Purposely Built - Introduction of a New Copolymer for Multifunctional Applications

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Abstract:

The use of synthetic polymers for mineral scale control in water treatment applications has progressed over the past 50 years. However, most developments occurred towards the onset of widespread use of synthetic polymers in our industry. Early polymers comprised of primarily carboxylate functionality such as polyacrylic acids, polymethacrylic acids, and polymaleic acids and their salts. The 1970's saw the development and use of copolymers that incorporated sulfonation and, separately, non-ionic moieties. This was further advanced in the late 1980's where all three functional types (carboxylate, sulfonate, non-ionic) were combined in a single copolymer in an effort to leverage functionality contribution from each monomer type. Over the past 30+ years, new polymer development has largely been variations upon this theme of the use of these three functionality types where incremental benefits have been realized. However, most of these benefits have largely been defined by the additive suppliers based upon narrow functionality targets without specific thought of formulation and field use implications. The intent of this paper is to introduce a new polymer that has been purposely designed to take advantage of industry learnings, post launch feedback from field use of incumbent technologies, and intentional structure function design. The paper will provide useful formulation and performance data to the AWT membership and provide comparisons of the new polymer to commonly utilized polymers using both bench top and pilot testing.

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Dr. Michael Singh is Senior Research Consultant at Eye-Dale Limited based in Bradford, UK. Dr. Singh has served in research leadership roles at Allied Colloids, Ciba Specialty Chemicals, BASF and International Specialty Products prior to joining Eye-Dale. Dr. Singh has over 39 years' experience in research. His work includes design, analysis and synthesis of organic intermediates, monomers, and polymers for use in water treatment, papermaking, textiles, agriculture, paints and coatings, pharmaceutical, personal care, construction, and oilfield applications. Dr. Singh holds multiple patents and has presented academic papers on monomer and polymer synthesis, polymerization processes, product design and end use applications. Dr. Singh received his BSc and Ph.D. in Chemistry from the University of Manchester Institute of Science and Technology.

It all Starts with Hexavalent Chromium

In 2015 we presented a paper to the AWT membership titled "*Rules of Three - Simplifying the Selection of Polymers.*"[1] The purpose of this paper was to simplify the selection of polymers out of the vast offerings in the water market. In this paper, we learned that carboxylate, sulfonate, and/or non-ionic monomers represent the overwhelming majority of building blocks utilized to manufacture polymers for mineral scale control. The 2015 paper did not discuss the historical progression of these polymer types. It is important to understand that prior to the 1970's, the predominant use of synthetic polymers in process applications were polycarboxylates such as polyacrylic acid or polymethacrylic acid. These types of polymers were utilized in boilers as dispersants and sludge conditioners and in cooling water for solids dispersants. In cooling water applications, mineral scale control was rarely needed due to the use of highly effective hexavalent chromium (Chromate or Cr^{6+}) for mild steel corrosion control. The use of hexavalent chromium allowed the water treater to have an essentially worry-free approach to controlling mild steel corrosion while operating at a low circulating water pH between 6.0-7.0 to avoid mineral scale formation. Polymers, when needed, were utilized simply to move solids in the system or when the sulfuric acid addition for pH control was sufficient to cause supersaturation and resulting precipitation of calcium, barium, or strontium sulfate. Generally, low molecular weight polycarboxylates such as polyacrylic and polymaleic acids that have an average molecular weight (M_w) of <3,000 Daltons and 1,000 Daltons respectively were and are highly effective as sulfate inhibitors while polycarboxylates such as polyacrylic acids and polymethacrylic acids with a M_w ranging from 4,500 – 30,000 Daltons are shown to be highly effective for dispersion and solids control. The structures for these carboxylate monomers are shown as follows:

Acrylic Acid   Maleic Acid   Methacrylic Acid
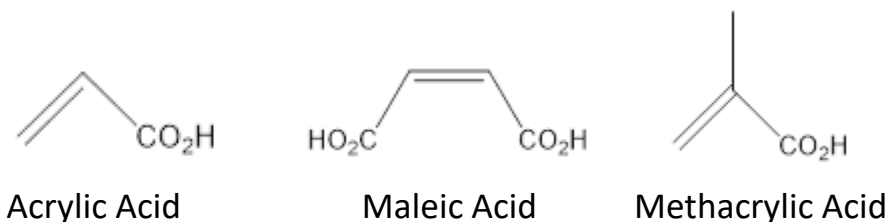
While not fully restricted by EPA rule 40 CFR.68 until 1990[2], the elimination of hexavalent chromium in cooling water began as early as the 1970's. One noted reference by Los Alamos National Laboratories in New Mexico cites the elimination of chromium in cooling systems by 1972.[3] The elimination hexavalent chromium and the general ability to operate systems at neutral or lower pH ranges has transformed how cooling water is treated and created both a need for non-chromate corrosion inhibitors a need great need for the additional polymer functionalities.

Ultimately, we know and live the post chromate story where higher circulating water pH ranges are necessary to mitigate mild steel corrosion potential while strongly increasing the potential for mineral scales such as calcium carbonate and calcium phosphate. However, before non-chromate and additional polymer functionalities are more fully explored, it is important to examine the interrelationship between mineral scale and mild steel corrosion. While corrosion can influence the formation and control of mineral scale and deposition of mineral scale can exacerbate corrosion, there is not a direct relationship between scale formation and the observed rates of corrosion. As an example, Figure 1 depicts a relationship between mild steel corrosion rate in mils/year, mpy (red line) and calcium carbonate scaling potential using LSI (black line). Most experienced water treatment

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[1] Rules of Three - Simplifying the Selection of Polymers, Michael L. Standish Radical Polymers – 2015 AWT Annual Convention, Nashville TN.

[2] https://www.law.cornell.edu/cfr/text/40/749.68#:~:text=Inhalation%20of%20hexavalent%20chromium%20air%20emissions%20increases%20the,heating%2C%20ventilation%2C%20and%20air%20conditioning%20or%20refrigeration%20systems.

[3] https://n3b-la.com/chromium/

professionals would agree, as a general rule, the potential for corrosion in cooling water systems decreases as the potential for calcium carbonate formation increases. While this is mostly true, we know that the Langelier Saturation Index (LSI) or more sophisticated saturation calculations are devoid from any inputs regarding corrosion. Additionally, these calculations only measure the tendency for scale formation and do not act as direct predictors of corrosion rates.

