Ground Up: Designing New Polymers for Independent Water Treatment Companies

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Abstract: This paper introduces two new polymers to the AWT membership and takes the membership through the process of design, development, and competitive evaluation of the polymers for mineral scale and deposit control. INITIA™ 585 is an Enhanced Poly-Maleic Acid (EPMA) polymer that exhibits exceptional crystal modification properties for calcium carbonate. INITIA™ 205 is a High Performance Sulfonated Polymer (HPSP) designed for calcium phosphate and iron stabilization. The insight into the development of these two new products provides a unique perspective into the primary considerations of monomer selection and ratio tradeoffs, molecular weight optimization, and the balance of performance versus multiple mineral scale types. The paper includes an overview of polymer functionality where structure-function properties of common water treatment polymers are detailed. The concepts of Threshold Inhibition, Crystal Habit Modification, and Particulate Dispersion are defined and applied to laboratory evaluation data for the new polymers for common mineral scales and deposits such as Calcium Carbonate, Calcium Phosphate and Iron. These data are then applied to suggested uses and formulations for cooling water and boiler applications.

About the Author: Michael Standish is founder of Radical Polymers, LLC, a business designed to specifically develop and provide technologies to the independent water treatment community. Mike has over 28 years experience in water treatment additive design, development and evaluation. Prior to forming Radical Polymers, Mike served as Senior Business Manager for International Specialty Products and Global Business Manager for National Starch's Alco Chemical business. Mike has served on the Board of Directors of AWT and holds a BS in Chemistry and Masters in Business Administration from the University of Tennessee at Chattanooga.

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Introduction

An Enhanced Polymaleic Acid (EPMA) and a High Performance Sulfonated Polymer (HPSP) are two new and powerful tools presented to the membership. The products have been specifically designed to deliver unambiguous benefits that allow the user to target specifically desired functionalities that are necessary in controlling today's most difficult scaling challenges.

The intent of this paper is to simplify the somewhat complex topic of polymer mediated mineral scale control by introducing the basic definitions of control mechanisms while providing an overview of polymer functionality. Once equipped with this baseline, the paper introduces the two new and differentiated technologies that are exceptional new tools for the membership's consideration. EMPA demonstrates crystal habit modification properties beyond that of the industry standard polymaleic acid and HPSP is a polymer designed from the ground up to optimize composition and monomer ratios that deliver best in class stabilization for calcium phosphate and iron.

Common Definitions and Mechanisms

One of the most important concepts to understand when selecting an additive for mineral scale control is *Threshold Inhibition*. **Threshold Inhibition is the extension of solubility of an otherwise insoluble salt beyond its saturation limits using an additive at sub-stoichiometric levels.** This concept of sub-stoichiometric functionality is very important and is what differentiates additives such as polymers and phosphonates from materials that function according to strict stoichiometric ratios such as EDTA. There are a few other key aspects of threshold inhibition that are important to recognize. Generally, threshold inhibition is a temporary effect with respect to time. For example, if uninhibited (untreated) water takes 60 seconds to begin to precipitate calcium carbonate in a given set of conditions (i.e. pH, temperature, calcium concentration, carbonate concentration….) and the same water, once treated, extends this time to 1 hour, then inhibition has occurred with respect to time. The extent and duration of threshold inhibition can be related to a number of factors or conditions. These include, but are not limited to:

- Driving Force for Precipitation (i.e. pH, temperature, concentration of scale forming ions)
- Particular Efficacy of the Selected Inhibitor
- Other Water Impurities (both dissolved and suspended)
- Rate of Water Concentration or Evaporation
- Frequency of Additive Dosage

Sequestration is another important function of many polymers and phosphonates. **Sequestration is the complexation of a metal ion such that the ion does not retain its original reactive properties.** Unlike threshold inhibition, sequestration does not have the connotation of either stoichiometry or specific functionality. In other words, sequestration does not describe how or how much of an additive is necessary; rather it describes what happens to the metal ion properties in solution. Phosphonates and polymers such as the ones common for mineral scale control can sequester ions such as calcium, magnesium and barium and prevent them from forming insoluble complexes with compounds such as carbonate and sulfate.

Chelation is an interesting term that is derived from the Greek word "khele" which means crab's claw.[1] A *Chelate* (meaning the system of the compound and the metal ion) is a coordination compound in which a central metal ion such as Ca^{2+} is attached by coordinate links to two or more non-metal atoms in the same molecule, called ligands. Thus, **a *Chelating Agent* is one that "grabs" a metal ion at two or more points within the agent molecule.** From a technical definition, polymers, such as polycarboxylates and sulfonated copolymers act as chelating agents with most muti-valent ions

[1] chelate. (n.d.). Online Etymology Dictionary. Retrieved July 18, 2014, from Dictionary.com website: http://dictionary.reference.com/browse/chelate

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due to the multiple binding sites along the polymer's backbone. However, using common water treatment vernacular, the term chelate tends to imply a more permanent or substantive relationship between the ion and the ligand (i.e. Calcium-EDTA.) In common water treatment terms, chelation also typically refers to stoichiometric relationships between the metal ion and the ligand. So the polymers, of the type discussed here, generally do not meet the common vernacular definition, as their association is generally temporary and their functionality is sub-stoichiometric.

Table 1: Simplified Definitions

Additive Functionality	Simple Definition
Threshold Inhibition	Extension of solubility of an otherwise insoluble salt beyond its saturation limits using an additive at sub-stoichiometric levels.
Sequestration	Complexation of a metal ion such that the ion does not retain its original reactive properties.
Chelation	Formation of a compound in which a central metal ion such as Fe^{2+} is attached by coordinate links to two or more non-metal atoms in the same molecule.
Stabilization	Colloidal Stabilization is where precipitation of a substance occurs but the additive prevents agglomeration of particles beyond 1 micron in size. Stabilization can also be a synonym for sequestration where coordination complexes between the additive and soluble ions or forming crystal lattices are formed and prevention of precipitation is achieved.
Particulate Dispersion	Particulate Dispersion is a suspension of particulates in an aqueous solution. These can be Inorganic (i.e. calcium carbonate), Organic (i.e. biomass) or a mixture of the two.
Crystal Habit Modification	Crystal Habit modification is where a "poison" such as a polymer, phosphonate, or other contaminant disrupts normal formation and produces crystals that either tend to re-dissolve or precipitate in abnormal forms.

Stabilization can be a tricky and controversial topic within the discussion of polymer functionality. The concept of Stabilization can have two meanings with respect to polymer interactions with metal ions: **Colloidal Stabilization is where precipitation in a fluid (water) occurs but the polymer prevents agglomeration of particles beyond 1 micron in size**. These particles are thus stabilized via electrostatic interactions with the polymer and remain suspended throughout the water phase. These sub-micron particles are typically not visible to the naked eye. A notable exception to this is stabilized iron particles, which can be visible due to the orange-brown color associated with most oxidized (Fe^{3+}) iron complexes. Colloidal stabilization can fail due to physical or chemical changes in the fluid, which results in particulate agglomeration beyond 1 micron in size and bulk settling of the precipitate. The term Stabilization can also be a synonym for sequestration where a coordination complex between the polymer and soluble ions or surface interaction between the polymer and forming crystal lattices occurs and prevention of precipitation is achieved. In this case, threshold inhibition is not the prevailing mechanism since stoichiometry is undefined. Iron Stabilization, Calcium Phosphate Stabilization, and Zinc Stabilization are all relevant examples.

Particulate Dispersion may be the most straightforward of the six concepts for scale control. A formal definition of **Particulate Dispersion is where a mixture of finely divided particles, called the internal phase (often of colloidal size) is distributed in a continuous medium, called the external phase**. More simply stated, Particulate Dispersion is a suspension of particulates in an aqueous solution. These can be Inorganic (i.e. calcium carbonate), Organic (i.e. biomass) or a mixture of the two. Polymer composition and Mw are key determinants in deriving functionality for effective particulate dispersion.

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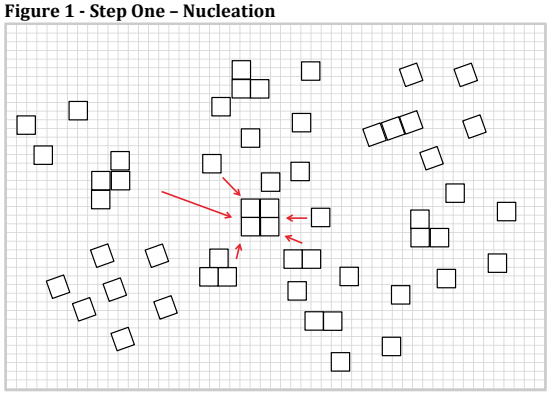
Crystal Habit Modification is the basis for the control of mineral scales such as calcium carbonate. A Crystal Habit is defined as the normal size and shape of a precipitated substance in a given set of environmental conditions. The formation of crystals such as calcium carbonate and their subsequent deposition onto surfaces follow a simplified process of Nucleation (Figure 1), Lattice Formation and Propagation (Figure 2), Bulk Precipitation (Figure 3), and Surface Deposition (Figure 4). **Crystal Habit modification can be described in instances where a "poison" such as a polymer, phosphonate, or other contaminant disrupts normal lattice formation. The crystal lattice poison, in turn, produces crystals that either tend to re-dissolve or precipitate in abnormal forms.** This effect reduces the cohesion of the crystals to each other (dispersion) and the adhesion of the crystal to system surfaces (scaling). Other primary qualities of crystal modification are as follows:

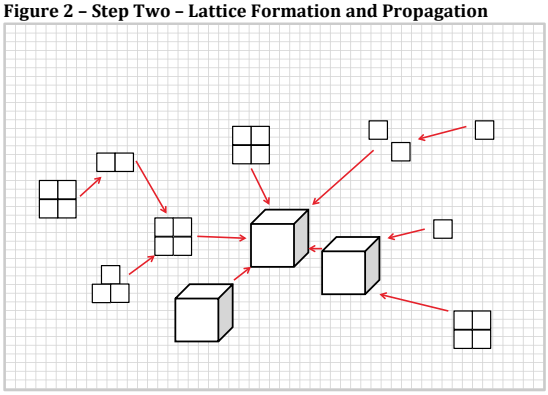
- Crystal growth is dynamic. Crystalloids that do not grow properly tend to re-dissolve.
- Polymers and other materials such as phosphonates can modify the size and shape of mineral crystal habits.
- Observed degree of modification that can be achieved follows the order:
  - $CaCO_3 > Ca_x(PO_4)_y$, $BaSO_4 >>> CaSO_4$
- Crystal Habit Modification is the basis for scale control using polymers
  - Threshold Inhibition – Crystal Modification is the mechanism that allows sub-stoichiometry.
  - Deposition Tendency – Crystal Modification is an in-situ mechanism that prevents or reduces particle cohesion.
  - Surface Adherence – The distortion that results from Crystal Modification limits surface to surface (i.e. particulate to tube wall) contact area thus limiting potential adhesion.

