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Factors Influencing the Precipitation of Calcium-Inhibitor Salts in Industrial Water Systems

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Introduction

The use of natural hard waters in industrial water systems (e.g., cooling, boiler, desalination, oil production, etc.) can cause severe scaling and corrosion of equipment surfaces and pose serious technical and economic challenges. The scales commonly encountered are sulfates, carbonates, and phosphates of calcium, magnesium, and barium. The precipitation and deposition of scale on equipment surfaces are influenced by various factors including feed and re-circulating water chemistry, pH, temperature, flow velocity, heat exchanger metallurgy, and types of additive used in the treatment program. Such scale deposits significantly reduce heat transfer efficiency, constricts flow (e.g., reduces internal pipe diameters), increase the operating pressure of pumps, and enhance the probability of corrosion damage. In many cases, the removal of deposits leads to discontinuous operation of the system, resulting in higher operating costs. In addition, treatment chemicals (i.e., flocculants and coagulants) used upstream to treat feed water also influence the performance of additives used to prevent the precipitation of scale forming salts.

Investigators have proposed several options for controlling scale formation including the use of acids, chelants, or the addition of threshold inhibitors. The most promising method is the addition of water soluble additives at very low concentrations such as few parts per million (ppm). Additives commonly used for scale control applications are polymers containing carboxylic acid groups such as poly(acrylic acid), poly(maleic acid), and both copolymers and terpolymers incorporating acrylic acid and/or maleic acid monomers. For carboxylic acid containing polymers, it appears that precipitation inhibition is greatest for polymers with molecular weights below 20,000 and the optimum molecular weight is dependent upon (a) polymer architecture (i.e., charge, size, and monomer ratio, etc.) and (b) scaling salt being formed.[1-3]

Mineral scale deposits are not the only challenges that adversely affect the operation of industrial water systems. Corrosion, suspended matter, and microbiological growth are equally important factors that have to be controlled along with scale formation. Deposition of suspended matter is typically controlled by the incorporation of a dispersant in the treatment formulation. Additives commonly used to control corrosion include polyphosphates, phosphonates, molybdate, zinc, etc.

To prevent the formation of biofilm and to achieve optimum system efficiency, microbiological growth within the water system must be controlled. Generally, biofilm formation is controlled by the addition of biocides, biostats, and biodispersants to the water system. Currently available biocides vary considerably in terms of their characteristics such as chemistry, biodegradability, compatibility with other additives, activity, and selectivity. Commonly used biocides include chlorine, ozone, chlorine dioxide, gluteraldehyde, and quaternary ammonium chloride.

Water treatment program design takes into consideration known factors that are common to most industrial water systems. These factors may include system water chemistry (e.g., pH, temperature, total dissolved solids), upstream treatment, and compatibility of the water treatment additives (i.e., biocide, dispersant, scale inhibitor, coagulant, flocculant, etc.), with each other as well as the compatibility of hardness ions with scale inhibitors, corrosion inhibitors, and biocides.

The control of mineral scale, suspended matter, corrosion, and microbiological growth in industrial water systems by different additives has been well researched.[4-6] However, the interactions of various treatment additives with water impurities have been mostly overlooked. One of the major concerns of industrial water technologists is the compatibility or tolerance limit of the treatment additives (e.g., anionic inhibitors). The tolerance or compatibility is defined as the maximum amount of the inhibitor that can be added to the water system without significant precipitation of calcium-inhibitor salt. If the compatibility is poor and the treatment used is higher than the recommended level, not only does calcium-inhibitor precipitation occurs, but also the overall scale formation becomes faster and could lead to many troubles (e.g., early shutdown, wasted time, reduced production, and low profitability).

In our previous reports, we presented information on the interaction of biocides, coagulating and flocculating agents, and metal ions such as iron, aluminum, and zinc, with a variety of scale/deposit control polymers.[7-10] It was shown that the performance of scale and deposit control polymers is influenced by the presence of various impurities present in the water. The present study is concerned with the interaction of hardness ions with both non-polymeric and polymeric inhibitors (see Tables 1 and 2) under a variety of operating conditions. In addition, an Fourier Transform Infrared (FT-IR) spectrophotometer was used to characterize the metal-inhibitor salt. It is hoped that the data presented in this paper will enable the water technologists to recognize the impact of a variety of operating conditions, water chemistry, interactions of anionic scale inhibitor/dispersant with biocide, coagulating/flocculating agent, and hardness ions in selecting the appropriate additives for their formulations.

Experimental

The chemicals used to prepare the solutions were Fisher Scientific ACS reagent grade. Stock solutions of known concentrations of calcium chloride, magnesium chloride, barium chloride, sodium chloride, hydrochloric acid, sodium hydroxide, and various polymeric and non-polymeric inhibitors were prepared and used to make up test solutions. The inhibitors were selected from commercial and experimental materials. All inhibitor solutions were prepared on dry weight basis. The desired concentrations were obtained by dilution, using double-deionized and distilled water. A Metrohm Brinkmann pH-stat unit equipped with a combination electrode was used to maintain the experimental solution pH. The pH electrode was calibrated before each experiment with standard buffers.

Inhibitor tolerance towards metal ions (i.e., calcium, magnesium, barium, etc.) was measured by monitoring turbidity. The test set-up used a constant water bath, double walled-glass reaction cell, and a Brinkmann (Westbury, New York) PC 802 Colorimeter with 420 nm filter (for transmittance measurements).

One hundred (100) mL of metal ions (Ca, Mg, or Ba) of known concentrations in deionized water containing varying amounts of inhibitor was placed in a 125-mL glass bottle. The pH of test solution was adjusted to a known value with dilute NaOH and/or HCl. The bottles were capped and placed in reaction cell. Appropriate time was allowed for temperature and pH to equilibrate. At known time intervals (typically 30 minutes) transmittance readings were taken using a fiber-optic probe. A range of pH values (7.5 to 10.5), temperatures (25 to 65^{O}C), hardness ion concentration (250 to 1,000 mg/L), and sodium chloride (1,000 to 5,000 mg/L) were studied. Duplicate/triplicate experiments were run to check the reproducibility of the compatibility data. In order to avoid faulty signals, extreme care was taken to maintain system pH and eliminate air bubbles in the solutions, especially in the vicinity of the turbidity probe. Tables 1 and 2 summarize the analytical characteristics of inhibitors evaluated in this investigation.

Metal-inhibitor salts formed during the compatibility experiments were characterized using a Nicolet Magna 560 Fourier Transform Infrared (FT-IR) spectrometer equipped with an ASI DuraSamplIR™.

Results and Discussion

Figure 1 shows the experimental set-up used in this investigation. Figure 2 illustrates the typical “% transmittance” (%T) as a function of inhibitor concentration (i.e., HEDP). The inflection point in the transmittance-inhibitor profile was used to calculate the point of onset of turbidity. The turbidity probe was interfaced with a colorimeter to determine a more accurate inflection point rather than relying on visual observations for the first appearance of turbidity (onset of calcium-inhibitor precipitation) or inflection point. Figure 2 illustrates the compatibility data obtained for a Ca-HEDP system and shows good reproducibility (± 5% or better).

Phosphonates and Polyphosphates (Non-Polymeric Inhibitors)

In water treatment processes, phosphonates and polyphosphates are used for a variety of reasons but most importantly because they inhibit the formation of scale forming salts and control mild steel corrosion. Phosphonates differ structurally from polyphosphates in that they have a P-C bond rather than P-O bond and this difference accounts for the superior stability of phosphonates (vs. polyphosphates) under extremes of pH and temperature.

