to different charge densities.

- ***Effect of Anionic Polymer Composition***

The influence of anionic polymer composition on compatibility with P-DADMAC (F-3) was studied by conducting a series of experiments with polymers containing a variety of monomers. Figure 8 presents turbidity data for carboxyl containing homopolymers (i.e., P-AA1, P-AA3, and P-MA). It is evident from the turbidity data that P-AA3 is less compatible with F-3 than P-AA1 and P-MA. The observed better tolerance of P-AA1 and P-MA compared to P-AA3 may be attributed to the difference in molecular weight.

Figure 8 also illustrates that polymers containing neutral monomer such as P-Am (polyacrylamide), and P-VP (polyvinylpyrrolidone), exhibit excellent compatibility with F-3 clearly suggesting that the electrostatic forces between P-VP and P-Am and F-3 are much weaker than observed between F-3 and carboxyl group containing polymers.

The effect of substituting the carboxyl group with other groups of varying chain length and ionic charge (e.g., 2-acrylamido-2-methylpropane sulfonic acid [SA], hydroxylpropyl acrylate [HPA], sulfonated styrene [SS], and acrylamide [Am]) was investigated for their ability to interact with F-3. Figure 8 clearly shows that type of monomer unit present in the polymer play key roles in influencing interactions with the cationic polymer. In general, acid groups such as sulfonic and carboxyl, make the polymer less compatible compared to non-ionic groups such as acrylamide and hydroxyl propyl acrylate.

- ***Effect of Polyphosphates and Phosphonates***

A series of experiments was conducted to evaluate the compatibility of several polyphosphates and phosphonates (see Table 4) at 5 and 50 ppm concentrations with 5 ppm of F-3 (1,400,000 M_w DADMAC). Figure 9 presents data for the compatibility of 5-ppm F-3 and 5-ppm polyphosphate or phosphonate. The turbidity data presented in Figure 9 clearly show that both polyphosphates and phosphonates are compatible with F-3 (cationic polymer) whereas P-AA3 (an anionic polymer) at 5 ppm exhibits incompatibility with F-3. Although not shown in Figure 9, experiments using up to 50 ppm phosphonates (anionic) suggests that these materials exhibit greater compatibility with F-3 than 5-ppm dosages of P-AA3 with F-3.

- ***Effect of Temperature***

It is well documented that various factors such as pH, total dissolved solids, water composition, and temperature affect the solubility of scale forming salts. It is also known that solubility of scale forming salts such as calcium carbonate, calcium sulfate, and calcium phosphate are inversely dependent on solution temperature. This solubility-temperature relationship suggests that scaling tendency is higher at heat exchanger surfaces than in the other parts of the re-circulating water system.

Figure 10 shows the effect of temperature on polymer-polymer salt precipitation for F-3 and P-AA/SA/SS under standard test conditions. As illustrated, temperature exhibits marked influence on the precipitation of polymer-polymer salt. For example, increasing the solution temperature by about 2.5 times (i.e., from 22 to 55°C) results in an approximately 25% increase in precipitation of polymer–polymer salt as evidenced by increased turbidity values. Thus, in cooling water system it is likely that the precipitation and deposition of polymer-polymer salt on heat exchanger surface would occur like other scale forming salts such as calcium carbonate, calcium phosphate, etc., due to favorable precipitation conditions.

- ***Effect of Ionic Strength***

The role of ionic strength (or total dissolved solids [TDS]) on the formation and precipitation of anionic polymer-cationic polymer complex salts was investigated using the turbidity titration. Figure 11 presents turbidity data for P-AA/SA/SS and F-3 systems in the presence of various concentrations of sodium chloride. It is evident that a system's ionic strength has a pronounced effect on the solubility of polymer–polymer salt as noted from the data in Figure 11 and in the table below:

NaCl (ppm)	Turbidity Reading	Turbidity Reduction vs. 0 ppm NaCl
0	17.3	N/A
5,580	14	≈20%
11,600	10	≈40%
23,400	0.2	>90%

Figure 11 and the data above suggest that the polymer-polymer salt solubility increases (i.e., turbidity decreases) with increasing salt concentration. This may be due to several factors: (a) the slight acidity of NaCl solutions, (b) the stabilization of anions through shielding of the charge-charge interactions by the sodium counter ions, and/or (c) the increase in neighboring-group effects due to random coil nature of the polymer chains in salt water.

- ***Effect of Solution pH***

It is generally accepted, that increasing the cooling system pH has a dual effect on system performance: (a) decreases metal corrosion rates and (b) increases scaling tendency (due to increased supersaturation of the scale forming salts such as calcium carbonate, calcium phosphate, and calcium phosphonates). It is also well documented that the degree of deprotonation explains the observed improvement in inhibitor (e.g., polymeric and non-polymeric inhibitors such as poly[acrylic acid] and acrylic acid-based copolymers, and phosphonates) performance with increase in solution pH from 4.5 to 9.0.

Figure 12 presents compatibility data for P-AA3 at 5-ppm as a function of solution pH in the presence of F-9 at 5 ppm. As illustrated, P-AA3 is very compatible (100% T or 0 turbidity) at pH 3. Increasing solution pH from 3.0 to 5.0 begins to show the incompatibility of P-AA3 with F-9 as indicated by the increased turbidity value. Figure 12 further shows that increasing the pH value from 5.0 to 9.0 results in an approximately 25% increase in the turbidity value. For example, turbidity values obtained at pH 7.0 and 9.0 were 14 and 16, respectively, compared to 13 obtained at pH 5. The excellent compatibility observed between P-AA3 and F-9 especially at pH <4 may be attributed to the presence of unionized carboxyl group present in P-AA3. It is interesting to note that increasing the solution pH from 5.0 to 9.0 increases the ionic charge on the P-AA3 whereas the cationic charge on F-9 is decreased thereby balancing out electrostatic interactions.

- ***Effect of Cationic Polymers on Calcium Phosphate Inhibition***

Cationic Polymer Dosage*:* Figure 13 presents results on the effect of varying concentration of two commonly used cationic polymers i.e., F-2 (P-DADMAC, M_W 700,000) and F-5 (M_W 750,000) for P-AA/SA/SS at a fixed calcium phosphate supersaturation. It can be seen that F-2 exerts a marked antagonistic influence on the performance of calcium phosphate inhibiting polymer. For example, % inhibition values obtained with 1.0 ppm of F-2 and F-5 are 82 and 95, respectively, compared to greater than 96% obtained in the absence of cationic polymer. It should be noted that increasing the cationic polymer concentration from 1.0 to 1.5 ppm results in 50% decrease in calcium phosphate inhibition with F-2 compared to a 25% reduction with F-5. It is interesting to note that at 2.0-ppm concentrations both cationic polymers exert similar antagonistic influence on the performance of P-AA/SA/SS.

