Effect of precipitation inhibitors on calcium phosphate scale formation

ZAHID AMJAD

*The BFGoodrich Company, Specialty Polymers and Chemicals Division, Avon Lake Technical Center,
Avon Lake, OH 44012, U.S.A.*

ZAHID AMJAD. Can. J. Chem. **67**, 850 (1989).

The highly reproducible pH-stat technique was used to study the influence of various types of inhibitors on the precipitation of calcium phosphate from solution. Three types of inhibitors were evaluated: (*1*) homo- and copolymers of acrylic acid, (*2*) polyphosphate and phosphonates, and (*3*) polycarboxylic acids. Experimental variables studied included pH, temperature, and inhibitor dosage all of which were found to greatly affect the precipitation of calcium phosphate. The role of polyacrylic acid molecular weight is addressed. Comparative data for the various types of inhibitors is discussed.

Key words: precipitation inhibitors, calcium phosphate scale formation.

ZAHID AMJAD. Can. J. Chem. **67**, 850 (1989).

On a utilisé la très reproductible technique du "pH-stat" pour étudier l'influence de divers types d'inhibiteurs sur la précipitation du phosphate de calcium à partir de solutions. On a évalué trois types d'inhibiteurs: (*1*) des homo- et des co-polymères de l'acide acrylique, (*2*) du polyphosphate et des phosphonates et (*3*) des acides polycarboxyliques. On a étudié l'influence des variables expérimentales suivantes: le pH, la température et la concentration des inhibiteurs; on a trouvé que tous ces facteurs avaient une grande influence sur la précipitation du phosphate de calcium. On a aussi examiné le rôle du poids moléculaire de l'acide polyacrylique. On discute de données comparatives concernant les divers types d'inhibiteurs.

Mots clés: inhibiteurs de précipitation, formation des écailles du phosphate de calcium.

[Traduit par la revue]

Introduction

Formation of mineral scales on equipment surfaces is a problem in many areas such as industrial water systems, secondary oil recovery utilizing water flooding techniques, desalination, and clothing washing machines. Precipitation of mineral salts such as calcium carbonate results in incrustation on clothes washed with hard water. Among the problems caused by scale deposits are obstruction of fluid flow, impedence of heat transfer, wear of metal parts, localized corrosion attack, and unscheduled equipment shutdown. The scales consist primarily of carbonates, sulfates, hydroxides, phosphates, and silicates of alkaline earth metals, particularly calcium and magnesium. The problem of scale formation is intensified at higher temperatures because of the peculiar inverse temperature – solubility characteristics of these minerals in water.

In addition to scaling problems, cooling water systems and boilers constructed of carbon steel also experience corrosion problems caused by the presence of dissolved oxygen. In the past, this corrosion problem was combated using chromate compounds. More recently, polyphosphate/orthophosphate compounds have been replacing chromates because of the toxicity problems associated with chromates. However, the use of phosphate compounds adds to scale formation of highly insoluble calcium phosphate.

Recently, the problem of calcium orthophosphate scaling in industrial water system has become increasingly important (1–3). Higher orthophosphate levels are being encountered in cooling waters due to increased water reuse, use of low quality make-up water such as waste water treatment plant effluent and the use of organic phosphonate scale and corrosion inhibitors which are degraded to orthophosphate. The increased orthophosphate levels, combined with alkaline operating conditions can lead to the formation of highly insoluble calcium phosphate scale deposits which are normally attributed to hydroxyapatite ($Ca_5(PO_4)OH$, HAP). In cooling water systems, however, it is not the HAP which is initially formed, but instead a precursor phase is obtained which is widely known as amorphous calcium phosphate.

The influence of trace amounts of polyphosphates and phosphonates on the precipitation of calcium phosphate has been the subject of numerous investigations. Results of previous studies have shown that hydroxyethane 1,1-diphosphonic acid, HEDP, is an effective inhibitor when added to barium sulfate (4), calcium fluoride (5), calcium carbonate (6), and calcium oxalate (7). However, with more soluble calcium sulfate dihydrate, this inhibitor appeared to have only a slight effect on the growth kinetics (8). Varsanik (9) reported that among various phosphonates studied in laboratory and pilot plant experiments, HEDP was the most effective inhibitor for limiting calcium phosphate scale formation. However, system pH had a dramatic effect upon inhibitor effectiveness. At neutral pH values, the performance of aminotri(methylene phosphonic acid), AMP, was comparable to that of HEDP.

