

Gypsum Scale Inhibitors Performance in the Presence of Impurities

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ABSTRACT

In the present work a variety of polymers with different functional groups and molecular weight (MW) were tested as gypsum scale inhibitors. The polymers tested include: poly(acrylic acid) PAA; poly(maleic acid), PMA; poly(aspartic acid), PASP; poly(epoxysuccinic acid), PESA; carboxymethyl inulin (CMI-25); copolymers of maleic acid:sulfonated styrene, PMAS); maleic acid:vinyl pyrrolidone, PMVP. The results indicated that performance of polymers strongly depends on the polymer architecture. Based on the data collected, the polymers may be ranked as follows: PAA > PMA > PASP > CMI-25 > PESA. Among the maleic acid based copolymers the performance ranking is as follows: PMA > PMAS > PMVP1 (MW 15k) > PMVP2 (MW 60k).

The influence of divalent metal ions (i.e., Cu, Zn, Mn) and trivalent metal ions (i.e., Al, Fe) as gypsum scale inhibitors was investigated. It was found that divalent and trivalent metal ions are ineffective gypsum scale inhibitors. Results also reveal that trivalent metal ions exhibit antagonistic effect on polymer performance. This study also presents results on the effect of a variety of surfactants (i.e., ionic, non-ionic, cationic) on polymers performance. Data reveal that whereas all surfactants are ineffective gypsum inhibitors, the presence of low concentrations of cationic surfactant (e.g., cetyltrimethyl ammonium chloride), CTAC, shows negative impact on polymer performance.

Keywords: gypsum, precipitation, inhibition, polymers, metal ions, surfactants

INTRODUCTION

Deposit formation on equipment surface in aqueous systems including domestic, commercial, and industrial processes is a common and expensive problem. Industrial processes affected by the deposition of unwanted materials such as mineral scales, suspended matter, and biomass include desalination by reverse osmosis process, pulp and paper manufacturing, sugar processing, cooling, boiler, geothermal, etc. Problems associated with deposits include blocking of pipes, pumps, plugging of membrane pores,

impedance of heat transfer, localized corrosion attack, often resulting in increased production and maintenance cost. The severity of deposit problem will vary depending on water chemistry, system operating conditions, metallurgy, and flow characteristics.

Calcium sulfate is one of the most commonly encountered scale deposits in desalination of seawater and is referred to as non-alkaline scale. It occurs in three different crystalline forms: calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, gypsum), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, plaster of Paris) and calcium sulfate anhydrite (CaSO_4). All these forms are more soluble than calcium carbonate and magnesium hydroxide.¹ In cooling water and reverse osmosis-based desalination process gypsum is most frequently encountered scale whereas calcium sulfate hemihydrate and calcium sulfate anhydrite are the most commonly formed salts in high temperature processes such as multistage flash distillation. The crystallization of calcium sulfate is a complex phenomenon influenced by various factors including supersaturation, total dissolved solids, temperature, impurities, organics, etc.

During the last four decades, the precipitation and inhibition of gypsum has been the subject of numerous investigations. Dogan et al.² using the spontaneous precipitation method, studied the influence of poly(ethyleneoxide-block-poly(methacrylic acid)) polymers as gypsum growth inhibitors. Results of their study show that inhibition increases with acid content of the polymer. Sethilmurugan et al.³ in their investigation on the evaluation of maleic acid:acrylic acid:acrylamide copolymers reported that these polymers are effective gypsum inhibitors. In another study, Amjad and Koutsoukos⁴ reported that polymer molecular architecture was an important parameter in determining the activity of the tested polymers. Low molecular weight (MW) proved to be more efficient than the higher MW polymers.

The presence of soluble impurities such as inorganic/organic flocculant, metal ions, and biocides present in cooling waters have been shown to influence the performance of polymeric scale inhibitors. Ahmad⁵ studied the efficacy of various additives (i.e., polyphosphate, phosphonate, polymer, polymer/phosphonate blend) as gypsum scale inhibitors. Among the various inhibitors tested, polyacrylate exhibited the best performance. In another study by Shih et al.⁶ it was reported that trace levels of aluminum ions show significant antagonistic impact on the performance of various gypsum scale inhibitors. Hamdona and his coworkers⁷ studied the kinetics of gypsum precipitation in the presence of divalent metal ions and reported that Mg^{2+} is a better gypsum inhibitor than Fe^{2+} probably due to the formation of MgSO_4 ion pairs. In contrast, Weijnen et al.⁸ observed that 63 mg/L of Cu^{2+} or 65 mg/L Zn^{2+} enhanced crystal growth rate of gypsum. Amjad and his coworkers⁹ studied the influence of recirculating cooling water system

impurities on the performance of calcium phosphate inhibiting polymers. It was shown that Mn^{2+} and Cu^{2+} ions are antagonistic to the performance of acrylate-based copolymers but the adverse effect is not as pronounced as with Fe^{3+} . In another study, Amjad¹⁰ reported that surfactant containing various functional groups perform poorly compared to polyacrylates as gypsum scale inhibitors. Results on the impact of cationic surfactant (e.g., cetyltrimethylammonium chloride, CTAC) suggest that CTAC exhibits an antagonistic effect on the efficacy of polymers. It has been found that cationic polymer (e.g., diallyldimethylammonium chloride, DMAC) shows much stronger antagonistic effect than the CTAC on the efficacy of polymers used as gypsum scale inhibitors.