Figure 1 does provide an empirical relationship relative to pH where the potential for mild steel corrosion is reasonably decreased with increasing pH and the potential for calcium carbonate precipitation is increased substantially with increasing pH.

As we know, LSI is calculated by subtracting the saturation pH (pH in which the water will neither precipitate or dissolve calcium carbonate) from the measured system pH where:

$$LSI = pH - pH_s$$

We can take a very simplistic example of a water with a saturation pH (pH_s) of 6.5 and compare the scaling potential of that same water in a chromate-based system versus a non-chromate-based treatment. In this example, we may find that our chromate-based treatment effectively controls mild steel corrosion at a pH of 6.5 or above while our non-chromate-based treatment requires that we mitigate corrosion potential by operating the system at pH 8.5 or above. The comparative LSI calculations are as follows:

<div align="center">

Chromate-Based
LSI = 6.5 – 6.5 = 0
Water is Not Scaling for Calcium Carbonate

Non-Chromate-Based
LSI = 8.5 – 6.5 = +2.0
Water is Moderately to Highly Scaling for Calcium Carbonate

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Figure 1- LSI versus Mild Steel Corrosion Rate

Empirical Relationship Between Scale and Corrosion
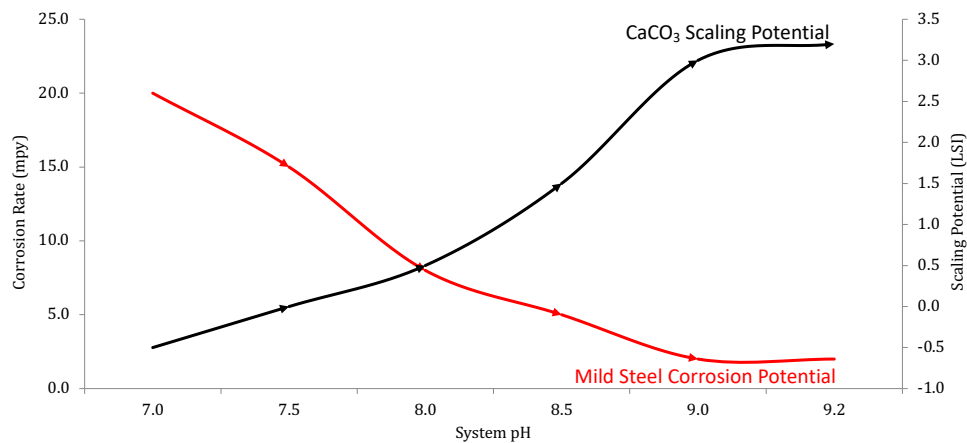
The primary point here is that when chromate was eliminated as a mild steel corrosion control additive, three main changes occurred in the industry:

- Cooling Water Circulating Water pH Ranges Increased to Mitigate Mild Steel Corrosion.
- Non-Chromate-Based Corrosion Inhibitors for Mild Steel were Required.
- New Polymer Functionalities were Needed to Stabilize the Corrosion Inhibitors AND Control Additional Mineral Scale.

Phosphates and Zinc – We Can Make This Work (with Adjustments)

The elimination of hexavalent chromium required a different approach to mild-steel corrosion control. If we look at today's toolbox for mild steel corrosion control in cooling water applications, we find a relatively short list of effective options. An overview list of the options is listed below. For the purposes of this paper, we will focus upon phosphorous and zinc chemistry with a full description and performance of these materials available in the 2018 AWT Paper titled "*A Survey of Phosphorous-Free Corrosion Inhibitors.*" Typical mild-steel corrosion inhibitors that are employed today include:

- Phosphorous Chemistry
    - Orthophosphate
    - Polyphosphates
    - Phosphonates
- Transition Metals
    - Zinc
    - Molybdenum
    - Tin
- All Organic
    - Organic Acids
    - Filming Amines
    - Polymeric
    - Azoles

While each of these technologies have advantages and disadvantages, the use of phosphorous chemistry has become the dominant approach to controlling corrosion in most industrial cooling systems. Where allowed, phosphorous chemistry has been paired with zinc to deliver highly successful results. The reason for this is efficacy and cost. Inorganic phosphates, polyphosphates and zinc are extremely low cost, have defined and proven mechanisms of action, and are highly efficacious as mild-steel inhibitors under neutral to alkaline conditions. In the 2018 paper presented to the AWT membership our team included a summary of phosphorous based corrosion inhibitors.[4] Basic mechanisms of these materials are described in this paper as follows:

Ortho-phosphate is a passivating, anodic inhibitor that reacts with ferric iron at the metal surface to form ferric phosphate dihydrate. This protective layer of ferric phosphate helps to reinforce the natural ferric oxide film and prevent further anodic reactions from occurring.[5] Ortho-phosphate forms a tenacious film that directly protects the corroding site, is easily repaired, and can be used in economical concentrations.[6] Effective dosages of ortho-phosphate usually fall in the range of 5-15mg/L as o-PO$_4$.

[4] A Survey of Phosphorous-Free Corrosion Inhibitors, Michael L. Standish, and Chelsea Farmer -Radical Polymers, Eric Ward-Consultant, and Rob Ferguson – French Creek Software, 2018 AWT Annual Convention

[5] Rey, S.P. "Carbon Steel Corrosion Control in the Past Twenty Years and in the New Millennium," The Analyst: Summer 2001

[6] Handbook of Industrial Water Treatment, Chap. 24, "Corrosion Control-Cooling Systems," Suez/GE Power & Water, Water Process Technologies Webpage

Polyphosphates are commonly used as precipitating, cathodic inhibitors that precipitate with calcium at cathodic sites, where the pH is high. This film forms a barrier that prevents dissolved oxygen from reaching the metal surface to accept the electrons generated by the oxidation of the metal. Their protective films are not as tenacious as passive films and do not repair themselves as quickly.[3] they can be good inhibitors for both steel and yellow metal pH values >7.5 and >50mg/L Ca.

Zinc has been used heavily as a corrosion inhibitor for many years. It acts as a cathodic, precipitating inhibitor by precipitating a film of zinc hydroxide or zinc hydroxycarbonate at cathodic sites where the pH is high. Zinc is not very effective when used alone but is synergistic with other inhibitors.[4] It has been used successfully for many years in combination with phosphorous-based chemistries, providing a good corrosion inhibitor blend of anodic and cathodic protection. Similar to calcium carbonate, zinc requires stabilization to prevent bulk precipitation in the process water; however, over stabilization can prevent the formation of the protective film.

