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Use of Sodium Polyaspartate for the Removal of Hydroxyapatite/Brushite Deposits from Stainless Steel Tubing

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This research investigates the use of sodium polyaspartate, a nontoxic, biodegradable polycarboxylic sequestrant, for removing calcium phosphate deposit consisting of hydroxyapatite (HAP) and brushite or dicalcium phosphate dihydrate (DCPD) from stainless steel surfaces. Cleaning studies show that the use of sodium polyaspartate under alkaline conditions significantly enhances the removal rates when compared to deionized water. In acidic solutions, sodium polyaspartate concentrations below 300 ppm inhibit removal of HAP/DCPD deposits whereas higher concentrations increase the removal rate. Comparative cleaning studies at alkaline pHs show that sodium polyaspartate cleans the surface at a rate comparable to sodium citrate but slower than in ethylenediaminetetraacetic acid. Supplementary dissolution experiments show that sodium polyaspartate enhances the HAP/DCPD dissolution rate while inhibiting the release of Ca^{2+}. On the basis of these findings, we have concluded that sodium polyaspartate improves the HAP/DCPD dissolution and cleaning rates by Ca^{2+} sequestration.

Introduction

Calcium orthophosphate deposition causes cleaning problems in a number of situations. In industrial water cooling systems, the use of water containing higher orthophosphate levels, i.e., recycled water or untreated makeup water, leads to calcium orthophosphate scaling. Due to the inverse solubility of the calcium phosphate at higher temperatures, soluble calcium and phosphate ions tend to form sparingly soluble calcium phosphate scales on the heat-exchange surfaces of heating towers and evaporators. Likewise, high-temperature (120−140 °C) dairy processing causes the formation of mineral-rich protein fouling deposits (70 wt % mineral, 15−20 wt % protein, 4−8 wt % fat) (Burton, 1968). Ninety percent of the mineral in milk deposits is calcium phosphate (Lyster, 1965). The precipitation and deposition of these hardness salts on industrial processing equipment lower the efficiency of heat-exchange surfaces and obstruct fluid flow in piping.

The precipitation of calcium phosphate in the body causes a number of medical problems. Pathological biological calcification causes cardiological problems including clinical failure of bioprosthetic heart valves (Webb et al., 1988) as well as dental problems, such as the formation of calculus on teeth (Gaffar et al., 1995). The calcium orthophosphates commonly encountered in mineral deposits are hydroxyapatite (HAP; $Ca_5(PO_4)_3OH$) and brushite or dicalcium phosphate dihydrate (DCPD; $CaHPO_4 \cdot 2H_2O$).

Use of Inorganic Acids in Mineral Cleaning. Typically, strong inorganic acids, such as hydrochloric acid and sulfuric acid, are used to remove mineral deposits from industrial processing equipment. The removal of mineral deposits can occur by dissolution and by mechanical cleaning. The dissolution process involves two steps: (1) an interfacial dissolution process in which the substance is transferred from the solid phase to the liquid phase followed by (2) a mass-transfer process in which the dissolved substance is transferred from the solid/liquid interface into the bulk fluid. Mass transfer may be controlled by a diffusive flux caused by a concentration gradient or by convective diffusion caused by fluid flow. Mechanical cleaning involves the removal of particles by the shear force imparted by the fluid flow past the deposit. Because strong acids are used in cleaning to enhance mineral solubility, the dissolution processes are of primary interest in acid cleaning.

In a previous paper, we studied the removal of DCPD deposits from stainless steel tubing in acidic solutions under turbulent flow (Grant et al., 1996). To determine the cleaning mechanism, real-time cleaning data were collected during the removal of ^{32}P-labeled calcium phosphate deposits from stainless steel tubing using a solid scintillation technique. The data were analyzed under the following assumptions:

(1) The removal of calcium phosphate occurs by dissolution only; i.e., it is not due to the mechanical removal of solid particles from the film due to shear forces.

(2) Interfacial dissolution is fast compared to mass transfer.

Gilliland and Sherwood's correlation for the mass-transfer coefficient for turbulent flow in tubes indicates that a removal rate based solely upon mass-transfer limitations is proportional to fluid average velocity to the 0.83 power (Welty et al., 1984). The data reported by Grant et al. (1996) showed that the cleaning rate was proportional to the average fluid velocity raised to a power of 0.7, suggesting that mass transfer controls the removal of DCPD.

Most of the previous work on the dissolution of calcium orthophosphates by strong acids has been performed in a batch mode in which the solid phase is a powder that is suspended by continuous stirring in a chemical reactor (Christoffersen et al., 1978, 1983;

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Gramain et al., 1989; Schaad et al., 1994; Thomann et al., 1990). Christoffersen et al. (1978) studied the dissolution mechanisms of HAP to determine whether the dissolution of seed HAP crystals in distilled water was controlled by interfacial dissolution or mass transfer. They found that the measured rate of HAP dissolution was much lower than the rate calculated for diffusion-controlled dissolution. From these results, they concluded that the dissolution of calcium phosphate was controlled by the interfacial process rather than by mass transfer. Thomann et al. (1990) also studied the kinetics of the dissolution of HAP powder. The dissolution of the powder was studied at constant pH in the range of 3.7−6.9. The proton uptake and calcium release were recorded continuously during the dissolution studies. According to Thomann et al. (1990), the dissolution rate was limited by the formation of a layer of adsorbed calcium ions on the crystal surface. This ionic layer restricts the diffusion of calcium, phosphate, and hydroxyl ions through the solid/liquid interface and thus limits the dissolution rate. Analogous batch dissolution studies showed that the dissolution of DCPD is a diffusion-controlled process (Nancollas and Marshall, 1971).

Although the experimental conditions and techniques differ, these results provide an indication of the mineral dissolution mechanisms under acidic conditions. Under the conditions of fast external mass transfer, the dissolution of HAP in acid solutions is controlled by interfacial processes. On the other hand, mass transfer plays a role in the dissolution of DCPD. If the solid consists of a mixture of HAP and DCPD, both mass transfer and surface reactions should be taken into account.

Use of Detergent Co-builders To Minimize Mineral Deposition. While strong inorganic acids effectively clean the mineral deposits, they are corrosive, toxic, and harmful to the environment. An alternate method is adding co-builders to detergent formulations to prevent the precipitation and the accumulation of calcium salts. These builders are calcium sequestrants that form water-soluble complexes with free calcium ions in solution to prevent crystal nucleation which occurs through the binding of calcium with phosphate. These inhibitors may also adsorb onto the crystal surface sites to retard or prevent crystal growth.

In the 1970s, sodium tripolyphosphate (STPP; $Na_2P_3O_{10}$) was the primary builder in detergent formulations used to prevent the precipitation of inorganic salts (Cahn, 1994). This builder was an effective sequestrant of free calcium cations and acted as a dispersant to keep the contaminant from redepositing on the surface. However, the use of STPP has been banned or restricted in many parts of the world, because it has been linked to the eutrophication of lakes and stagnant waters. Thus, substitutes for STPP are currently used in detergent formulations. In applications where a strong, water-soluble chelating agent is required, ethylenediaminetetraacetic acid (EDTA) is the preferred sequestrant. As shown in Figure 1, EDTA has six bonding functional groups (four carboxylic acid groups and two nitrogen groups). EDTA also degrades slowly and may cause heavy-metal mobilization in groundwater (Means et al., 1980; Xue et al., 1995). Sodium citrate may be chosen when a biodegradable, nontoxic, and water-soluble calcium sequestrant is required. Sodium citrate acts as a dispersant, but it is a weak sequestering agent. Citrate ions have only four bonding functional groups (three carboxylic acid groups and one hydroxyl group). The search for detergent co-builders to replace STPP is ongoing.