Cationic Polymer Architecture: Figure 14 illustrates the performance of P-AA/SA/SS in the presence of several cationic polymers used in the cooling water treatment applications. These tests were run under the same calcium phosphate supersaturation with 10 ppm of P-AA/SA/SS and 1.5 ppm of several cationic polymers (various compositions and molecular weights). As illustrated, all cationic polymers have varying degrees of antagonistic influence on the calcium phosphate inhibiting polymer. It is evident from Figure 14 that 300,000 to 1,400,000 M_W P-DADMAC decreases % inhibition values by 50%. Whereas, the low M_W (100,000) P-DADMAC exerts an even stronger antagonistic effect (>75% reduction in

% inhibition) compared to higher M_W P-DADMACs. For example, % inhibition values obtained in the presence of M_W 300,000 and 1,400,000 P-DADMAC are about 50% compared to only 16% in the presence of M_W 100,000 P-DADMAC. A similar M_W dependence was observed with P-EPI/DMA/EDA copolymers.

Figure 14 shows the effect of cationic polymers of varying composition on the performance of P-AA/SA/SS. The data indicate that terpolymer performance is dramatically reduced in the presence of 1.5 ppm of various cationic polymers. It is worth noting that under similar experimental conditions the presence of Fe(III), a commonly used inorganic flocculant, does not show significant adverse affects on the performance of P-AA/SA/SS. The comparative data on inorganic and organic flocculants clearly show that organic flocculants, compared to inorganic flocculant exhibit stronger antagonistic effect on the terpolymer's calcium phosphate inhibiting performance. Figure 14 also shows the effect of a non-ionic polymer or polyacrylamide (M_W 2,000,000 P-Am, F-13). As expected, compared to cationic polymers tested, P-Am does not exert any antagonistic influence on the performance of terpolymer.

Characterization of Polymer-Polymer Salt

Polymer-polymer salts appear to be of enduring interest to macromolecular, colloid, and water technologists. From a water treatment perspective, understanding the interactions between common formulation ingredients with other chemicals that are separately fed to water systems is especially important for cooling water systems operating under stressed conditions. As discussed above, cationic polymers are incompatible with commonly used polymeric antiscalants and this leads to the formation of insoluble salts that can potentially foul the heat exchanger surfaces.

The polymer-polymer salt formed during the turbidity experiment was characterized using a Nicolet Magna 560 Fourier Transform Infrared (FT-IR) spectrophotometer equipped with a fixed-angle horizontal Attenuated Total Reflectance (ATR) accessory. These data were compared with the ATR-IR spectra for individual anionic and cationic polymer additives used in turbidity experiments. Specifically, concentrated solutions of the P-AA3 and F-3 components were vacuum dried for ATR-IR analysis. Figure 15 shows the ATR-IR spectra for the P-AA3 (11.a), F-3 (11.b), and the P-AA3-F3 polymer-polymer salt (15.c). Although the bands attributable to the P-AA3 dominate the spectrum in Figure 15.c, the shoulders near 3400, 1470, and 950 cm^{-1} suggest the presence of F-3 in the salt. These shoulders correspond roughly to absorption bands for the F-3 shown in Figure 15.b.

Summary

Currently, a wide variety of chemicals (e.g., flocculants, coagulants, scale inhibitors, dispersants, biocides, corrosion inhibitors, etc.) with different ionic charges and molecular architecture are available to water technologists to develop formulations capable of achieving desired performance objectives of the water treatment programs. This paper provided some insight on the formation and precipitation of cationic polymer-anionic polymer salt under cooling water conditions.

The results of study show that scale inhibitors and polymeric dispersants used to control various foulants interact with water clarification chemicals (i.e., cationic flocculants and coagulants) as well as biocides resulting in the formation of an insoluble salt. The driving forces in the formation of such insoluble salts of anionic and cationic polymers are electrostatic in nature. Other factors that influence the formation of these insoluble salts (i.e., [anionic polymer}-[cationic polymer] salts) include pH, temperature, and TDS.

The data from this study also suggest that interaction between anionic and cationic polymers strongly depends upon both cationic and anionic polymer architecture (e.g., composition and molecular weight). In addition, it has been shown that low concentrations (e.g., 0.1 to 2.0 ppm) of either cationic coagulants/flocculants or biocides exhibit strong antagonistic effects on the performance of calcium phosphate inhibiting polymers. Finally, the [anionic polymer]--[cationic polymer] salts formed have been characterized.

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Table 1
Cationic Coagulants/Flocculants Evaluated

Cationic Material	Acronym	Chemical Name	Cationic Charge (%)	Molecular Weight (x 1,000)
P-DADMAC	F-1	Poly(diallyldimethyl ammonium chloride)	100	300
P-DADMAC	F-2	Poly(diallyldimethyl ammonium chloride)	100	700
P-DADMAC	F-3	Poly(diallyldimethyl ammonium chloride)	100	1,400
P-DADMAC	F-4	Poly(diallyldimethyl ammonium chloride	100	100
P-EI	F-5	Poly(ethyleneimmine)	100	750
P-Am/AETAC	F-6	Poly(acrylamide:2- (acryloyloxy)ethyltrimethyl ammonium chloride)	10	4,000 to 6,000
P-Am/AETAC	F-7	Poly(acrylamide:2-(acryloyloxy)ethyltrimethyl ammonium chloride)	50	4,000 to 6,000
P-Am/AETAC	F-8	Poly(acrylamide:2-(acryloyloxy)ethyltrimethyl ammonium chloride)	50	8,000 to 10,000
P-EPI/DMA	F-9	Poly(2-hydroxypropyl:N,N-dimethylammonium chloride)	100	25
P-PI/DMA/EDA	F-10	Poly(2-hydroxypropyl:N,N- dimethyl ammine:ethylene diammine)	100	50
P-PI/DMA/EDA	F-11	Poly(2-hydroxypropyl:N,N- dimethyl ammine:ethylene diammine)	100	100
P-PI/DMA/EDA	F-12	Poly(2-hydroxypropyl:N,N- dimethyl ammine:ethylene diammine)	100	200
P-Am	F-13	Poly(acrylamide)	0 (non-ionic)	2,000
P-Am/AA	F-14	Poly(Acrylamide:acrylic acid)	0 (anionic)	2,000