Phosphonates and polyphosphates prevent scale formation at "sub-stoichiometric" dosages by adsorbing onto crystal growth sites of micro-crystallites thereby interfering with crystal growth and altering the crystal growth morphology. In addition, both phosphonates and polyphosphates have been shown to exhibit metal chelation and dispersancy activities.

Although there are many types available, the three (3) of the most commonly used phosphonates in water treatment formulations are as follows:

- Aminotris(methylene phosphonic acid) or AMP,
- Hydroxyethylidine 1,1-diphosphonic acid or HEDP, and
- 2-phosphonobutane 1,2,4-tricarboxylic acid or PBTC.

The precipitation of Ca-phosphonate salts can (a) cause fouling of heat exchanger and reverse osmosis membrane surfaces and (b) decrease the phosphonate concentration in the system to the extent that severe calcium carbonate scaling can occur. It should be noted that Ca-inhibitor scales usually have the same inverse solubility features commonly observed with scales and they also impede heat transfer. Table 1 summarizes the types of phosphonates investigated in the present study.

Ca-inhibitor salt precipitation is well known for phosphonates, polyphosphates, and polycarboxylates.[11,12] Figure 3 shows the calcium ion compatibility data obtained for AMP, HEDP, and PBTC. As illustrated, all phosphonates form insoluble salts with calcium ion. Based on their calcium ion tolerance in the presence of 250 mg/L Ca, pH 9.50, $25^{O}C$ these phosphonates can be ranked (in descending order) as follows:

PBTC (98 ppm) >> AMP (26 ppm) > HEDP (12 ppm).

Figure 4 shows comparative compatibility data for phosphonates and polyphosphates. It is evident from Figure 4 that all phosphorus-containing inhibitors form insoluble salts with calcium ions. Among the polyphosphates (i.e., sodium tripolyphosphate or STPP and tetra potassium pyrophosphate or TKPP), calcium tolerance increases with an increase in P-O-P concentration. For example, under similar experimental conditions, calcium compatibility values obtained for TKPP is 10 ppm compared to 29 ppm obtained for STPP. It is interesting to note that the only inhibitor that exhibits greater tolerance to calcium ion is PBTC which contains three (3) carboxyl group and one (1) phosphono group. This suggests that both the nature as well as number of functional groups present in the inhibitor play important roles in Ca-inhibitor salt formation.

The influence of a polymeric dispersant on Ca-HEDP precipitation was studied by conducting a series of experiments in the presence of varying concentrations of a high performance terpolymer (P-AA/SA/SS, K798). Figure 5 illustrates that the precipitation of Ca-HEDP is strongly influenced by the presence of K798. For example, under similar experimental conditions (i.e., 250 mg/L Ca, 40 ppm HEDP, pH 9.5, $25^{O}C$) the %T readings obtained in the presence of 10, 20, 30, and 50 ppm of K798 are 72%, 79%, 90%, and 99%, respectively, compared to 71% obtained in the absence of K798. The data in Figure 5 clearly show negligible Ca-HEDP precipitation in the presence of 50 ppm of K798. The ability of the K798 to exhibit excellent calcium tolerance under stressed conditions and provide superior Ca-HEDP inhibition is an important polymer performance characteristic.

Figure 6 illustrates the performance of various polymeric inhibitors on Ca-HEDP precipitation. It is evident that under similar experimental conditions employed that all polymers tested inhibit Ca-HEDP precipitation but varying degrees. The data clearly show that the polymer (K752) containing only one (1) functional group (i.e., -COOH) exhibits poor inhibitory activity. Replacing a portion of the "–COOH" in PAA with a bulkier group (i.e., sulfonic acid) thereby creating a copolymer (K775) markedly improves the Ca-HEDP inhibition performance. However, under the same conditions, PPC (promoted as a multi-functional terpolymer) exhibits poor Ca-HEDP inhibition activity.

Figure 6 also shows that incorporating another hydrophobic group (i.e., SS) in the polymer structure (thereby creating terpolymers; i.e, K797 and K798), further improves Ca-HEDP inhibition activity. Based on the data presented in Figure 6, the polymers may be ranked as follows (in terms of decreasing effectiveness):

terpolymers > copolymers > homopolymers

It should be noted that the same polymer ranking was observed for Ca-STPP when evaluated under similar test conditions (i.e., 250 mg/L Ca, pH 9.50, 25 ^{O}C) with higher inhibitor and STPP (i.e.,100-ppm polymer and 300-ppm STPP) concentrations.

Polymeric Inhibitors

Homopolymers

Figure 7 shows the calcium ion compatibility of various PAAs (Noveon's and competitive) and poly(maleic acid). These data clearly suggest that all PAAs evaluated form insoluble salts with calcium ion and the compatibility of these PAAs with Ca^{2+} depends on polymer characteristics (i.e., molecular weight [MW] and polymerization method). In general, solvent polymerized PAAs exhibit better tolerance to calcium ion than do water polymerized PAAs. For example, under the experimental conditions employed (1,000 mg/L Ca, pH 9.5, 25^{O}C), calcium tolerance values obtained for K752 (solvent-polymerized 2,000 MW PAA) is greater than 700 ppm compared to 55 ppm obtained for K7028 (water-polymerized 2,300 MW PAA). A similar trend in increased calcium ion tolerance was also observed for K732 (solvent-polymerized 6,000 MW PAA) and K7058 (water-polymerized 7,300 MW PAA). As demonstrated in Figure 7, the polymerization process plays an important in imparting calcium ion tolerance to PAAs. Further work is underway to understand the factors responsible for calcium-polymer precipitation for polymers made in different media.

Figure 7 also shows that the calcium ion tolerance values for competitive PAAs (i.e., PAA8, PAA9, PAAP), are similar to PAAs of comparable MW and polymerization media. Under similar experimental conditions, the poly(maleic acid) or PMA exhibits a calcium ion tolerance greater than the 6,000 and 7,300 MW PAAs but less than the PAAs with

MWs below 3,000. The observed calcium ion tolerance for PMA versus the PAAs may be attributable to MW and/or the polymerization media.

Copolymers and Terpolymers

Figure 8 shows the influence of polymer architecture for Ca^{2+} tolerance in a series of experiments carried out in the presence of 1,000 mg/L Ca, pH 9.5, and $25^{O}C$. It is evident from Figure 8 that calcium ion tolerance strongly depends upon polymer composition. For example, replacing a portion of the AA in K7058 with SA groups (e.g., K775, AA/AA1, and AA/SA2) results copolymers with an order of magnitude increase in calcium ion tolerance values.

As illustrated in Figure 8, adding either acrylate and/or vinyl acetate groups to PMA decreases the calcium ion compatibility. Therefore, it appears that both the monomer's charge and size play roles in a polymer's calcium ion tolerance.

In addition, the calcium ion tolerance values for several terpolymers (K797, K798, PABC, and PASN) were investigated. Figure 8 show the results of these experiments and the data indicate that all four terpolymers tested are extremely compatible with calcium ions. These data suggest that the incorporation of large and greater amounts of anionic and non-ionic monomer groups increase the calcium ion tolerance of polymers. In practice, if when high hardness ions levels are encountered in re-circulating waters, incorporating high performance polymers in the water treatment program will help ensure better overall system performance.

Polymer Molecular Weight

In recent years, many studies have been undertaken concerning the influence of MW on the precipitation of scale forming salts. Studies of polymers as scale inhibitors have shown that polymer performance in industrial water treatment is strongly affected by polymer MW. For carboxylic acid containing polymers, it appears that precipitation inhibition is greatest for polymers with MWs below 20,000 with the optimum MW being dependent upon on the particular polymer composition and salt being formed.

