PERFORMANCE OF POLYMERIC AND NON-POLYMERIC ADDITIVES AS DISPERSANTS FOR CALCIUM HYDROXYAPATITE IN AQUEOUS SYSTEMS

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Keywords: Ca-hydroxyapatite, dispersion, polymeric, non-polymeric dispersants

Abstract: The influence of polymeric and non-polymeric additives as dispersants for calcium hydroxyapatite, HAP, was investigated in an aqueous system. The polymeric additives tested include: homo-polymers of acrylic acid (AA), maleic acid, methacrylic acid, 2-acrylamido 2-methylpropane sulfonic acid, (SA); co-polymer of AA:SA and ter-polymers of AA:SA:t-bAM (tertiary butyl acrylamide) and AA:SA:SS (sulfonated styrene). It was found that polymer architecture i.e., monomer type, monomer content, molecular weight, and polymerization solvent, strongly influences the performance of polymer as HAP dispersant. The non-polymeric additives investigated include: phosphonates and surfactants. The dispersancy data reveal that non-polymeric additives are inferior to polymeric additives in dispersing HAP.

(Received January 14, 2006; Accepted July 24, 2006)

INTRODUCTION

One of the major challenges encountered in operating industrial water systems (i.e., cooling, boiler, desalination, oil production) is the accumulation of unwanted deposits on heat transfer surfaces¹. These deposits can be categorized into the following four groups: (a) Mineral scales i.e., calcium phosphate, calcium carbonate, barium sulfate, etc., (b) Suspended matter (i.e., clay, silt, mud, etc.) (c) Corrosion products (i.e., iron oxides, zinc oxide, copper oxides, iron phosphates, etc.) and (d) Microbiological mass.

In a boiler, these deposits normally accumulate in low circulating areas, i.e., bottom of the steam drum in two drum boiler. These deposits may become immobilized during upset conditions resulting in deposit build up in high input area. HAP has been reported to be a major scale forming salt in boilers operating on phosphate based treatment program². In desalination of sea/brackish waters by reverse osmosis process, deposition of calcium phosphate, calcium carbonate and other inorganic salts may result in a decrease in productivity, poor water quality, and premature membrane failure³. In the oil industry carbonates, sulfates, and phosphates salts of calcium barium and strontium are very common. The development of these salt layers on heat

exchanger surfaces results in production losses. Thus, the effective operation of industrial water systems continues to depend on the control of deposits in these systems.

Calcium phosphate deposits have also been encountered on heat exchangers during pasteurization of milk⁴. The formation of calcium phosphate is an important process in physiological situations such as formation of pathological stones, teeth, and bones. In addition, calcium phosphates are widely produced in industry, in such forms as ceramics, nutrient supplements, medicine, dentrifices, and stabilizers for plastics.

Historically, the influence of polymers as precipitation inhibitors for calcium phosphates has been heavily researched. However, the effect of polymer architecture on dispersion of calcium phosphates, especially hydroxyapatite has been mostly overlooked. This paper explores the influence of polymeric and non-polymeric additives as dispersants for HAP particles in an aqueous system.

EXPERIMENTAL

Grade A glassware and reagent grade chemicals were used. Hydroxyapatite used in the present study was obtained from Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA. The polymeric

additives used as dispersants were selected from commercial and experimental materials. All dispersant solutions were prepared on a dry weight basis. The desired concentrations were obtained by dilution.