Figure 1 - Step One – Nucleation



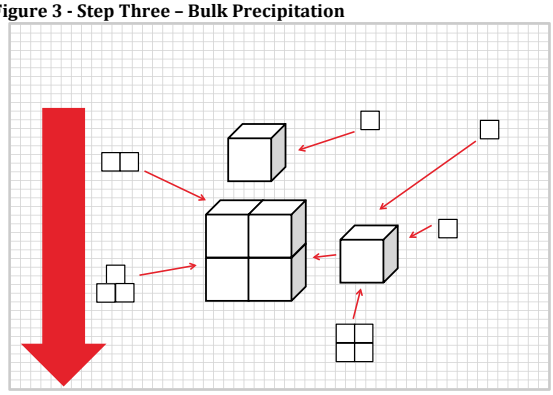
Nucleation - Diffusion from Solution to Solid Surface

Figure 2 – Step Two – Lattice Formation and Propagation



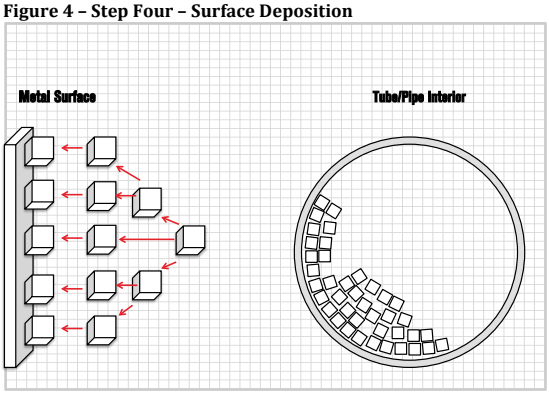
Lattice Formation - Disorder to Order

Figure 3 - Step Three – Bulk Precipitation



Macro Calcite Formation - Bulk Precipitation Exhaustion of Soluble Ions

Figure 4 – Step Four – Surface Deposition



Deposition - Maximum Surface Contact Area

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A strong case is made that threshold inhibition would not be possible without crystal modification. Further, what is recognized as stabilization and, in some cases, dispersion would also not be possible without the functionality of crystal habit modification. These concepts, in the context of polymer functionality, are explored further in the following sections.

Polymer Functionality Overview

Polymer functionality is largely either overestimated or underestimated by the producer, seller and/or user. Rarely, is the polymer's exact functionality well understood. On one hand, it is common to observe producers and sellers to make claims of functionality for everything. At the same time, there are always those that think of the functionality of polymers as essentially one-dimensional. For the skeptic, polymers are typically viewed as either good threshold inhibitors, or as good dispersants, or as good crystal modifiers, or as good stabilizers, etc.…(Figure 5.) The truth here, as with most things, lies somewhere in-between the extremes.

The mechanisms, which enable the specific functionalities of polymers, are largely interconnected such that the overall scale control means is achieved by employing multiple mechanisms either sequentially or simultaneously (Figure 6.) Taking an example of a carboxylated homopolymer (such as polymaleic acid) for calcium carbonate control, we can see that all six functionalities could easily be relevant to the scale management process.

Figure 5 – Typical View of Polymer Functionality

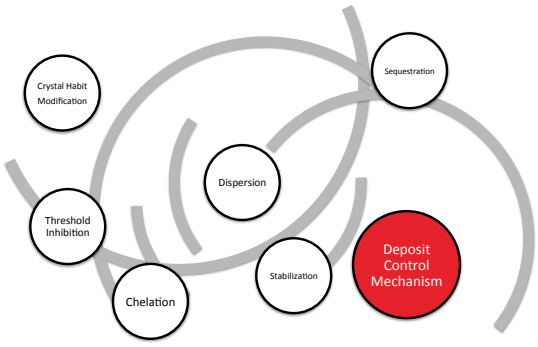
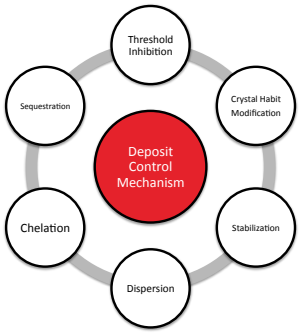


Figure 6 – Interconnected View of Polymer Functionality



Sequestration is likely the first interaction employed in the battle of the polymaleic acid and calcium carbonate. Figure 7 illustrates this first line of defense where the polymer is sequestering calcium ions such that they are unavailable for combination with carbonate ions. By definition, *Chelation* is also employed here. The carboxylic acid (H-O-C=O or COOH) functional groups on the polymer backbone carry a minus one charge. Because of this, two carboxylic acid groups are required to fully sequester each divalent (2+) calcium ion. It is this coordination of the polymer at two sites along the molecule with the calcium ion (central metal ion) that meets the formal definition of chelation.

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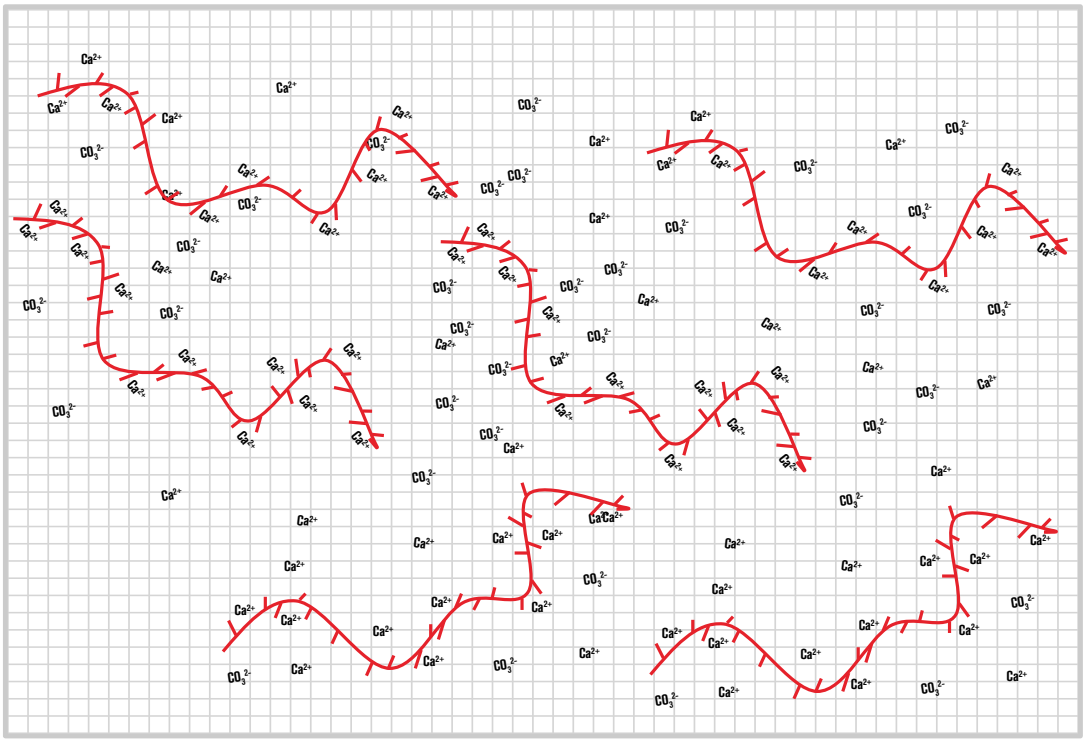
Figure 7 – Sequestration and Chelation of Divalent Calcium



The functionality of sequestration and chelation by such polymers is typically temporary in process water treatment applications such a cooling towers and boilers. The duration (how long?) and extent (how much?) the polymer can maintain solubility of calcium in an environment where carbonate species is present is dependent upon many factors. The primary of these are the concentration of the scale forming ions (in this case $[Ca^{2+}][CO_3^{2-}]$), pH, temperature, polymer concentration, polymer efficacy (design), presence and concentration of suspended solids, presence and concentration of other soluble ions, the rate in which the water (and its impurities) are concentrated and the frequency of polymer addition.

As calcium carbonate begins to precipitate in this example, it is necessary for the polymer to interact with both the soluble calcium that remains in solution (sequestration, chelation) and also the forming crystal lattices, which are sometimes referred to as crystalloids (Figure 8). These calcium carbonate crystalloids can be thought of as "pre-crystals" as they have begun to form crystal lattices that are necessary for formation of macro, insoluble calcium carbonate scale. However, these crystalloids are considered soluble or, at least, at the precipice of precipitation and highly vulnerable to re-solubilization. In this case, the polymer can begin to exhibit *Stabilization* functionality. The polymer may not be able to fully sequester all of the calcium ions present, nor may it be able to prevent crystalloid formation or repeated dissolution (partial threshold inhibition mechanism) but it may be effective in preventing growth of the crystalloids beyond that of colloidal particles.

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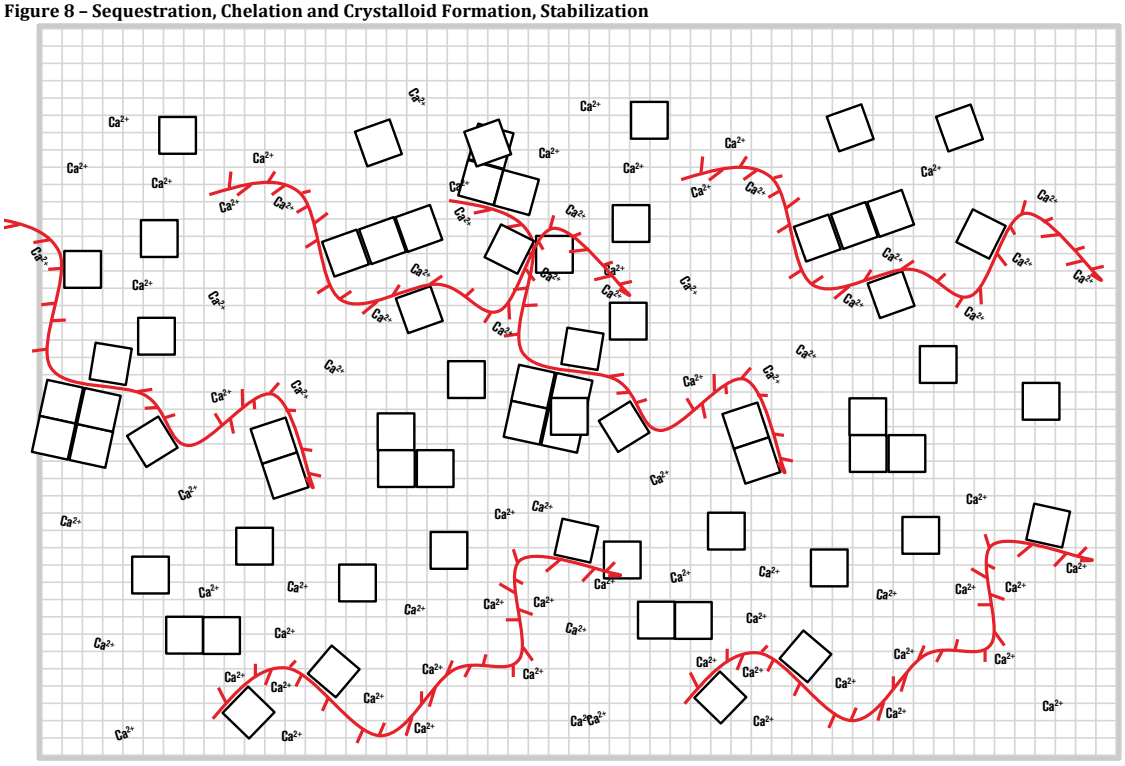
Figure 8 – Sequestration, Chelation and Crystalloid Formation, Stabilization