Chromates Are Out – Sulfonated Polymers Are In!

Elimination of chromate and substitution with phosphate, polyphosphate, and zinc approaches have significant implications on how water must be treated. Specifically, these non-chromate approaches are not as effective. As such, cooling water systems that had been operating at pH ranges from 6.0-7.5 are now required to operate at higher pH ranges to help mitigate the rate of mild steel corrosion. Today's typical circulating water pH can range from 7.0-9.2 with >8.0-9.2 being most typical. This change, as illustrated, has a significant impact upon calcium carbonate saturation and the potential for scale formation. This now requires the use of polymers and/or phosphonates for calcium carbonate control. From a polymer standpoint, calcium carbonate control does not require the development of new technologies. At low LSI (<2.0) and Calcite Saturation (<125X), low molecular weight polyacrylic acids (<3,000 Daltons) and or HEDP phosphonate can be utilized. At high LSI (>2.0-3.0) and Calcite Saturation of <225X, polymaleic acid and/or PBTC phosphonate are effective choices. ***The real issue is that polycarboxylates are extremely poor to ineffective for the stabilization of calcium phosphate and zinc.*** This is important for two reasons:

1) Phosphates and Zinc Must Be Stabilized in Cooling Recirculating Waters in Order to be Available as Mild Steel Corrosion Inhibitors.
2) Bulk Water Precipitation of Calcium Phosphate Forms Mineral Scale, Bulk Water Precipitation of Zinc Forms a Deposit.

Essentially, the industry had solved the issue of removing chromate by utilization of increased system pH and the use of phosphates and zinc but did not have in place a polymer technology to manage all of the resulting problems. However, our industry is pretty resourceful, and technology was soon developed to address these issues. For the purposes of this paper, the polymer technologies described are those with wide-commercial use and do not represent all of the different sulfonated polymer types developed for calcium phosphate and zinc stabilization. However, the following overview is believed to represent the primary milestones in the development of sulfonated polymers for these applications.

According to patent records, early uses of 2-acrylamido-2-methylpropane sulfonic acid (AMPS®)[7] copolymers were developed in the mid-1960's by Lubrizol Corporation, Bayer, and Union Carbide.[8] However, Calgon is credited for applying this technology for mineral scale control in the form of copolymers with acrylic acid in 1973 in US Patent 3,928,196. While this patent does not specifically detail the efficacy of copolymers of acrylic acid and AMPS, it does establish the copolymer as a highly effective scale inhibitor for water treatment applications. As we know today, acrylic acid AMPS copolymers are specifically known as industry standard polymers for the effective stabilization of calcium phosphate and transition metals such as zinc. Alternate polymer technologies was developed

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[7] The AMPS Monomer is a registered trademark of The Lubrizol Corporation.

[8] US3506707A (Lubrizol), US3332904(Union Carbide), DE1595658(Bayer AG)

along the same time frame by Betz Laboratories which included copolymers of acrylic acid and hydroxypropyl acrylate (HPA) marketed as Dianodic II™. Dianodic II was marketed as follows: "Betz Dianodic II is a new breakthrough in nonchromate cooling water treatment technology. It is a two-component treatment program featuring a truly effective calcium phosphate inhibitor that permits higher phosphate concentrations necessary for proper mild steel corrosion protection."[9] While this technology was proven highly effective, it had a major disadvantage versus Calgon's acrylic acid copolymers with AMPS.   The hydroxypropyl acrylate component of the Betz polymer was hydrolytically instable when formulated. This resulted in the II in Dianodic II where the non-chromate approach required a two drum treatment. Later, Betz Laboratories developed another alternate technology using a monomer similar in structure to AMPS. This monomer, sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS), was copolymerized with acrylic acid and is claimed to have better hydrolytic stability than either HPA or AMPS. COPS copolymers are still utilized today but are largely specific to Betz (now Veolia).   Chemical structures for these monomers are shown below:

Acrylic Acid   2-acrylamido-2-methyl propane sulfonic acid (AMPS)   Hydroxypropyl acrylate   sodium 1-allyloxy-2-hydroxypropane sulfonate (COPS)
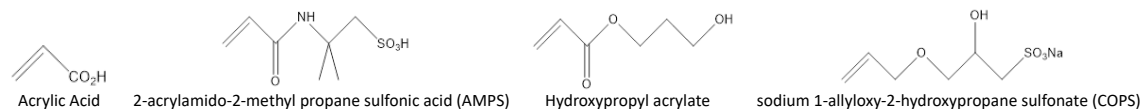
Summarizing the polymer developments to date, we find that acrylic acid copolymers of COPS are largely used by Betz Laboratories and Calgon has pioneered the use of acrylic acid copolymers with AMPS.   As evidenced by Calgon filings with the FDA under 21 CFR 173.310 and current common knowledge, the preferred Calgon polymer has a Mw of ~12,000 – 15,000 and ratio of respective monomers of 60:40 percent by weight. This copolymer, which is still utilized heavily today, was largely produced, and used exclusively by Calgon during this time period. Shortly after, Rohm and Haas Company began producing and selling to the general market an acrylic acid copolymer with an Mw of ~ 4,500 Daltons at a monomer ratio of 75:25 percent by weight. There continues to be much debate about the benefits of both the Mw differences and monomer ratios in these polymers. This paper will explore these differences and report the resulting performance in the experimental section.

Introduction of the "Terpolymer" and Beyond

In 1987, Rohm and Haas Company essentially combined (author's opinion) the good ideas of Betz and Calgon to deliver terpolymers containing carboxylate, sulfonate, and non-ionic (hydrophobic) groups. This is reported in US Patent 4,711,725 (issued 12/08/1987) where the resulting terpolymer is reported to provide "improved phosphate, iron, and zinc stabilization while maintaining their water solubility. Certain preferred polymers also exhibit a high degree of hydrolytic stability at high pH conditions."   This quote and thinking correlate with the known efficacy of acrylic acid copolymers of AMPS for phosphate, iron and zinc stabilization and the known limitations of hydroxypropyl acrylate's hydrolytic stability.   More simply, it was known that acrylic acid/AMPS copolymers (carboxylate/sulfonate) and acrylic acid/HPA copolymers (carboxylate/hydrophobic) were both highly effective for calcium phosphate, iron and zinc stabilization. Rohm and Haas cleverly combined these concepts while using a more hydrolytically stable hydrophobic monomer to develop a best of both worlds type technology. The resulting material, which is widely utilized today with a common composition of a copolymer of acrylic acid, AMPS, and tertiary butyl acrylamide (t-BAM). Monomer structures are shown below:

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[9] Betz Technical Bulletin 787 – Questions and Answers Dianodic II™

Acrylic Acid | 2-acrylamido-2-methyl propane sulfonic acid (AMPS) | Tertiarybutyl acrylamide (t-BAM)
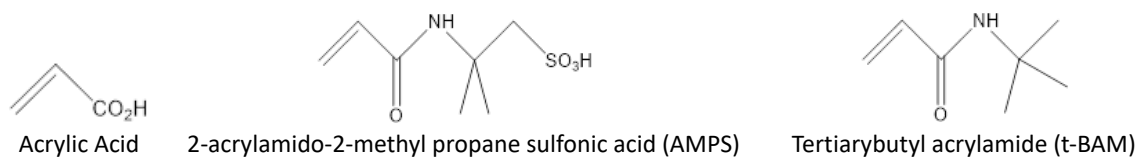
Along the same time period, B.F. Goodrich Company developed terpolymers that included acrylic acid, AMPS, and sodium styrene sulfonate (SSS) covered under US Patent 4,885,097. In addition to a demonstrated high degree of efficacy for calcium phosphate stabilization, this polymer claimed improved metal ion stabilization versus competitive technologies. Monomer structures for this polymer type are shown as follows:

Acrylic Acid | 2-acrylamido-2-methyl propane sulfonic acid (AMPS) | Sodium Styrene Sulfonate (SSS)
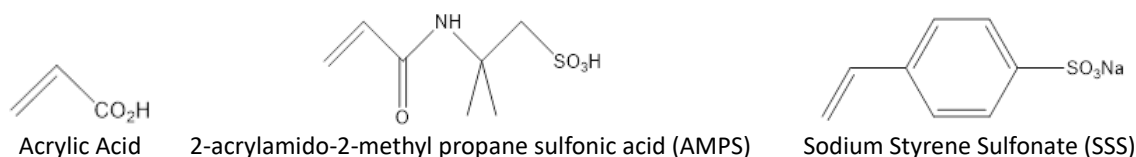
Coincidental with these developments in polymer chemistry, the Association of Water Technologies was founded in 1985.[10] This is important in that this period represented both an expansion of the number of water treatment service companies and the use (read dependance) of AMPS copolymers and terpolymers for phosphate and zinc stabilization. This was also a time where virtually all polymers and building block monomer were produced domestically in the United States. This is critical in that AMPS, at this time, was exclusively manufactured by Lubrizol at their Bayport, TX facility. In the early 1990's there was a supply issue with AMPS monomer from Lubrizol which essentially set the industry scrambling for alternative technologies. This led to the development of non-AMPS containing copolymers containing alternate sulfonate monomers. One primary example of this was developed by National Starch's Alco Chemical Division around 1993-1994. Based on described preferred embodiments in US Patent 5,547,612 which issued in 1995, this polymer applied the same approach of use of carboxylate (acrylic acid), sulfonate (p-sulfophenyl methallyl ether (SPME) and sodium methallyl sulfonate (SMS), and hydrophobic (methyl methacrylate (MMA). The patent reports that "the inventive polymers have been found to be as effective, and in some cases, more effective, in the inhibition of calcium phosphate scale formation and deposition than commercial water treatment polymers prepared from acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid monomer." Monomer structures for this polymer are presented below:

Acrylic Acid | p-sulfophenyl methallyl ether (SPME) | sodium methallyl sulfonate (SMS) | methyl methacrylate

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[10] https://www.awt.org/join/membership-info/
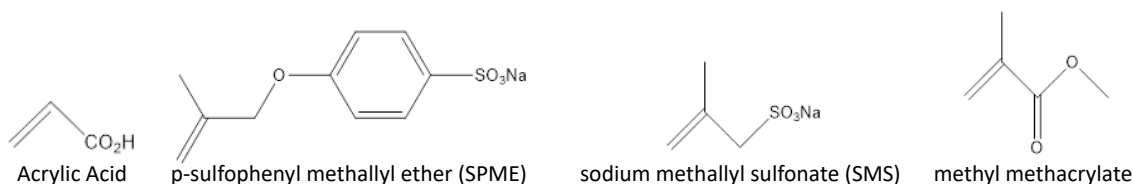
Wrapping Up History

Looking through the rear-view mirror, we can observe that a series of events over about 25 years lead us to the current state of sulfonated polymer offerings into our market. The 1970's initiated the events with the limitation and eventual elimination of the use of hexavalent chromium as a mild steel corrosion inhibitor in cooling waters. This set off a series of events where alternate corrosion inhibitors were required. Phosphate, polyphosphate, and zinc were implemented as primary substitutes and the last piece of the puzzle is put in place as new classes of sulfonated polymers were developed to effectively stabilize these mild steel corrosion inhibitors. This development of polymers introduced the sulfonated monomer AMPS in the 1970's which was further derivatized by copolymerizing with hydrophobic and aromatic monomers in the 1980's. In the 1990's a non-AMPS based polymer was introduced during a shortage of AMPS monomer.

Purposefully Building a New Polymer

The overall objective of this work is to develop a more optimized copolymer incorporating the learnings from previous threads of work in the industry. The obvious thread here is the use of the common polymer functional groups of carboxylates, sulfonates, and non-ionics/hydrophobics. Specifically, we know that polycarboxylates provide good functionality for metal carbonate and metal sulfate scales and provide effective functionality for inorganic solids control. We also know from the history described that the addition of sulfonate functional groups added a dimension of efficacy for stabilization of phosphate and transition metals such as iron and zinc. Empirically, we also know that 2-acrylamido-2-methyl sulfonate monomer (AMPS) is the primary building block for most widely commercialized sulfonated copolymers utilized today and that typical ratios are either 60:40 or 75:25 acrylic acid:AMPS with molecular weights of 12,000-15,000 or 4,500 respectively. Finally, we know that these materials can be enhanced in one way or another by utilization of either hydrophobic monomers or other sulfonate types such as sodium styrene sulfonate.