The effect of trace amounts of polymeric scale inhibitors on both the rate of precipitation and crystal modification of scale forming minerals has been the subject of numerous investigations (10–12). McCartney and Alexander (10) showed that polymers containing carboxyl groups such as carboxymethyl cellulose, aliginic acid, polymethacrylic acid, and polyacrylic acid (PAA) were particularly effective as $CaSO_4 \cdot 2H_2O$ crystal growth inhibitors. Electrophoretic studies (11) suggest that the inhibitory effect of polyelectrolytes such as PAA (11), is due to the adsorption of the molecules on the surfaces of calcium sulfate crystals. Amjad (12), in a recent study on the influence of polyacrylic acids (PAAs) in controlling $CaSO_4 \cdot 2H_2O$ scale formation on heat transfer surfaces, reported that the molecular weight (mol wt) plays an important role on the inhibitory effect of PAAs on $CaSO_4 \cdot 2H_2O$ (gypsum) crystal growth from aqueous solution.

The work discussed in this paper focuses on the precipitation of calcium phosphate in the presence of PAAs of varying molecular weights over a range of temperature, pH, and polymer concentration using a pH-stat technique. The influence of functional groups originating from the monomers, other than carboxylic acid attached to the polymer backbone, on the inhibiting activity of the polymers has also been investigated.

TABLE 1. Inhibitors tested

Description	Acronym
Polymers	
Acrylic Acid (AA) homopolymers	PAA
AA/methacrylic acid (MAA) copolymer	AA/MAA
AA/carbitol acrylate (E)	AA/E
Polyphosphate and phosphonates	
Sodium pyrophosphate	PP
Aminotri (methylene phosphonic acid)	AMP
Hydroxyethane 1,1-diphosphonic acid	HEDP
Polycarboxylic acids	
Benzene hexacarboxylic acid or mellitic acid	MA
1,3,5-Benzene tricarboxylic acid (trimesic acid)	TMA
Citric acid	CA

For quantitative comparison, precipitation studies were also performed in the presence of polyphosphates, phosphonates, and polycarboxylic acids (e.g., citric acid, benzene hexacarboxylic acids, etc.). Table 1 identifies the inhibitors used in this study. As shown, the inhibitors vary appreciably in terms of both the functional group and the molecular weight. The purpose of this study was to quantify the effectiveness of these inhibitors and provide an explanation for the mechanism of inhibition of calcium phosphate precipitation in aqueous systems.

Experimental

Grade A glassware and reagent grade chemicals were used. Stock solutions of calcium chloride and disodium hydrogen phosphate were prepared using distilled water, filtered through 0.22 micron filter paper (Millipore Corp.) and analyzed for calcium and phosphate as described previously (9). Sodium pyrophosphate (PP) and citric acid (CA) were prepared from reagent grade chemicals. The AMP and HEDP used in this study were provided by The Monsanto Company. The polymeric inhibitors used were selected from commercial and experimental materials supplied by The BFGoodrich Company, Specialty Polymers and Chemicals Division. Polymer solutions were prepared on a dry weight basis. The desired concentrations were obtained by dilution.

Subsaturated calcium phosphate solutions were prepared in a double-walled glass cell maintained at constant temperature by adding stock solutions of calcium chloride and disodium hydrogen phosphate to the distilled water to attain initial calcium and orthophosphate concentrations of 140 and 9.0 parts per million (ppm), respectively. Spontaneous precipitation was induced by raising the pH of this acidic solution with 0.10 M NaOH. The pH of the solution was maintained at a constant value (± 0.01) using a Metrohm pH stat (pH meter Model 632, dosimat Model 655, impulsomat Model 616, Brinkmann Instruments, Westbury, NY). Hydrogen ion measurements were made with a combination electrode equilibrated at the required temperature. The electrode was calibrated before and checked after each experiment using NBS standard buffer solutions. The solutions were continuously stirred with a Teflon-coated stirring bar at ~400 revolutions per minute. Experiments involving inhibitors were performed by adding the inhibitor to the subsaturated calcium phosphate solution before inducing spontaneous precipitation. Precipitation of calcium phosphate in this supersaturated solution was monitored by analyzing aliquots of the filtered (0.22 micron filter paper) solution for phosphate by spectrophotometric method (9).

Percent inhibition attained was then calculated using the following equation:

[1] $\quad \% \text{ Inhibition} = \dfrac{(PO_4)_{exp} - (PO_4)_{final}}{(PO_4)_{initial} - (PO_4)_{final}} \times 100$

where

$(PO_4)_{exp}$ = concentration of phosphate in the filtrate in presence of the inhibitor at known time

$(PO_4)_{final}$ = concentration of phosphate in filtrate in absence of the inhibitor at 20 h

$(PO_4)_{initial}$ = concentration of phosphate ion at the beginning of the experiment

Results and discussion

The initial conditions used and the results of typical precipitation experiments made in the presence of inhibitors are summarized in Table 2. The experiments reported here had good reproducibility ($\pm 6\%$ or better). Initiation of precipitation by foreign particles, which are always present, does not seem likely, since the experiments were reproducible. Furthermore, the experiments were repeated after having filtered the solutions prior to mixing through 0.1 micron membrane filters without any change in the observed results. However, the possibility of heterogeneous nucleation on the walls of the glass vessels used cannot be precluded, although experiments were conducted in two different experimental set-ups.