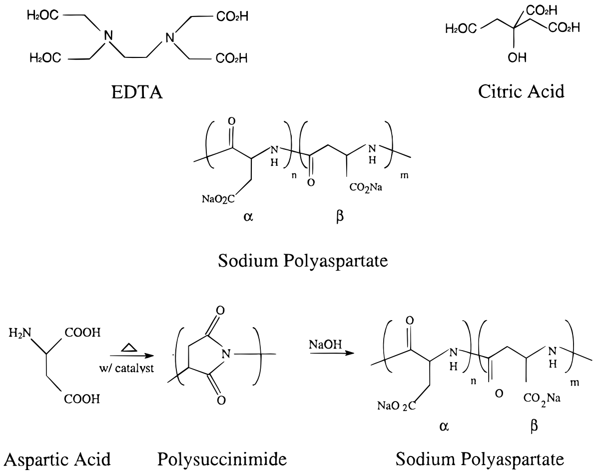

Figure 1. Chemical structures.

Studies have shown that some sequestering agents promote the dissolution of HAP crystals (Christoffersen and Christoffersen, 1983; Arbel et al., 1991). Christoffersen and Christoffersen (1983) investigated the effects of citrate ion concentration on the dissolution kinetics of HAP at a neutral pH. At low citrate concentrations, they found that HAP dissolution is inhibited by sodium citrate. This inhibition was attributed to the adsorption of citrate ions onto the crystal surface. At higher concentrations citrate ions caused an increase in the rate of dissolution. This increase was attributed to complexation of citrate ions with free calcium ions in solution. Arbel et al. (1991) studied the dissolution of HAP by complexing agents, including EDTA and sodium citrate, at the physiological pH (pH 7.4). Scanning electron microscopy (SEM) micrographs of HAP powder revealed the formation of concave holes on the crystal surface following exposure of the mineral to the complexing agent. According to Arbel et al. (1991), these findings showed that the complexants adsorbed onto the crystal surface, enwrapped the calcium cation, and leeched out the calcium. The ability of the calcium complexing agent to dissolve HAP was described in terms of the sequestration ability of the molecule. Thus, sodium citrate was found to be a weaker dissolving agent than EDTA. The knowledge that sequestrants may dissolve calcium phosphate under certain conditions opens up new opportunities for the investigation of the use of sequestrants as mineral-removal agents.

Investigation of Sodium Polyaspartate for Mineral Cleaning. Our research explores the use of sodium polyaspartate (PASP), the sodium salt of poly(aspartic acid), for the removal of HAP and DCPD deposits from stainless steel. Polyaspartate is a promising developmental polycarboxylic sequestrant that is nontoxic, biodegradable, and water-soluble (Freeman et al., 1996). As shown in Figure 1, the sequestrant consists of polymerized α and β aspartyl residues, each containing a carboxylic functional group.

The use of polyaspartate for the inhibition of crystal growth originated from studies of the regulation of biomineralization in oyster shells (Sikes and Wheeler, 1988). Sikes and Wheeler extensively studied the organic matrix of an oyster shell in order to understand the principal function of the organic matrix on the growth of the oyster shell structure which is 99% $CaCO_3$. They found that polyaspartate, a natural component of the organic matrix, inhibited the growth of the shell.

Sodium polyaspartate has been synthesized for commercial use. Polyaspartate is commonly synthesized by a two-step process (Figure 1) (Mosig et al., 1997; Wolk et al., 1994). First, aspartic acid undergoes acid-catalyzed thermal polymerization to produce poly(anhydroaspartic acid) or polysuccinimide. Then, polysuccinimide is hydrolyzed in a caustic solution to form sodium polyaspartate. The resulting polyaspartate has a linear polyamide backbone structure that enables the polymer to biodegrade rapidly and completely (Freeman et al., 1996). Ecotoxicity studies on polycarboxylates have shown that these polymers are nontoxic and do not adversely impact the environment (Freeman et al., 1996).

Currently, sodium polyaspartate is used as the following: a dispersant to prevent the redeposition of minerals (Garris and Sikes, 1993), an inhibitor of the salt crystallization and precipitation (Mueller and Sikes, 1993), a water softener, and a corrosion inhibitor (Silverman et al., 1995). To our knowledge, sodium polyaspartate has not been studied as a means of dissolving calcium phosphate in alkaline solvents.

In the first part of our work, we measured the effect of sodium polyaspartate on HAP/DCPD removal. In these experiments, real-time measurements of the amount of radiolabeled calcium phosphate remaining on the surface as a function of time were conducted. The experiments were carried out using an on-line solid scintillation detection technique in a continuous-flow system. Comparative cleaning studies were carried out in the presence of EDTA and sodium citrate. To ascertain whether sodium polyaspartate affected the mineral dissolution rate, supplementary batch HAP/DCPD dissolution experiments were carried out. During the dissolution experiments, the total calcium content and the free calcium concentration in the solvent were measured. Measurements of the total analytical calcium concentration in the supernatant were used to track the dissolution rate. The free calcium activity levels illustrate the role of sequestration in the dissolution/removal of HAP/DCPD.

Experimental Section

Materials. Polysuccinimide synthesized by the acid-catalyzed thermal polycondensation of L-aspartic acid ($M_w = 10\,000$, $M_n = 2730$) was prepared by Rohm & Haas as described by Freeman et al. (1996). Crystalline aqueous suspensions of HAP (25% solids) and DCPD (25% solids) were obtained from the Sigma Chemical Co. The radiolabeled DCPD used for the cleaning studies (described below) was obtained by irradiating a 10-g sample of a DCPD suspension (Sigma Chemical Co.) to 10 mCi in a Pulstar nuclear reactor at North Carolina State University. EDTA was obtained from Sigma Chemical Co. Sodium citrate was obtained from Fisher Scientific. All analytical chemicals were reagent-grade and were used without further purification.

The polysuccinimide was washed repeatedly in deionized water to remove the phosphoric acid catalyst until the pH of the supernatant of two consecutive washes was the same. The concentration of residual phosphate remaining was measured by UV spectrophotometry and was found to be negligible. Then, the powder was dried under an infrared lamp at 60 °C. A preweighed amount of the washed succinimide was suspended in deionized water. The suspension was agitated constantly to keep the particles suspended and heated to 90 °C using a Fisher magnetic stirrer/hot plate. The polysuccinimide was then hydrolyzed by adding a 50% sodium hydroxide solution dropwise to maintain a pH of about 11. The reaction was complete when all of the polysuccinimide particles had completely dissolved. The resulting sodium polyaspartate was a red solution.