Figure 9 shows the calcium ion tolerance for PAAs with molecular weights ranging from 1,600 to 345,000. It is evident that the same calcium ion tolerance trend (i.e., increasing calcium ion tolerance with decreasing PAA molecular weight) applies for both types (solvent and water polymerized) of PAAs. In order to observe the molecular weight effect for PAAs made in different polymerization media (solvent and water), two sets of experimental conditions were employed as follows:

- High stress (500 mg/L and $45^{O}C$) for solvent polymerized PAAs, and
- Low stress (100 mg/L calcium and $25^{O}C$) for water-polymerized PAAs.

For example, calcium tolerance values obtained for solvent-polymerized PAAs are 195 ppm for K752 (MW 2,000) and 10 ppm for K732 (MW 6,000) compared to

>1,000 ppm for PAA1 (MW 1,600). As illustrated in Figure 9, similar molecular weight dependence is observed for PAAs made in an aqueous medium. It is interesting to note, that a similar molecular-weight trend was observed in studies involving the interaction of anionic polymers (i.e., PAA) with cationic polymers (i.e., quaternary ammonium chloride).[13]

Effect of Solution pH

It is generally accepted that increasing the re-circulating water pH has a two-fold effect on system performance: (a) it tends to decrease the rates of metal corrosion, and (b) it increases the scaling tendency by increasing the supersaturation of scale forming salts such as calcium carbonate, calcium phosphate, calcium phosphonates, etc. It is also well recognized for polymeric inhibitors such as poly(acrylic acid) and acrylic acid-based copolymers that the degree of de-protonation explains the observed improvement in polymer performance as the solution pH increases from 4.5 to 9.0. Studies involving phosphonates as crystal growth inhibitors show that an increase in the pH of the crystal growth solution over a pH 4.5 to 9.0 range results in an improvement in inhibitor performance that parallels the phosphonic acid titration curve.

Figure 10 shows the calcium ion compatibility data for three (3) structurally different but commonly used inhibitors namely: K732, K775, and PBTC. As illustrated, solution pH in the 7.5 to 10.5 range influences to varying degrees the compatibility of these inhibitors with calcium ion. For polymeric inhibitors such as K732 and K775 compatibility values decrease by a factor of about 1.4 as the pH is increased from 7.5 to 10.5. Under similar experimental conditions, increasing the pH from 7.5 to 10.5 results in about a two-fold decrease in calcium ion tolerance for PBTC. The observed difference in calcium ion tolerance observed between polymeric and non-polymeric inhibitors may be attributed to the characteristics (number, type, and ionization constants) of the functional groups present in the inhibitors. It is interesting to note that calcium ion tolerance decreases for PBTC, K732 and K775. However, it has been reported that phosphonate performance increases directly with increases in pH values.[14]

Effect of Solution Temperature

It is well documented that various factors (e.g., pH, total dissolved solids, 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 phosphates are inversely dependent on solution temperature. This solubility-temperature relationship suggests that the scaling tendency will be higher at the heat exchanger surface than in the other parts of the re-circulating system.

Figure 11 presents the data for our investigations to determine the influence of solution temperature (25 to 65^{O}C) in the presence of 500 mg/L calcium ion at pH 9.5 for three inhibitors (i.e., K732, PBTC, and K775). The data clearly indicate that solution temperature has a pronounced effect on the compatibility of inhibitors with calcium ion. As noted in Figure 11, increasing the temperature from 25 to 45^{O}C results in a ~40%

decrease in the calcium ion tolerance of K775 and K732 compared to a ~10% decrease in performance for PBTC. The observed difference in calcium ion tolerance between polymeric and non-polymeric inhibitors may be attributed to difference in solubility behavior of Ca-polymer versus calcium-PBTC salts.

Effect of Ionic Strength

The role of ionic strength or total dissolved solids (TDS) in influencing the calcium ion tolerance of the polymeric and non-polymeric inhibitors was studied by carrying out a series of experiments with inhibitors containing varying functional groups (i.e., --COOH, ---SO_3H, and ---PO_3H_2). The data in Figure 12 indicate that an inhibitor's calcium ion tolerance is strongly dependent upon the type of the functional group and system TDS. It is worth noting for polymeric inhibitors that increasing the TDS from 0 to 5,000 ppm NaCl results in about a 12-fold increase in calcium ion tolerance for polymeric inhibitors (i.e., K732 and K775) compared to doubling in the calcium ion tolerance of PBTC. The observed increase in calcium ion tolerance with increasing TDS suggests that Ca-polymer salts are more soluble in NaCl (or high TDS water) than Ca-PBTC salt. This is an interesting observation and should be considered during the selection of inhibitor and formulation development for water systems operating at cycles of concentrations.

Effect of Water Hardness

Hardness Ion Concentration

From a water conservation viewpoint, there has been an increasing trend towards operating cooling water systems at higher cycles of concentration resulting in greater driving force for the precipitation of scale forming salts. Figure 13 demonstrates the effect of hardness ion in the range 250 to 1,000 mg/L Ca on the compatibility of K732, K775, and PBTC. It is evident that tolerance of these inhibitors decreases as the calcium ion is increased. For example, in the presence of 500 mg/L calcium ion the tolerance values obtained for K732, K775, and PBTC are 18, 210, and 75 ppm, respectively compared to 10, 75, and 26 ppm obtained in the presence of 1,000 mg/L calcium ions. Thus, calcium ion tolerances decrease by a factor of two to three times for K732, K775 and PBTC with two-fold increase in calcium ion concentrations (from 500 to 1,000 mg/L). It is interesting to note under similar experimental conditions and at low hardness ion concentration (i.e., 250 mg/L), that K775 is significantly more tolerant to calcium ion than either K732 or PBTC.

Hardness Type

The compatibility of commonly encountered divalent metal ions (e.g., magnesium, calcium, and barium ions) in re-circulating cooling water was investigated by carrying out a series of experiments under similar conditions (i.e., pH 9.5, 25^{O}C, divalent metal ions 250 mg/L). Figure 14 shows the results for two comparable MW PAAs (i.e., K732 and K7058) made by different polymerization processes (i.e., solvent and water polymerization media, respectively). Both PAAs form insoluble salts with metal ions and based on the compatibility data, the metal–polymer salt may be ranked (in terms of decreasing solubility or tolerance) as follows:

Mg >> Ca >> Ba

The observed order of PAA tolerance with various metal ions is consistent with metal reactivity and metallic character.

Metal-Polyacrylate Salt Characterization

Precipitates formed during the metal-inhibitor compatibility experiments were filtered using a 0.22-micron filter paper. The hot-air dried samples of K7058, sodium-K7058 salt, and K7058-barium salts were characterized using an FT-IR spectrophotometer according to the procedure described previously.[13] Figure 15 present IR spectra for K7058 and the K7058-metal ion salts. The band near 1699 cm^{-1} represents the acid carboxylate of acrylic acid in K7058. The bands near 1543 and 1533 cm^{-1} represent the carboxylate salt carbonyl bands for the sodium and barium salts, respectively. It can be seen that there is significant shift in band for barium salt (1533 cm^{-1}) versus 1543 cm^{-1} for the sodium salt of K7058. This confirms that barium forms an insoluble salt in the presence of K7058. Additional work is underway to characterize the polyacrylate salts of calcium, magnesium, and strontium ions.

Summary

Our results advance the water treatment industries' understanding of the factors that influence the precipitation of calcium-inhibitor salts under cooling water conditions. The following should be kept in mind when considering the use of scale inhibitors and dispersants in developing high performance water treatment formulations and programs.