Table 2
Cationic Biocides Evaluated

Biocide	Acronym	Chemical Name	Molecular Weight
Poly-Quat	B-1	Proprietary	N/A
TKHP	B-2	Tetrakishydroxymethyl phosphonium chloride	406
DAMAC	B-3	Dialkyldimethyl ammonium chloride	347
ADMAC	B-4	n-alkyldimethyl benzyl ammonium chloride	329

Table 3
Polymeric Scale Inhibitors and Dispersants Evaluated

Acronym	Chemical Name	Molecular Weight
P-AA1	Poly(acrylic acid)	1,500
P-AA2	Poly(acrylic acid)	2,000
P-AA3	Poly(acrylic acid)	5,000
P-MA	Poly(maleic acid)	1,200
P-Am	Poly(acrylamide)	10,000
P-VP	Poly(vinylpyrrolidone)	30,000
P-AA/HPA	Poly(acrylic acid/hydroxylpropyl acrylate)	20,000
P-MA/SS	Poly(maleic acid/sulfonate styrene)	20,000
P-AA/SA	Poly(acrylic acid/sulfonic acid)	N/A
P-AA/SA/SS	Poly(acrylic acid/sulfonic acid/sulfonated styrene)	N/A
SLS	Sodium lignosulfonate	N/A

Table 4
Phosphonates and Polyphosphates Evaluated

Acronym	Chemical Name	Molecular Weight
AMP	Amino tris(methylene phosphonic acid)	299
HEDP	1-hydroxyethylidine 1,1-diphosphonic acid	206
PBTC	2-phosphono butane 1,2,4-tricarboxylic acid	270
SPYP	Sodium pyrophosphate	266
STPP	Sodium tripolyphosphate	388
SHMP	Sodium hexametaphosphate	611