Polymer Interaction - Sequestration, Chelation, Crystalloid Stabilization

Revisiting the definition of *Threshold Inhibition* reveals that a key determinant in this functionality is a sub-stoichiometric relationship between the level of polymer and the scale forming species. A strict mechanism of sequestration and/or chelation would not allow for this relationship. Rather, a process of partial and/or temporary sequestration, formation of the crystalloid, and re-dissolution of the interrupted crystal lattice formation is necessary to accomplish this phenomenon at sub-stoichiometric ratios. Thinking through the process, it can be envisioned, as in Figure 8, that the polymer is fighting a battle on two fronts: the water soluble battle with divalent calcium and the water insoluble battle against calcium carbonate crystalloids. As it has been defined, threshold inhibition is a temporary effect. Thus, the polymer is winning and losing each of these battles simultaneously until bulk precipitation occurs. The polymer essentially wins as it sequesters divalent calcium ions (water soluble battle) and as it adsorbs onto crystalloid surfaces (water insoluble battle) disrupting crystal lattice formation. The effective polymer concentration is constantly being depleted as the polymer wages war on both fronts. However, as crystalloids re-dissolve, the polymer too is freed to continue the battle on the water soluble front. This process is continued to the point where crystalloids tend to form lattices that do not re-dissolve, where larger macro-structures of calcium carbonate form, and bulk precipitation occurs. Again, the rate and duration of this polymer-calcium carbonate war is dependent upon the factors previously mentioned. Threshold inhibition is an extraordinarily unique event that is somewhat specific to certain polymers and phosphonates. Other materials that can have much stronger sequestering or chelating properties or a much higher affinity for adsorption onto forming calcium carbonate do not exhibit threshold inhibition properties.

Once bulk precipitation has occurred, the two remaining mechanisms for mineral scale control may be employed. *Dispersion* is possibly the most simple of the two although nuances exist here. It is important to separate the concept into two pieces: in-situ dispersion and post precipitation dispersion. In both cases, the polymer is effective in maintaining a suspension (dispersion) in solution by electrostatic repulsion. In each case, the polymer interacts with the precipitate and itself

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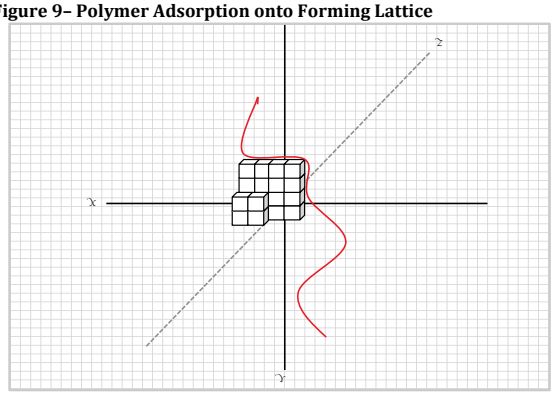
to prevent agglomeration and resultant separation from solution. However, in some cases, where the polymer is present in-situ, another benefit can be employed. If the polymer is effective in modifying or distorting crystals as precipitation occurs, those crystals are much less likely to cohere to themselves and thus are much more easily dispersed. Polymaleic acid is a prime example of this in-situ mechanism. Polymaleic acid is actually exceptionally poor at suspending solids due to its very low (typically 500-800 Daltons) molecular weight. In contrast, polymaleic acid is effective at preventing agglomeration of solids such as calcium carbonate when it is present as a crystal habit modifier during the precipitation process.

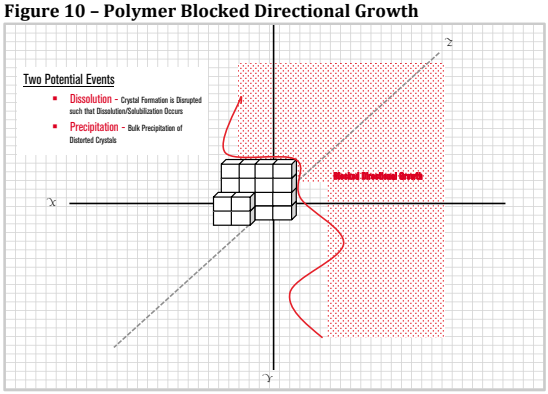
The ability of a polymer to modify the habit of mineral scales has been known for decades. Folklore suggests that prior to the invention of synthetic polymers for this purpose, starch (a naturally occurring polymer) from potatoes was utilized to soften scale in the boilers of steam locomotive engines. More recently, synthetic polymers such as polycarboxylates (polyacrylic acids, polymaleic acids), sulfonated copolymers, and various other polymers have been used specifically for this purpose in virtually all water treatment applications. The concept of *Crystal Habit Modification* is simple and qualitative. Essentially, the expectation for the polymer is to adsorb onto the surface of a forming crystal lattice, impede the directional growth of the lattice, and subsequently promote the formation of precipitated crystals that are abnormal in shape, size, and overall appearance. This can be illustrated in Figures 9-13. Figure 9 shows a three dimensional illustration of a forming crystal lattice where a polymer begins to adsorb onto the lattice surface. It can be observed in Figure 10 how this adsorption of the polymer "blocks" directional growth in several dimensions or directions. The directional blocking then causes one of two events with the forming crystal lattice. The lattice is either unstable, such that it tends to re-dissolve (Figure 11), or bulk precipitation occurs and crystal habit modification of the bulk precipitate is observed (Figure 12). Figure 13 illustrates the benefit of crystal habit modification in the bulk precipitate.

Figure 9– Polymer Adsorption onto Forming Lattice



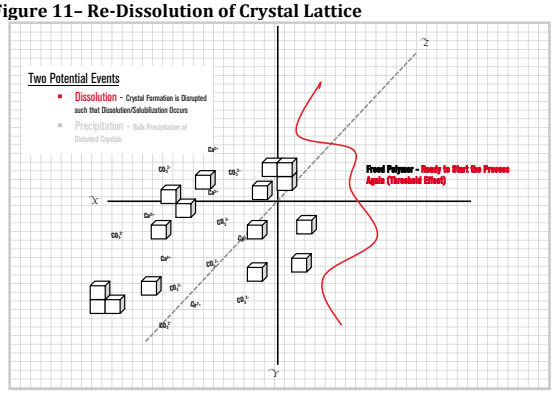
Polymer Interaction – Adsorption onto Forming Crystal Lattice

Figure 10 – Polymer Blocked Directional Growth



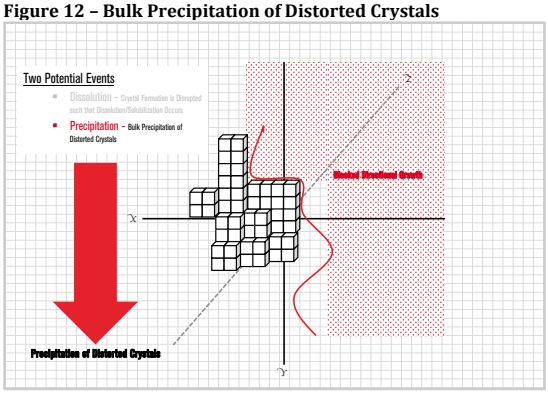
Polymer Interaction – Blocked Directional Growth

Figure 11– Re-Dissolution of Crystal Lattice



Polymer Interaction – Re-Dissolution

Figure 12 – Bulk Precipitation of Distorted Crystals



Polymer Interaction – Bulk Precipitation of Distorted Crystals

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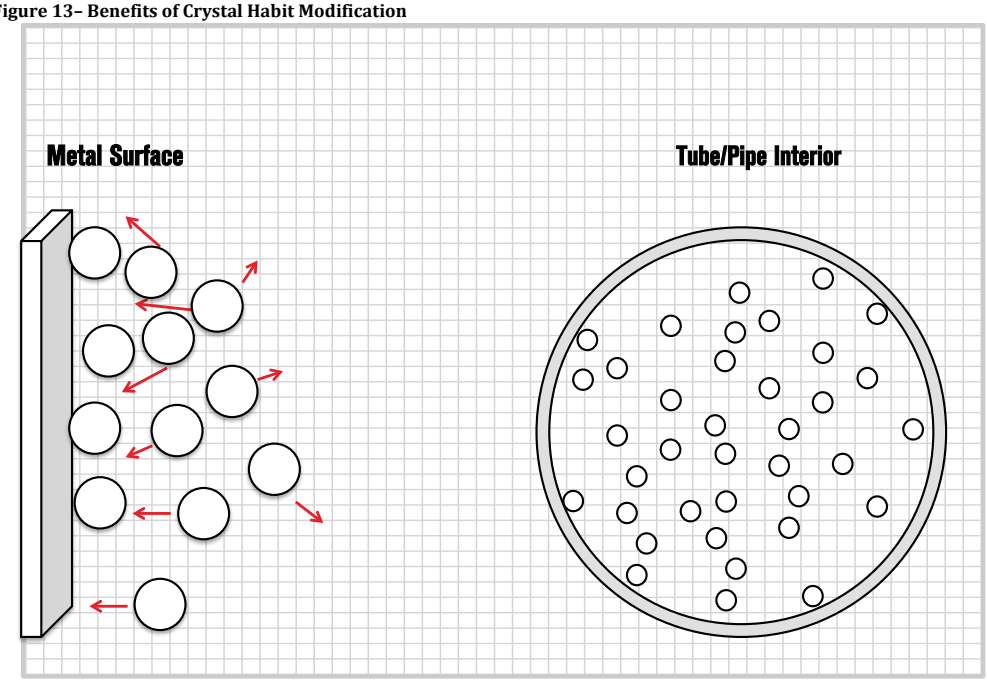
Figure 13– Benefits of Crystal Habit Modification