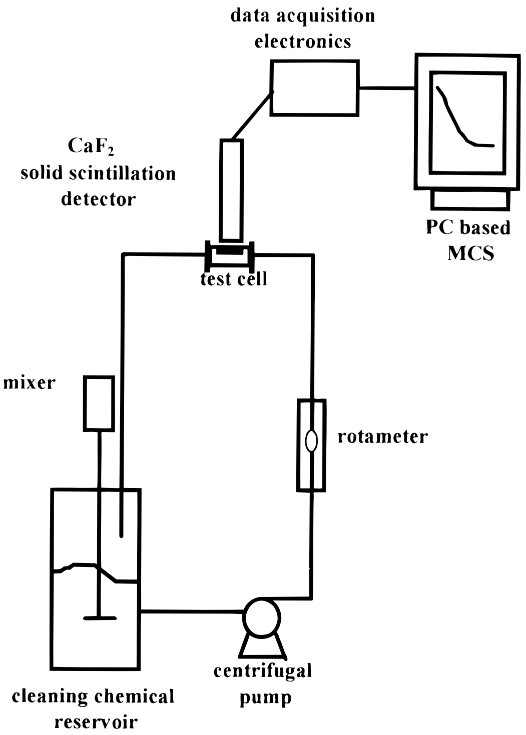

Figure 2. Diagram of the experimental flow system.

Cleaning Studies. (a) Experimental Flow System. An on-line solid scintillation technique was used to continuously measure the amount of contaminant remaining on the inner surface of stainless steel tubes. This technique involves the use of an experimental flow system equipped with solid scintillation detection equipment. We have used this system previously to study the removal of both mineral (e.g., calcium phosphate) and oil contaminants from stainless steel tubes (Yan et al., 1997; Grant et al., 1996, 1997).

Figure 2 shows a diagram of the experimental flow system. It consists of type 304 stainless steel tubing (10.5-mm i.d.). The cleaning solvent was recycled to a 20-L solvent tank. The volume of the cleaning solvent used in the cleaning experiments (5 L) was chosen so that the total concentration of calcium phosphate present in the bulk solution could be assumed to be zero at all times. An EMI lab stirrer agitator was used to keep the contents of the solvent tank well mixed. The tank was also equipped with a pH probe connected to a Fisher Accumet model 915 pH meter for the continuous measurement of pH during the cleaning experiments. The pH readings were acquired on an IBM-compatible computer using Omega Data Collect for Windows. A Micropump centrifugal pump with a variable-speed flow controller was used to control the solvent flow rate. A glass rotameter (Omega) was used to measure the flow rate.

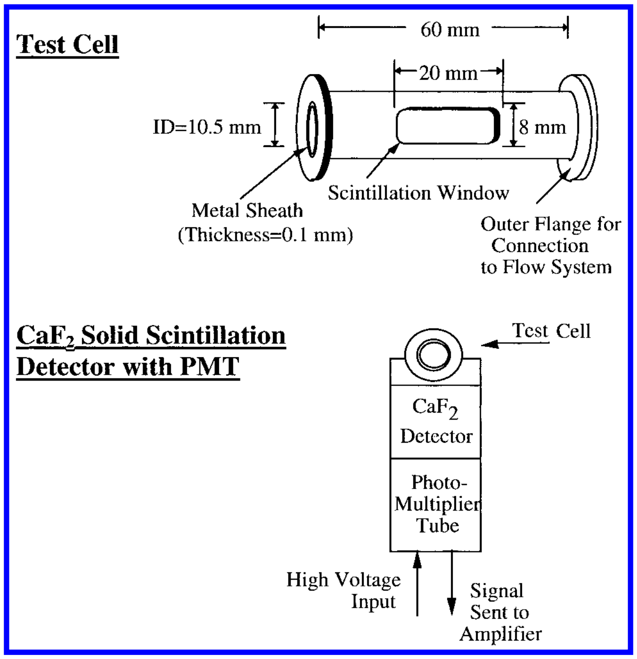

Figure 3. Test cell and the detector for solid scintillation measurements.

Within the stainless steel tubing, there was a removable section of tubing referred to as the test cell (Figures 2 and 3). To ensure fully developed turbulent flow in the test cell, an entrance length of tubing of 1.3 m was used. The test cell was made up of a 60-mm-long section of type 304 stainless steel. The ^{32}P-labeled calcium phosphate was deposited within this test cell (see below). To allow for a higher percentage of β emissions to be transmitted through the cell for efficient ^{32}P detection during the cleaning experiments, the tubing contained a 20 mm 8 mm × 0.1 mm stainless steel scintillation window created from a metal sheath. The test cell was held firmly in place by placing C-clamps around flanged outer connections. The removable flow cell enabled controlled application of the deposit. The calcium fluoride (CaF$_2$) scintillation detector (Bicron) shown in Figures 2 and 3 was positioned against the scintillation window on the outside of the test cell. This position allowed on-line measurements of the film remaining on the surface as a function of time without disturbing the flow field in the tube.

(b) Detection System. The emissions of β-particles from the ^{32}P-labeled calcium phosphate deposit on the inner surface of the flow cell were detected by the CaF$_2$ solid scintillation detector and transmitted in an electronic signal to a preamplifier (Tennelec TC145), an amplifier (Tennelec TC241), and a multichannel scalar (MCS) (Oxford). The MCS counted the number of β-particles per channel transmitted from the window of the test cell every 10 s. The data were recorded on an IBM-compatible computer in units of β-particle counts per channel. The units were proportional to the amount of radioactive material remaining in the test cell.

Prior to starting the cleaning experiments, the test cell containing a dried, radiolabeled calcium phosphate deposit was mounted in the flow system. The CaF$_2$ detector was mounted flush with the scintillation window of the test cell. The β-emissions in the ^{32}P-labeled deposit readily permeate through air. Thus, in the dry system, the CaF$_2$ detector detected the β-particles emitted by the deposit immediately adjacent to the scintillation window and on the surface of the test cell opposite the scintillation window.

The cleaning experiments were initiated by starting the flow of solvent through the test cell. During the first 30 s of exposure of the contaminated surface to an aqueous solvent, the counts dropped rapidly. This drop was due to the attenuation of the β-particles by the presence of the liquid inside the test cell. After the signal dampening, the detection system only read the radioactivity of the deposit remaining on the surface immediately adjacent to the scintillation window. The readings taken immediately after the attenuation of the signal were chosen as time zero. The counts at time zero, C_0, represent the amount of film deposited. As the cleaning process progressed, the amount of radiolabeled deposit remaining on the surface decreased. This decrease was quantitatively recorded by a lowering of the β-particle counts.

The data were normalized using the following equation:

$$\frac{M(t)}{M_0} = \frac{C(t) - B}{C_0 - B} \tag{1}$$

where $M(t)$ is the mass of contaminant on the surface at time t, M_0 is the mass of the contaminant at time zero, $C(t)$ is the β-particle count at time t, B is the background count, and C_0 is the β-particle count at time zero. Background counts were evaluated by measuring the β-particle count in the absence of a radiolabeled deposit. All analysis of the data only included readings taken after time zero. The normalized counts were time-averaged over 5-min intervals and plotted as a function of time. Thus, the graphical representations of the data consist of a smoothed-curve fit through the time-averaged data.