Figure 1
Experimental Set-Up for Turbidity Titrations

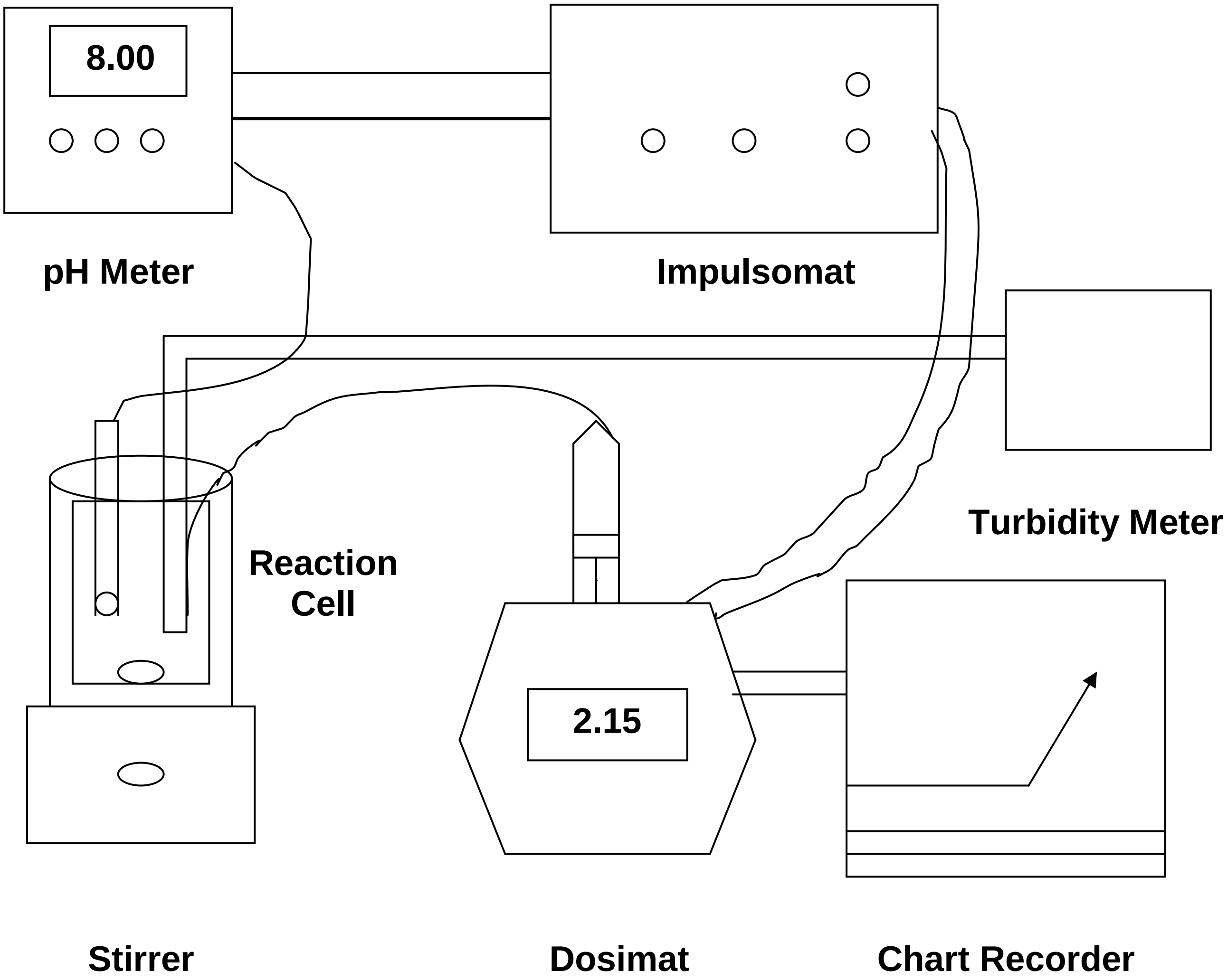


Figure 2. Compatability of P-DADMAC (F-3) with Several Anionic Polymers vs. Time

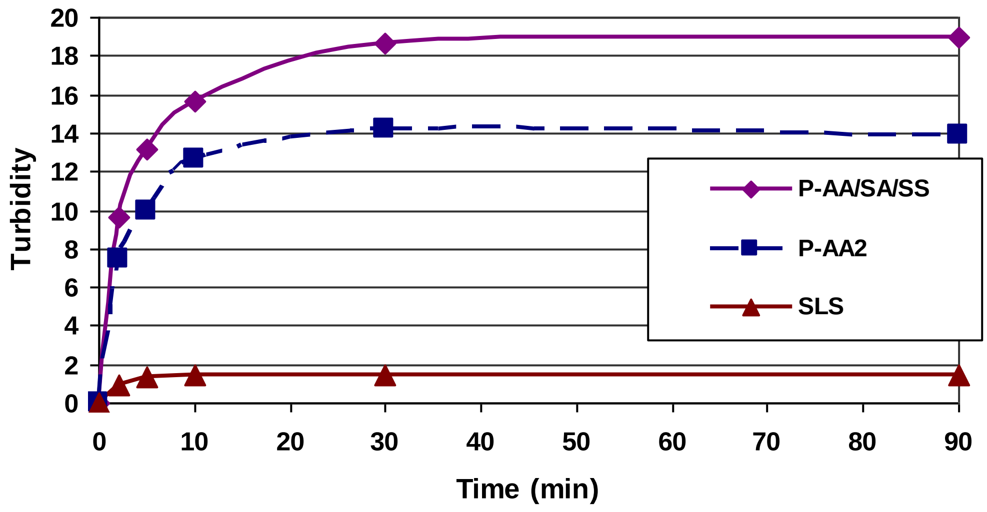


Figure 3. Compatibility of P-EPI/DMA (F-9) with Several PAAs at Varying Dosages

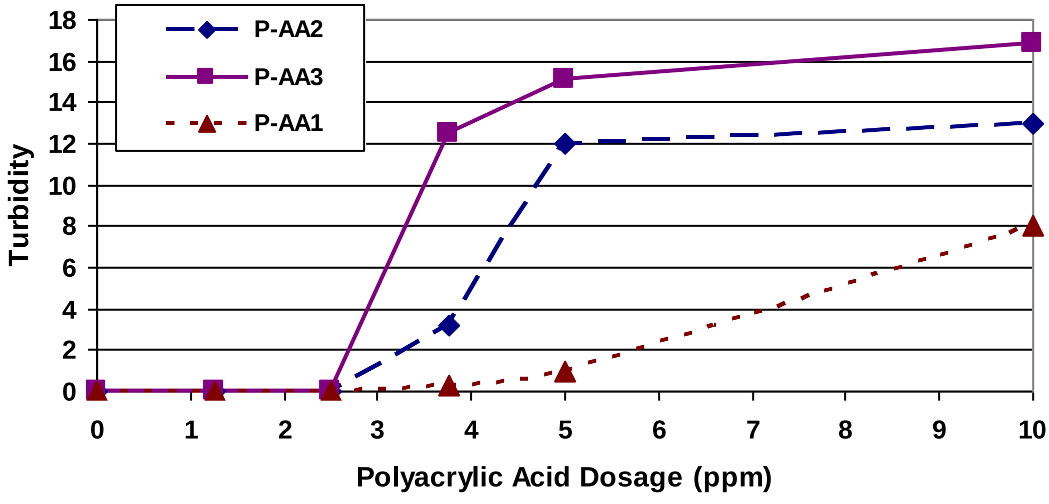


Figure 4. Compatibility of P-AA/SA/SS with Various Cationic Polymers

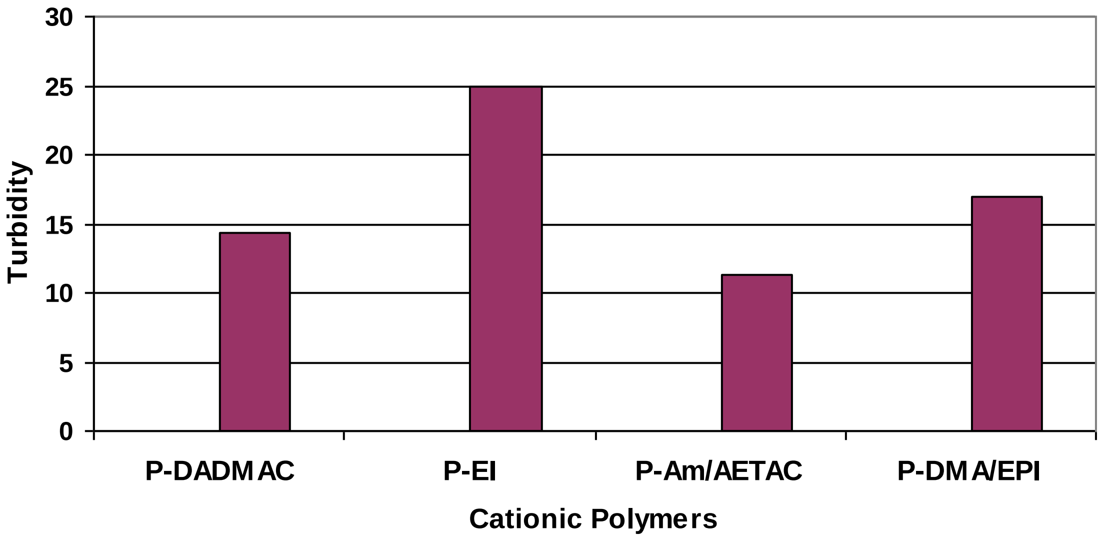


Figure 5. Compatibility of P-AA/SA/SS with Cationic Flocculants of Varying Ionic Charge