Effect of concentration of polyacrylic acid

Results of precipitation experiments made in the presence of varying concentrations (5–50 ppm) of polyacrylic acid (PAA-1, mol wt 2 100), are summarized in Table 2 and shown in Fig. 1. It can be seen (Fig. 1) that the precipitation reaction in the presence of 15 ppm of PAA-1 is reduced by ~50% compared to that in the absence of PAA-1. Figure 1 further indicates that an increase in polymer concentration results in an increase in inhibition value and at 50 ppm of polymer concentration, the precipitation of calcium phosphate was completely inhibited (>95% inhibition) for at least 20 h.

Effect of polyacrylic acid molecular weight

Recently the influence of PAAs as antiscalants for controlling scale formation in industrial water systems has attracted the attention of several investigators. It has been shown that one of the factors determining the effectiveness of PAA is its mol wt (12–14). Based upon the results for similar mol wt polyelectrolytes, Smith and Alexander (15) reported that PAA was more effective than polymethacrylic acid in inhibiting the precipitation of calcium sulfate from supersaturated solutions. Furthermore, growth inhibition results for series of experiments with styrene/maleic anhydride copolymers suggest an optimum effectiveness at a mol wt of 1 600.

Precipitation experiments made in the presence of PAAs of varying mol wt (2 100 – 60 000) are summarized in Table 2. Figure 2 shows precipitation curves in the presence of 10 ppm of various PAAs. The curves in Fig. 2 show that at constant temperature and polymer concentration, the phosphate inhibition value increases with decreasing mol wt, reaches a maximum at a mol wt about 2 100, and thereafter decreases with decreasing mol wt (2 100 to 800). It is interesting to note that Amjad and Masler (14) in their study on the evaluation of PAAs (mol wt 800 – 12 000) as $CaSO_4 \cdot 2H_2O$ crystal growth inhibitors showed optimum performance with an ~2 000 mol wt PAA. Similarily, Amjad (12) in a recent study on the influence of PAA in controlling gypsum ($CaSO_4 \cdot 2H_2O$) scale formation on heat transfer surfaces, reported that the molecular weight of PAA plays an important role in the inhibition of $CaSO_4 \cdot 2H_2O$ crystal growth from aqueous solution. The amount of gypsum scale formed on heat exchanger surface was found to be higher

TABLE 2. Phosphate inhibition data in the presence of inhibitors*

Expt. No.	Inhibitor	Concentration (ppm)	Temperature (°C)	Residual phosphate concentration (ppm) at			% Inhibition at 20 h
				1 h	5 h	20 h	
2	none	0	50	0.16	0.06	0.05	0
3	none	0	50	0.18	0.07	0.05	0
5	PAA-1	5	50	1.92	1.32	1.02	11
4	PAA-1	10	50	2.48	1.86	1.62	18
6	PAA-1	15	50	6.82	5.52	4.45	49
7	PAA-1	15	50	6.75	5.45	4.67	52
8	PAA-1	20	50	8.22	7.45	7.29	81
10	PAA-1	50	50	8.86	8.72	8.65	96
9	PAA-2	10	50	1.67	1.52	1.06	11
12	PAA-2	15	50	1.98	1.66	1.26	14
11	PAA-2	20	50	3.91	2.76	1.94	21
14	PAA-3	10	50	2.84	1.72	0.72	8
15	PAA-3	20	50	4.55	3.91	2.43	27
16	PAA-4	10	50	1.91	1.63	0.49	5
17	PAA-5	10	50	1.02	0.50	0.09	1
19	PAA-6	10	50	0.75	0.34	0.06	0
22	AA/E	10	50	8.22	7.93	7.49	83
29	AA/MAA	10	50	2.63	1.75	1.35	15
30	none	0	40	2.43	0.34	0.04	0
31	PAA-1	10	40	5.98	5.45	4.38	48
32	PAA-2	5	40	1.81	1.64	1.38	15
33	PAA-2	10	40	5.98	4.47	2.67	29
36	PAA-2	15	40	5.72	5.16	4.72	52
35	PAA-3	10	40	6.15	4.73	3.06	34
34	PAA-4	10	40	2.02	1.75	1.39	16
37	PAA-5	10	40	2.02	1.75	0.72	8
38	none	0	30	5.15	3.64	0.22	0
39	PAA-1	5	30	6.78	5.92	4.63	50
40	PAA-1	10	30	7.89	7.55	6.75	74
42	PAA-2	10	30	7.85	7.17	4.91	54
41	PAA-2	15	30	9.26	9.21	8.83	98
44	PAA-3	10	30	6.22	5.45	5.15	56
43	PAA-4	10	30	3.88	3.73	2.88	32
45	PAA-5	10	30	2.06	1.80	0.75	9