When the counts decrease to the background radioactivity level (~30 counts/channel), the contaminant had been completely removed from the stainless steel surface. The experiment was concluded either when the counts decreased to the background radioactivity levels or after 10 h of continuous cleaning.

(c) Hydroxyapatite/Brushite Deposit Preparation. Typically, calcium phosphate deposits consist of a mixture of different forms of calcium phosphate. The deposits used in this study consisted of a 1:1 weight ratio of HAP and DCPD. From this composition, we calculated the Ca/P ratio of the deposit to be approximately 1.4. This deposit is similar to the mineral composition of milk-fouling residues. The mineral component of milk-fouling residues has a Ca/P ratio of approximately 1.5 (Jeurnink and Brinkman, 1994).

To prepare the HAP/DCPD stock slurry, 4 g of the HAP suspension, 4 g of the DCPD suspension, and 12 g of deionized water were mixed. The HAP/DCPD slurry was radiolabeled by mixing 20 g of the HAP/DCPD stock slurry with 0.01 mL of ^{32}P-labeled DCPD. Next, 0.50 mL of the radiolabeled HAP/DCPD slurry was injected into the test cell. Then, the test cell was capped and positioned horizontally on a roller assembly. The test cell was simultaneously rotated at 60 rpm and heated under an infrared lamp at 90 °C for 8 h. The dried deposit had a mass of $M_0 = 57 \pm 0.5$ mg. Previously, we found that coatings formed under rotation yielded a smoother, more even deposit than those in the absence of rotation (Grant et al., 1996). In the current studies,

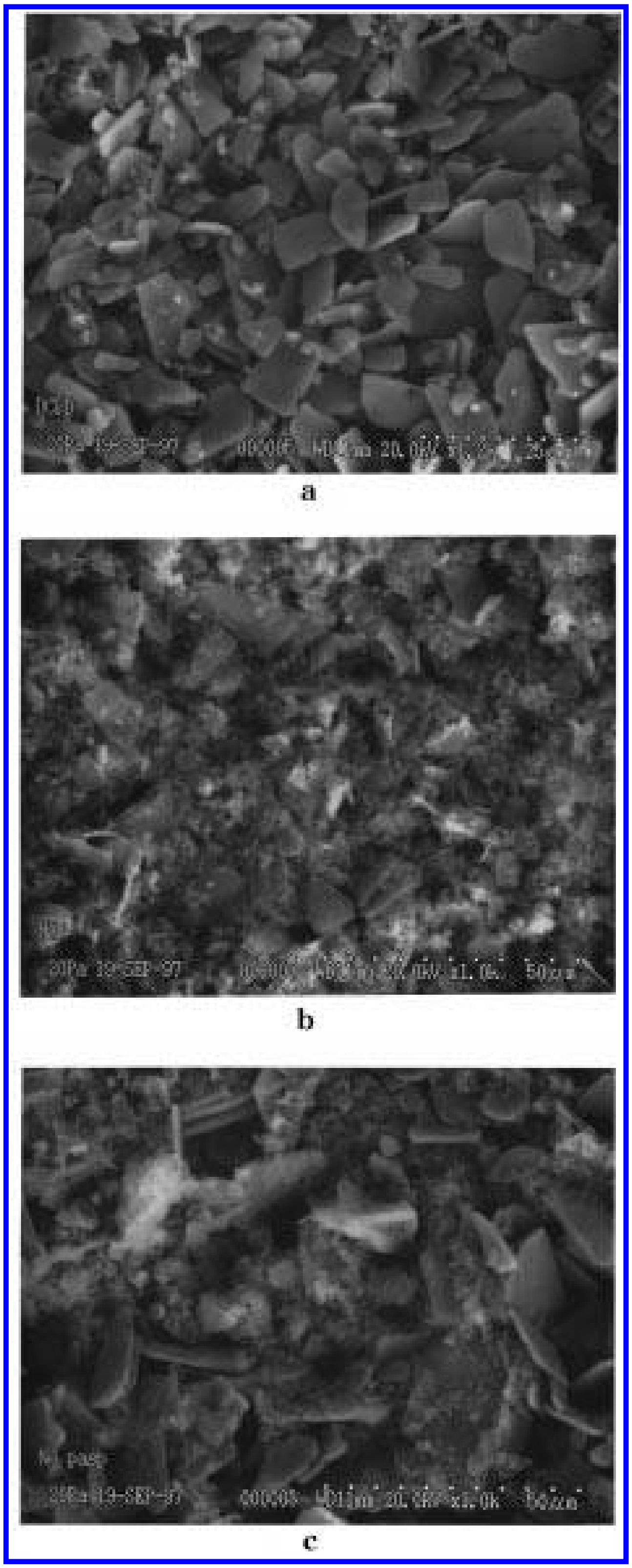

Figure 4. SEM micrographs of HAP and DCPD.

we visually observed that this coating technique did not totally eliminate differences in film morphology (i.e., surface area and thickness of the deposit). These differences in the coating account for the variability observed between duplicate runs.

Scanning electron microscopy micrographs were taken of HAP, DCPD, and a 1:1 weight ratio of HAP/DCPD deposited on stainless steel strips. Figure 4a shows that the DCPD deposit consists of rounded platelets. On the other hand, the HAP deposit, shown in Figure 4b, consists of flat, thin fragments and fiberlike crystals. Figure 4c shows a deposit consisting of the HAP/DCPD mixture used in these experiments. The examination of the deposit shows that the HAP and DCPD are evenly dispersed within the deposit.

(d) Procedure for the Cleaning Experiments. The HAP/DCPD cleaning studies were carried out in aqueous sodium polyaspartate, EDTA, and sodium citrate solutions. The purpose of these studies was to determine the effect of the sequestrants on the mineral cleaning rate. A concentrated solution of the sequestrant was diluted to the desired concentration in the solvent tank. To promote dissolution and to minimize rate limitations due to mass transfer of the sequestrants, relatively high concentrations of the sequestering agents (on the order of hundreds of parts per million) were used.

After adding 600 ppm of sodium polyaspartate to deionized water, the pH of the solvent was approximately pH ∼8. Thus, to compare the removal of HAP/DCPD in sodium polyaspartate with EDTA and sodium citrate, the initial pHs of solvents containing EDTA and sodium citrate were adjusted to pH 8 prior to carrying out the cleaning experiments. Lower pH studies were carried out within the pK_a region of sodium polyaspartate (pH 4). The pH of the deionized water was approximately 6. In experiments where the initial pH was adjusted, 1 M sodium hydroxide or 1 N sulfuric acid was added prior to starting the experiment. Following the adjustment of the initial pH, no further pH adjustment was made in these experiments. The pH was monitored continuously throughout the cleaning experiment using an Accumet pH meter. These pH readings were acquired every 10 s and recorded by an IBM-compatible computer. In an effort to simulate industrial pipe cleaning, the rate of contaminant removal was studied within the region of fully developed turbulent flow ($Re = 15\,000$). These experimental conditions corresponded to a flow rate of 0.095 L/s. Experiments were carried out at room temperature (25 °C).

