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Use of polymers for deposit control in once-through utility systems

Michael L. Standish of Radical Polymers describes a newly patented alternative to chelating agents such as EDTA and HEDP

Mineral scale inhibitors have been used in once-through utility systems since at least the 1970s. In recent years, the industry has predominantly employed phosphonates such as hydroxyethylidene diphosphonic acid (HEDP) for calcium carbonate (CaCO_3) control, along with secondary levels of sulfonated copolymers to help manage transition metals such as iron and manganese.

Recently, supply chain issues, notably COVID, labour shortages, regulations and restrictions, transportation bottlenecks, port congestion and energy costs, have limited the availability of HEDP and raised costs to two to three times historic levels. Users have had to search for alternatives. This paper describes the viability of a combination of a PEPMA patented enhanced polymaleic acid (PEMPA)¹ and a high purity sulfonated polymer (HPSP) as an alternate for HEDP.

Function of polymers & phosphonates

In once-through and recirculating cooling applications, mineral scale control is mainly achieved with phosphonates, polymers or, more commonly, a combination. This is due to the increased functionality of polymers and phosphonates and the ability to apply these materials at sub-stoichiometric levels with exceptional results.

Traditional chelating agents such as ethylenediaminetetraacetic acid (EDTA) and other discrete or non-polymeric small molecules require

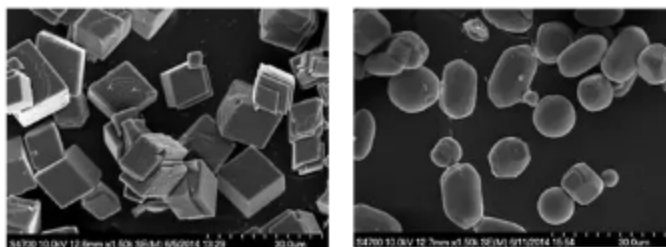


Figure 1 - Untreated calcite (left) & calcite treated with PEPMA (right)

dosages based on a stoichiometric relationship with the metal ions present in the treated water. As such, chelating agents are typically only employed in applications like boiler water treatment, where hardness levels are typically low and make-up water volume is minimised.

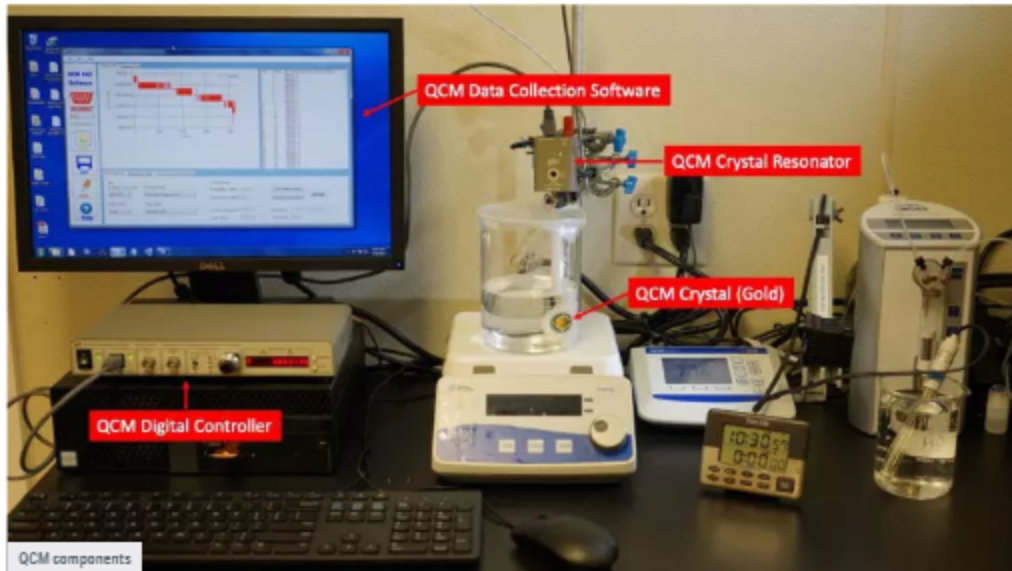
Polymers and phosphonates provide mineral scale control using the primary functionalities of threshold inhibition, sequestration, chelation, stabilisation, dispersion and crystal modification. **Threshold inhibition** involves extending the solubility of an otherwise insoluble salt beyond normal saturation limits by using an additive which functions at sub-stoichiometric levels to delay the onset of precipitation.