*See Table 1 for inhibitor acronyms. Note: the number following PAA- refers to the PAA's mol wt as follows: 1 = 2 100; 2 = 5 100; 3 = 800; 4 = 10 000; 5 = 26 000; 6 = 60 000. Experimental conditions: calcium = 140 ppm, phosphate = 9.0 ppm, pH = 8.50.

in the case of a high (240 000) mol wt PAA than that obtained on the presence of 2 100 mol wt PAA.

The phenomenon of a markedly decreasing PAA effectiveness with increasing mol wt as observed in the present study may be due to several factors including different rates and degrees of adsorption/desorption of PAA molecules on the precipitating calcium phosphate particles. Other factors such as coiling/uncoiling of the polymer molecule and the type of end groups in the polymer could also influence the adsorption processes. Adsorption studies are currently underway in our laboratories to better understand the role of PAA mol wt in inhibiting the precipitation of sparingly soluble salts from aqueous solutions.

Effect of polymer composition

The effect of polymer composition at a constant concentration of 10 ppm was studied using the pH-stat technique. The results are summarized in Table 2 and illustrated in Fig. 3. As shown in Fig. 3, the copolymer of acrylic acid/methacrylic acid (AA:MAA) shows better performance than PAA-4. For example, % inhibition values obtained for AA:MAA and PAA-4 are 5

and 15, respectively (expts. 29, 16). The slight performance increase observed for AA:MAA over PAA-4 may be attributed to the presence of additional methyl groups attached to carbon atoms between carboxylate carrying carbon atoms.

The next polymer in order of increasing inhibitor effectiveness is a copolymer of acrylic acid and an acrylate ester (carbitol acrylate) or AA/E. Compared with PAA, the acrylic acid segments for AA/E are partially substituted by a carbitol acrylate group. The carboxylic acid group concentration and thus the anionic charge density are significantly lower than PAA-4. The effectiveness of AA/E as calcium phosphate inhibitor (Table 2, expt. 22) is surprisingly better than PAA-4, suggesting that the carbitol acrylate group is more effective in improving the inhibitory activity of AA/E than the corresponding carboxyl group in PAA-4. Phosphate inhibition data (Table 2, expts. 16, 29, 22) indicate the following order of polymer effectiveness:

$$AA/E > > AA/MAA > PAA$$

Effect of temperature

The results on the effect of temperature on the inhibition of
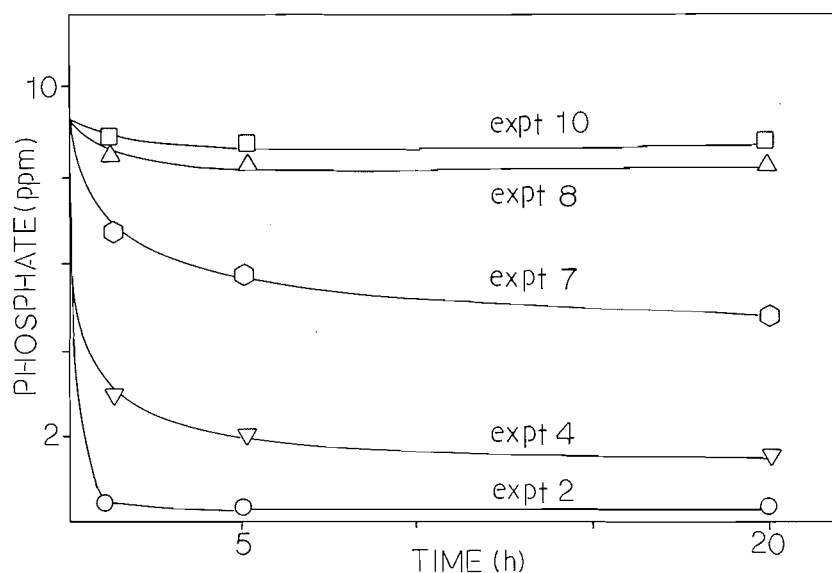
FIG. 1. Plots of phosphate concentration as a function of time at 50°C in the presence of PAA-1 of varying concentrations (ppm): (O) 0; (∇) 10; (◯) 15; (△) 20; (□) 50.
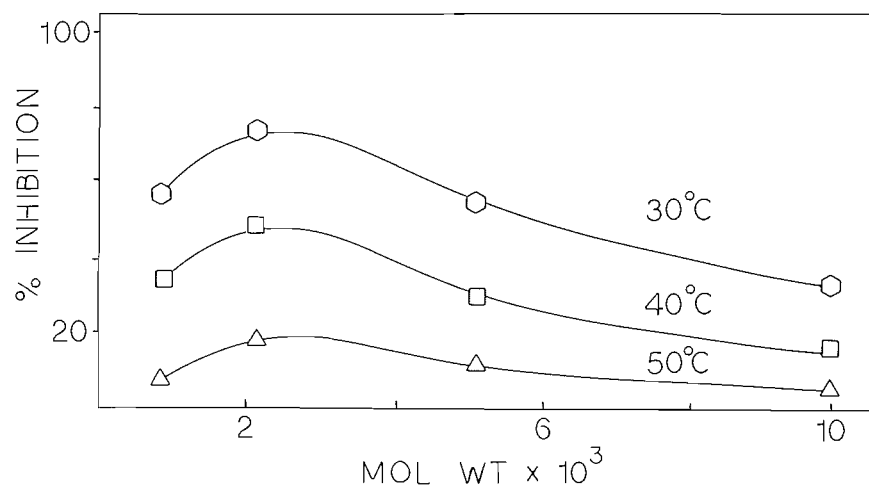
FIG. 2. Relationships of % inhibition with polyacrylic acid molecular weight for calcium phosphate inhibition at temperatures from 30–50°C.