- All inhibitors evaluated (polymeric and non-polymeric) form insoluble salts with hardness ions under cooling water conditions.

- The calcium ion compatibility of PAAs strongly depends upon polymerization solvent and polymer molecular weight.

- Replacing acrylic acid with sulfonic acid containing monomers results in an increased calcium ion tolerance of the copolymer.

- Charge, size, and amount of co-monomers present in polymers affect the interactions that occur between polymeric inhibitors and metal ions.

- Terpolymers compared to both homopolymers and copolymers are more tolerant to calcium ions and are more effective Ca-phosphonate and Ca-polyphosphate inhibitors.

- System pH significantly impacts the interaction of an inhibitor with calcium ion to form an insoluble salt.

- Polymeric and non-polymeric inhibitors show marked decrease in calcium tolerance with increasing temperature.

- Inhibitor tolerance toward metal ion strongly depends upon metal ion concentration and the character of the metal ion.

- Solubility of metal-inhibitor salt increases with increasing TDS.

Future Work

Our ongoing studies are directed toward further understanding the mechanistic aspects of calcium-inhibitor precipitation, the solubility behavior of calcium inhibitor precipitates, and the influence of precipitates on the overall scale formation process. The results on these studies will be presented at future conferences.

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References

1. Z. Amjad, "Development of Calcium Phosphate Inhibiting Polymers," Chapter No. 16, "*Calcium Phosphates in Biological and Industrial Systems*", Kluwer Academic Publishers, Boston, MA (1998).

2. D. Wilson, "Influence of Molecular Weight on Selection and Application of Polymeric Scale Inhibitors," CORROSION/94, Paper No. 48, NACE International, Houston, TX (1998).

3. Z. Amjad, J. F. Zibrida, and J. A. Thomas-Wohlever, "Inhibition of Calcium Phosphates by Polymers in the Presence of Iron (III). The Influence of Chelating Agents," Chapter Number 2 in "Advances in Crystal Growth Inhibition Technologies," Kluwer Academic Publishers, Boston, MA (2001).

4. J. A. Wohlever, Z. Amjad, and R. W. Zuhl, "Performance of Anionic Polymers as Precipitation Inhibitors for Calcium Phosphonates," in Advances in Crystal Growth Inhibition Technologies, Kluwer Academic Publishers, New York, NY (2001).

5. Z. Amjad, D. Butala, and J. Pugh, “The Influence of Recirculating Water Impurities on the Performance of calcium Phosphate Inhibiting Polymers,” CORROSION/99, Paper No. 118, NACE, Houston, TX (1999).

6. L. Downward, T. K. Haack, and R. E. Talbot, “TetrakisHydroxymethyl-Phosphonium Sulfate (TKHP) – A New Industrial Biocide with Low Environmental Toxicity,” Paper No. 401, CORROSION/97, NACE International, Houston, TX (1997).

7. A. Marshal and B. Greaves, “The Effect of water Quality on the Performance of Extended Phosphate technology,” CORROSION/86, Paper No. 399, NACE International, Houston, TX (1986).

8. Z. Amjad, R. W. Zuhl, and J.F. Zibrida, “The Effects of Biocides on Deposit Control Polymers,” AWT 2000 Annual Convention, Oct-2000, Honolulu, HI (2000).

9. Z. Amjad and R. Zuhl, “The Influence of Water System Impurities on the Performance of Deposit Control Polymers as Particulate Dispersants,” AWT 2001 Annual Convention, Oct 9-13, Dallas, TX (2001).

10. R. W. Zuhl, Z. Amjad, and W. F. Masler, “A Novel Polymeric Material for Use in Minimizing Calcium Phosphate Fouling in Industrial Water Systems,” *Journal of the Cooling Technology Institute*, Vol. 8 (2), Houston, TX (1987).

11. B. P. Boffardi and G. W. Schweitzer, “Advances in the Chemistry of Alkaline Cooling Water Treatment,” CORROSION/85, Paper No. 132, NACE International, Houston, TX (1985).

12. Richard H. Ashcraft, “Scale Inhibition under Harsh Conditions by 2-Phosphonobutane-1,2,-4 tricarboxylic Acid,” CORROSION/85, Paper No. 123, NACE International, Houston, TX (1985).

13. Z. Amjad and R. Zuhl, “A New Look at Industrial water System Fouling Caused by the Interaction of Anionic Deposit Control Agents and Cationic Water Treatment Chemicals,” CORROSION/2002, Paper No. 02401, NACE International, Houston, TX (2002).

14. W. Griffith and S. D. Roberts, “Inhibition of Calcium Sulfate Dihydrate by Phosphonic Acids – Influence of Inhibitor Structures and Solution pH,” Paper No. SPE 7862, Society of Petroleum Engineers (1979).

Table 1
Non-Polymeric Scale and Deposit Control Agents (Phosphonates and Polyphosphates) Evaluated

Acronym	Chemical Name	Molecular Weight
HEDP	1-hydroxyethylidine -1,1-diphosphonic acid	206
AMP	Amino tris(methylene phosphonic acid	299
PBTC	2-phosphono butane 1,2,4-tricarboxylic acid	270
TKPP	Tetra potassium pyrophosphate	330
STPP	Sodium tripolyphosphate	368