Design of the New Polymers

When designing a polymer for mineral scale control it is important to recognize the desired primary functionalities, their impact upon efficacy, and nuances that might enhance overall performance. Polymers can be particularly sensitive to a wide range of design factors. Among these are considerations such as composition, molecular weight, molecular weight distribution, polymer end-groups, and the manufacturing or polymerization process utilized. Each of these considerations can have substantial consequences upon overall performance, the emphasized functional feature (i.e. threshold inhibitor, dispersant, crystal modifier), the polymer's stability/retained performance in severe service conditions, and the type of mineral scale or deposit the polymer will control. A brief insight to how composition relates to functionality is provided in Table 2. There it can be observed that a carboxylate group, such as from acrylic acid and maleic acid, provides the basis of functionality for calcium carbonate and calcium sulfate. Further, sulfonate groups, provide the primary functionality for calcium phosphate, iron, and zinc stabilization. Non-ionic groups are typically utilized to enhance polymer performance by increasing interaction with a particular surface. Examples of this include the addition of a non-ionic to enhance calcium carbonate crystal modification properties, improve calcium phosphate and iron stabilization, or to add a viable interface to organics or biomass. The implications of molecular weight can be over simplified to state that lower molecular weight (<3,000 daltons) polymers tend to provide better threshold inhibition properties while polymers with an average molecular weight (M_w) between 5,000 and 10,000 daltons tend to function better as stabilizers and particulate dispersants. Of course there are exceptions to these rules of thumb but they largely hold true throughout the range of polymers offered in the industry. Other aspects such as the polymerization process, end-group selection, and molecular weight distribution can have a tremendous impact upon polymer performance as well. One good example of this is the use of hypophosphite in the preparation of polyacrylates. These polymers are known as phosphinocarboxylates but, more accurately, they are polyacrylates prepared using sodium hypophosphite. These polymers are well known as having better thermal stability and tolerance to iron and salts than typical polyacrylates prepared by more conventional methods.

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Table 2: Simplified Polymer Functionality for Common Mineral Scales and Deposits

	$CaCO_3$	$CaSO_4$	$Ca_x(PO_4)_y$	Iron	Zinc	Organics	Salt Stab
Carboxylate	+++	++	-	-	-	-	++ MA - AA
Sulfonate	-	+	+++	+++	+++	-	+ Conc. Dependant
Non-Ionic	++ Crystal Mod. - Threshold Chelation	-	+++	+	-	+++	+

Design and Evaluation of an Enhanced Polymaleic Acid (EPMA)

The use of Polymaleic Acid (PMA) for calcium carbonate scale control dates back to at least the 1920's according to patent literature. German, British, and American scientist seemingly recognized the potential efficacy and commercial benefits of the material along the same timeframe. Widespread use of PMA began in the 1970's – continues in present time. PMA is well known, accepted, and utilized for the treatment of water and, in particular, the control of calcium carbonate. Further, PMA has become the leading choice for service companies seeking an effective additive for severe service applications in cooling waters, boilers, oilfield operations, and large-scale thermal desalination activities.

EPMA, an Enhanced Polymaleic Acid, improves upon the exceptional performance of PMA, and is differentiated from mono-carboxylic acid polymers such as polyacrylic acid. Specifically, EPMA exhibits:

- Exceptional Polymer Stability in Harsh Water Conditions
- Best-in-Class Crystal Habit Modification for Calcite (cubic form of calcium carbonate)
- Highly Effective Calcium Carbonate Threshold Inhibition in Harsh Waters

In contrast to mono-carboxylic polymers such as polyacrylic acid, the stability of EPMA in harsh water systems is enhanced due to the presence and proximity of di-carboxylic acid groups along the EPMA backbone. The negative charge inherent within each carboxylic acid functional group provides effective repulsion along the backbone of the polymer. This electrostatic repulsion, in turn, provides rigidity and stability along the polymer that prevents the EPMA from coiling or collapsing upon itself as it encounters high levels of hardness and/or salinity in an aqueous environment. Figure 14 illustrates this comparison between EPMA and mono-carboxylic acid polymers such as polyacrylic acid. The continued extension of the EPMA polymer conformation in harsh water environments is critical in that the polymer not only remains stable (soluble) in such conditions, but it also retains its functional properties. This is in contrast to polymers such as polyacrylic acid which can lose both solution stability and efficacy in comparable environments.

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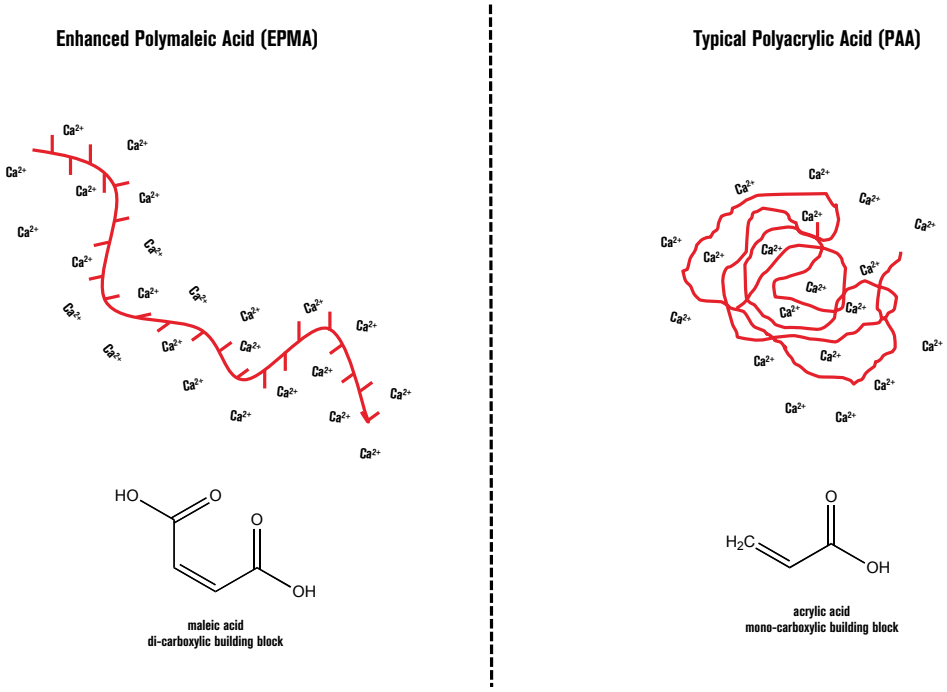
Figure 14– EPMA Stressed Water Stability



The modification of calcium carbonate crystals is especially important in today's water treatment applications. Beyond being the underlying mechanism that enables threshold inhibition, crystal modification is the primary functionality controlling mineral scale deposition in failure situations. Industry initiatives such as water conservation, use and reuse of poorer quality make-up water, and elimination of phosphorous dramatically increase the likelihood of bulk precipitation and ultimate formation of deposited mineral scale. EPMA exhibits extraordinary crystal modification properties for calcite compared to well known industry standards such as PMA and Multifunctional One Polymers (MOP).

Crystal Modification - Laboratory Experiments

To demonstrate the effect of polymers as crystal habit modifiers, experiments were conducted to determine the relative modification properties of EPMA, PMA, and MOP polymers at 15 mg/l and 30 mg/l dosages relative to a blank (no polymer treatment.) Since EPMA, PMA, and MOP are all effective threshold inhibitors in severe conditions, it was necessary to conduct the laboratory work under exceptional conditions to ensure precipitation occurred and crystal modification properties could be observed. In the experiment, 50ml of a solution containing 1200 mg/l of Ca^{2+} (Using $CaCl_2 \bullet 2H_2O$) was treated with the designated polymer dosage. Using $Na_2CO_3 \bullet H_2O$, 50 ml of a 1200 mg/l solution of CO_3^{2-} was then added to the Ca^{2+}, polymer dosed solution. The final solutions contained 600 mg/l of Ca^{2+} and 600mg/l of CO_3^{2-}. Each solution was measured to have a pH of 9.5 – 10.2 and was heated in a water bath at 70°C for 18 Hours. The samples were allowed to cool and the precipitate was collected using a plastic transfer pipette and were examined by both compound and Scanning Electron Microscopy using a Hitachi S-4700 Type II cold field emission SEM. Table 3 details the severe service conditions of the experiments.

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Table 3 – Crystal Modification Experimental Conditions

Condition	Value
Calcium Concentration	600 mg/l Ca^{2+} Solution (Using $CaCl_2 \bullet 2H_2O$)
Carbonate Concentration	600 mg/l CO_3^{2-} Solution (Using $Na_2CO_3 \bullet H_2O$)
Sample pH	~9.5-10.2
Temperature	70°C
Duration of Heating	18 Hours
Polymer Dosage	15 mg/l and 30 mg/l as Active (as indicated in images)
Calcite Saturation (IAP/Ksp)	857.45 at pH 9.5
Calculated Free Calcium	218.0 mg/l
Calculated Free Carbonate	62.5 mg/l
Langelier Saturation Index (LSI)	>3.0 (Calculated to be 4.3)
Ryznar Stability Index (RSI)	0.90

The exclusive formation of calcite is shown in Images 1 and 2 for the blank (no polymer treatment.) Similarly, the SEM micrographs shown in Images 3 and 4 reveal that the conditions of the experiments produce a uniform calcite (cubic calcium carbonate) precipitate.

Image 1 – Compound Microscopy – Blank (No Treatment)

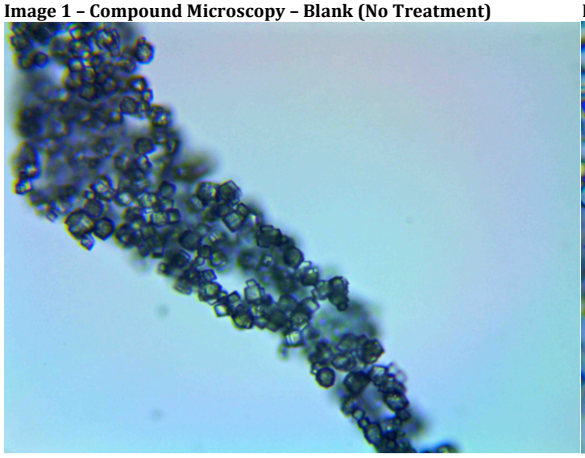


Image 2 – Compound Microscopy – Blank (No Treatment)

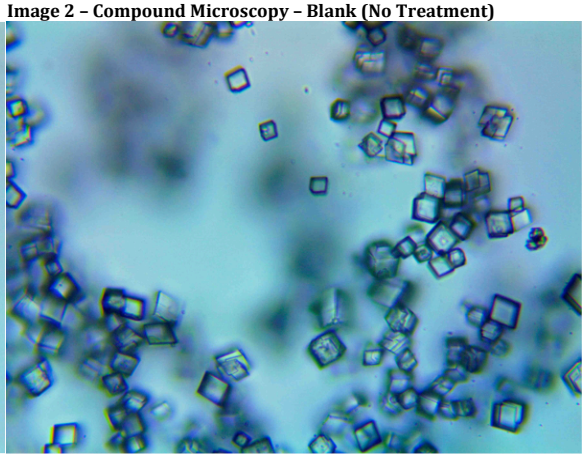


Image 3 – SEM Micrograph– Blank (No Treatment)