Dispersancy experiments were run in 100 mL graduated cylinders and at room temperature ($\sim 23^{\circ}\text{C}$). The HAP dispersion test was conducted by adding 0.25 g of HAP to known volume of synthetic water containing varying amount of dispersant. After the addition of HAP, cylinders were covered with parafilm and manually mixed with a motion similar to repeatedly turning over an hourglass for 1 minute and left to stand. The synthetic water contained calcium chloride, magnesium chloride, sodium chloride, sodium sulfate and sodium bicarbonate. The experimental solution in the cylinder totaled 100 mL and was comprised of varying dosage (1.0 to 10 parts per million, ppm) of dispersant, 0.25 g HAP, 105 mg/L Ca, 31 mg/L Mg, 353 mg/L Na, 600 mg/L Cl, 209 mg/L sulfate, and 116 mg/L bicarbonate. The structures of polymeric dispersants used in the present investigation are shown in Table 1. The polymers tested include: Homo-polymers of acrylic acid (HPAo and HPAw of varying molecular weight, MW, made in organic (o) solvent and water (w) respectively, and maleic acid (HPM); copolymer of acrylic acid:2-acrylamido 2-methylpropane sulfonic acid, CP-1, CP-2; and ter-polymers of acrylic acid:2-acrylamido 2-methyl propane sulfonic acid:tertiary butyl acrylamide, TP-1; and acrylic acid:2-acrylamido 2-methyl propane sulfonic acid:sulfonated styrene, TP-2.

A standard HAP dispersion experiment consisted of eight tests running simultaneously in eight cylinders. At hourly intervals transmittance (%T) readings were taken using a Binkmann PC/910 colorimeter using a 420 nm filter. Results from these experiments have shown good reproducibility within $\pm 5\%$. Dispersion (%D) was calculated from %T readings as a function of HAP dispersed compared to control, which was a test run, with no dispersant. Therefore, greater dispersion was indicated by greater %D. The %D was calculated using the following equation:

$$\% \text{Dispersion} = [100 - \{ \% T \times (1/80) \times 100 \}]$$

RESULTS AND DISCUSSION

A. Duration of Dispersion Time: In order to study the effect of time on HAP dispersion, a

series of experiments were carried out and %D was measured at known time intervals. Starting

Table 1. Polymers tested.

Structure	
$\left(\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right)_n$	poly(acrylic acid)
HPAo HPAw	
$\left(\underset{\text{COOH}}{\text{CH}} - \underset{\text{COOH}}{\text{CH}} \right)_n$	poly(maleic acid)
HPM	
$\left(\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right)_m \left(\text{CH}_2 - \underset{\text{CO}}{\text{CH}} \right)_n$ $\text{NH} \text{---} \text{C} \text{---} \text{CH}_3$ $\text{CH}_2\text{SO}_3\text{H}$	poly(acrylic acid: 2-acrylamido 2-methylpropane sulfonic acid)
CP-1 (75:25) CP-2 (60:40)	
$\left(\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right)_m \left(\text{CH}_2 - \underset{\text{CO}}{\text{CH}} \right)_n \left(\text{CH}_2 - \underset{\text{CO}}{\text{CH}} \right)_y$ $\text{NH} \text{---} \text{C} \text{---} \text{CH}_3$ $\text{CH}_2\text{SO}_3\text{H}$ $\text{C}(\text{CH}_3)_3$	poly(acrylic acid: 2-acrylamido 2-methylpropane sulfonic acid: tertiary butyl acrylamide)
TP-1	
$\left(\text{CH}_2 - \underset{\text{COOH}}{\text{CH}} \right)_m \left(\text{CH}_2 - \underset{\text{CO}}{\text{CH}} \right)_n \left(\text{CH}_2 - \underset{\text{CO}}{\text{CH}} \right)_y$ $\text{NH} \text{---} \text{C} \text{---} \text{CH}_3$ $\text{CH}_2\text{SO}_3\text{H}$ SO_3H	poly(acrylic acid: 2-acrylamido 2-methylpropane sulfonic acid: sulfonated styrene)
TP-2	

Table 2. Phosphonates and surfactants tested.