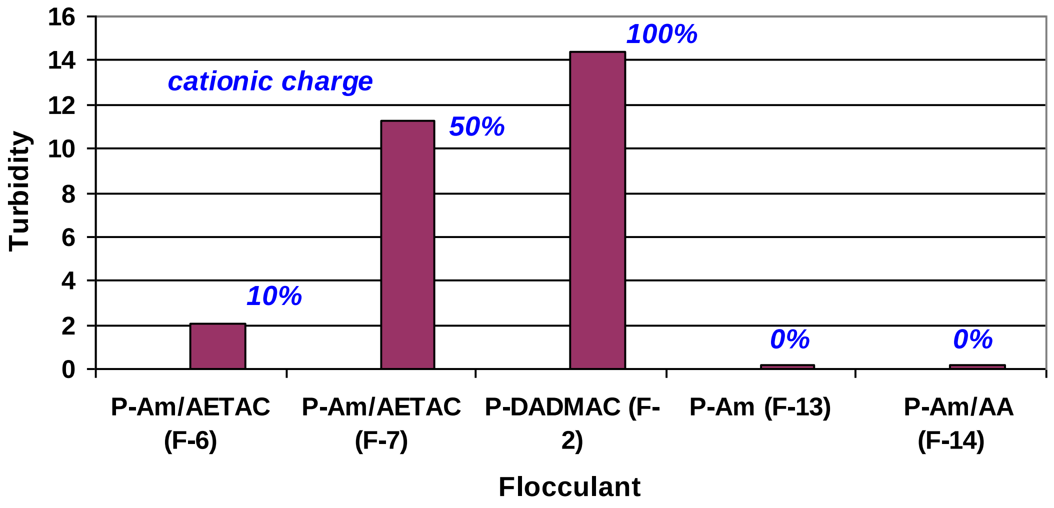


Figure 6. Compatibility of P-AA/SA/SS as a Function of P-DADMAC Molecular Weight

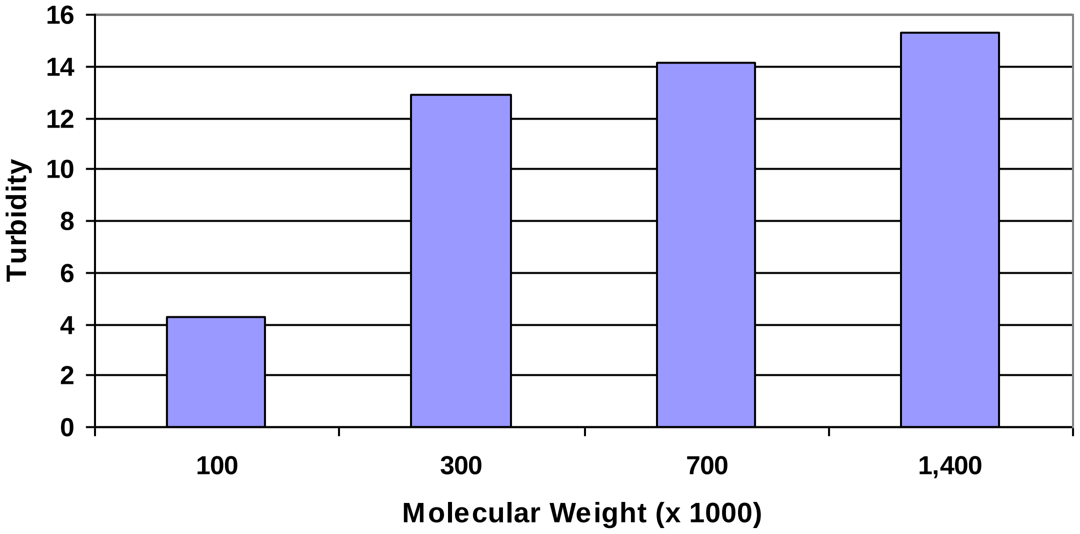


Figure 7. Compatibility of P-AA/SA/SS as a Function of Cationic Biocide Dosage

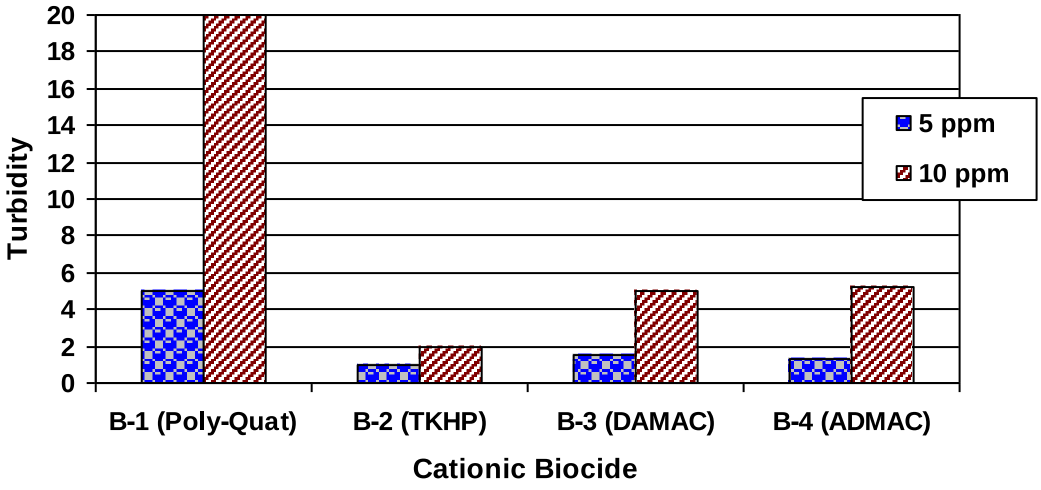


Figure 8. Compatibility of P-DADMAC (F-3) with Several Anionic Polymers

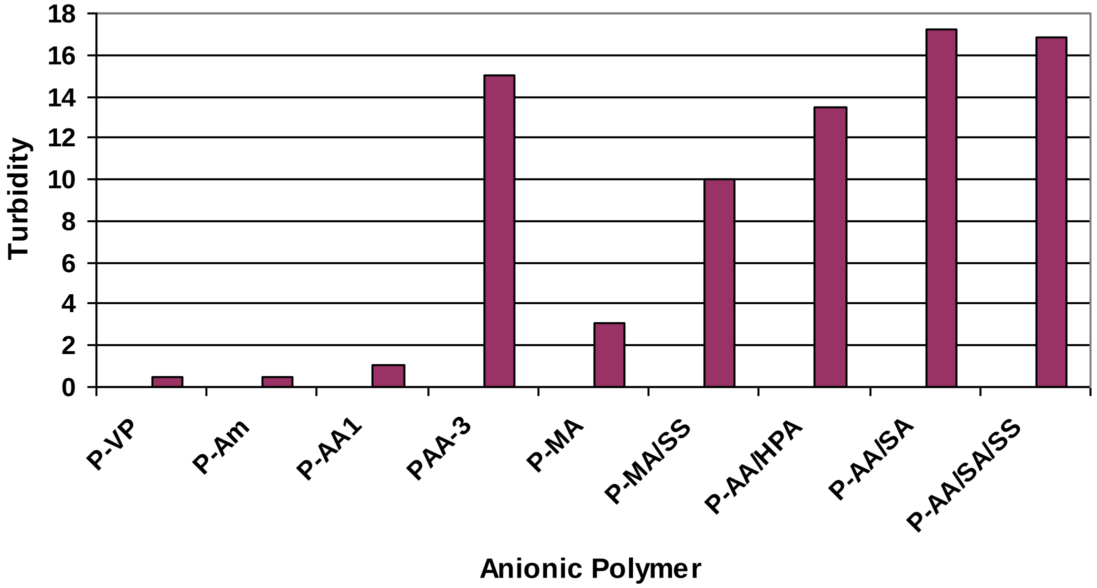