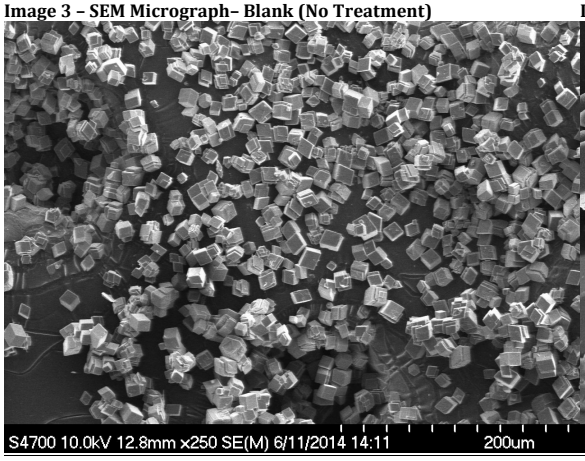
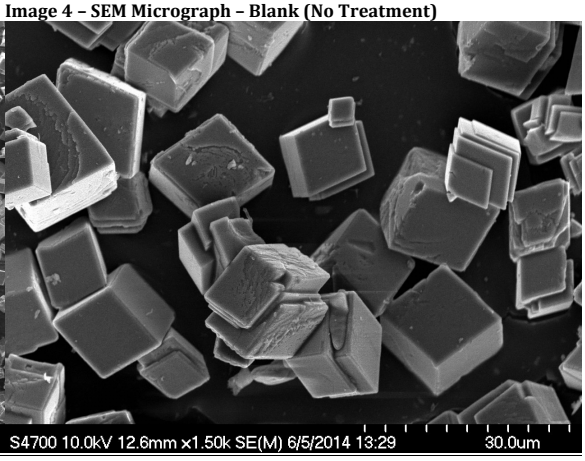


Image 4 – SEM Micrograph – Blank (No Treatment)



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Polymaleic Acid (PMA) is widely recognized as the industry standard crystal habit modifier to cubic calcium carbonate (calcite.) As can be observed in Images 5-8 both polymer dosages "soften" the calcite and begin showing modification features. The presence of unmodified calcite is prominent in the 15 mg/l dosage and are still observable at the 30 mg/l treatment level. At both dosages, the modification that is achieved by PMA manifests as a "boulder" type shape.

Image 5 – Compound Microscopy – PMA 15 mg/l Treatment

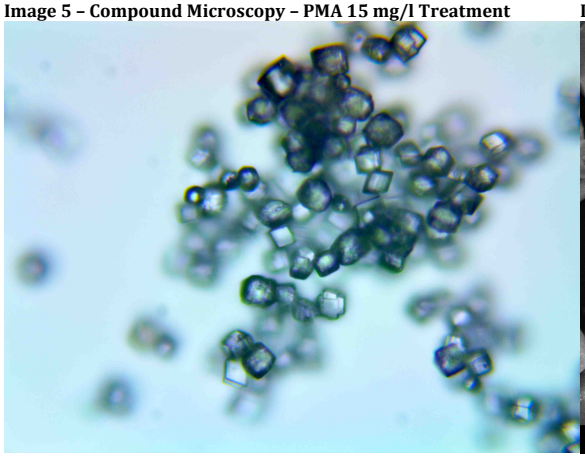


Image 6 – SEM Micrograph – PMA 15 mg/l Treatment

Image 7 – Compound Microscopy – PMA 30 mg/l Treatment

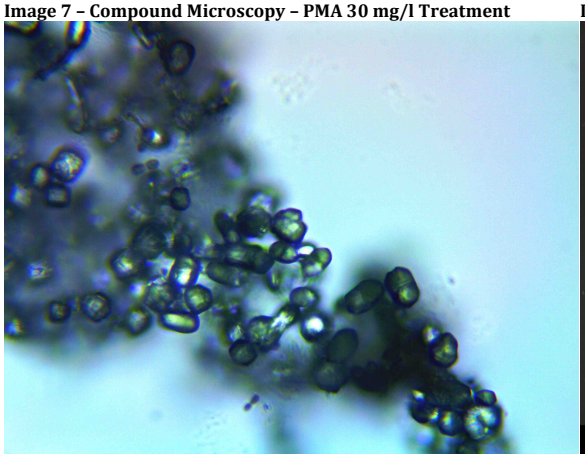
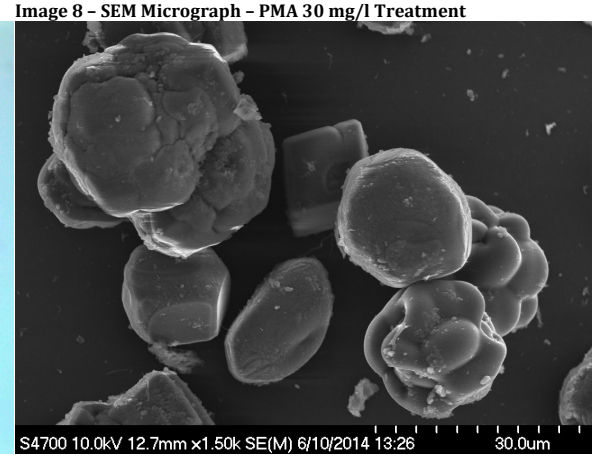


Image 8 – SEM Micrograph – PMA 30 mg/l Treatment



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Multifunctional One Polymers (MOP) are relatively new technologies, which are designed for multiple use purposes rather than specific performance as crystal habit modifiers. Images 9-12 show that MOP does not demonstrate the same level of modification as the PMA. At the both the 15 mg/l and 30 mg/l dosages, the MOP treated samples retain much of their original, untreated cubic form. One explanation for this could be the polymer architecture and design. Typical MOP materials are ~2,000 – 3,000 Mw and contain sulfonated monomers. These design features may limit the interaction of the polymer with forming calcite crystalloids and thus reducing the overall level of observed crystal habit modification.

Image 9 – Compound Microscopy – MOP 15 mg/l Treatment

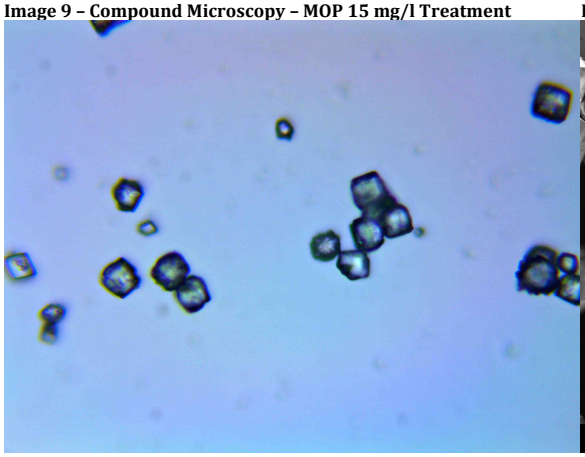


Image 10 – SEM Micrograph – MOP 15 mg/l Treatment

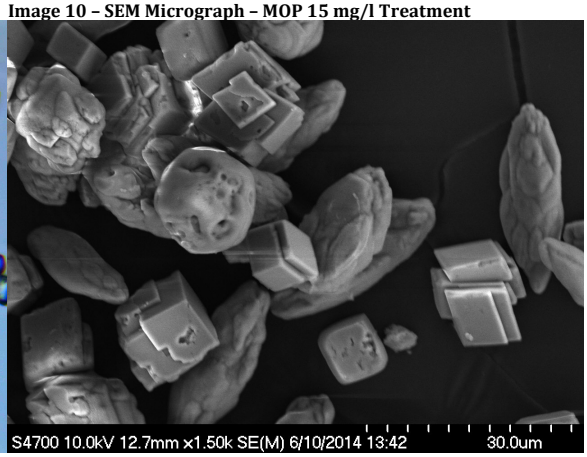


Image 11 – Compound Microscopy – MOP 30 mg/l Treatment

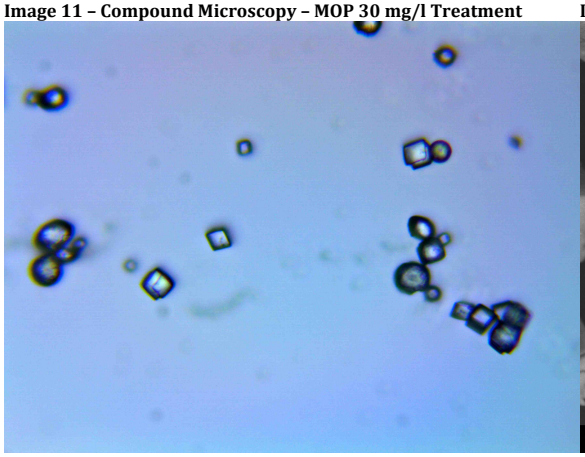
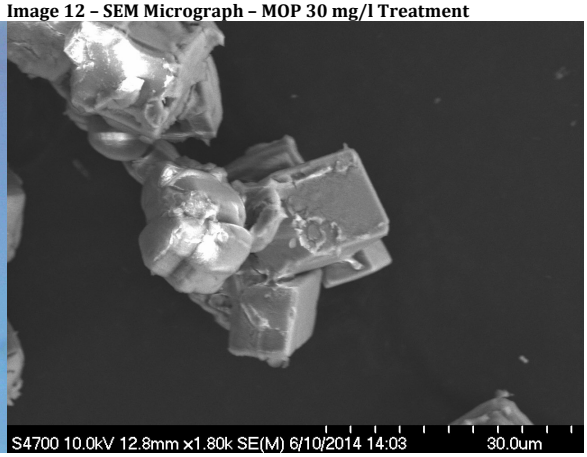


Image 12 – SEM Micrograph – MOP 30 mg/l Treatment



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The degree, type and quality of crystal distortion observed with the new EPMA polymer were unique and unmatched by either the PMA or MOP polymers. Distinctive to the EPMA is the formation of spherical and rounded pill shaped macro structures. Such structures are unlikely to form strong adhesions onto metal surfaces and require less mechanical energy to remove those that are deposited (refer to Figure 13). Remarkably, it can be observed that the EPMA shows a greater degree of distortion at lower treatment levels. Images 13 and 14 show EPMA at a dosage of 15 mg/l with resulting distortion of over 50% of the potential cubic macro-lattices. Further, Images 15 and 16 show near total distortion of all potential cubic macro-lattices at the 30 mg/l dosage.