Building upon this history, our team set out to look at potential optimization of these types of sulfonated polymers. In this work, we examined several critical factors such as % sulfonated monomer, polymer molecular weight (Mw), use of a Functional Polymerization Aid (FPA) and incorporation of one of three distinct hydrophobic monomers. We judged the impact of these changes by looking at calcium phosphate stabilization. Table 1 provides an overview of the leading candidates from this research project.

Table 1: Summary of Leading Candidates

| Sample ID	Carboxylate	Sulfonate	Hydrophobe A	Hydrophobe B	Hydrophobe C	FPA	Mw
RPX-3377	Moderate	Highest	Yes	No	No	High	<5,000 Daltons
RPX-3378	Moderate	Highest	Yes	No	No	High	<5,000 Daltons
RPX-3379	Moderate	Highest	Yes	No	No	Moderate	5,000-10,000 Daltons
RPX-3406	High	Highest	No	No	No	Moderate	5,000-10,000 Daltons
RPX-3425	Moderate	Highest	No	No	Yes	Moderate	<5,000 Daltons
RPX-3428	High	Highest	No	No	No	Moderate	5,000-10,000 Daltons
RPX-3432	Moderate	Highest	No	No	Yes	Moderate	<5,000 Daltons
RPX-3438	Moderate	Highest	No	Yes	No	Moderate	5,000-10,000 Daltons
RPX-3440	Moderate	Highest	No	Yes	No	Moderate	5,000-10,000 Daltons
RPX-3536	High	Highest	No	No	No	Low	>10,000 Daltons
RPX-3544	Moderate	Highest	No	Yes	No	Low	>10,000 Daltons
RPX-3546	Moderate	Highest	No	No	Yes	Low	>10,000 Daltons

Experimental Data and Analysis

The original and continued primary purpose of these classes of sulfonated polymers is to stabilize calcium phosphate in cooling water applications. In today's applications, this tends to involve more highly alkaline waters than were widely common once the technology was introduced. For these reasons, we chose a screening method with a high saturation ratio with respect to calcium phosphate. In this method, a solution containing 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}) and 2ppm Ferrous (Fe^{2+}) Iron is treated at dosages of 12 – 30ppm active polymer. The solution pH of the test samples is maintained 8.8-9.0 throughout the duration of the test using a borate buffer. After 18 hours Incubation at 70º C, the samples are filtered using a 0.45-micron membrane and subsequently analyzed for residual phosphate and iron content.

Figure 2 shows data for commercial 75:25 and 60:40 AA:AMPS Copolymers where % phosphate stabilization (y-axis) is compared to dosage of active polymer (x-axis). It can be observed that the 60:40 AA:AMPS shows better stabilization at lower polymer dosages than the lower AMPS containing material. Similarly, Figure 3 compares commercially available polymers comprised of AA:AMPS:t-BAM, AA:AMPS:SSS and AA:MMA:SMS:SPME. The incorporation of hydrophobic monomers is shown to have a particular benefit in further reducing the dosage demand versus the AA:AMPS copolymers.

Figure 2: Calcium Phosphate Stabilization – AA:AMPS Copolymers

Calcium Phosphate Stabilization
Commercial AA:AMPS Copolymers
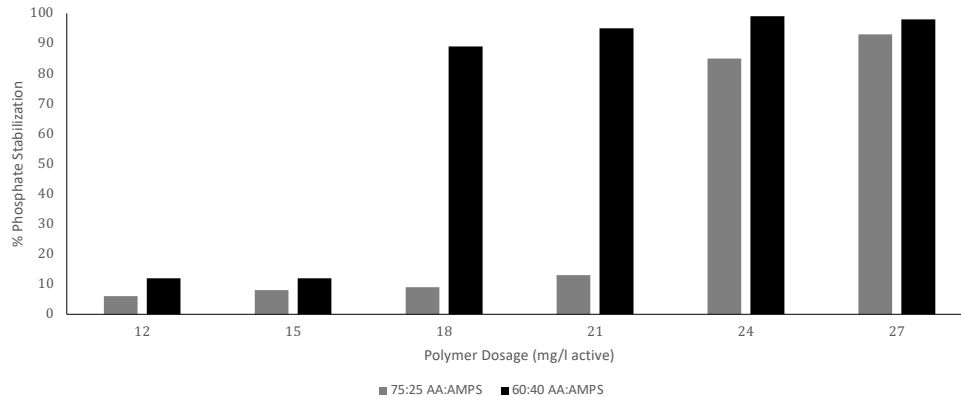
Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 3: Calcium Phosphate Stabilization – Sulfonated Copolymers with 3 or More Monomers

Calcium Phosphate Stabilization
**Commercial Sulfonated Copolymers – 3 or More Monomers**
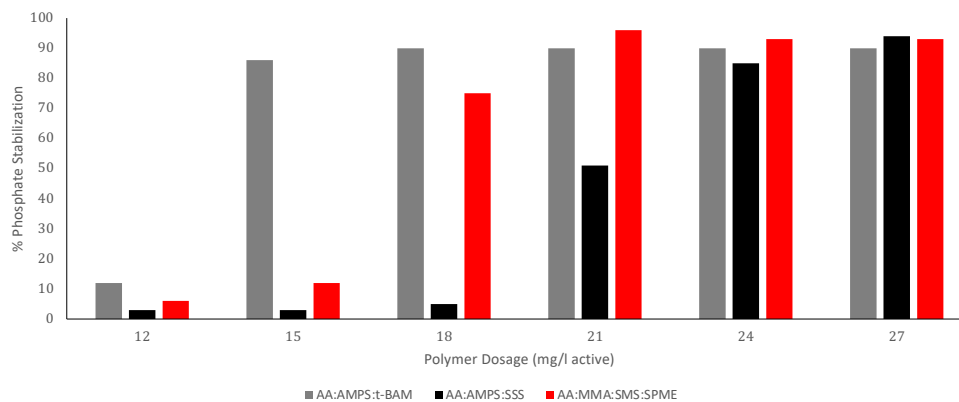
Experimental Conditions – 500ppm Ca (as CaCO$_3$), 10ppm Phosphate (as PO$_4{}^{3-}$), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70° C.