calcium phosphate precipitation in the presence of PAAs are shown in Table 2. It can be seen (Table 2) that as the temperature is raised, there is a concomitant marked decrease in the phosphate inhibition. At a given calcium phosphate and PAA concentration, the relationship between the temperature and the phosphate inhibition can roughly be expressed quantitatively by an empirical equation:

[2] $\%$ Inhibition $= a(1/T) + b$

where T is the absolute temperature; a and b are constants. The linear plots of % inhibition against $1/T$ for PAA-1 and PAA-2 are illustrated in Fig. 4.

Effect of solution pH

The influence of pH on the performance of several phosphonic acids as $CaSO_4 \cdot 2H_2O$ crystal growth inhibitors has been studied by seeded growth technique (16). Results of this study show that an increase in the pH of the crystal growth medium over a pH 4 to 9 range brings about an improvement in inhibitor performance that runs parallel to the phosphonic acid titration curve.

For polymeric inhibitors, such as polyacrylic acid and acrylic acid based copolymers, the degree of protonation should, just as phosphonate inhibitors, be considered in explaining their action. Unfortunately, their acid dissociation constants are not available. It can nevertheless be expected that the affinity of polymeric molecules towards the crystal surface should also be influenced by the solution pH due to the dissociation of carboxylic acid group.

