

# INFLUENCE OF HUMIC COMPOUNDS ON THE CRYSTAL GROWTH OF HYDROXYAPATITE

Zahid Amjad<sup>1</sup> and Michael M. Reddy<sup>2</sup>

<sup>1</sup>The Advanced Technology Group  
The BFGoodrich Company  
9921 Brecksville Road  
Brecksville, Ohio 44141

<sup>2</sup>U. S. Geological Survey  
3215 Marine Street  
Boulder, Colorado 80303

## 1. ABSTRACT

The influence of several natural and synthetic additives containing hydroxy and/or carboxyl groups on the kinetics of crystal growth of hydroxyapatite (HAP) at sustained supersaturation has been investigated using the constant composition method. Addition of low levels (0.25 to 5 parts per million) of fulvic acid, tannic acid, benzene hexacarboxylic acid, and poly(acrylic acid) to supersaturated calcium phosphate solutions has an inhibitory influence upon the rate of crystal growth of HAP. Salicylic acid, under similar experimental conditions, is an ineffective HAP growth inhibitor. Kinetic analysis suggests Langmuir-type adsorption of added ions on the HAP surfaces with a relatively high affinity for the substrate in the concentration range investigated.

## 2. INTRODUCTION

The influence of inhibitors on the crystallization of hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , HAP) has been extensively studied in relation to calcification in biological systems and mineral scale formation in industrial water systems. HAP, a mineral prototype for teeth and bones, is also encountered as a deposit on heat exchanger surfaces in industrial applications (cooling, boiler, pulp and paper) where alkaline pH accelerates the conversion of initially precipitated amorphous calcium phosphate to HAP. Results of previous investigations using both seeded growth and spontaneous precipitation techniques have shown that

both pyrophosphate and organophosphonates are effective crystal growth inhibitors for di-calcium phosphate dihydrate (DCPD) ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) and HAP phases.<sup>1-4</sup>

Several studies have been reported pertaining to the influence of di-, tri, and hexa-carboxylic acids on the crystal growth of HAP. Nancollas et al.<sup>5</sup> investigated the influence of tricarboxylic acids on calcium phosphate precipitation using the seeded growth method. Comparison of the effect of citric acid, isocitric acid, and tricarboxylic acid suggests that the hydroxyl group in the molecular backbone plays a key role in the effectiveness of two of these tricarboxylate ions. A study on the influence of benzene hexacarboxylic acid, benzene tricarboxylic acid, glycolic acid, malic acid, and malonic acid as crystal growth inhibitors for HAP reported that the inhibitory power of these additives strongly depends on the ionic charge (or the number of carboxyl and/or hydroxyl groups) of the inhibitor.<sup>6,7</sup> Effects of additives containing hydroxy, phosphonic, and carboxylic group as HAP and DCPD crystal growth inhibitors have recently been reported. Results of these studies reveal that additives containing both phosphono and carboxy groups exhibit stronger inhibitory activity than those containing hydroxy and/or carboxy groups.<sup>7,8</sup>

The influence of polymeric inhibitors (e.g., poly(acrylic acid), poly(maleic acid), and acrylic acid-based copolymers) as crystal growth inhibitors for sparingly soluble salts has attracted the attention of several researchers. Smith and Alexander<sup>9</sup> have reported that calcium sulfate crystal growth is inhibited by poly(acrylic acid), poly(methacrylic acid), and carboxycellulose. Amjad<sup>10-13</sup> has reported that the effectiveness of a polymer as a crystal growth inhibitor for sparingly soluble salts (e.g., HAP, DCPD,  $\text{BaSO}_4$ ,  $\text{CaF}_2$ ), is inversely proportional to its molecular weight. In addition, it has also been reported that substituting the carboxyl group with bulky groups (for example, hydroxyl propylacrylate, tertiary butyl acrylamide, 2-acrylamido-2-methyl propane sulfonic acid) results in increased inhibitory power of the copolymer in preventing the precipitation of calcium phosphates.<sup>14</sup> A study of water-soluble polymers<sup>15</sup> reported phosphorylated polyvinyl alcohol and sulfated polyvinylalcohol retarded transformation of amorphous calcium phosphate to hydroxyapatite. The adsorption of citrate (CA) and phosphocitrate (PC) ions by HAP surfaces and their influence on constant-composition growth kinetics have been reported. According to Williams et al.,<sup>16</sup> PC was strongly adsorbed to HAP and inhibited crystal growth and the two additives, PC and CA, behaved synergistically in their HAP crystal growth inhibition.

Humic and fulvic acids, commonly found in the natural environment, are polymeric molecules whose molecular weights range from several hundred to several thousand. They mostly contain carboxylic and phenolic acid functionalities, and can behave as negatively charged colloids or anionic polyelectrolytes in surface waters. Nystrom et al.<sup>17</sup> in their study on the filtration of process waters containing humic acid by membrane-based filtration procedures reported that humic acid forms a gel-like layer on the filter and blocks the pores of the filter. Recently, using a constant-composition method, Lacout et al.<sup>18</sup> reported that low levels of fulvic acid markedly inhibit DCPD crystal growth.