For our experimental work, the leading candidates all had high levels of sulfonated monomer. This criteria was quickly observed in our own testing and could be built upon from the previous research and performance history of 60:40 AA:AMPS versus 75:25 AA:AMPS copolymers. Our work then focused upon optimization of molecular weight, the use of a non-ionic monomer, and potential benefits of incorporation of a Functional Polymerization Aid (FPA). A series of polymers were synthesised, analyzed, and subjected to calcium phosphate scale inhibition testing. It was suggested that a widely used multivariate data analysis technique known as principal components analysis (PCA) and its regression equivalent PLS (projection to latent structures by means of partial least squares analysis) could be employed. PCA and PLS are projection statistical techniques, they breakdown and 'project' the dimensionality of large datasets down to much fewer dimensional plots which show how the variables and samples under study interrelate to each other. In our study we have 13 measured variables, where the experiments can be considered as distributed within this 13th dimensional 'reaction space'.

PCA/PLS regression analysis looks for patterns of best fit (principal components) through this type of reaction space, ideally to pick out the most optimal 2- or 3-dimensional principal component plots to capture as much of the trend patterns as possible. In summary, PCA/PLS methods can project experimental data to lower dimensional spaces for easy inspection to highlight clusters and trends evident in the experimental data, allowing subsequent identification of correlations among key variables and measured responses. PLS regression model coefficients are of interest because they make the model interpretation easier. The size and the sign of the of the coefficients indicate the influence of each model term. Figure 4 shows the PLS regression model coefficients for the % calcium phosphate stabilization response.
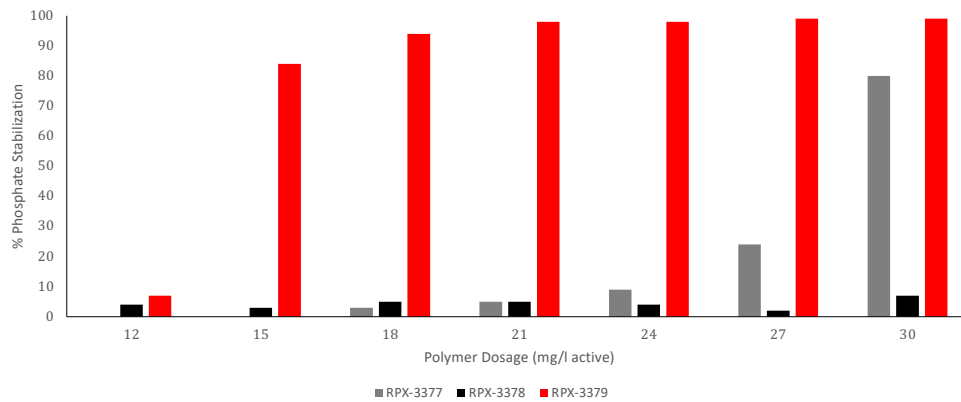
Figure 4: % Calcium Phosphate Stabilization Response Model
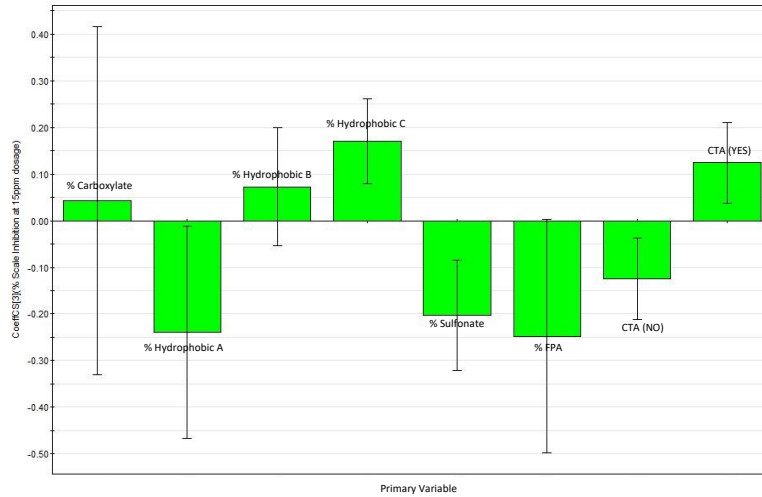
This graphic shows that scale inhibition is predominately affected by % FPA, % Hydrophobic A and % Sulfonate variables which are strongly negatively correlated. Alternately, %Hydrophobic C and the use of a Chain Transfer Agent (CTA) are positively correlated to higher calcium phosphate stabilization. In this dataset, there is no statistically significant evidence that % Carboxylate or % Hydrophobic B are correlated to calcium phosphate stabilization. Figures 5, 6, and 7 present the calcium phosphate stabilization data for the three hydrophobic monomers added compared to polymer with no hydrophobe added in Figure 8.

Figure 5: Calcium Phosphate Stabilization – Hydrophobic Monomer A Incorporation

**Calcium Phosphate Stabilization
Primary Variable - Hydrophobic A**

Experimental Conditions – 500ppm Ca (as CaCO$_3$), 10ppm Phosphate (as PO$_4^{3-}$), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

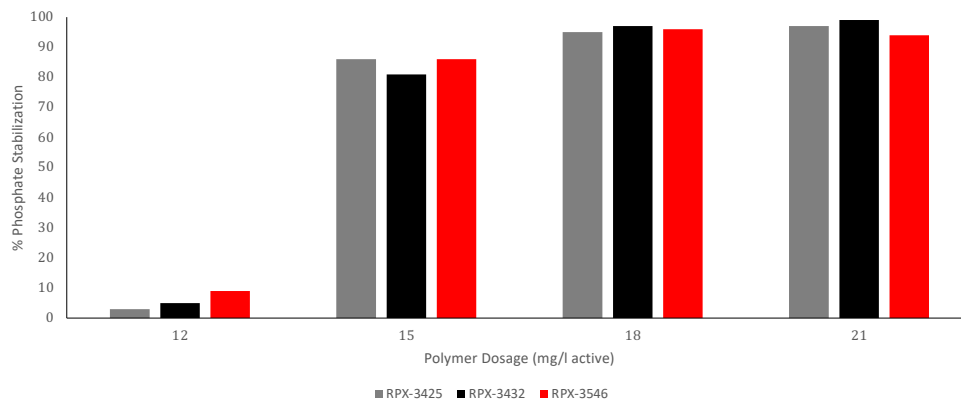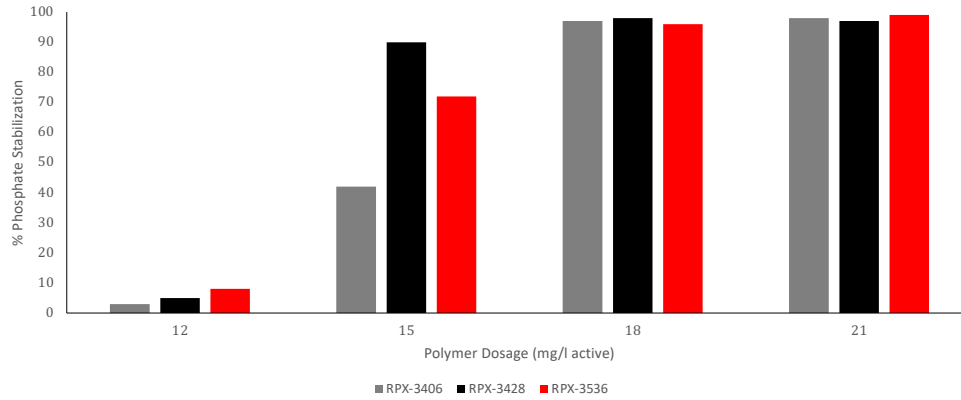Figure 6: Calcium Phosphate Stabilization – Hydrophobic Monomer B Incorporation