Figure 9. Compatibility of P-DADMAC (F-3) with Phosphonates and Polyphosphates

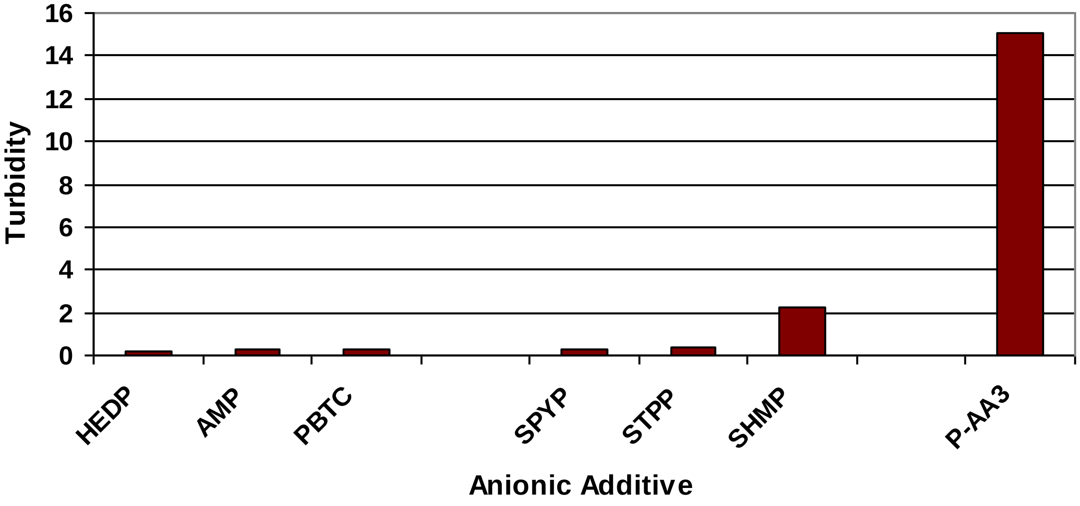


Figure 10. Effect of Temperature on Compatibility of P-DADMAC (F-3) with P-AA/SA/SS

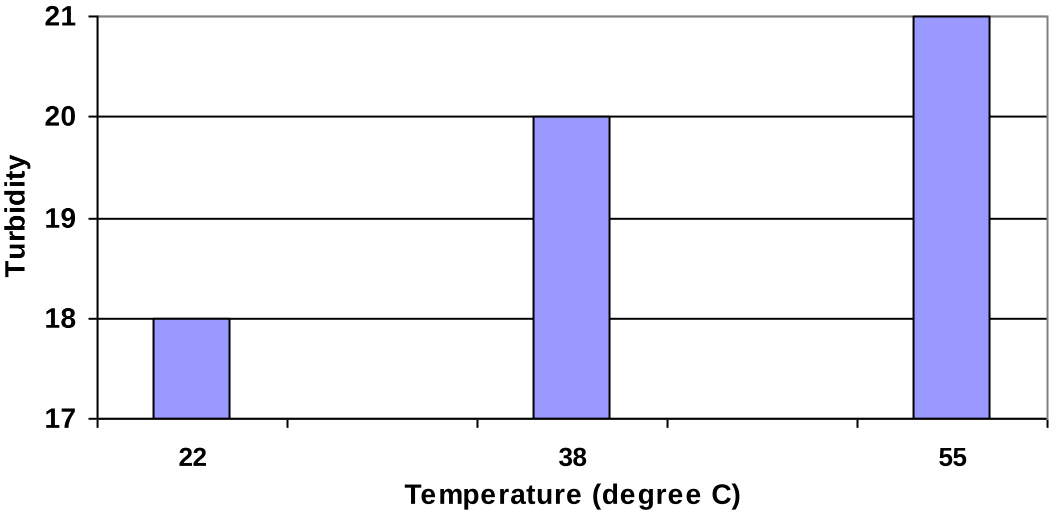


Figure 11. Effect of Total Dissolved Solids (NaCl) on Compatibility of P-DADMAC (F-3) with P-AA/SA/SS

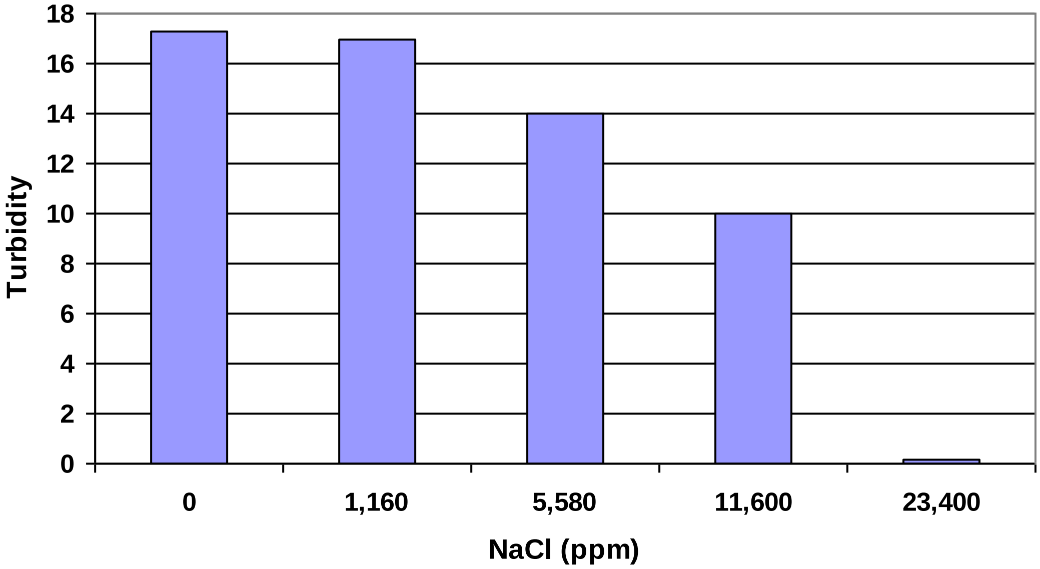


Figure 12. Effect of Solution pH on the Compatibility of P-EPI/DMA with P-AA/SA/SS