Chemical Name
Aminotris(methylenephosphonic acid) (AMP)
1-Hydroxyethylidene 1,1-diphosphonic acid (HEDP)
2-Phosphonobutane 1,2,4-tricarboxylic acid (PBTC)
Sodium dodecyl sulfate (SDS)
Sodium xylene sulfonate (SXS)

at time zero, the %D of any dispersant or control (no dispersant) steadily declines as time increases due to HAP settling. The trend of time versus %D is apparent in Figure 1. As evident

from Figure 1, %D strongly depends upon settling time. For example, %D values obtained in the presence of 5 ppm (parts per million) of HPAo5 [poly(acrylic acid), organic solvent polymerized, molecular weight, MW, 5000] at 1hr and 3hr are 65% and 33%, respectively. As shown in Figure 1 increasing the dispersion time from 3hr to 5hr resulted in ~40% additional decrease in %D value. In our experiments we selected 3hr for comparing the performance of various dispersants.

FIGURE 1. HAP dispersion as a function of time in the presence of 5 ppm HPAo5.

FIGURE 2. HAP dispersion by varying dosages of HPAo5.

B. Dispersant Concentration: In Figure 2 profiles of %D versus dispersant concentration for HPAo5 are illustrated. The data clearly indicate that dispersant concentration strongly affects the ability of a dispersant to disperse HAP. For example, at a 1.0 ppm concentration, HPAo5 shows poor dispersancy (<5%). However, as the dispersant concentration is increased from 1 ppm to 5 ppm (five folds) concentration, dispersant performance significantly improved (>five folds) and maximum dispersancy is obtained at 7.5 ppm.

C. Polymerization Solvent: The effect of polymerization solvent on the dispersing ability

of HPA (homo-polyacrylic acid) was investigated. Results presented in Figure 3 show that in the presence 5 ppm of polymers polymerized in organic solvent (i.e., HPAo2, MW 2,000) and HPAo5, MW 5000) perform better than water polymerized homo-polymers (i.e., HPAw2 and HPAw5) of similar molecular weights. For example, under similar experimental conditions, %D values obtained for HPAo2 and HPAw2 are 42% and 13%, respectively. Similar trend in polymer performance between HPAo5 and HPAw5 was also observed. The difference in performance may be attributed to several factors including branching, end groups, and the carboxyl groups available for adsorption on to HAP. It should be pointed out that in our studies on the compatibility of HPA with calcium ions, solvent polymerized HPA showed better tolerant to calcium ion than the water polymerized HPA⁵.

D. Effect of Polymer Molecular Weight: The role of molecular weight on the performance of polymer as precipitation inhibitor, dispersant, metal ion stabilizer, and complexing agent has been the subject of numerous investigations⁶⁻⁸. It is generally agreed that an optimum performance is achieved with a 2000 MW HPA. For co-polymers the optimum molecular weight is ~10000 to 20000 depending upon the type of co-monomers used. Figure 4 presents HAP dispersion data for poly(acrylic acids) of varying molecular weights. As illustrated in Figure 5 the %D value increases as the polymer molecular weight is increased from 800 to 2000. The data also show that %D value decreases as the MW of P-AA is increased from 2000 to 10000 for HPAo polymerized in organic solvent. It should be noted that similar MW dependence was also observed for water polymerized P-AAs.

FIGURE 3. Effect of polymerization solvents on the performance of homo-polymers.

FIGURE 4. HAP dispersion by poly(acrylic acids) of varying molecular weight.

E. Effect of Homo-Polymers: The influence of homo-polymers containing different functional groups on HAP dispersion was studied by conducting a series of experiments under similar conditions. The data presented in Figure 5 for a number of carboxyl and sulfonate groups containing homo-polymers (i.e., poly(acrylic acid), HPA; poly(methacrylic acid), HPMA; poly(maleic acid), HPM; poly(sulfonated styrene), HPSS; and poly(2-acrylamido 2-methylpropane sulfonic acid), HPS indicate that these polymers disperse HAP but to a varying degree.

Among all the homo-polymers containing carboxyl group tested HPMA compared to HPA and HPM exhibits the poor performance. The observed poor performance shown by HPMA may be attributed to the interference in carboxyl group adsorption on HAP by methyl group. It is interesting to note that polymers devoid of carboxyl group (i.e., HPS and HPSS) perform better than carboxyl group containing polymers of similar molecular weights.