Table 2
Polymeric Inhibitors Evaluated

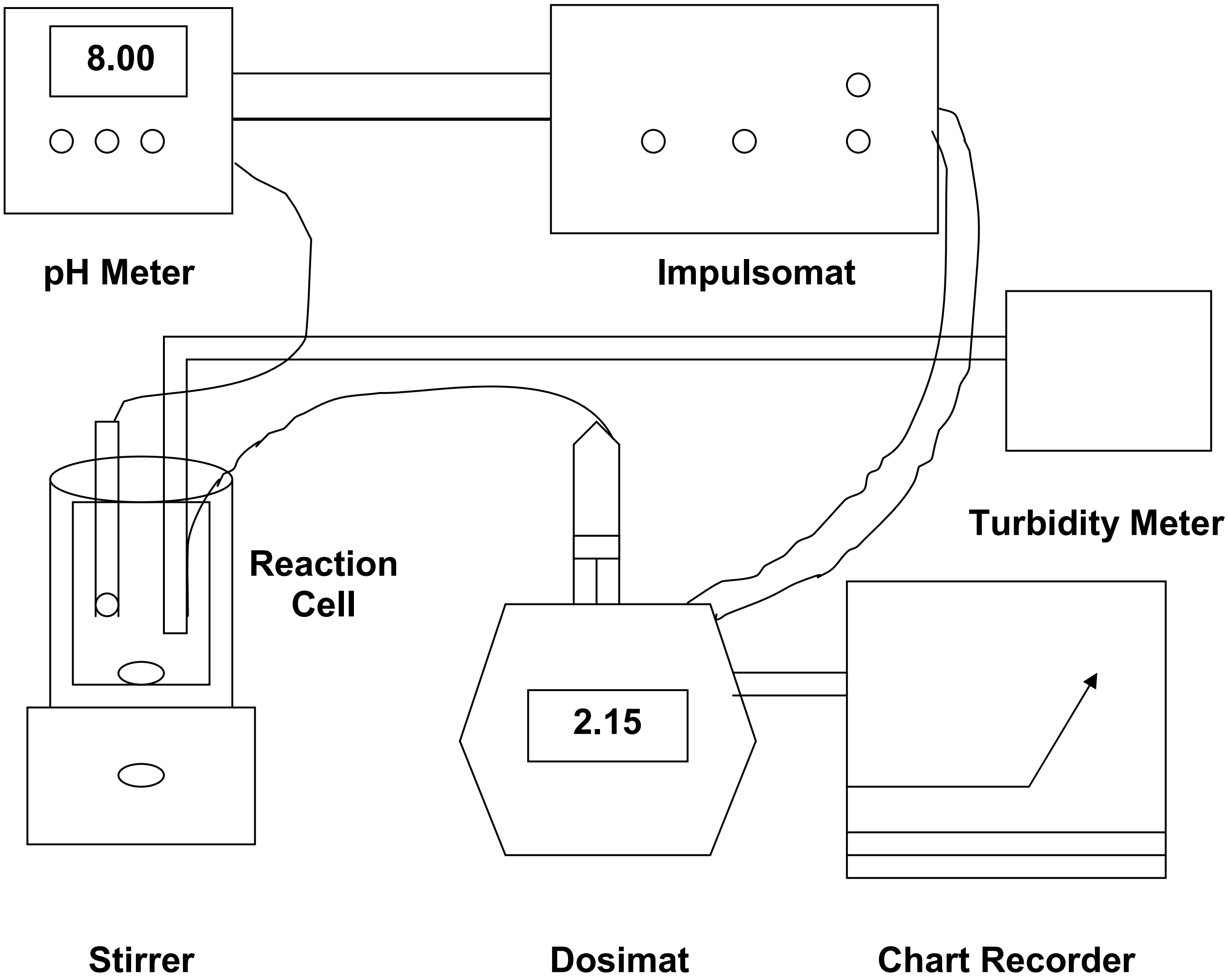
Acronym	Chemical Type	Mol. Wt.	Notes**
PAA1	Poly(acrylic acid)	1,600	L, Exp
K752*	Poly(acrylic acid)	2,000	L, SP
K732*	Poly(acrylic acid)	6,000	L, SP
K7028*	Poly(acrylic acid)	2,300	L, WP
K7058*	Poly(acrylic acid)	7,300	L, WP
K7600N*	Poly(acrylic acid)	120,000	L, WP
K702*	Poly(acrylic acid)	345,000	L, WP
PAA8	Poly(acrylic acid)	4,500	C
PAA9	Poly(acrylic acid)	2,600	C, SP
PAAP	Poly(acrylic acid) with phosphinate groups	N/A	C
PMA	Poly(maleic acid)	<4,000	C
PAA/MA	Poly(acrylic acid/maleic acid)	2,800	C
PMCP	Poly(maleic acid/ethyl acrylate/vinyl acetate)	N/A	C
K775*	Poly(acrylic acid/sulfonic acid)	<20,000	L
AA/SA1	Poly(acrylic acid/sulfonic acid)	<20,000	C
AA/SA2	Poly(acrylic acid/sulfonic acid)	<20,000	C
PABC	Poly(acrylic acid/B/C)	<20,000	C
PASN	Poly(acrylic acid/sulfonic acid/substitute acrylamide)	<20,000	C
K797*	Poly(acrylic acid/sulfonic acid/sulfonated styrene)	<20,000	L
K798*	Poly(acrylic acid/sulfonic acid/sulfonated styrene)	<20,000	L
PPC	Proprietary polycarboxylate	N/A	C

* Lubrizol Advanced Materials, Inc. (formerly Noveon, Inc.) Carbosperse™ (formerly Good-Rite) K-700 polymer.

** Key to Notes:

Exp = Experimental polymer
L = Lubrizol Advance Materials, Inc.
C = Competitive polymer
SP = Solvent polymerized polymer
WP = Water polymerized polyacrylate

Figure 1
Experimental Set-Up for Turbidity Titrations



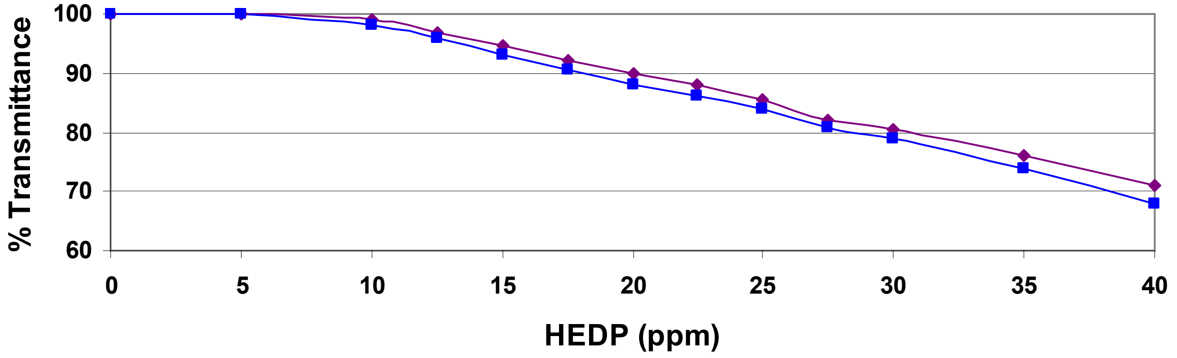


Figure 2. Ca-HEDP Precipitation vs. HEDP Concentration
(250 mg/L Ca, pH 9.5, 25°C)

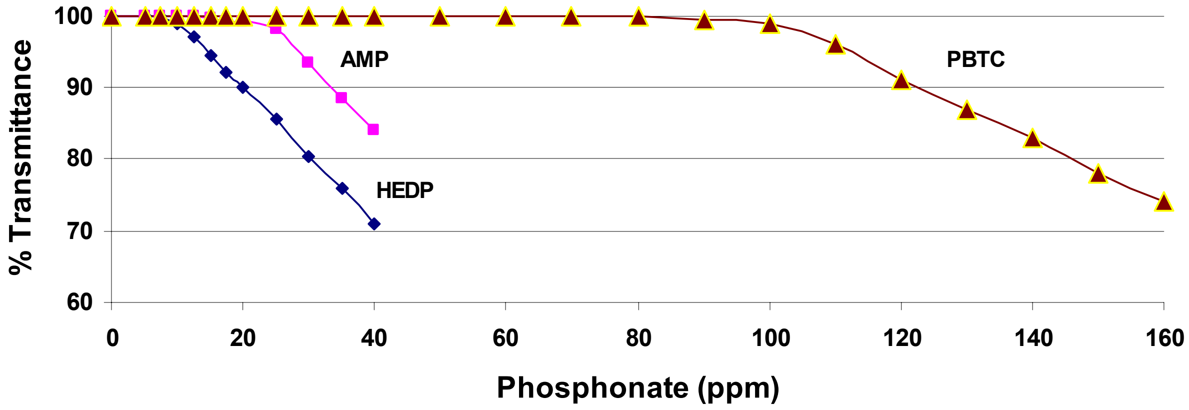


Figure 3. Calcium Phosphonate Precipitation vs. Phosphonate Concentration (250 mg/L Ca, pH 9.5, 25°C)