In a once-through system, untreated or uninhibited water passing through a condenser may take less than five seconds to begin precipitating mineral scale in a given set of operating conditions. Alternatively, effectively treated water containing a few hundred ppb of phosphonate or polymeric inhibitor may prevent the onset of precipitation by 30 seconds

or more. This difference is referred to as induction time.

In a once-through cooling application, the residence time of water passing through the condenser is typically less than ten seconds. Thus, treating a system with ppb levels of an effective polymer and/or phosphonate that extends the induction time to over ten seconds would mean the difference between scaling and not scaling the condenser. By comparison, in a recirculating system with a holding time of 24 hours or more, the level of polymer or phosphonate needed to inhibit formation of scale can range between 3 and 10 ppm on an active basis.

The extent and duration of threshold inhibition may be related to a variety of factors or conditions. These include: the driving forces for precipitation (pH, temperature, concentrations of scale-forming ions, etc.); the particular efficacy of the threshold inhibitor; other water impurities (dissolved gas and/or suspended solids); the rate of water concentration or evaporation; and the frequency of additive dosage.



Sequestration, the complexation of a metal ion such that the ion does not retain its original reactive properties, can be another important function of treatment additives, particularly of many polymers and phosphonates. Unlike threshold inhibition, it does not specify stoichiometry or specific functionality. Some phosphonate or polymer additives commonly used for mineral scale control can sequester

ions like calcium, magnesium and barium, preventing them from forming insoluble complexes with compounds such as carbonate and sulfate.

A **chelate** 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 an additive that links to a metal

ion at two or more points within the agent molecule.

In practice, polymers such as polycarboxylates and sulfonated copolymers and phosphonates act as chelating agents with most multivalent ions, due to the multiple anionic binding sites within the molecules. In common usage, chelation further implies a more permanent or substantive relationship between the ion and the ligand, and refers to stoichiometric relationships between them.

Stabilisation may refer to two distinct mechanisms. In colloidal stabilisation, precipitation in a fluid occurs, but the polymer additive prevents agglomeration of particles of $<1 \mu\text{g}$ in size. These are stabilised via electrostatic interactions with the polymer and remain suspended throughout the water phase. Colloidal stabilisation can fail due to physical or chemical changes in the fluid that result in particulate agglomeration beyond $1 \mu\text{g}$ and bulk settling of the precipitate.

The alternate usage of 'stabilisation' is as a synonym for sequestration, where a coordination complex