The effect of the solution pH on the precipitation of calcium phosphate in the presence of 10 ppm of PAA-1 and AA/C polymers was studied using the spontaneous precipitation technique. Results are summarized in Table 3. Figure 5 compares phosphate inhibition values for PAA-1 and AA/E at pH 7.5, 8.0, and 9.0. As shown in Fig. 5, at pH 7.5, both polymers (Table 3, expts. 53, 55) exhibit excellent performance (>90% inhibition). However, at pH 8.5, AA/E shows 85% inhibition vs. 30% obtained for PAA-1 (Table 3, expts. 60, 61). Data presented in Table 3 also shows that increasing the solution pH to 9.0 does not significantly affect the performance of AA/E whereas a marked performance decrease occurs for PAA-1 (Table 3, expts. 62, 66).
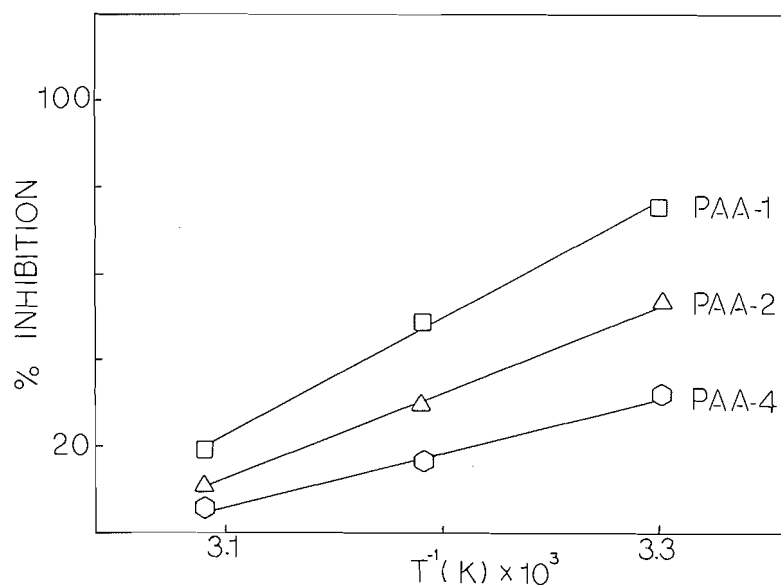
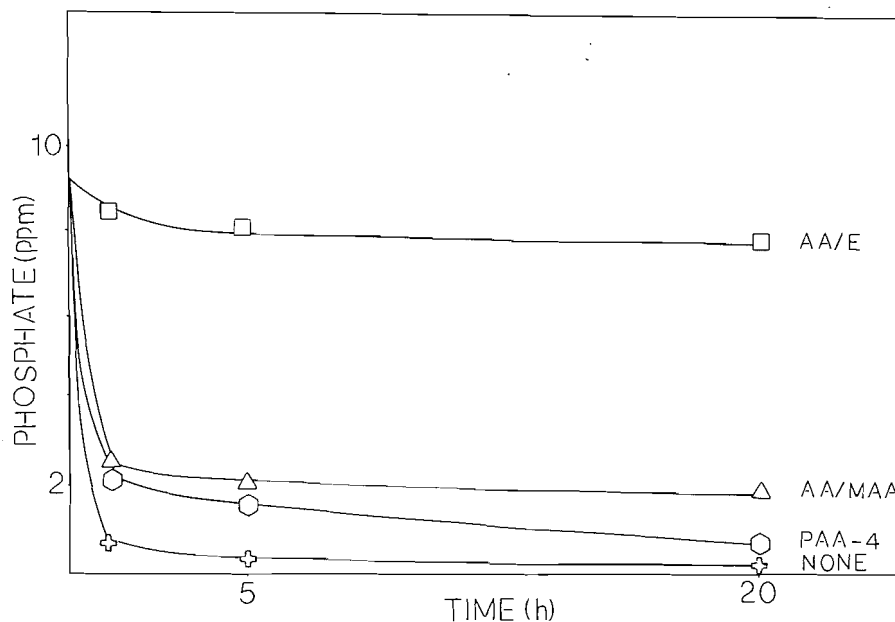FIG. 3. Plots of % inhibition as a function of 1/T for PAA-1, PAA-2, and PAA-4.

FIG. 4. Plots of phosphate concentration as a function of time at 50°C in the presence of 10 ppm of PAA-4, AA/MAA, and AA/E.

It is interesting to note that in the seeded growth study of $CaSO_4 \cdot 2H_2O$ in the presence of PAA, the inhibitory effect of PAA was found to increase with increasing solution pH (17). This is inconsistent with the results obtained in the present study. The observed difference in PAA performance for two different sparingly soluble salts as a function of solution pH may be explained in terms of differences in solubility values of calcium phosphate and calcium sulfate salts (i.e. an increase in solution pH results in an increased supersaturation in the case of calcium phosphate, whereas pH does not significantly affect the calcium sulfate supersaturation).

Effect of polyphosphate, phosphonate, benzene polycarboxylic acid, and citric acid

The inhibiting properties of condensed phosphates of both the meta- and polyphosphate types have been extensively studied in

relation to scale formation and biological calcification processes. In the former case it has been shown that sodium pyrophosphate is an effective growth inhibitor when added to $CaCO_3$ (6) and $BaSO_4$ (18) systems. In biological calcification processes, pyrophosphate ion has been found to be an effective crystal growth inhibitor for calcium phosphate (19) and calcium oxalate (7) systems. A surface adsorption mechanism has been found useful in describing the effect of pyrophosphate in many of these systems.

Precipitation experiments made in the presence of pyrophosphate (PP) are summarized in Table 4. It can be seen (Table 4, expt. 47) that at 10 ppm, PP exhibits a smaller inhibiting effect compared to PAA-1 (Table 2, expt. 40). For example, % phosphate inhibition values obtained for PP and PAA-1 are 28 and 74, respectively. It is interesting to note that PP, which exhibits strong inhibitory effect for calcium oxalate (7), barium
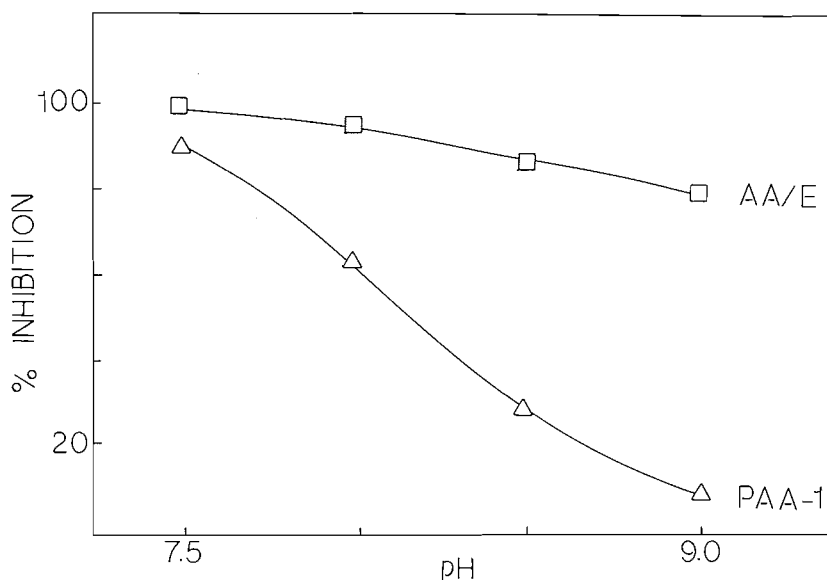
FIG. 5. The effect of solution pH on the inhibition of calcium phosphate at 50°C in the presence of 10 ppm of PAA-1 and AA/E polymers.