Calcium Phosphate Stabilization
Primary Variable - Hydrophobic B
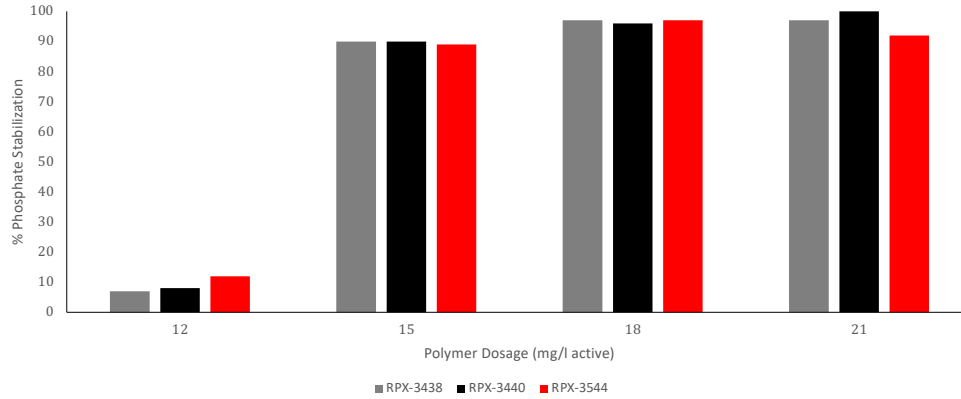
Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 7: Calcium Phosphate Stabilization – Hydrophobic Monomer C Incorporation

Calcium Phosphate Stabilization
Primary Variable - Hydrophobic C

Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 8: Calcium Phosphate Stabilization – No Hydrophobic Monomer Incorporation

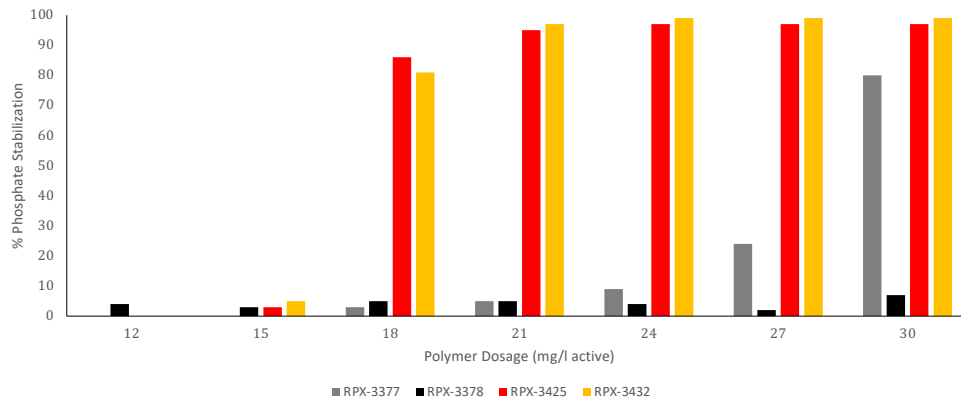**Calcium Phosphate Stabilization
Primary Variable – No Hydrophobe Added**

Experimental Conditions – 500ppm Ca (as CaCO$_3$), 10ppm Phosphate (as PO$_4^{3-}$), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Our work next focused on the impact of average molecular weight (Mw). This is effectively also related to the use of the FPA and CTA which also impact regulation of molecular weight. In figures 9, 10, and 11, we can see the impact of molecular weight where the materials grouped at <5,000 Daltons show relatively poor performance versus polymers >5,000 Daltons.

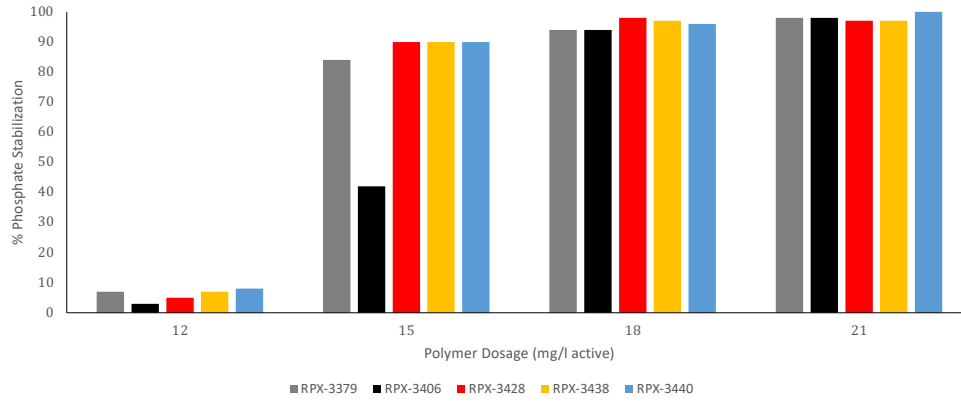Figure 9: Calcium Phosphate Stabilization – Polymers <5,000 Daltons