Dissolution Studies. Supplementary HAP/DCPD dissolution experiments were carried out under controlled conditions to investigate the kinetics of HAP/DCPD dissolution in alkaline media. In contrast to the cleaning studies in which the amount of contaminant remaining on a stainless steel surface was monitored in a continuous flow system, these studies involve small-scale batch studies of the dissolution rate of the HAP/DCPD powder. The objective of our studies was to determine whether the anionic polyaspartate ligand enhances or inhibits mineral dissolution. To isolate the effects of the organic ligands in the dissolution process, the dissolution studies were carried out in pH 10 buffered solutions. The buffered solution was prepared by adding 1 M NH_3OH to 1 M NH_3Cl until the desired pH was attained. Potassium chloride (0.08 M) was added to the ammonia buffer to minimize ionic strength variations and reduce electric field gradients in the diffusion layer (Thomann et al., 1990). This salt was chosen because of its lack of effect on the dissolution process (Gray, 1962).

(a) Hydroxyapatite/Brushite Powder Preparation and Sample Conditioning. For the dissolution studies, nonradiolabeled HAP/DCPD stock slurry (described above) was dried under an infrared lamp overnight. The dried HAP/DCPD was ground into a fine powder. To study sample conditioning effects, equilibrated and dry HAP/DCPD were used. Equilibrated HAP/DCPD studies involved the addition of sodium polyaspartate to a pH-buffered solution that had equilibrated with HAP/DCPD for 3 h. In the dry HAP/DCPD studies, dry HAP/DCPD powder was added directly to a pH-buffered solution containing sodium polyaspartate.

(b) Measurement of Dissolution Kinetics. The dissolution kinetics was measured by continuously recording the calcium ion release and by measuring the total calcium content in the bulk solution. An Orion pH/ISE meter model 290A equipped with an Orion calcium electrode was used to measure the free calcium concentration during the dissolution studies. The electrode detects calcium ion concentrations ranging from 0.02 to 100 ppm. Because ions bound to calcium sequestering agents and phosphates are not detectable by this technique, these readings correspond to the activity of the free calcium ions present in the bulk solution. The total calcium measurements were carried out by removing 3-mL samples of the suspension at regular time intervals. The samples were immediately filtered through a 20-μm syringe filter to remove the solid particles from the suspension. The resulting sample was clear and contained no visible particles. The total calcium content of the solution was then measured using inductively coupled plasma (ICP) spectrophotometry.

(c) Batch Dissolution Experimental Parameters. HAP/DCPD powder (5 or 10 mg) was dissolved in 200 mL of pH-buffered solutions (pH 10). Experiments carried out in the presence of calcium sequestering agents contained sodium polyaspartate, EDTA, or sodium citrate. Relatively high sequestrant concentrations were used in the dissolution studies (up to 2000 ppm) because HAP/DCPD powder was added in excess. The solutions were stirred continuously to keep the crystals suspended and dispersed within the solution and minimize mass-transfer limitations. The dissolution experiments were carried out at room temperature (25 °C).

Results and Discussion

Cleaning in the Presence of Sodium Polyaspartate. To determine the effectiveness of sodium polyaspartate on the removal of HAP/DCPD deposits from stainless steel tubes, cleaning studies were performed with and without sodium polyaspartate. Experiments carried out in the presence of sodium polyaspartate consisted of a solution containing 600 ppm of sodium polyaspartate in deionized water (pH $\sim$8). Cleaning experiments carried out in the absence of sodium polyaspartate used deionized water only.

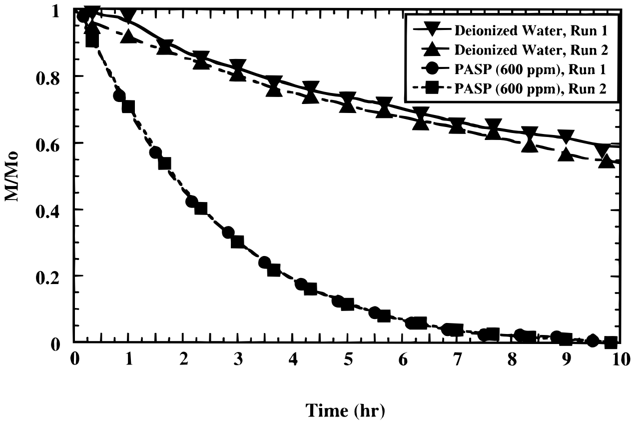

Figure 5. Effect of the presence of sodium polyaspartate on the removal of HAP/DCPD deposits from stainless steel (flow rate = 0.095 L/s).

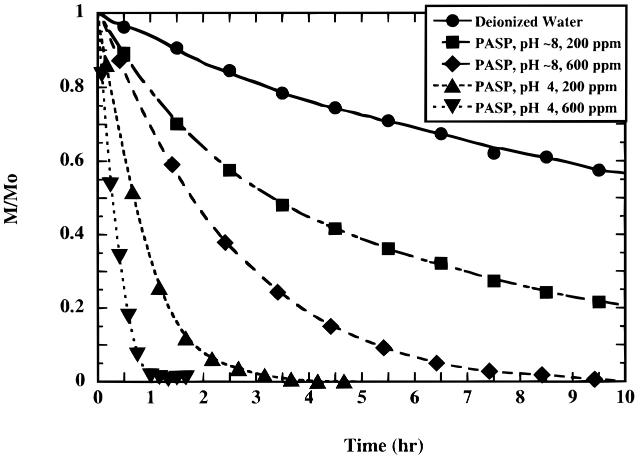

Figure 6. Removal of HAP/DCPD deposits from stainless steel at alkaline and acid solvent pHs (flow rate = 0.095 L/s).

Figure 5 shows the results of cleaning studies carried out in the presence and absence of sodium polyaspartate. The data are represented in terms of the fraction of film remaining as a function of time. Selected data points are shown in order to differentiate the data sets. As shown in Figure 5, the presence of sodium polyaspartate has a pronounced effect on the mineral-removal process. The initial removal rates (measured during the first 30 min of cleaning) were calculated by multiplying the initial slope of the normalized curve by the initial mass of the deposit. In the presence of sodium polyaspartate, the initial removal rate was 0.47 mg/min as compared with only 0.049 mg/min without the sodium polyaspartate. After 10 h of cleaning in 600 ppm of sodium polyaspartate, the HAP/DCPD had been completely removed from the stainless steel. By comparison, over 65% of the deposit remained after cleaning with deionized water over the same time period. This discovery shows that, under these conditions, sodium polyaspartate can be used as an additive to improve the mineral-removal rates over deionized water.

To further investigate the effect of the presence of sodium polyaspartate on HAP/DCPD removal, comparative cleaning studies were carried out at alkaline and acidic pHs. The results are show in Figure 6. The effects of acids on mineral dissolution are well-known. The increased removal rates at the low pH are due to enhanced mineral solubility and hydrogen-ion catalysis. At alkaline pHs, however, the improved removal rate in the presence of sodium polyaspartate compared to deionized water cannot be attributed to proton-promoted dissolution. To develop an understanding of the effects of the polyaspartate on the removal rates, these studies were expanded to determine the effects of sequestrant concentration.