TABLE 3. Phosphate inhibition data in the presence of inhibitors: effect of solution pH*

Expt.	Inhibitor	pH	% Phosphate inhibition at 20 hr
53	PAA-1	7.5	91
55	AA/E	7.5	99
56	PAA-1	8.0	62
58	AA/E	8.0	96
60	PAA-1	8.5	30
61	AA/E	8.5	85
62	PAA-1	9.0	10
66	AA/E	9.0	80

*Experimental conditions: calcium = 140 ppm, phosphate = 9.0 ppm, inhibitor = 10 ppm, 50°C.

TABLE 4. Phosphate inhibition data in the presence of inhibitors*

		Residual phosphate concentration (ppm) at			% Inhibition at 20 h
Expt. No.	Inhibitor	1 h	5 h	20 h	
47	PP	3.41	2.99	2.58	28
49	HEDP	4.02	3.75	3.16	33
48	AMP	5.17	4.29	3.65	40
52	MA	4.66	4.31	3.85	41
51	TMA	2.02	1.60	0.45	5
50	CA	4.72	2.09	0.27	1

*See Table 1 for acronyms. Experimental conditions: calcium = 140 ppm, phosphate = 9.0 ppm, pH = 8.50, 30°C, inhibitor = 10 ppm.

sulfate (18), and calcium carbonate (6) systems, only has moderate inhibitory effect on calcium phosphate precipitation.

Organophosphonates such as HEDP have been found to markedly inhibit the crystallization of calcium carbonate (6), calcium oxalate (20) and barium sulfate (18). Inhibition data summarized in Table 4 show that AMP is a better inhibitor than HEDP. For example, % inhibition values obtained at 10 ppm inhibitor concentration, 30°C, and at 20 h for AMP and HEDP are 40 and 33, respectively. It is noteworthy that for HAP crystal growth in the presence of polyphosphates and phosphonates (19), the relative order of effectiveness reported was:

HEDP > AMP > PP

The above order of inhibitor effectiveness is inconsistent with the results obtained in the present study (expts. 47, 48, 49). It should be noted that for dicalcium phosphate dihydrate, (DCPD), seeded growth on DCPD seed crystals (21) in the presence of PP and phosphonates, the order of effectiveness suggested was:

AMP > HEDP > PP

The differences observed in the order of phosphonates effectiveness for HAP, DCPD, and this investigation, may be due to several factors including different rates of adsorption/ desorption of inhibitors on different types of substrates.

Results summarized in Table 4 for the inhibitory effect of benzene hexacarboxylic acid (mellitic acid, MA) show that compared to PAA, MA is a moderately effective calcium phosphate inhibitor. However, under similar experimental conditions, MA exhibits a much greater effectiveness compared to citric acid (CA) but is significantly less effective than PAA-1. For example, % inhibition values obtained at 30°C for 10 ppm concentration of PAA-1, MA, trimesic acid, and CA are 74, 41, 5, and 1, respectively. These results are consistent with those reported by Coffey (22) which indicate that the best inhibitors for barium sulfate precipitation were those that imparted the most negative electrophoretic mobility to the barium sulfate particles. Similar observations have been reported in recent seeded growth studies on the effect of polycarboxylic acid on the crystal growth of calcium carbonate (23), dicalcium dihydrogen phosphate (24), and hydroxyapatite (25) from aqueous solutions.

Mechanism of inhibitor action

The results discussed above show that trace quantities of certain inhibitors markedly reduce the precipitation of calcium phosphate. The influence of these inhibitors on precipitation reaction may be explained in terms of three effects, (*a*) direct

complexation of inhibitor with crystal lattice ions in solution; (b) adsorption of inhibitor on the crystal surface either generally or at the active growth sites; (c) inhibitor may change the ionic strength of the solution and hence the effective solubility of the calcium phosphate.