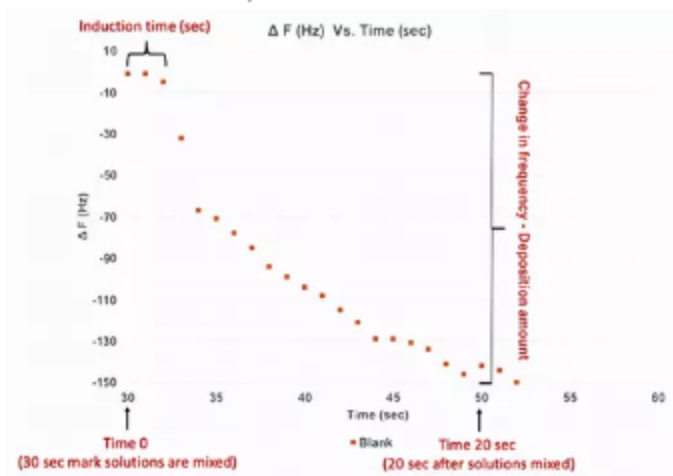


Figure 2 - Example of blank QCM experiment

Table 1 - Synthetic water conditions

Parameter	Utility A	Utility B	Utility C
Calcium (mg/l as Ca ²⁺)	91.2	83.2	170.0
Magnesium (mg/l as Mg ²⁺)	42.9	42.2	NR
Bicarbonate (mg/l as HCO ₃ ⁻)	301.5	86.9	255.0
Carbonate (mg/l as CO ₃ ²⁻)	(total as CaCO ₃)	100.0	(total as CaCO ₃)
Sulfate (mg/l as SO ₄ ²⁻)	0.0	166.9	NR
Chloride (mg/l as Cl ⁻)	NR	147.2	NR
Phosphate (mg/l as PO ₄ ³⁻)	0.0	1.0	0.0
Final Solution pH	9.0-9.2	8.8-8.9	9.2-9.3
Temperature (°C)	50°C	7°C	50°C
Calcite Saturation	94.4X	43.5X	140.3X
Langelier Saturation Index	2.5	2.0	2.7
Calcite Momentary Excess (mg/l)	46.1	19.2	35.4
Treatments	Blank 500ppb PBTC 500ppb PEPMA/HPSP	Blank 500ppb HEDP 500ppb PEPMA/HPSP	Blank 500ppb HEDP 500ppb PEPMA/HPSP

between a polymer additive and soluble ions, or surface interaction between polymer and forming crystal lattices, occurs, preventing precipitation. Typically, phosphonates do not have stabilisation properties.

Particulate dispersion is a suspension of particulates in an aqueous solution. It involves a mixture of finely divided particles, called the internal phase (often of colloidal size), being distributed in a continuous medium, called the external phase. These can be inorganic (e.g. CaCO₃), organic (e.g. biomass) or a mixture of the two.

While phosphonates do not have true particulate dispersion functionalities, polymers can be quite effective. Polymer composition and molecular weight are key determinants in deriving functionality for effective particulate dispersion.

The final mechanism discussed here in relation to scale control is

crystal habit modification. A crystal habit is the normal size and shape of a precipitated substance in a given set of environmental conditions. The formation of crystals such as CaCO₃ and their subsequent deposition onto surfaces follow a process of nucleation, lattice formation and propagation, bulk precipitation and surface deposition.

Modification of crystal habit involves introducing a 'poison' or contaminating additive that disrupts normal lattice formation. This, in turn, yields crystals tending either to re-dissolve or to precipitate in abnormal forms that deviate from the substance's untreated crystal habit. This effect tends to reduce cohesion of the crystals to each other (dispersion) and adhesion of crystals to system surfaces (scaling).

In some ways, crystal modification is the basis for mineral scale control using phosphonates and polymers.

Crystal modification impacts threshold inhibition in that it disrupts the growth and propagation of the crystal lattice such that crystalloids tend to redissolve. This frees up the polymer or phosphonate molecules to interact with other forming crystal lattices, which supports the sub-stoichiometric relationship.

Additionally, distorted crystals tend to be more easily stabilised (colloidal) and dispersed as particulates. Finally, the modified crystals themselves are much less likely to form permanent attachments to surfaces. The comparative modification was demonstrated in an earlier publication.² It can be readily shown in a comparison of untreated calcite versus a sample precipitated in the presence of PEMPA (Figure.).

In the case of once-through cooling applications, the functionalities of polymers and phosphonates described do not necessarily all come in to play due to the short retention time in the condenser, high water flow velocities and ultra-low additive dosage. For example, at ppb dosage levels and high velocities, the polymers would not be expected to provide much functionality for dispersion or stabilisation.