Figure 7 shows the effects of polyaspartate concentration on cleaning at acidic conditions. Notice that, as the polyaspartate concentration increases, the cleaning rate substantially decreases, goes through a minimum, and then increases again at 400 ppm. These results indicate that polyaspartate is not an effective additive in the cleaning process at low pHs in the range of

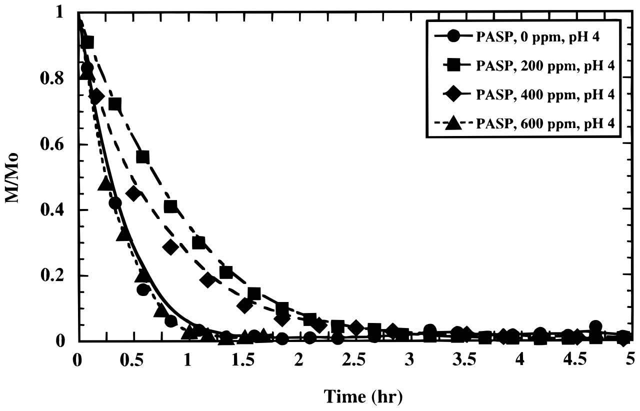

Figure 7. Effect of poly(aspartic acid) concentration on the removal of HAP/DCPD deposits from stainless steel at an acidic pH (flow rate = 0.095 L/s).

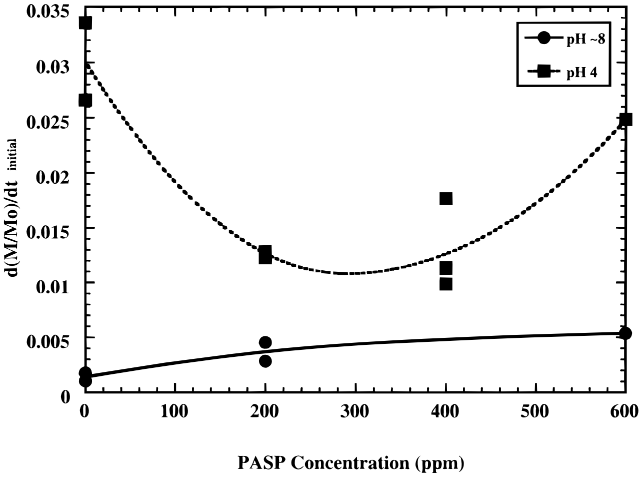

Figure 8. Effect of poly(aspartic acid) concentration on the initial removal rates of HAP/DCPD deposits from stainless steel (flow rate = 0.095 L/s).

concentrations studied. Two factors contribute to this behavior. First, the adsorption of polyaspartate ions on the HAP/DCPD interface forms a protective layer that inhibits calcium phosphate dissolution. This effect is similar to the well-known inhibition of crystallization due to the presence of sequestering agents (Christoffersen and Christoffersen, 1983; Schaad et al., 1994). Second, at low pHs, the polyaspartate ions in solution tend to remain protonated, which inhibits the formation of Ca−PASP complexes. The trends observed in Figure 7 are analogous to the results obtained by Christoffersen and Christoffersen (1983) in the dissolution of HAP in the presence of sodium citrate.

A comparison of the initial removal rates at low and high pHs is presented in Figure 8. The lines represent smoothed-curve fits of the data. Variability in duplicate runs is attributed to differences resulting from the coating technique. The lower curve indicates that, at a high pH, the initial removal rate increases as the sodium polyaspartate concentration increases. By contrast, at the low pH, the removal rate goes through a minimum. In the acidic solvent, the addition of the sequestrant does not improve the rate beyond that which was measured in the absence of the sequestrant for the concentration range studied. Thus, while the overall dissolution rate is more rapid at the lower pH, this enhancement is due to enhanced solubility rather than the effects of the sequestrant. Sodium polyaspartate proves to be more effective at the alkaline pH. At the high pH, the removal rate at 600 ppm is about 4 times higher than the rate obtained in the absence of polyaspartate ions. This suggests that improved cleaning of HAP/DCPD can be achieved in practice under alkaline conditions by adding polyaspartate.

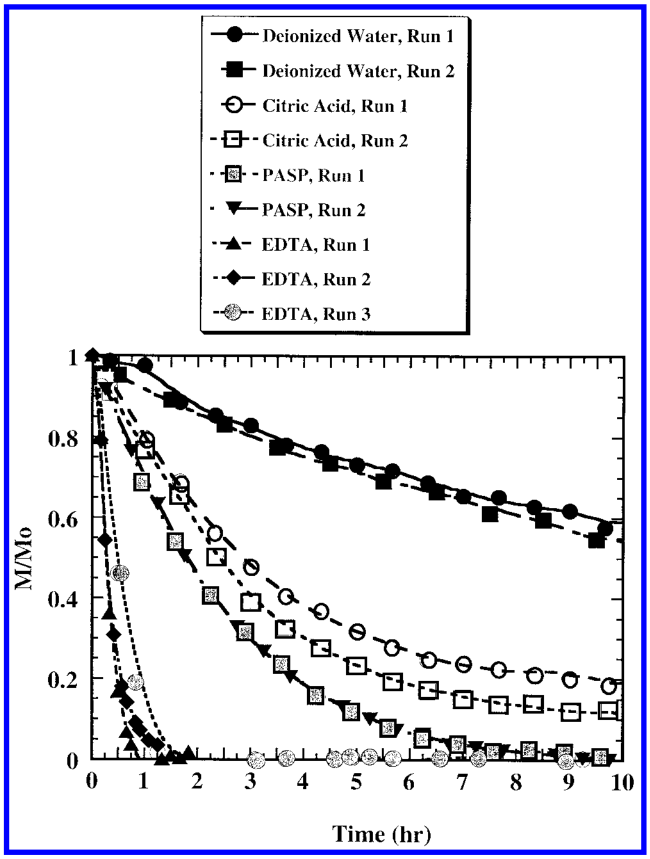

Figure 9. Comparison of the ability of the sodium salts of poly(aspartic acid), EDTA, and citric acid to remove HAP/DCPD deposits from stainless steel (pH ~8, 600 ppm, 0.095 L/s).

Studies were carried out to discern the effectiveness of the sodium polyaspartate relative to commonly used calcium sequestering agents. Figure 9 compares the removal rates of HAP/DCPD in sodium polyaspartate with sodium citrate and EDTA at an alkaline solvent pH and a sequestrant concentration of 600 ppm. In all cases studied, the sequestering agents improved the cleaning rate over deionized water but to varying degrees (Figure 9). EDTA, a strong sequestrant, removed the deposit faster than both sodium polyaspartate and sodium citrate. Sodium polyaspartate and sodium citrate have similar performances. The sodium polyaspartate completely removed the calcium phosphate in the time range studied. Approximately 18% of the deposit remained after 10 h of cleaning the HAP/DCPD deposit in sodium citrate. An additional advantage of sodium polyaspartate is its ability to act as a corrosion inhibitor (Silverman et al., 1995).