Factors governing the performance of polymers can be divided into two distinct categories: (1) those that affect the solubility of the scale forming salts and (2) those that affect the action of the polymer. Solution pH affects the deprotonation of polymer, the affinity of polymer towards ionic species, and the adsorption of polymers onto growing crystal surfaces. Solution ionic strength also affects polymer performance. Additionally, all open cooling towers using natural waters contain certain levels of contaminants such as transition metal ions and particulate matter, can affect polymer performance. The present work is a quantitative investigation of the effects of various impurities present at low concentrations (<20 mg/L) of metal ions i.e., Al^{3+} , Fe^{3+} , Mg^{2+} , Mn^{2+} , and Zn^{2+} , on the performance of gypsum scale inhibitors. This study also reports on the influence of cationic polymeric coagulant/flocculant on the inhibitory activity of synthetic, natural, and hybrid polymers. Additionally, the impact of commercial surfactants (anionic, non-anionic, cationic, etc.) on polymers performance was also studied.

EXPERIMENTAL

Materials

Reagents grade chemicals and grade A glassware were used. Stock solutions of calcium chloride and sodium sulfate were prepared using distilled, CO_2 -free water and filtered through 0.22 μm filter paper. The calcium ion concentration was determined by atomic absorption spectrophotometry. The standardization of sodium sulfate was done by ion chromatography. Polymers and surfactants evaluated in this study were commercial materials and their stock solutions were prepared on dry active solids basis.

Gypsum Precipitation Procedure

Gypsum precipitation experiments were carried out by adding known volume of stock solution of sodium sulfate to known volume of water in a glass bottle maintained at 66°C.

Following temperature equilibration, a known volume of calcium chloride solution was added with continuous stirring. In experiments involving the inhibitor and impurities, a known volume of the stock solution of inhibitor and/or impurities were added to the sodium sulfate solution prior to the addition of calcium chloride. The total volume of the supersaturated solutions (CaCl_2 0.225M, 20 mL; Na_2SO_4 0.225M, 20 mL) containing varying amounts of polymer and impurities was 100 mL. The progress of gypsum precipitation in the absence and presence of inhibitors was followed by analyzing aliquots of the filtered (0.22 μm filter paper) solution for calcium by EDTA titrations. The pH value of the gypsum supersaturated solution was adjusted to 7.00 ± 0.05 by the addition of standard HCl and/or NaOH solutions as needed. Experiments were run in duplicate/triplicate and results showed good reproducibility ($\pm 7\%$).

Polymer Efficacy as Gypsum Inhibitor

The driving force for gypsum precipitation from supersaturated solutions depends upon the saturation index, SI, defined as: $\text{SI} = \text{IAP}/K_s^\circ$, where IAP is ion activity product and K_s° is the thermodynamic solubility product. Under the experimental conditions used, SI values for gypsum and calcium sulfate anhydrite were 2.09 and 1.78, respectively. It should be noted that in our experiments it was only gypsum that was found in precipitated solids.

The performance of the tested additives as gypsum inhibitors was calculated using the following equation:

$$\text{Percent inhibition (\%I)} = (C_1 - C_2) / (C_3 - C_2) \times 100 \quad (1)$$

Where:

C_1 = Concentration of calcium in the filtrate in the presence of an inhibitor at 20 hr.

C_2 = Concentration of calcium in the filtrate in the absence of an inhibitor at 20 hr.

C_3 = Concentration of calcium at the beginning of the experiment.

RESULTS AND DISCUSSION

Gypsum Inhibition by Homopolymers

In industrial installations and domestic applications (i.e., water treatment, geothermal, oilfield, desalination, sugar processing, laundry, membrane cleaners, etc.) polymeric and non-polymeric additives are used for a variety of reasons including scale inhibition, scale removal, dispersancy of suspended matter, corrosion inhibitors, metal ions chelators, etc.

The incorporation of scale inhibitor in water treatment formulation which inhibits gypsum formation is a reliable approach to prevent deposition of unwanted materials on equipment surface. The inhibitors commonly employed fall into two main categories mainly phosphonates and acrylic acid, maleic acid-based homo- and copolymers containing different functional groups. Figure 1 lists the polymers tested. It can be seen that polymers vary markedly in terms of molecular structure, composition, and MW.