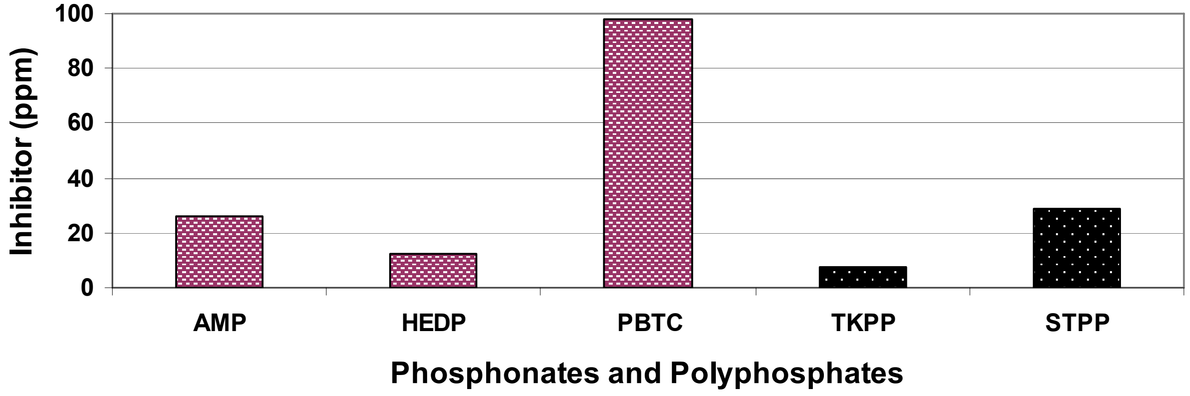


Figure 4. Calcium Ion Tolerance of Phosphonates and Polyphosphates (250 mg/L Ca, pH 9.5, 25°C)

Figure 5. Effect of Terpolymer (K798) Dosage on Ca-HEDP Precipitation (250 mg/L Ca, pH 9.5, 25°C)

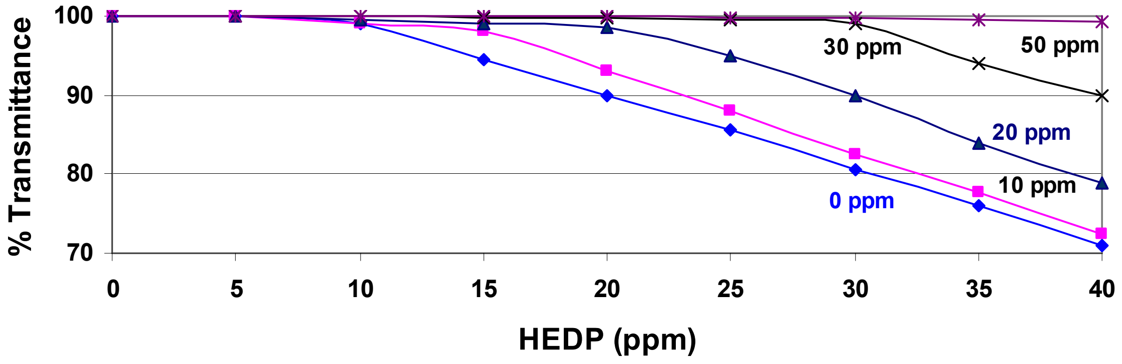


Figure 6. Ca-HEDP Inhbition by Various Polymers (250 mg/L Ca, 40 ppm HEDP, 50 ppm polymer, pH 9.5, 25°C)

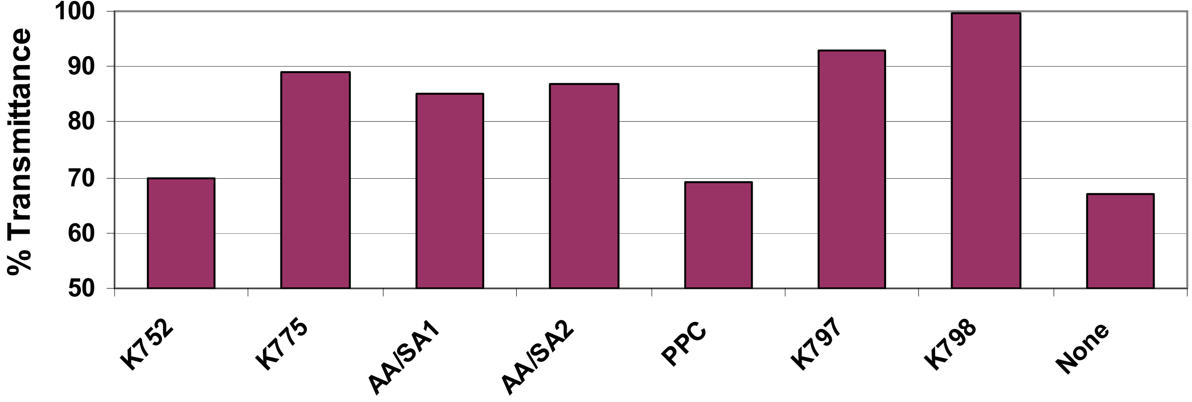


Figure 7. Ca-Ion Tolerance of Homopolymers (1,000 mg/L Ca, pH 9.5, 25°C)

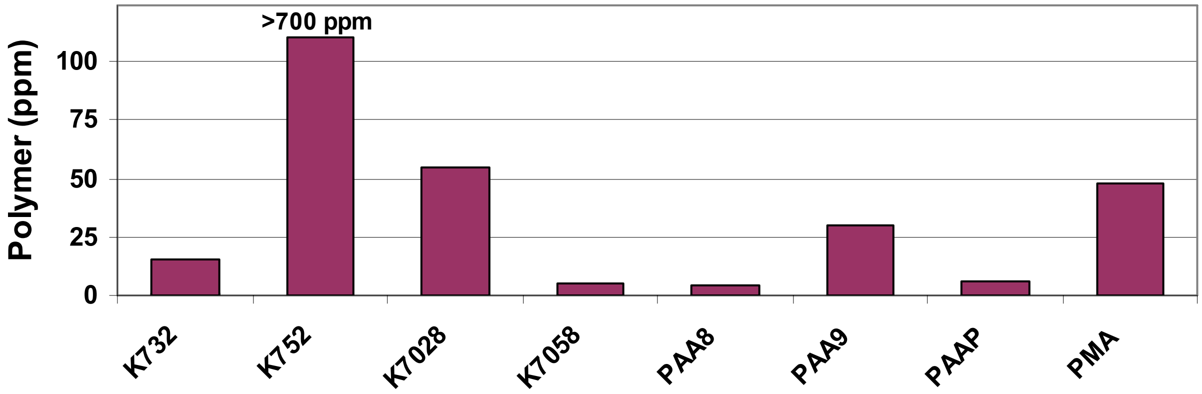


Figure 8. Calcium Ion Tolerance of Homopolymers, Copolymers, and Terpolymers (1,000 mg/L, pH 9.5, 25°C)

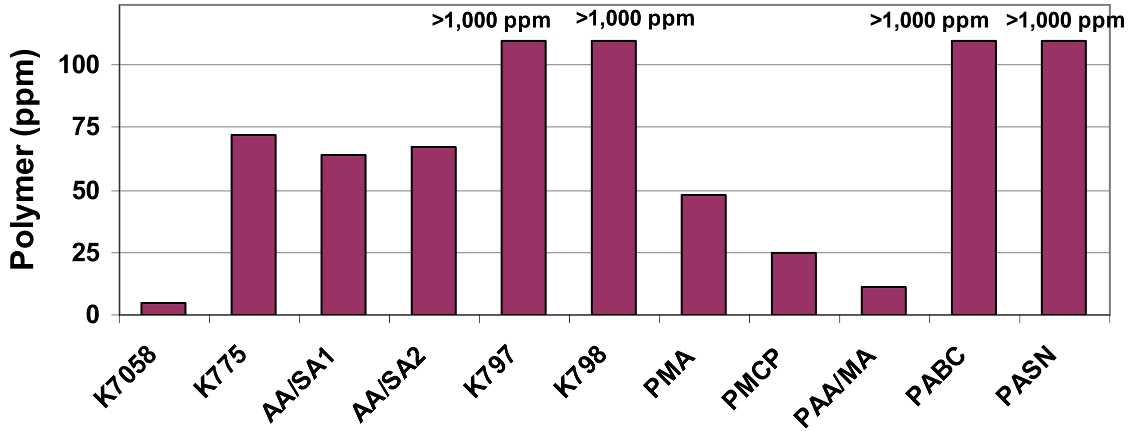


Figure 9. Calcium Ion Tolerance vs. PAA Molecular Weight and Polymerization Process