Under the experimental conditions employed in the present investigation, the marked reduction in calcium phosphate precipitation must be attributed to surface adsorption factor rather than the calcium–inhibitor complex formation or the concomitant increase in ionic strength of the supersaturated solution in the presence of inhibitors.

If the action of the inhibitor, which stabilizes supersaturated solutions of calcium phosphate, is to be adsorbed on the crystal embryos and prevent their growth, the question arises why the nuclei do not go on forming until all the stabilizing material (i.e. inhibitor) has been used up, since the formation of nuclei involves a negligible change in the concentration of the solution. There are two possible reasons for this. Nucleation may take place only on a limited number of "stray nuclei", or it may be that the inhibitors stop development of the nuclei below the critical size and they redisperse, forcing the inhibitor to interact with other embryos. An adsorption mechanism is also indicated in many systems by an appreciable habit modification of crystals grown in the presence of impurities (12).

Summary

In the present work it has been shown that low levels of both polymeric and non-polymeric type inhibitors can significantly inhibit the precipitation of calcium phosphate from aqueous solution. The results on the performance of PAAs of varying molecular weight (800 to 60 000) suggest that optimum effectiveness for PAAs occurs at a mol wt ~2 000. The results of the present study also suggest that the inhibition of calcium phosphate precipitation strongly depends upon the concentration of polymer, solution pH, and polymer composition. In addition, it has also been shown that the presence of pyrophosphate, phosphonates, and mellitic acid at low concentrations can significantly inhibit calcium phosphate precipitation. A mechanism based upon surface adsorption has been proposed to explain the influence of inhibitors on calcium phosphate precipitation.

Acknowledgements

1. G. H. NANCOLLAS. Corrosion/82 Paper No. 20. National Association of Corrosion Engineers, Houston, TX. 1982.
2. W. J. BEER and J. F. ERTEL. Corrosion/85, Paper No. 125. National Association of Corrosion Engineers, Houston, TX. 1986.
3. R. ZUHL, Z. AMJAD, and W. F. MASLER. J. Cooling Tower Institute, 8, 41 (1987).
4. S. T. LIU and G. H. NANCOLLAS. J. Colloid Interface Sci. 52, 582 (1975).
5. L. SHYU. Ph.D. Thesis, State University of New York at Buffalo, New York. 1982.
6. M. M. REDDY and G. H. NANCOLLAS. Desalination, 12, 61 (1973).
7. E. N. RIZKALLA and M. M. MOAWAD. J. Chem. Soc. Faraday Trans. 80, 1617 (1984).
8. S. T. LIU and G. H. NANCOLLAS. J. Colloid Interface Sci. 44, 422 (1973).
9. R. G. VARSANIK. Mater. Perform. 14, 16 (1975).
10. E. R. MCCARTNEY and A. E. ALEXANDER. J. Colloid Sci. 13, 383 (1958).
11. C. H. NESTLER. J. Colloid Interface Sci. 26, 10 (1968).
12. Z. AMJAD. J. Colloid Interface Sci. 123, 523 (1988).
13. P. FLESHER, E. L. STREETFIELD, A. S. PEARCE, and O. D. HYDES. 3rd Int. Symp. Fresh Water Sea 1, 493 (1970).
14. Z. AMJAD and W. F. MASLER. Corrosion/85, Paper No. 357, National Association of Corrosion Engineers, Houston, TX. 1985.
15. B. R. SMITH and A. E. ALEXANDER. J. Colloid Interface Sci. 34, 81 (1970).
16. D. W. GRIFFITHS, S. D. ROBERTS, and S. T. LIU. Int. Symp. Oilfield Geothermal Chem. Society of Petroleum Engineers. 1979. Paper 7861.
17. Z. AMJAD. Corrosion/88, Paper No. 421. National Association of Corrosion Engineers, Houston, Tx. 1988.
18. E. N. RIZKALA. J. Chem. Soc. Faraday Trans. 79, 1857 (1983).
19. Z. AMJAD. Langmuir, 3, 1063 (1987).
20. G. L. GARDNER. J. Phys. Chem. 82, 864 (1978).
21. Z. AMJAD. Can. J. Chem. 66, 2181 (1988).
22. M. D. COFFEY. Paper No. SPE 5302, Inter. Symp. Oilfield, Soc. Pet. Eng. Dallas, 1975.
23. Z. AMJAD. Langmuir, 3, 224 (1987).
24. Z. AMJAD. J. Colloid Interface Sci. 117, 98 (1987).
25. Z. AMJAD. In Adsorption on and surface chemistry of hydroxyapatite. Edited by D. N. Misra. Plenum Press, New York. 1984.