In the presence of alkaline sequestrants, the cleaning process is accompanied by a pH drop (Figure 10). It is well-known that a pH drop accompanies the sequestration of cations by the EDTA anion in unbuffered alkaline solutions (Schwarzenbach and Flaschka, 1959). The sequestrant releases hydrogen ions as the ligand binds to cations. Also, sodium citrate and EDTA have been shown to dissolve calcium phosphate by calcium sequestration (Arbel et al., 1991). By association, sodium polyaspartate may also act as a deprotonated ligand to

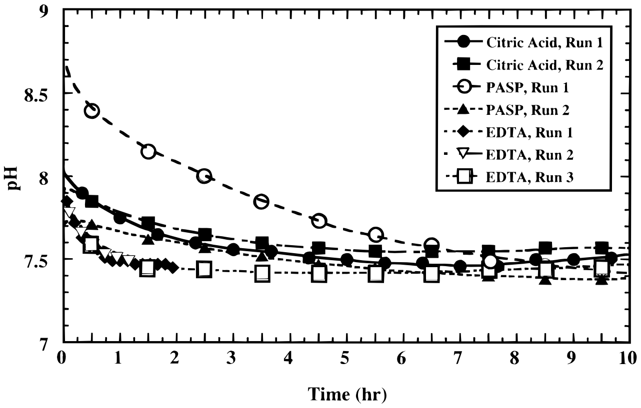

Figure 10. pH changes during the removal of HAP/DCPD deposits from stainless steel in the presence of the sodium salts of poly(aspartic acid), EDTA and citric acid (600 ppm, 0.095 L/s).

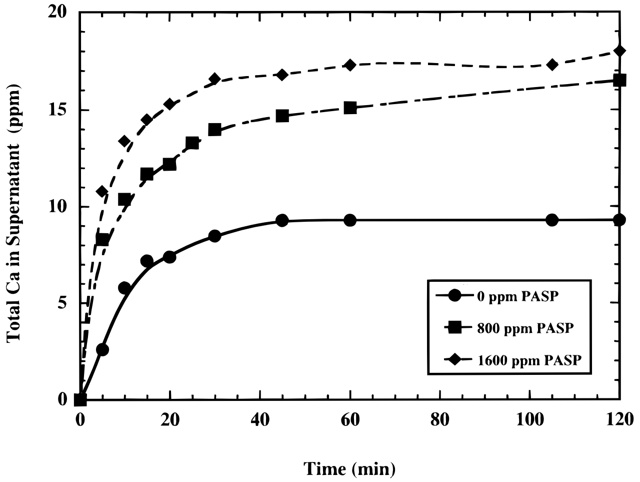

Figure 11. Effect of sodium polyaspartate concentration on the dissolution of dry HAP/DCPD powder (10 mg of HAP/DCPD, pH 10, 0.08 M KCl).

enhance HAP/DCPD dissolution by calcium sequestration in alkaline solutions.

Batch Dissolution Experiments in the Presence of Sodium Polyaspartate. To investigate the possibility of enhanced dissolution rates due to ligand-promoted dissolution, batch dissolution studies were carried out in the presence of alkaline solutions containing sodium polyaspartate and an excess of HAP/DCPD powder. As stated previously, these dissolution studies were carried out in dry and equilibrated HAP/DCPD. The purpose of these studies was to determine whether the sodium polyaspartate affected the HAP/DCPD dissolution rate and the degree of calcium ion sequestration.

Figure 11 shows the total calcium concentration in the supernatant as a function of time during the dissolution of dry HAP/DCPD in sodium polyaspartate at concentrations ranging from 0 to 1600 ppm. Increasing the concentration of sodium polyaspartate increased the initial mineral dissolution rate and the total calcium dissolved at long times. Thus, these results confirm that sodium polyaspartate improves the removal rate by enhancing the rate of HAP/DCPD dissolution.

The next step was to determine whether the enhanced dissolution rate was due to calcium sequestration. Figure 12 shows the results of parallel dissolution experiments in which the rate of Ca^{2+} release and the total Ca concentration were monitored after introducing an excess of dry HAP/DCPD into the sodium polyaspartate solution. Notice that, during the dissolution of the HAP/DCPD powder in the sodium polyaspartate, the concentration of free Ca^{2+} ions is appreciably lower than the total Ca concentration of the supernatant. Initially, the total Ca concentration in the supernatant increases at a rate of 0.8 ppm/min while the Ca^{2+} concentration level increases at only 0.045 ppm/min after an initial lag time. After 30 min, the total calcium concentration was 6.2 ppm compared to a Ca^{2+} concentration of only 0.32 ppm. The free Ca^{2+} concentration and the total Ca concentration differ due to the formation of calcium ion complexes.

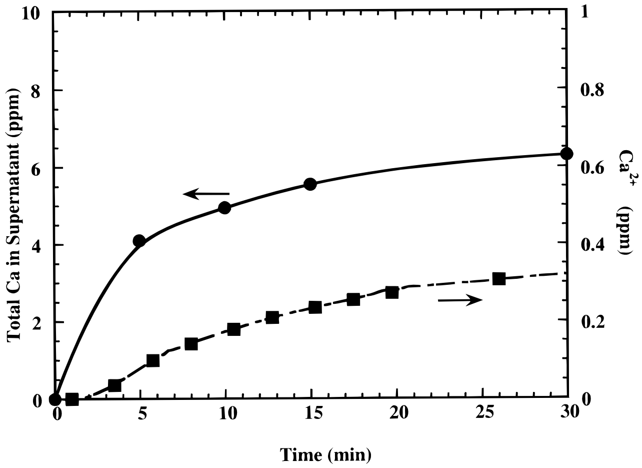

Figure 12. Comparisons of free Ca^{2+} and total Ca during the dissolution of HAP/DCPD in sodium polyaspartate (2000 ppm of PASP, 5 mg of HAP/DCPD, pH 10, 0.08 M KCl).

The sequestration of Ca^{2+} enhances the dissolution rate. During the first 5 min of the dissolution studies, a relatively high dissolution rate, shown by the increase in the total calcium accumulation in the solution, corresponded to a low Ca^{2+} concentration. The enhanced dissolution rate indicates that low Ca^{2+} levels in the bulk solution increase the concentration gradient which drives mass transfer. Thus, the data show that high rates of sequestration correspond to improved HAP/DCPD dissolution rates.

To investigate the rate of Ca^{2+} sequestration, the Ca^{2+} levels were monitored after the addition of sodium polyaspartate to HAP/DCPD that had been exposed to a pH-buffered solution for 3.5 and 6 h. During the equilibration of the HAP/DCPD powder in a pH-buffered solution in the absence of sodium polyaspartate, there was an accumulation of calcium ions in the bulk solution. However, as shown in Figure 13, the concentration of free Ca^{2+} dropped immediately upon the addition of sodium polyaspartate to the solution.