Evaluation methodology & results

In once-through cooling applications, threshold inhibition is primary mechanism of both polymers and phosphonates. These additives are typically used at ultra-low dosages in the ppb range, due to the short retention time of the water through the condensers. Therefore, the quantification of induction time versus additive dosage is a valuable comparison tool.

Parameter	Induction time (seconds)	Frequency change (delta Hz)	Induction time (seconds)	Frequency change (delta Hz)	Induction time (seconds)	Frequency Change (delta Hz)
Blank	<5	>250	<5	190	30	140
500 ppb PBTC	<5	100	<5	50	<10	20
500 ppb PEPMA/HPSP	>60	0	10	20-25	120	15

Table 2- Comparative QCM data for the untreated blank, 500 ppb phosphonate treatment & 500 ppb PEPMA/HPSP blend

There are several ways to compare additives using induction time experiments. For CaCO_3 , the measurement of pH inflection is one tool that indicates the onset of precipitation. As it forms in waters that are not highly buffered, a decrease in pH can be observed shortly after precipitation, due to the removal of alkalinity from the water via CaCO_3 formation.

This is one of the simplest ways to screen additives in a lab environment but with the limitations of sensitivity and the lag between actual precipitation and observance of a pH inflection. Another tool is turbidity. As insoluble CaCO_3 forms, an increase in turbidity is observed, which indicates precipitation. This method also has limitations of sensitivity and being a lagging indicator of precipitation.

A third possible method would be to examine mass balance changes in calcium and/or alkalinity via water analysis. This method is least preferred due to the need for collection, stabilisation and rapid analysis of samples within the short time frame in once-through cooling applications.

One potential way to overcome these issues is with the use of ion-specific electrodes. However, my experience is that these lack stability and accuracy. Furthermore, as with pH electrodes, they are a lagging indicator of the onset of precipitation.

The use of a quartz crystal microbalance (QCM) is a low-cost, somewhat novel, effective and highly sensitive tool for the purposes of evaluating ultra-low dosages of additives.³ In this, a quartz crystal is set to oscillate at a specific high frequency. Data collection software continuously records and reports the data.

The QCM resonator can detect changes in frequency due to deposition of foreign matter onto the surface QCM crystal at a level down to $\mu\text{g}/\text{cm}^2$. These levels can be measured in real time and observed within the residence time of typical condenser operations. Where the

other aforementioned techniques are lagging indicators of scale formation, QCM can measure real-time changes and observe the onset of scale formation and deposition.

For the experiment, a Stanford Research Systems QCM-200 instrument was used with a gold-plated quartz crystal wafer. Separate solutions of the desired cationic and anionic components of the water chemistry were prepared and heated to the indicated temperature. The former was prepared with 83 ppm calcium (as ion), 42 ppm magnesium (as ion) and heated to 71°C. The latter was prepared with 87 ppm bicarbonate, 100 ppm carbonate, 167 ppm sulfate, 147 ppm chloride, and 1 ppm orthophosphate and heated to 71°C.

After stabilisation of the baseline QCM frequency, the cation solution was treated with inhibitor and then mixed at 30 seconds (Time 0) with the anion solution to begin the experiment. Frequency changes were then observed and recorded versus time to compare inhibitors. The resulting pH from the combined solutions was 8.8-8.9. The leading industry software for scaling indices for once-through waters shows this water to have a calcite saturation of about 43.5 times, a Langelier saturation index of 2.01 and a momentary excess for calcite of about 19.18 mg/l.

This index is a good indication of the driving force for precipitation, while the calculation of momentary excess provides an understanding of how much calcite will precipitate (untreated) before the water returns to equilibrium, defined as the condition in which precipitation and dissolution rates are equal, resulting in net zero precipitation of CaCO_3 .

In this and all of the experiments presented in this paper, the QCM probe was allowed to stabilise in the cation solution until a steady baseline frequency was observed. The experiment was then started and data recording initiated. The anion solution was then added to the cation solution

at 30 seconds, which becomes Time 0, since this is the first opportunity for precipitation and potential deposition.