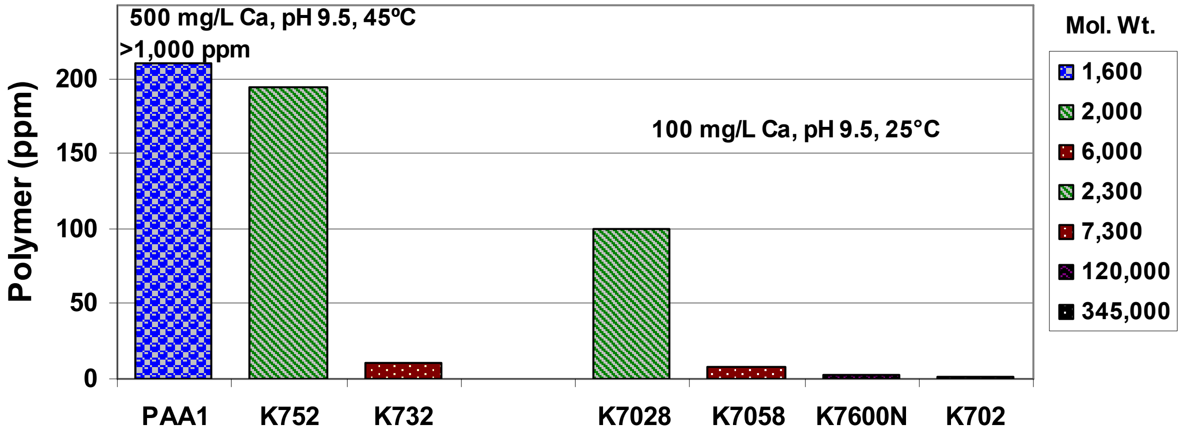


Figure 10. Effect of Solution pH on Ca-Inhibitor Precipitation (500 mg/L Ca and 25°C)

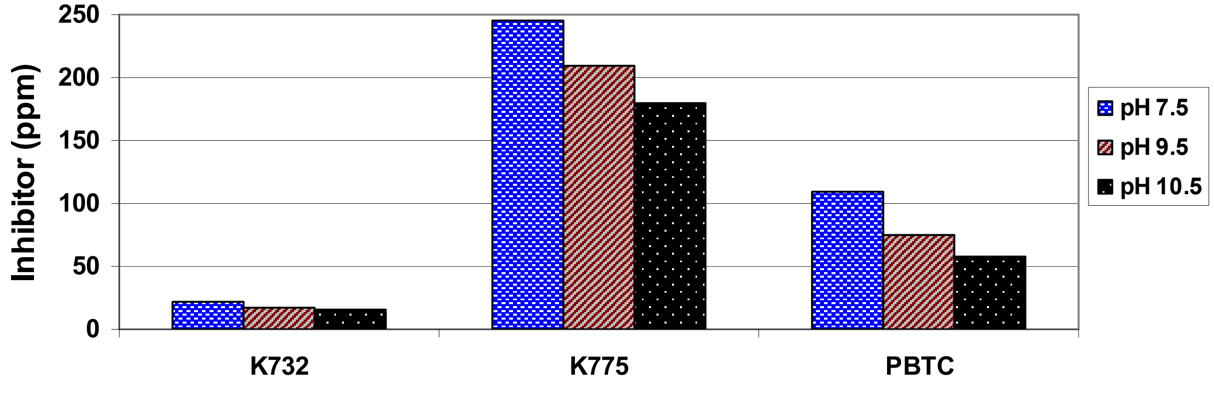


Figure 11. Calcium - Inhibitor Precipitation at Various Temperatures (500 mg/L Ca and pH 9.5)

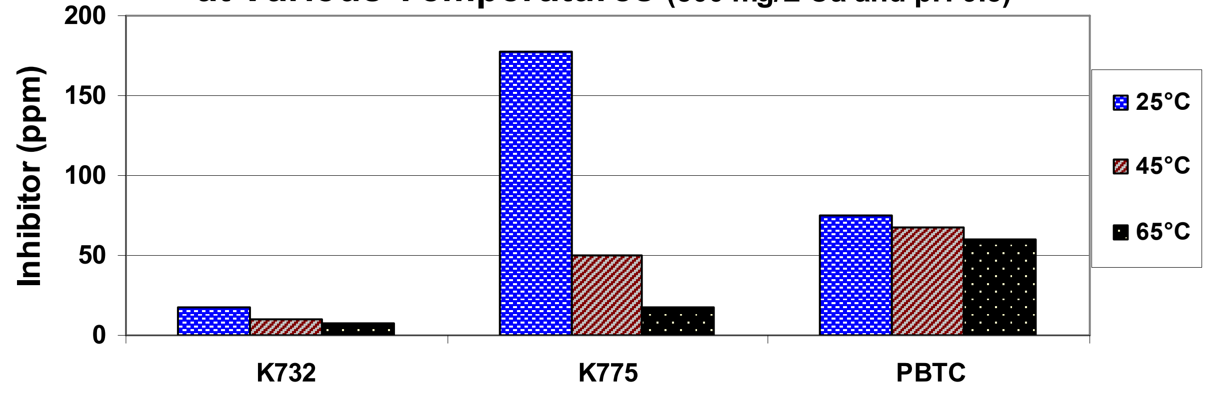


Figure 12. Effect of NaCl Conc. on Ca-Inhibitor Precipitation (500 mg/L Ca, pH 9.5, 25°C)

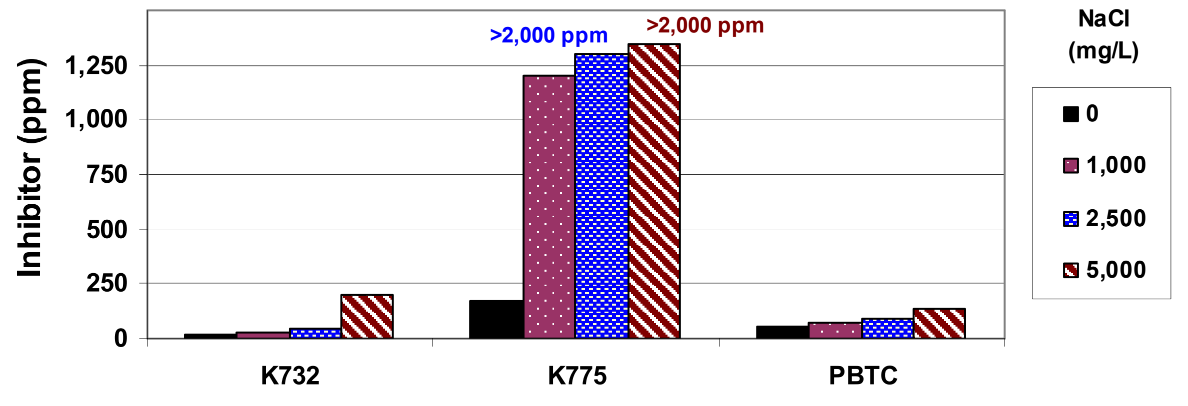


Figure 13. Effect of Calcium Ion Concentration of Ca-Inhibitor Precipitation (pH, 25ºC)