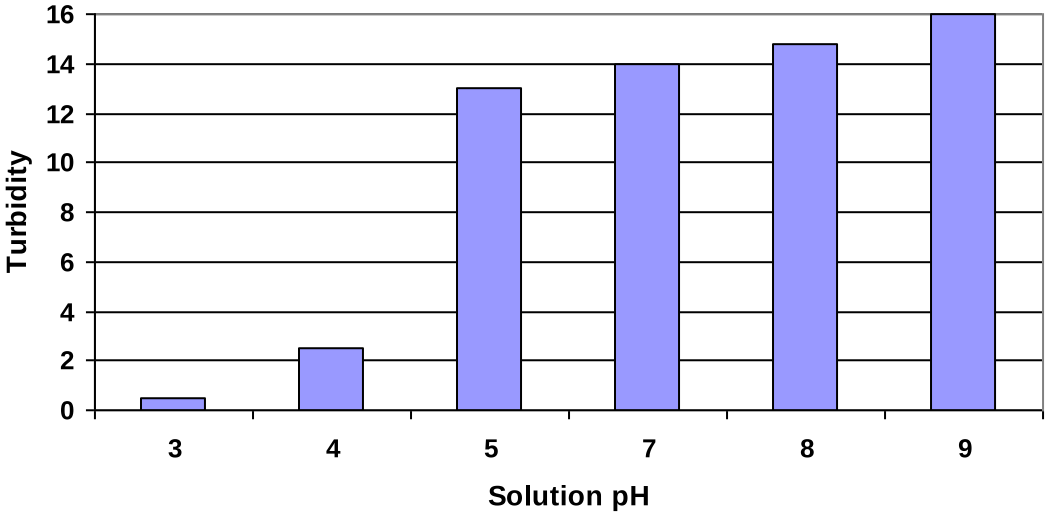


Figure 13. Effect of Cationic Polymer Dosage on Calcium Phosphate Inhibition of P-AA/SA/SS (Conditions: 140 mg/L Ca, 9 mg/L phosphate, pH 8.5, 50 deg C, 20 hr, 10 ppm P-AA/SA/SS)

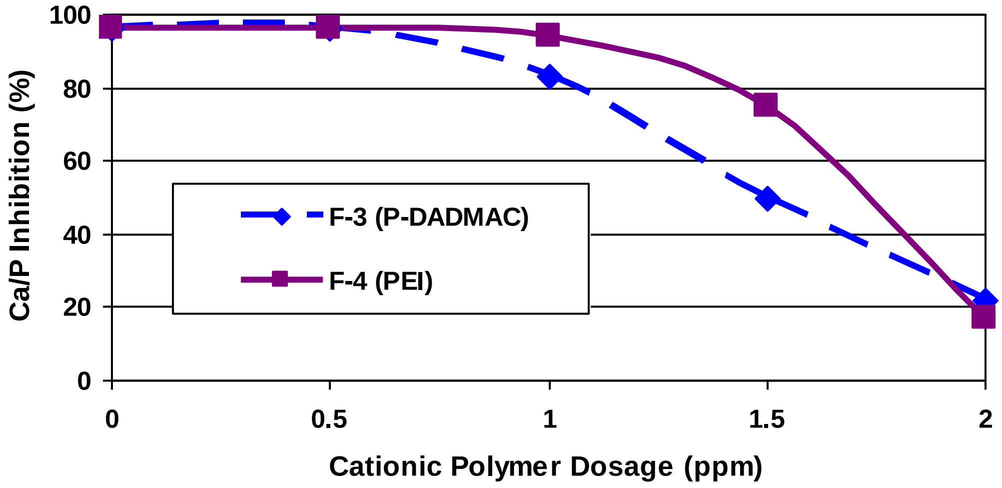


Figure 14. Calcium Phosphate Inhibition by P-AA/SA/SS - Effect of *Polymer Composition* & Molecular Weight (x 1,000)

(Conditions: 140 mg/L Ca, 9.0 mg/L phosphate, pH 8.5, 50 deg C, 20 hr, 10 ppm P-

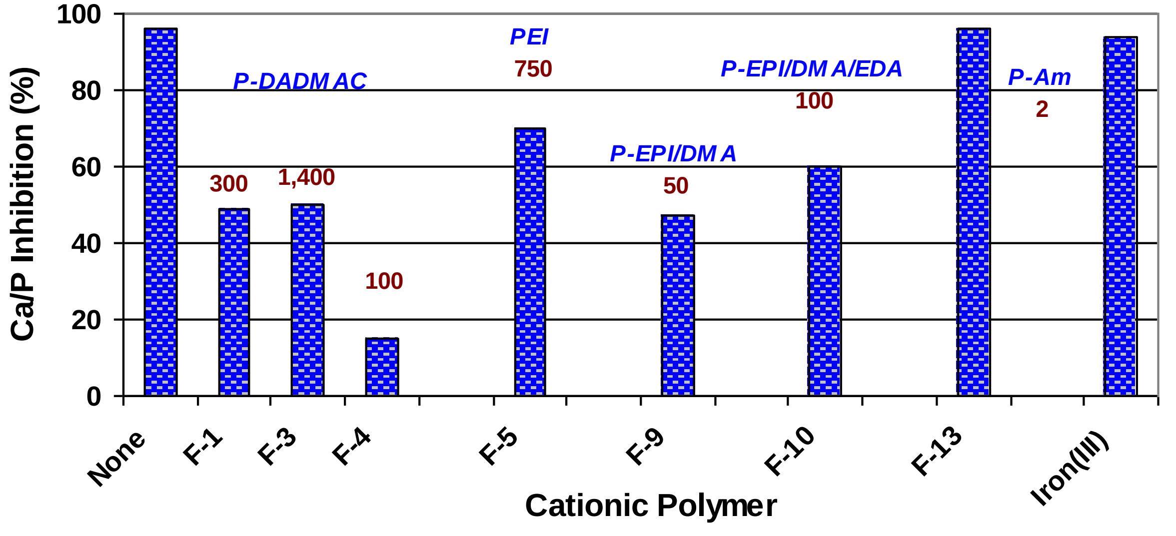


Figure 15
ATR-IR Spectra for P-AA3 (15.a), C-2 (15.b), and P-AA3 – C-2 Salt (15.c)