**Calcium Phosphate Stabilization
Primary Variable – M$_w$ <5,000 Daltons**

Experimental Conditions – 500ppm Ca (as CaCO$_3$), 10ppm Phosphate (as PO$_4^{3-}$), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 10: Calcium Phosphate Stabilization – Polymers 5,000 – 10,000 Daltons
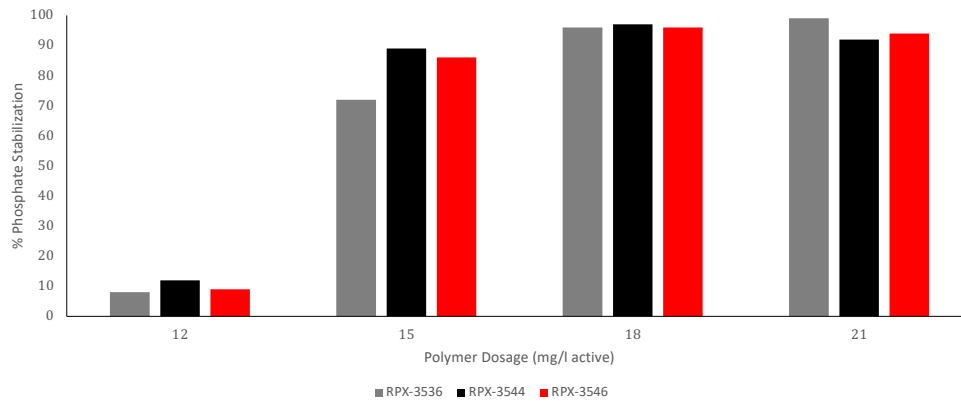
Calcium Phosphate Stabilization
Primary Variable – M_w 5,000-10,000 Daltons

Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 11: Calcium Phosphate Stabilization – Polymers >10,000 Daltons

Calcium Phosphate Stabilization
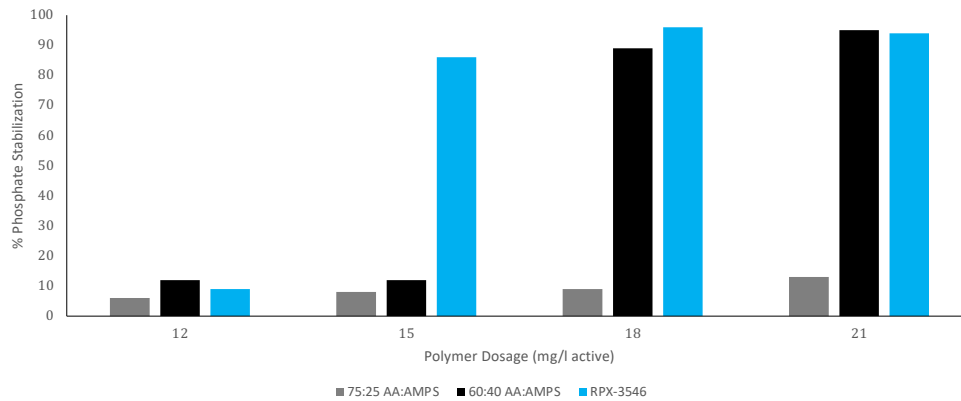**Primary Variable – M_w >10,000 Daltons**

Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Comparison of Leading Candidate to Commercial Materials

From these data, the leading candidate material is RPX-3546 which contains Hydrophobic Monomer C, a low level of FPA, and a molecular weight of >10,000 Daltons.   Compared to 60:40 and 75:25 AA:AMPS copolymers, we can see improved efficacy at 15ppm polymer dosage in Figure 12. Similarly, Figure 13 shows RPX-3546 versus commercially available AA:AMPS:t-BAM, AA:AMPS:SSS and AA:MMA:SMS:SPME copolymers.   RPX-3546 is shown to work better than both AA:AMPS:SSS and AA:MMA:SMS:SPME and comparably to AA:AMPS:t-BAM for calcium phosphate stabilization.

Figure 12: Calcium Phosphate Stabilization – RPX-3546 Versus AA:AMPS Copolymers

Calcium Phosphate Stabilization
RPX-3546 Versus - Commercial AA:AMPS Copolymers

Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Figure 13: Calcium Phosphate Stabilization – RPX-3546 Versus Sulfonated Copolymers

Calcium Phosphate Stabilization
RPX-3546 Versus Commercial Sulfonated Copolymers
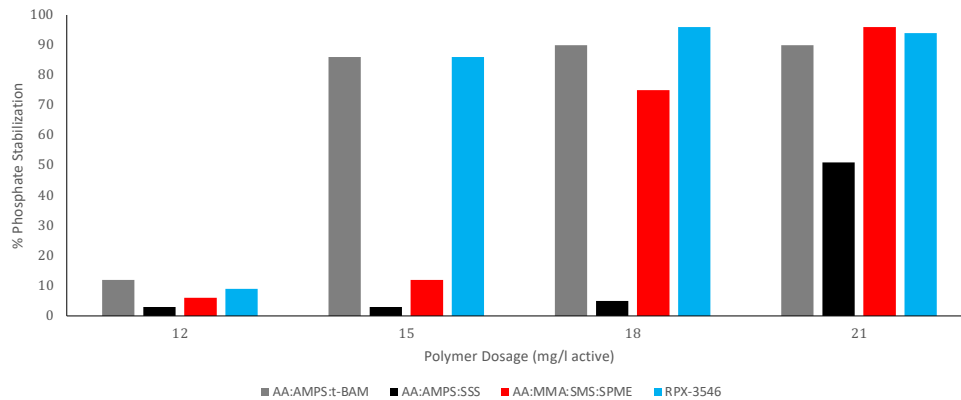
Experimental Conditions – 500ppm Ca (as $CaCO_3$), 10ppm Phosphate (as PO_4^{3-}), 2ppm Ferrous (Fe^{2+}) Iron, pH 8.8-9.0, 18 hours Incubation at 70º C.

Summary and Future Work

The work presented in this paper is limited to evaluation of a range of sulfonated copolymers for calcium phosphate stabilization using a laboratory screening method. This work has led to the development of a new polymer that demonstrates significant improvement of performance versus incumbent commercial products such as 60:40 AA:AMPS, 75:25 AA:AMPS, AA:AMPS:SSS, and AA:MMA:SMS:SPME copolymers. Additionally, the new polymer shows similar performance to industry leading AA:AMPS:t-BAM copolymers. The evaluations have shown that the concentration of sulfonated monomer, incorporation of a specific hydrophobic monomer, polymer molecular weight, and the selective use of FPA can contribute to improved efficacy. Based upon several unique properties of the new polymer, the authors believe that more extensive evaluations will further differentiate this material from all existing materials. Future work will include pilot cooling evaluations, particulate dispersion, iron stabilization testing, pKa comparison, and evaluation of functionality for other mineral scales such as calcium carbonate and calcium sulfate.