The untreated blank, an inflection or reduction in frequency of about 10 Hz, is recorded within three seconds of the solutions being mixed (Figure 2). This is indicative of the onset of precipitation and actual deposition onto the QCM probe. This is the time in which induction of CaCO_3 precipitation is observed and recorded.

While the initial reduction of vibrational frequency was observed at just three seconds, the test is typically continued until a full inflection is observed and no further decrease in frequency is measured. In the untreated blank test, this occurred at about 50-55 seconds. At this point, the overall change in delta frequency (ΔF) over the duration of the test provides an indication of the relative deposition quantity.

Using the same methodology described above, the QCM instrument was utilised to compare the efficacy of a PEPMA/HPSP blend to phosphonate and an untreated blank in synthetic solutions, all at 50 ppb, replicating specific water and operating conditions of three once-through utility applications.

Table 1 shows the water conditions. The final pH is that of the solution once the cation and anion solutions were combined and treated. Reporting of alkalinity is based upon customer-provided detail and was replicated in the synthetic solutions.

Figure 3 shows the comparative QCM data. In each synthetic utility water tested, the untreated blank exhibited the highest amount of deposition, as would be expected. Both PBTC and HEDP treatments at 500 ppb indicated an improvement in deposition amounts but did not necessarily delay the onset of precipitation.

In all cases, PEPMA/HPSP significantly limited the amount of total deposition observed and substantially increased the induction time where the onset of CaCO_3



Figure 3 - QCM delta frequency: Utilities A, B & C

precipitation was recorded. Table 2 shows the comparison between the treated and untreated experiments with respect to induction time and ΔF change (amount of deposition). Based upon computer modelling and momentary excess calculations, Utility A would be expected to show the greatest amount of deposition and resulting decrease in frequency. This was indeed the case where a negative ΔF of >250 Hz was observed over the 60-second duration of the test (Figure 3). Utility C would have been expected to show the next greatest drop in frequency followed by Utility B. In fact, C showed a drop of about 140 Hz compared to 190 for B. As mentioned, calcite saturation can be a gauge of the potential for precipitation or driving force. Utility C shows a calcite saturation of about 140 times versus 94 for A and about 44 for B. As such, it would be expected that the induction time

and subsequent measurement of deposition for the untreated blanks would follow this same order. In fact, C showed the longest induction time for the untreated blank, whereas A and B had similar observed induction times. At this point, there is not enough experimental data to suggest why this is the case and propose a mechanism for cause and effect.

Conclusions

Given the current issues with supply of phosphonates, the use of certain polymer treatments in once-through applications seems to be a viable option for utilities. In particular, PEPMA/HPSP shows efficacy when compared to untreated blank and phosphonate-treated samples in three synthetic once-through cooling waters. Further, a QCM proved to be a valuable tool for the evaluation of additives in short holding time applications due to its sensitivity.

The work presented in this paper provides a good start to proving both the use of the PEPMA/HPSP alternative treatment, as well as the use QCM as a laboratory evaluation tool. However, this methodology does not consider many important factors such as surface discontinuities, pre-existing deposition, resulting in increases nucleation sites, or fluid dynamics.

Additional work is also needed to understand causes of deviation from saturation models, correlation to field use of scale inhibitors, the examination of different polymeric additives, the evaluation of the combination of phosphonate and polymeric, and the investigation of additional water chemistries.

This future work will help bolster the methodology and develop data sets to support dosage model development. Despite the limitations of the data and work conducted thus far, the approach demonstrates promise and has led to a commercially successful product in the field. •

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Mike Standish
 VICE PRESIDENT - WATER ADDITIVES

RADICAL POLYMERS - DIVISION OF MFG CHEMICAL, LLC

+1 423 316 9877
 mike.standish@radicalpolymers.com
 www.radicalpolymers.com



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