Image 13 – Compound Microscopy – EPMA 15 mg/l Treatment

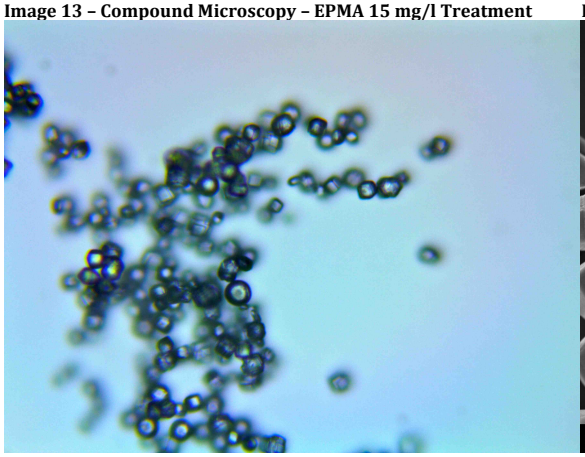


Image 14 – SEM Micrograph – EPMA 15 mg/l Treatment

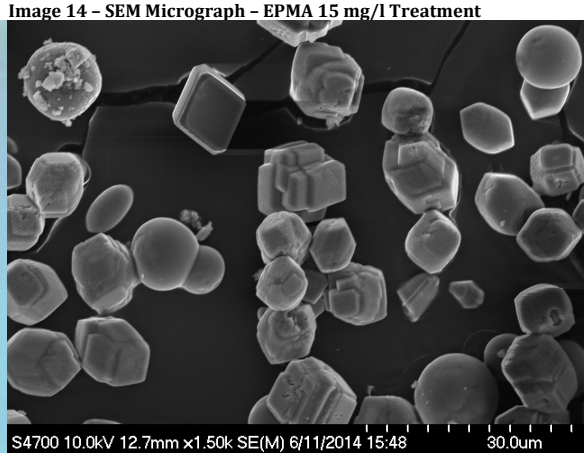


Image 15 – Compound Microscopy – EPMA 30 mg/l Treatment

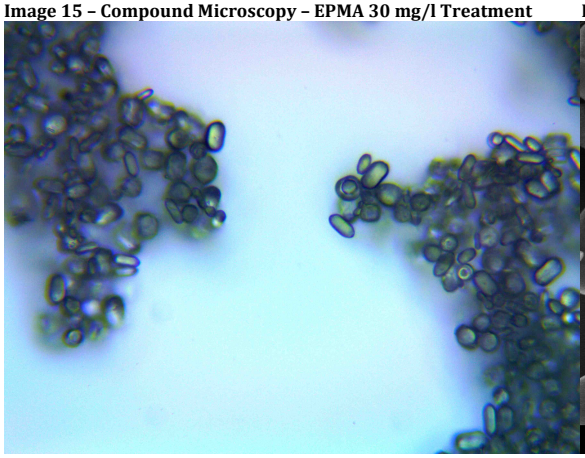
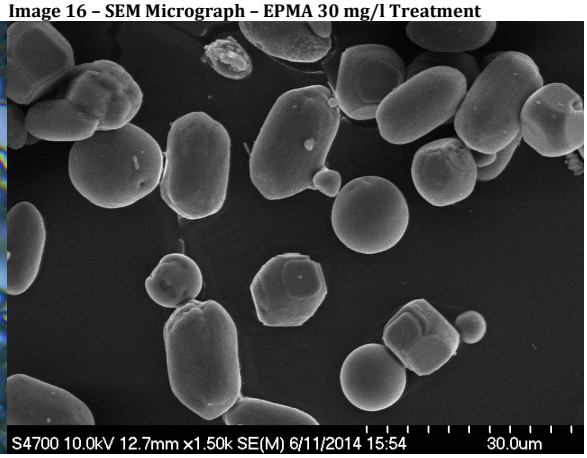


Image 16 – SEM Micrograph – EPMA 30 mg/l Treatment



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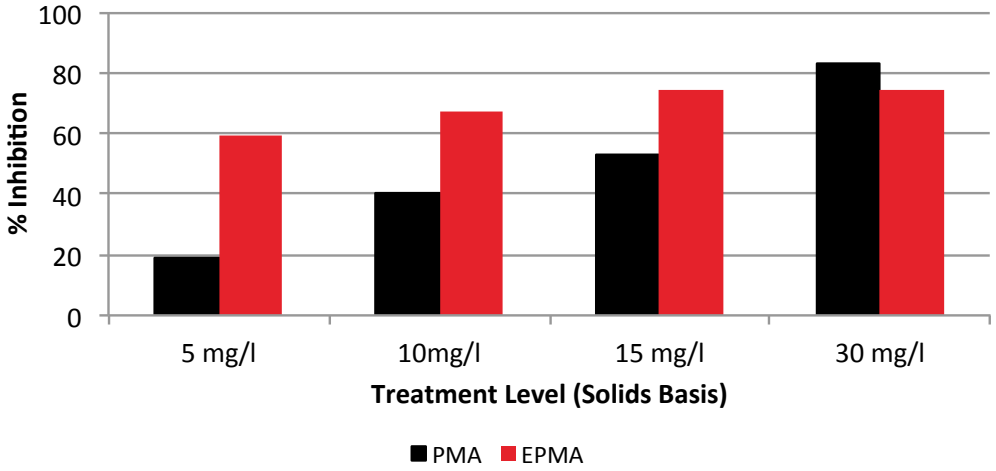
Threshold Inhibition - Laboratory Evaluation

A comparison of Enhanced Polymaleic Acid (EPMA) and Polymaleic Acid (PMA) as threshold inhibitors was conducted using a "Severe Calcium" laboratory bottle testing method. In this method, 50 ml of a solution containing 1200mg/l Ca^{2+} was added to a French square bottle and treated with the indicated polymer dosage (as active.) Then 50 ml of solution containing sodium carbonate (150 mg/l as CO_3^{2-}), sodium bicarbonate (450 mg/l as CO_3^{2-}), and a borate buffer (98 mg/l $B_4O_7^{2-}$) was added to the calcium/polymer solution. All samples had a measured pH of ~9.0 and were capped and placed in a water bath at 50° C for 18 hours. The Langelier Saturation Index was calculated to be ~ 3.0. In this evaluation, EPMA and PMA were compared across increasing dosages of 5, 10, 15, and 30 mg/l on an active polymer basis. The results are shown in Graph 1.

Graph 1: PMA versus EPMA – Calcium Carbonate Inhibition



Within this severe calcium test, EPMA demonstrates good stability in harsh conditions (i.e. high calcium, high alkalinity) and shows functionality as a threshold inhibitor. EPMA showed slightly better results at the lower treatment levels but performed slightly lower than PMA at the 30 mg/l dosage. The inherent limitations of bottle testing for calcium carbonate inhibition and the small sampling of data at the time of this writing make it difficult to draw conclusive opinions beyond that of EPMA and PMA equivalence. More testing is required and planned prior to claiming superiority or defining the boundaries of EPMA performance as a threshold inhibitor. As with PMA or any other inhibitor of this type, it is recommended that EPMA be formulated with PBTC (preferred) or HEDP to enhance threshold inhibition functionality. A recommended ratio is ~3:1 EPMA to PBTC with a typical delivery ~ 10 mg/l active polymer and 3 mg/l active PBTC as a starting point for most applications.

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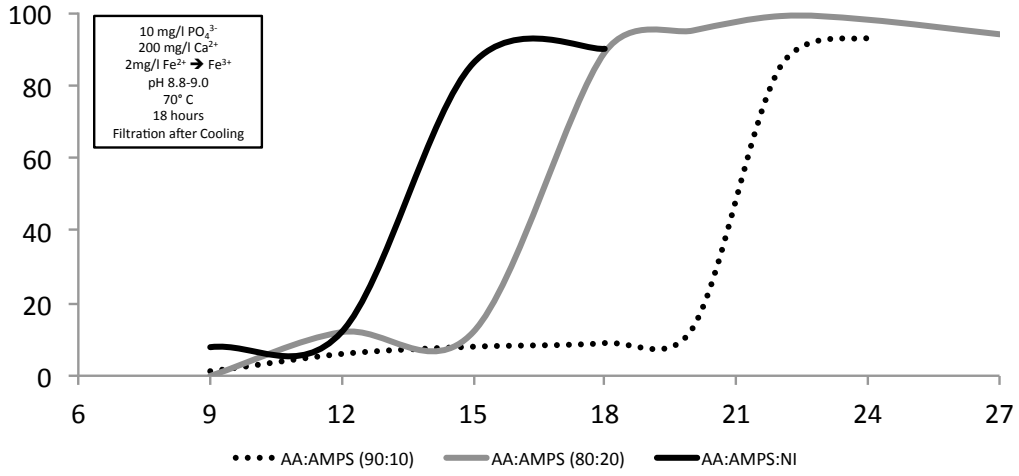
Design and Evaluation of a High Performance Sulfonated Polymer (HPSP)

Water treatment service companies have many choices when selecting a polymer additive for calcium phosphate and iron stabilization. Most commonly a polymer containing a sulfonated monomer is utilized when facing control issues for phosphate and/or iron. While a wide-range of choices in any market place is generally good for the consumer, too many choices combined with complex product marketing can lead to confusion and misapplication. The aim here is to clarify and simplify these choices and introduce a new High Performance Sulfonated Polymer (HPSP) to the membership.

As defined by IUPAC (International Union of Pure and Applied Chemistry), ***a copolymer is a polymer derived from more than one species of monomer***.[2] As such, a copolymer may have two, three, four, …or even more monomers. A survey of the commercially available polymers in this area reveals that copolymer types range from more generic acrylic acid copolymers with 2-acrylamido-2-methyl propane sulfonic acid (AA:AMPS®[3]), to copolymers of acrylic acid, AMPS, and a Non-Ionic (NI) monomers (AA:AMPS:NI), to various copolymers which may include acrylic acid, a non-ionic monomer and one or more sulfonated monomers such as sulfonated styrene (SS), sodium methallyl sulfonate (SMS) and allyl-oxy-benzene sulfonate (ABS). In marketing terms, these polymers may manifest themselves as copolymers, ter-polymers, or as tetra/quad polymers. However, it is critical to understand that, more monomers, in and of themselves, are not necessarily better. What is most important is that the most effective functionality in such copolymer design is employed. More specifically, it is the monomer type, ratio and manner in which these monomers are combined (polymerization conditions) that ultimately defines overall polymer efficacy in a given water treatment application.

A comparison of the calcium phosphate stabilization properties in Graph 2 demonstrates the effect of both monomer combination and ratio. Here a standard AA:AMPS copolymer (90:10 molar ratio AA:AMPS) is represented by the black dotted line. It can be observed that 21- 24 mg/l active polymer is required to stabilize 10 mg/l PO_4^{3-}. Increasing the AMPS level in the polymer improves the performance dramatically for phosphate stabilization. As can be seen with the 80:20 AA:AMPS copolymer (presented in grey) only 15-18mg/l of active polymer is required to stabilize the 10 mg/l PO_4^{3-}. Further, the addition of a non-ionic group (presented in black), enhances the performance of the polymer to where only 12-13 mg/l of active polymer is required to fully stabilize the phosphate.