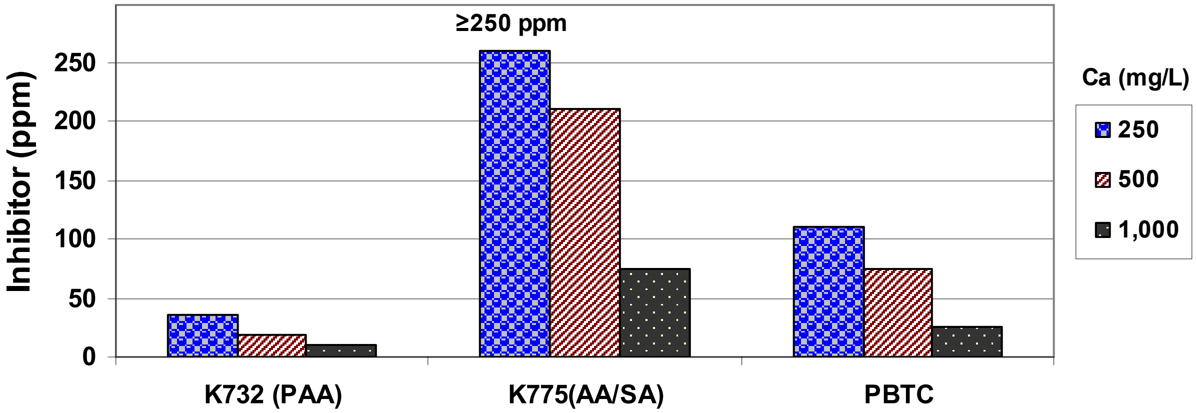


Figure 14. Divalent Cation-PAA Precipitation
(250 mg/L divalent cation, pH 9.5, 25°C)

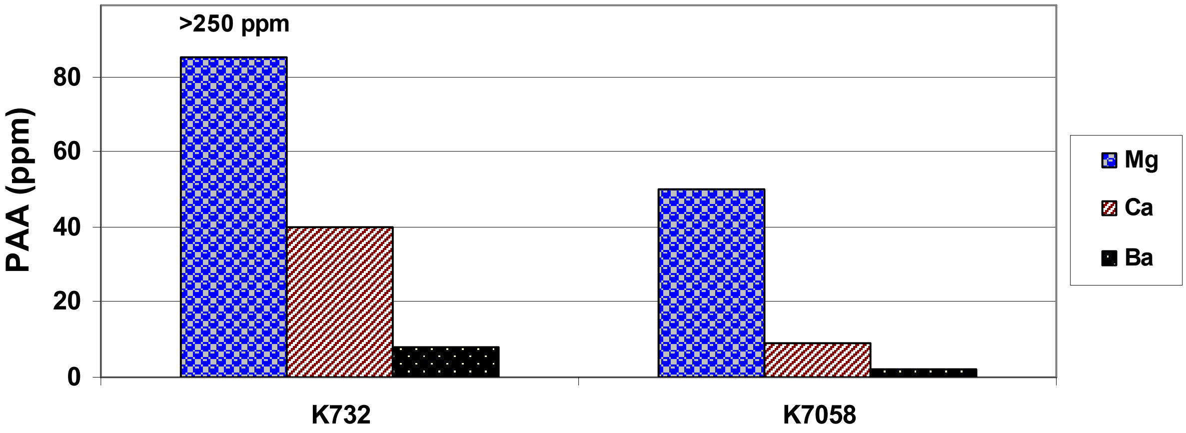
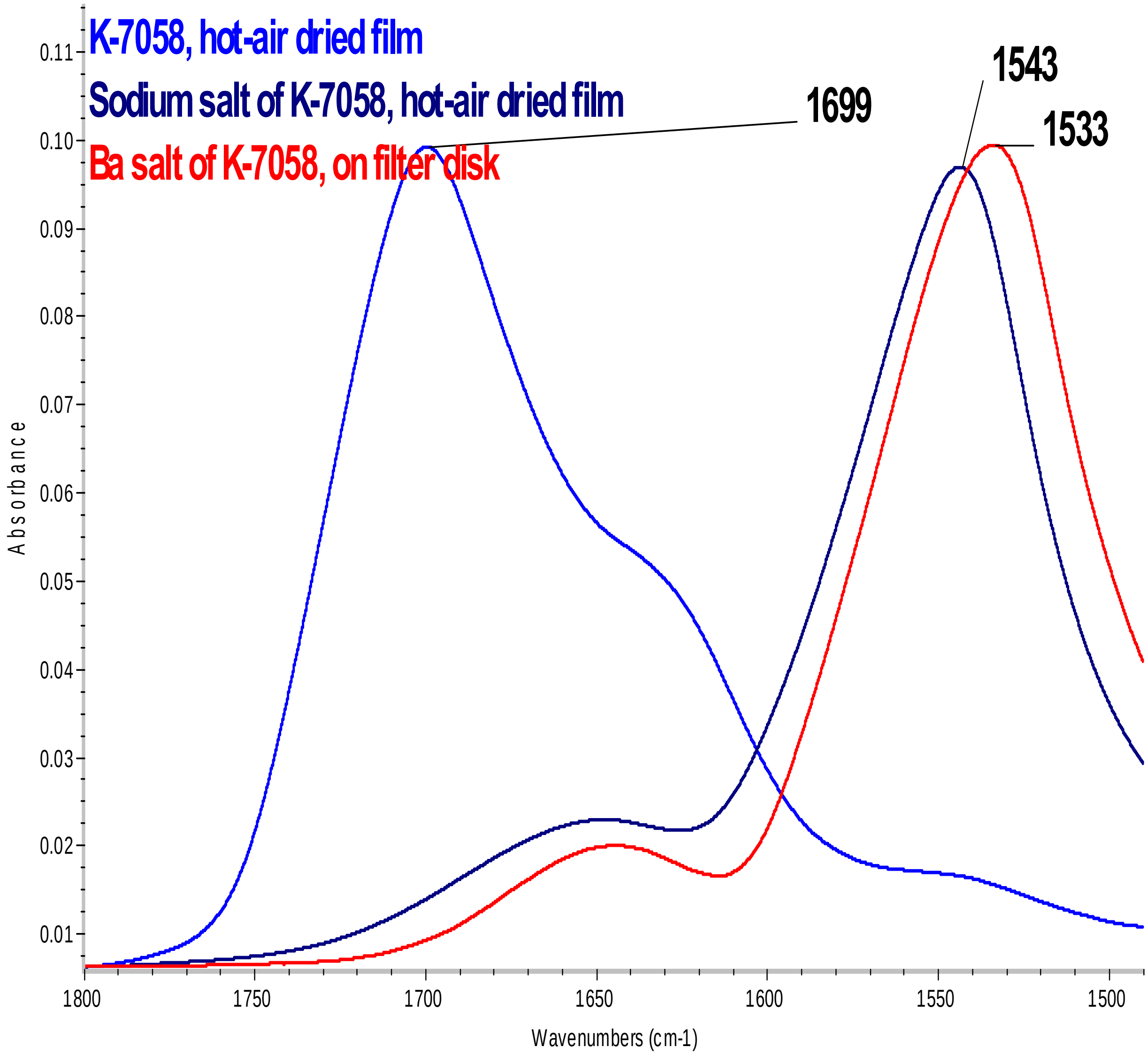


Figure 15. FT-IR Spectra of K-7058, K-7058 (Na), and K-7058 (Ba) Salts



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