FIGURE 5. HAP dispersion by various homo-polymers.

F. Effect of Co-polymers: The influence of substituting the carboxyl group with other groups of varying chain length and ionic charge (i.e., sulfonated styrene, SS; 2-acrylamido 2-methylpropane sulfonic acid, SA) was investigated for their ability to disperse HAP. Results presented in Figure 6 clearly show that polymers containing sulfonate group compared to homo-polymers, exhibit good to excellent dispersion power for HAP. For example, %D values obtained for CP-1 (AA:SA, 75:25) and CP-2 (AA:SA, 60:40) are 69% and 78% compared to 8% and 28% obtained for homo polymer of acrylic acid (HPA) and homo-polymer of 2-acrylamido 2-methyl propane sulfonic acid (HPS). The data suggest that sulfonate group present in CP-1 and CP-2 adsorb strongly on HAP than the carboxyl group present in poly(acrylic acid). In addition, sulfonate group being more acidic than carboxyl group imparts more negative charge to HAP particles resulting in stronger repulsion between the charged HAP particles.

FIGURE 6. HAP dispersion by homo- and co-polymers.

FIGURE 7. HAP dispersion by homo- and ter-polymers.

G. Effect of Ter-polymers: Figure 7 presents HAP dispersion data on two ter-polymers. As illustrated both ter-polymers exhibit good to excellent performance as HAP dispersing agents. The excellent dispersion power observed for ter-polymers may be attributed to sulfonate group present in the polymers.

H. Effect of Solution Temperature: Figure 8 shows data on the effect of solution temperature on the dispersing ability of homo-, co-, and ter-polymers. It is evident from the data that poly(acrylic acid) lost ~80% dispersing ability compared to ~10% loss observed for co- and ter-polymers. It is interesting to note similar temperature dependence of polymers has been reported for calcium carbonate dispersion by low molecular weight poly(acrylic acid)⁹.

FIGURE 8. Effect of solution temperature on the performance of polymeric additives.

I. Effect of Non-polymeric Additives: The influence of phosphonates, non-polymeric ingredients commonly used in water treatment formulations, was investigated by conducting a series of dispersion experiments under similar experimental conditions. Figure 8 shows the plots of %dispersion for three different phosphonates. It is evident from the data that phosphonates compared to acrylic acid based co- and ter-polymers (Figures 5 to 8) exhibit poor dispersancy ability for HAP. It should be pointed out that phosphonates has been shown to exhibit superior performance compared to co- and ter-polymers in inhibiting the precipitation of calcium carbonate from aqueous solutions. This suggests that phosphonate group compared to carboxyl group present in polymeric additives has a strong adsorption affinity for calcium carbonate.

Surfactants are commonly used in shampoos, laundry detergents, dentrifices, and hard surface cleaners. The impact of surfactants (i.e., sodium lauryl sulfate, SLS; sodium dodecyl sulfate, SDD,

and sodium xylene sulfonate, SDS, on HAP dispersion was studied under similar experimental conditions. Dispersion data presented in Figure 8 reveal that sulfonate containing surfactant (SXS) exhibit better performance than sulfate containing surfactants such as SDS. The observed better performance shown by SXS is consistent with earlier results (Figures 5, 6, and 7) on the performance of polymers containing sulfonate groups (i.e., CP-1 and TP-2).

FIGURE 9. HAP dispersion by phosphonates and surfactants.

SUMMARY

This study has shown that:

- The dispersion of HAP increases with increasing dispersant concentrations.
- Polymer architecture i.e., monomer type, monomer content, polymerization solvent, and molecular weight plays an important role on the dispersion power of polymer.
- Solution temperature exhibits marked negative influence on the dispersing power of poly(acrylic acid).
- Non-polymerized dispersants such as phosphonates and surfactants, are inferior to acrylic acid-based homo-, co-, and ter-polymers.

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