Graph 2: Comparison of AA:AMPS and AA:AMPS:NI Copolymers



[2] IUPAC Macromolecular Division Commission on Macromolecular Nomenclature, Basic Definitions and Terms Relating to Polymers - 1974

[3] AMPS® and The AMPS Monomer® are registered trademarks of The Lubrizol Corporation.

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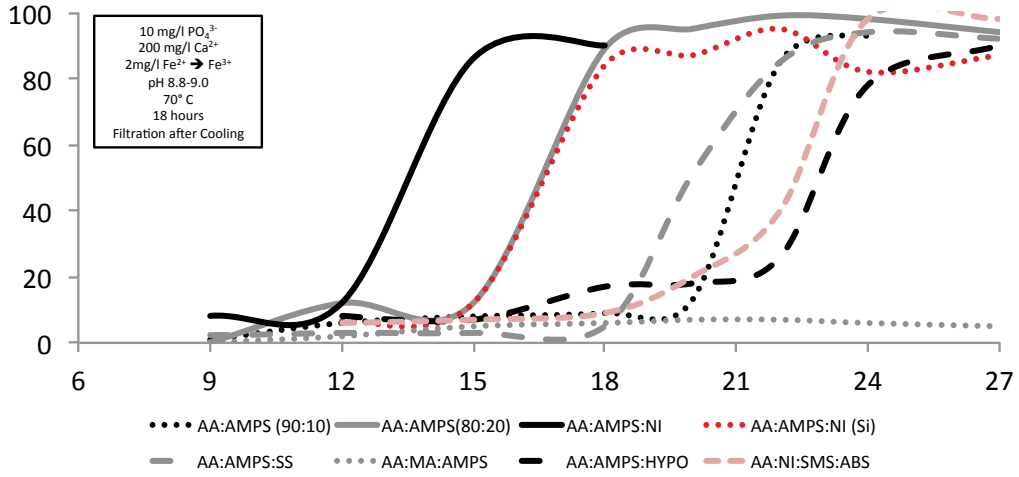
These straightforward results show that performance for calcium phosphate stabilization within this class of polymers is impacted by both the concentration of sulfonate group and the enhancement with non-ionic functionality. Expanding the field of materials evaluated can be observed in Graph 3 where an overall survey of eight commonly utilized polymers where a range of composition and polymerization techniques are employed.

Graph 3: Survey of Commonly Utilized Calcium Phosphate Stabilizers



A ranking and further description of these industry-leading polymers is presented in Table 4 below:

Table 4: Ranking of Commonly Utilized Calcium Phosphate Stabilizers

Polymer Description	Comments	Ranking (Required Dosage)
AA:AMPS:NI	Industry Standard "terpolymer"	**1** (12-15 mg/l)
AA:AMPS (80:20)	Meets 21 CFR 173.310 for Boilers	**2** (15-18 mg/l)
AA:AMPS:NI (Si)	"terpolymer" recommended for silica control	**2** (15-18 mg/l)
AA:AMPS:SS	Sulfonated Styrene "terpolymer"	**4** (18-21 mg/l)
AA:AMPS (90:10)	Most Widely Utilized Composition for Phosphate Stabilization	**5** (18-21 mg/l)
AA:NI:SMS:ABS	"tetra/quad" polymer	**6** (21-24 mg/l)
AA:AMPS:HYPO	Phosphino version of 90:10 AA:AMPS	**7** (21-24 mg/l)
AA:MA:AMPS	Multifunctional One Polymer	Did Not Function

Several primary conclusions can be drawn from the survey of results in Graph 3 and Table 4. First, it is clear that the level of sulfonated monomer is a key determinant of performance. Additionally, it is clear that certain additions of non-ionic functionality can enhance efficacy. Moreover, it can be concluded that the concept of more monomers does not necessarily improve functionality for calcium phosphate stabilization alone. To this point, materials such as the AA:NI:SMS:ABS and the AA:AMPS:HYPO do have other benefits such as thermal stability that are not represented here. Similarly, the AA:MA:AMPS (Multifunctional One Polymer) is primarily designed to control calcium carbonate with incidental efficacy for calcium phosphate stabilization. The test conditions represented here were too severe for the MOP polymer to act as a stabilizer.

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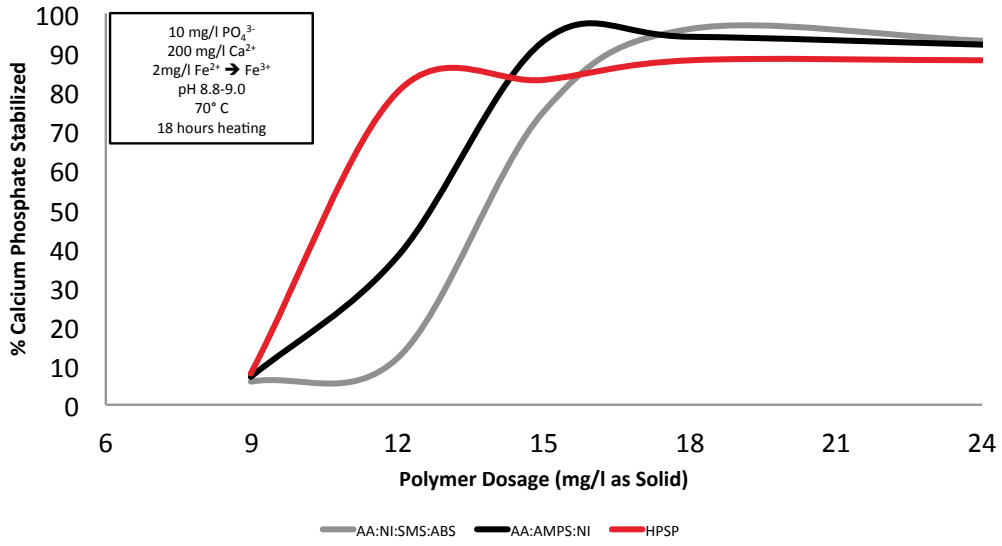
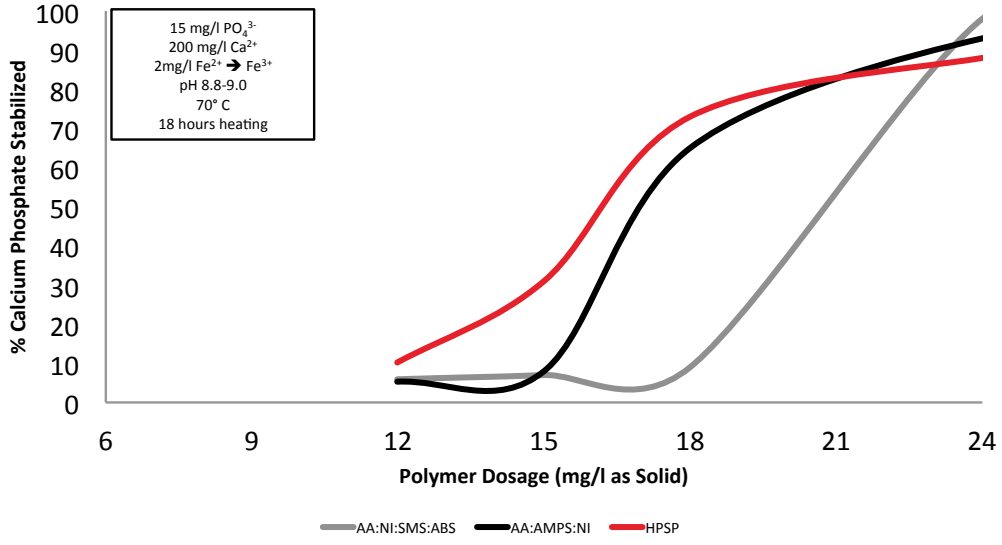
Calcium Phosphate and Iron Stabilization Comparison - New HPSP

The new HPSP material introduced here is has been designed to optimize monomer type, monomer ratio, and polymerization conditions for specific functionality as a phosphate and iron stabilizer for water treatment applications. The new HPSP material has been thoroughly evaluated versus the industry leading specialty copolymers containing AA:AMPS:NI and AA:NI:SMS:ABS. For the purposes of this paper, a sampling of the data generated is presented for comparison. For calcium phosphate, two severe service applications were chosen where 10 mg/l PO_4^{3-} and 15 mg/l PO_4^{3-} were evaluated at a pH range of 8.8 – 9.0 in waters containing 200 mg/l calcium (as Ca^{2+} or 500 mg/l calcium as $CaCO_3$) and 2 mg/l Fe^{2+}. In each test, the samples were treated with polymer at increasing dosages. The samples where then placed in a water bath at 70° C for 18 hours. After allowing the samples to cool, each sample was filtered through a 0.2µm membrane filter and measured to determine ortho-phosphate concentration using a Hach spectrophotometer. Further, each filter was preserved, imaged, and compared for iron stabilization using imaging software. Graph 4 shows the comparison of HPSP to AA:AMPS:NI and AA:NI:SMS:ABS at 10 mg/l PO_4^{3-}. Graph 5 shows the comparison at 15 mg/l PO_4^{3-}.

Graph 4: HPSP Versus Industry Standards – 10 mg/l PO_4^{3-}



Graph 5: HPSP Versus Industry Standards – 15 mg/l PO_4^{3-}



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At both 10 and 15 mg/l PO_4^{3-} levels, the High Performance Sulfonated Polymer (HPSP) exceeds the performance of both the industry benchmark AA:AMPS:NI terpolymer and the AA:NI:SMS:ABS quad polymer. Specifically, the HPSP stabilizes 10 mg/l PO_4^{3-} at between 9-12 mg/l dosage and 15 mg/l PO_4^{3-} at a dosage between 15-18 mg/l. Comparatively, the HPSP polymer stabilizes orthophosphate under severe conditions at a ratio of ~ 1:1 polymer to orthophosphate level whereas a ratio of ~1.2:1 to 1.5:1 is required for the competitive materials. The optimization of the levels of the monomer component types (carboxylate, sulfonate, non-ionic) in the HPSP provides performance at lower dosage levels than the competitive materials.

Images 17 -19 show the iron stabilization properties of polymers relative to a blank (No Treatment.) In these images, the amount of iron captured on the 0.2µm membrane filter can be visually observed with increasing dosage. Less color collected on the membrane surface is an indication that the iron has been effectively stabilized and particles sufficiently less than 0.2µm in size. As with the phosphate stabilization results, it can be observed that the HPSP product functions more effectively at a lower overall dosage. This comparison is especially prominent when observing the 9, 12, and 15 mg/l treatments for each polymer. All polymers demonstrate efficacy at dosages greater than 15 mg/l.