Sequestration is improved by increasing the concentration of the sodium polyaspartate. This was shown by the Ca^{2+} readings taken when dry HAP/DCPD powder was added directly to the alkaline pH-buffered sodium polyaspartate solution (Figure 14). The sodium polyaspartate concentrations ranged from 0 to 2000 ppm. In this case, no free Ca^{2+} ions are initially present in the bulk solution, and the polyaspartate is present during the initial stages of HAP/DCPD equilibration and dissolution. The data show that no free Ca^{2+} is measured during the first few minutes of the experiment after adding the sodium polyaspartate even though HAP/DCPD dissolution is occurring (Figure 14). In the absence of sodium polyaspartate, there is only a minor

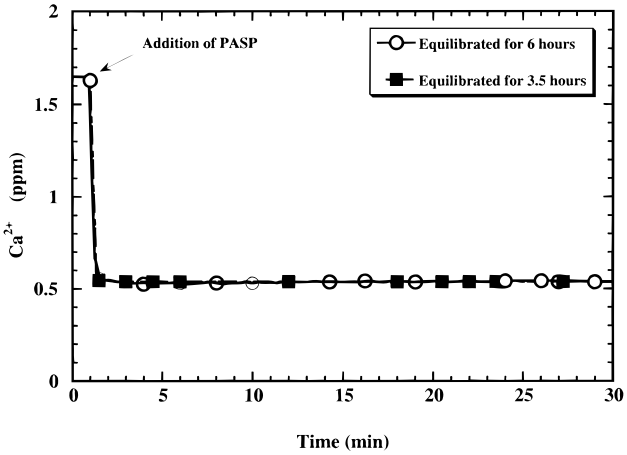

Figure 13. Effect of sodium polyaspartate on the Ca^{2+} changes of equilibrated HAP/DCPD (800 ppm of PASP, 5 mg of HAP/DCPD, pH 10, 0.08 M KCl).

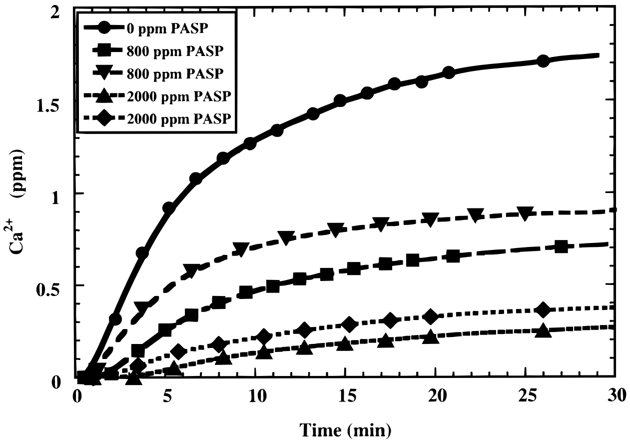

Figure 14. Effect of sodium polyaspartate concentration on the Ca^{2+} profile during the dissolution of dry HAP/DCPD powder (5 mg of HAP/DCPD, pH 10, 0.08 M KCl).

delay time (<0.5 min). The length of this time delay increases with increasing concentrations of sodium polyaspartate. Following this initial delay, a measurable quantity of free calcium ions is released into the bulk solution. The rate of accumulation and the final concentration of Ca^{2+} measured decreases with increasing ligand concentration.

The delay times may be caused by the release of calcium as complexed ions rather than as free ions. During the dissolution of calcium phosphate, calcium is present in the crystal lattice structure and in the bulk solution. We have observed previously in the discussion of Figure 13 that sodium polyaspartate binds instantly to free calcium ions. Thus, sodium polyaspartate binds to free calcium ions after they are transferred from the crystal surface to the bulk solution. In addition, the negatively charged carbonyl groups of sodium polyaspartate can bind to the calcium on the crystal surface (Mueller and Sikes, 1993) to form a soluble complex ion. The complex then desorbs, bringing calcium into the bulk solution. The net result is the release of complexed calcium ions rather than free ions, which leads to the observed increase in the HAP/DCPD dissolution rate. Thus, in the cleaning studies, the increase in the initial cleaning rates in the presence of polyaspartate may be due to complexation of free calcium cations in the bulk solution and to the direct removal of calcium from the solid/liquid interface.

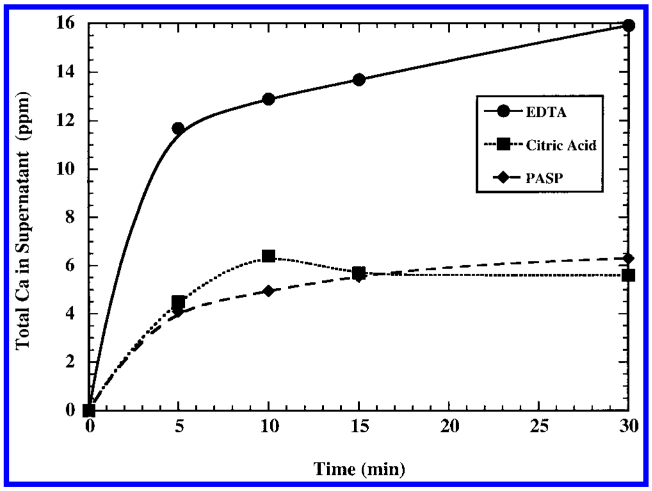

Figure 15. Dissolution of HAP/DCPD powder in the sodium salts of poly(aspartic acid), EDTA and citric acid (2000 ppm of sequestering agent, 5 mg of HAP/DCPD, pH 10, 0.08 M KCl).

As shown in Figure 14, higher sodium polyaspartate concentrations result in a more effective calcium sequestration. Higher sequestration rates lead to higher dissolution rates. Thus, it is likely that increasing the sodium polyaspartate concentration in the alkaline cleaning studies leads to a more rapid calcium phosphate dissolution by a ligand-promoted dissolution mechanism.

Dissolution studies were also carried out to determine whether a relationship existed between the cleaning rate in the presence of various calcium sequestering agents and the dissolution rates. Figure 15 shows the total calcium content of the supernatant during the dissolution of HAP/DCPD in sodium polyaspartate, sodium citrate, and EDTA. In both the cleaning and the dissolution studies, EDTA dissolved HAP/DCPD more rapidly than citric acid and sodium polyaspartate. Sodium polyaspartate and sodium citrate have similar effects on calcium phosphate dissolution ability (Figure 15). Similarly, the cleaning studies showed that sodium polyaspartate and sodium citrate had similar cleaning capabilities (Figure 9). Thus, the dissolution behavior appears to be directly related to the cleaning behavior and thus provides an indication of the cleaning mechanism.

In summary, these findings demonstrate the sodium polyaspartate, a biodegradable polycarboxylate, is effective in dissolving HAP/DCPD deposits at alkaline pH. The enhanced cleaning rate is due to ligand-promoted dissolution. Because sodium polyaspartate also acts as a dispersant, the presence of sodium polyaspartate may simultaneously enhance the dissolution rate and prevent the redeposition of minerals in hard surface cleaning applications.

Conclusions

The results presented in this work show that sodium polyaspartate can be used to remove HAP/DCPD deposits from stainless steel. Sodium polyaspartate, a nontoxic, biodegradable polycarboxylic sequestrant, significantly enhances the removal of HAP/DCPD deposits from the stainless steel under alkaline conditions. Under acidic conditions, the presence of sodium polyaspartate partially inhibits dissolution in the range of concentrations studied. Comparative cleaning studies show that the removal rate using sodium polyaspartate is similar to that of sodium citrate and slower than that of EDTA. Batch dissolution experiments carried out in alkaline sodium polyaspartate solutions show that sodium polyaspartate enhances the HAP/DCPD dissolution rate by sequestering free Ca^{2+} ions in solution instantaneously during the dissolution process.

Future work will expand upon these findings in order to assess the rate-limiting step in the removal process. Experiments will be carried out at various flow rates to determine the relative contributions of mechanical removal, dissolution by mass transfer, and interfacial dissolution in the mineral-removal process. A cleaning model will be developed based on the mechanisms involved in the removal process.

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