Figure 15.a

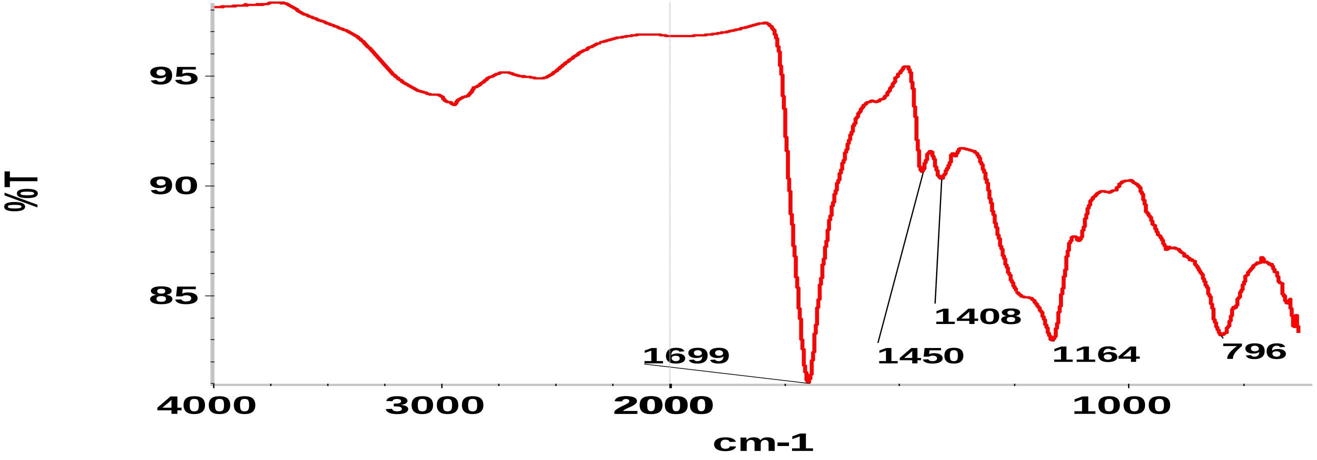


Figure 15.b

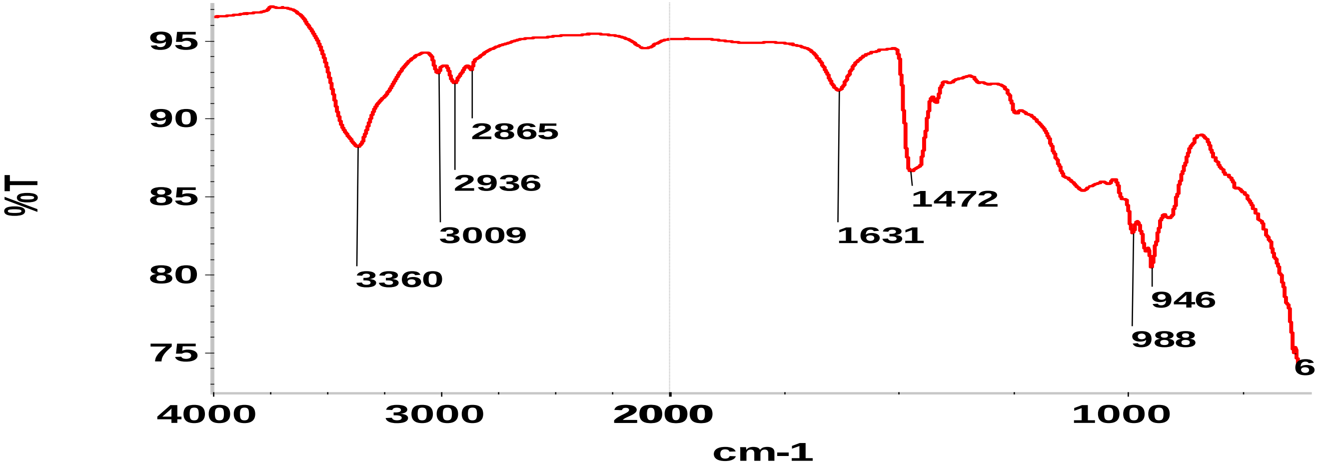
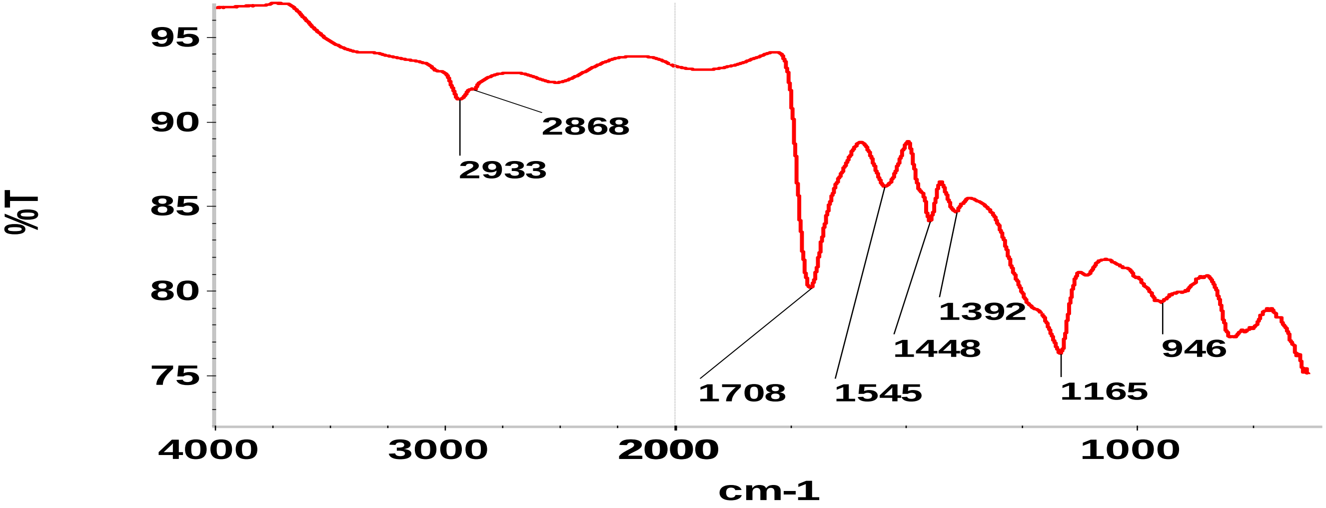


Figure 15.c



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