Image 17: AA:AMPS:NI – Iron Collection on 0.2µm membrane filter

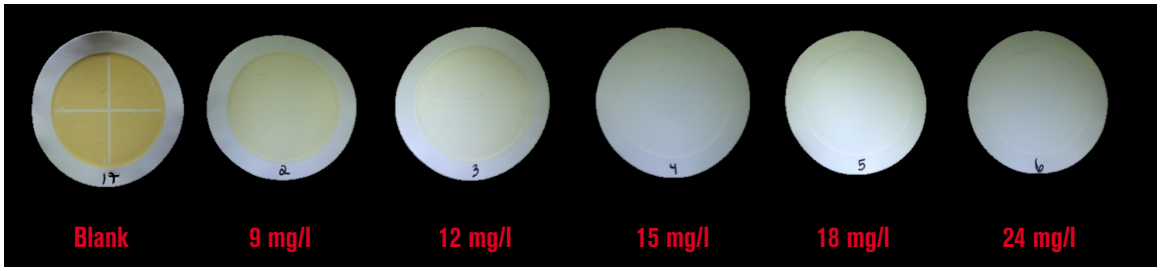


Image 18: AA:NI:SMS:ABS – Iron Collection on 0.2µm membrane filter

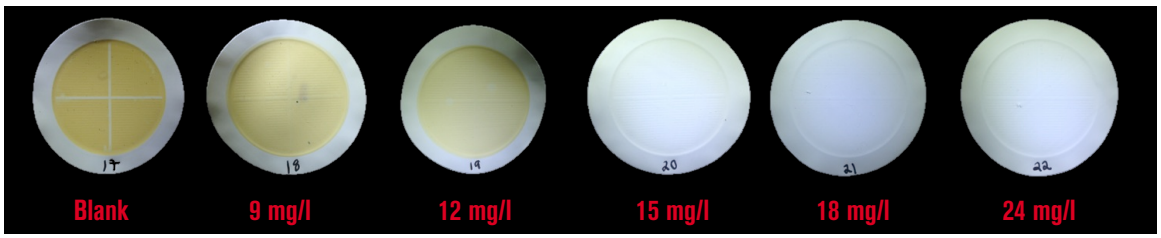
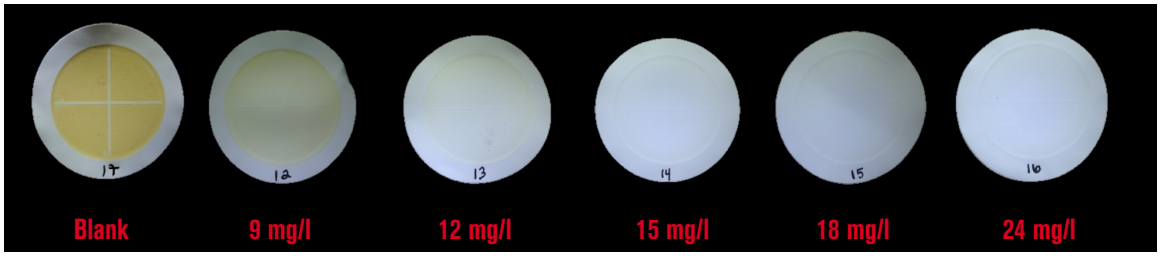


Image 19: HPSP – Iron Collection on 0.2µm membrane filter



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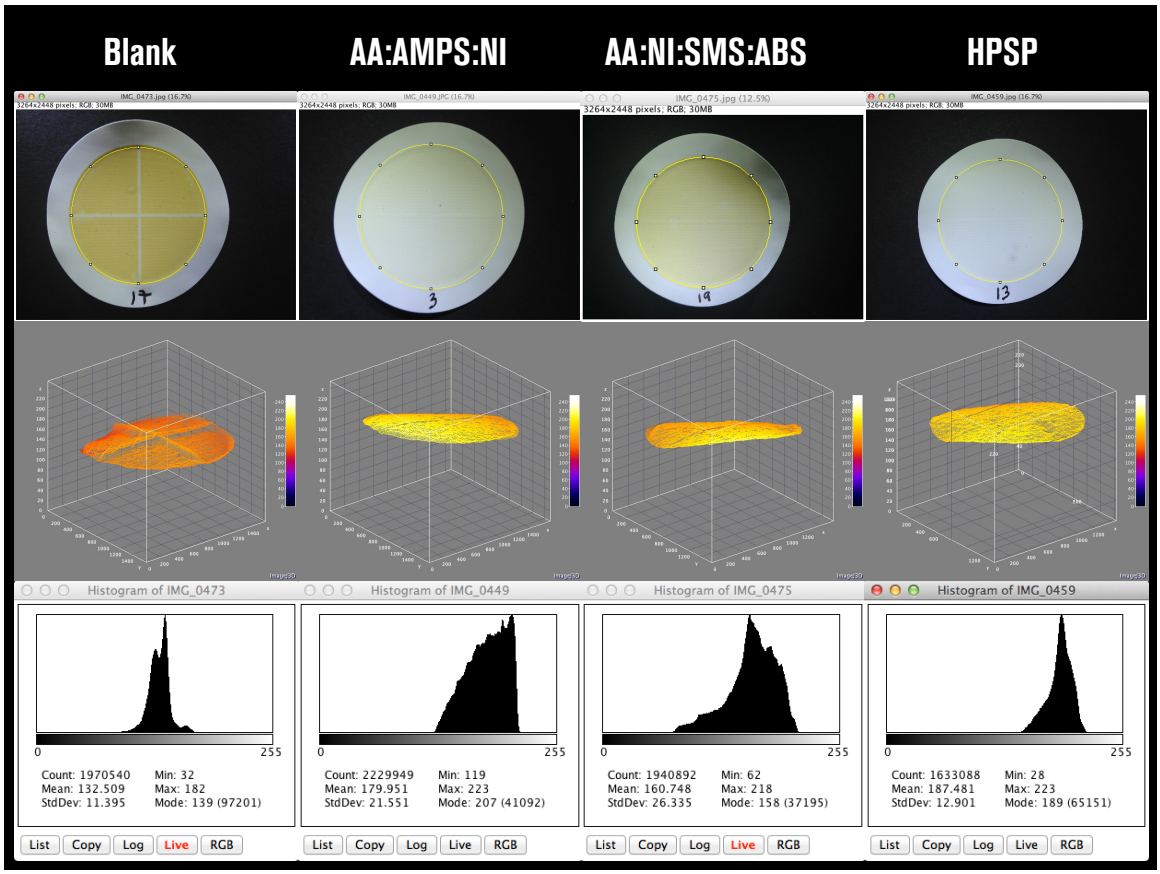
While visual observations are a powerful means of examination, the filter membranes were also examined using image analysis software to develop a quantitative comparison. In this case, the filter membrane from 12 mg/l dosage of each polymer was analyzed. Image 20 shows a collection of the data gathered from the analysis where the top row consists of comparative images of the filter membranes that have been imported into the software. The yellow, circular, multipoint line on each image defines the area selected for analysis. The center row shows three-dimensional images where the digitization of the analyzed area is calculated. Essentially, the software is converting the selected area of the image into values along the RGB (Red, Green, Blue) color scale. The RGB color scale is additive scale where each component of the three primary colors is used to define the observed color. Values for each of the three components can range between 0 and 255. A value of R=0, G=0, and B=0 produces total blackness while a value of R=255, G=255, and B=255 produces total whiteness. Using these RGB values, the software calculates color and intensity along thousands of data points within the coordinate area analyzed. These values can then be simplified as shown in the bottom row of two-dimensional histogram images. Here the same RGB values are calculated across the whole coordinate area and an intensity value is provided.

Image 20: Image Analysis Comparison



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For the purposes of determining comparative iron stabilization properties of the polymers, the histograms can be compared relative to approaching total whiteness at an RGB value of 255. Graph 6 shows an overlay of these values for the blank (No Treatment) and the three polymers evaluated. The orange color associated with the iron collected on the filter membrane has an approximate RGB composite mean value of 132 versus total whiteness equaling 255. It is within this range of 132 to 255 the efficacy of each polymer can be compared. More simply, a value closer to 132 indicates the sample looks more like the blank whereas a mean value closer to 255 indicates the sample looks more like a pure, white membrane with no iron present. It can be seen that the best performer is the HPSP with a mean value of 187, followed by the AA:AMPS:NI (179) and the AA:NI:SMS:ABS at 160.

Graph 6: Iron Stabilization Comparison using Image Analysis

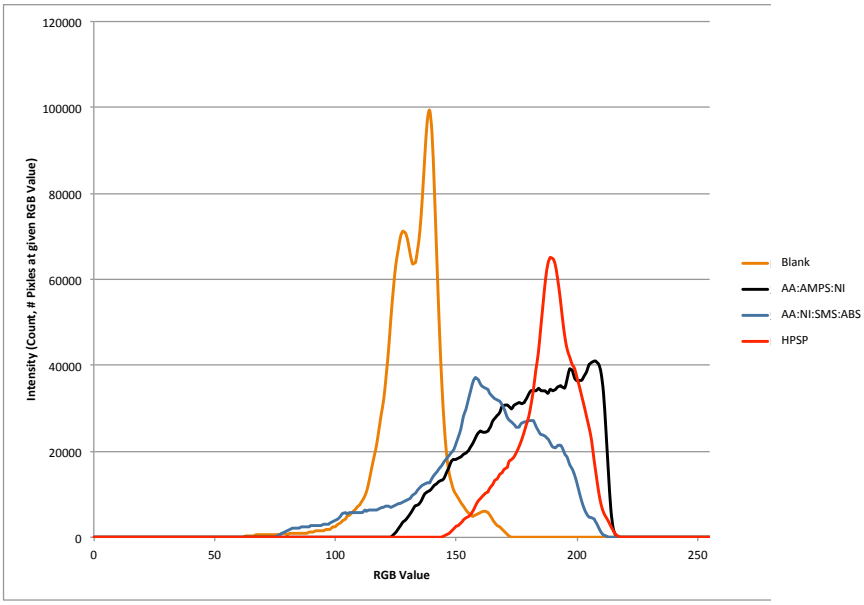

Image Analysis - Comparative Iron Stabilization

Summary

Enhanced Polymaleic Acid (EPMA) and High Performance Sulfonated Polymer (HPSP) are two new and powerful tools now available to the membership. The products have been specifically designed from the ground up to deliver unambiguous benefits that allow the user to target specific and desired functionality. EMPA demonstrates crystal habit modification properties beyond that of the industry standard polymaleic acid while HPSP is a polymer designed to optimize composition and monomer ratios that deliver best in class stabilization for calcium phosphate and iron. Equipped with these new tools, the understanding of the complex aspects of scale control mechanisms, and a working knowledge of polymer functionality, users now have a powerful means to gain a performance and market advantage for their businesses.

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