In our laboratory, several studies have been conducted on the effect of synthetic polymers containing a variety of functional groups (including hydroxyl, carboxyl, ester, sulfonic) on the precipitation of sparingly soluble salts using the constant composition (CC) technique. It has been found that the overall efficacy of the polymer as a crystal growth inhibitor strongly depends on ionic charge, polymer composition, and molecular weight. Humic and fulvic acids commonly present in many surface waters are known to affect the efficiency of industrial water systems (cooling, boiler, desalination) and agricultural fertilization. To understand humic substance interactions with various scale-forming salts, we examined fulvic acid growth inhibition effectiveness on HAP crystals. This study

also presents results on the effect of tannic acid and salicylic acid on the crystal growth of HAP at constant supersaturation. For performance comparison, crystal growth experiments were also carried out in the presence of low molecular weight poly(acrylic acid) and benzene polycarboxylic acids.

### 3. EXPERIMENTAL

Solutions were prepared using reagent grade chemicals with deionized, distilled,  $\text{CO}_2$ -free water. Calcium ion concentrations were determined by atomic absorption spectroscopy and phosphate solutions were analyzed spectrophotometrically. Fulvic acid used in this study was characterized as described previously.<sup>19</sup> Tannic acid was obtained from Fisher Scientific and was used without further purification. Benzene hexacarboxylic acid and benzene-1,3,5-tricarboxylic acid were obtained from Sigma Chemical Company. Poly(acrylic acid) was a commercial sample from the BFGoodrich Company (the use of trade-names in this report is for identification purposes only and does not constitute endorsement by the USGS).

HAP seed crystals were prepared and characterized as described previously.<sup>10</sup> All experiments were conducted at  $37 \pm 0.1$  °C in doubled-walled, water-jacketed, Pyrex cells (Figure 1). The crystal growth experiments were made at constant supersaturation as described previously.<sup>10</sup> Hydrogen ion activity measurements were made with a glass/Ag - AgCl electrode pair equilibrated at 37 °C. The electrode pair was standardized before each experiment. In a typical crystal growth experiment, the stable supersaturated solution of calcium phosphate with a calcium to phosphate molar ratio of 1.67 was prepared by adjusting the premixed subsaturated solution of calcium phosphate to a pH of 7.40 by the slow addition of 0.10 M potassium hydroxide. The supersaturated calcium phosphate solutions were continuously stirred while nitrogen gas presaturated with water was bubbled through the solution to exclude carbon dioxide.

After the pH adjustment and a waiting period of about 45 minutes, the crystallization was initiated by the addition of well-characterized HAP seed crystals. To investigate the effect of inhibitors, stock solutions were diluted to the desired concentrations in the working solutions. In all cases, the precipitation reaction started immediately following the introduction of the seed crystals in the crystallization medium. During HAP forma-

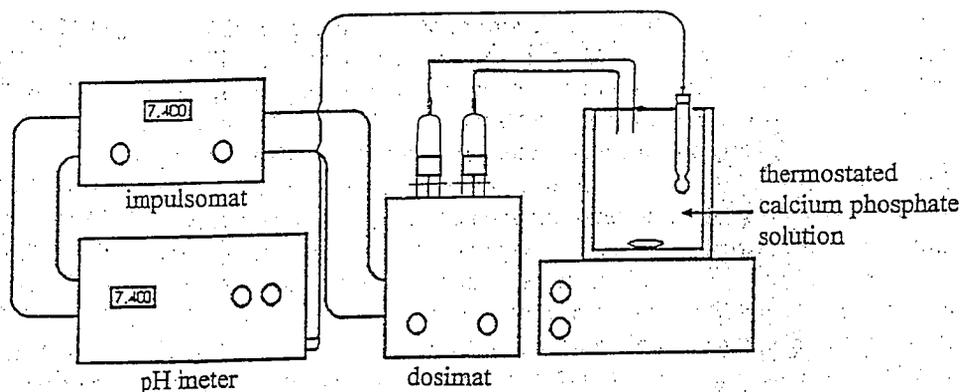


Figure 1. Constant composition experimental apparatus.

Table 1. Substances evaluated for inhibition of HAP crystal growth onto HAP seed crystals at constant supersaturation

Inhibitor	Acronym
Fulvic acid	FA
Tannic acid	TA
Salicylic acid	SA
Benzene Hexacarboxylic Acid	BHCA
Benzene-1, 3, 5-Tricarboxylic acid	BTCA
Poly (Acrylic acid)	PAA

tion, protons are released in the solution thus offering a very sensitive means of monitoring its crystallization process. This increase in hydrogen ion activity accompanying crystallization, was sensed by the pH electrode, which triggered an automatic titrator potentiostat (Brinkmann Instruments, Westbury, NY) to add titrant solutions of calcium chloride, potassium phosphate, potassium hydroxide, and inhibitor. The molar concentration ratios of the titrants corresponded to the stoichiometry of the HAP phase. Potassium chloride was added to calcium phosphate supersaturated solutions to maintain constant ionic strength. Periodically, aliquots of the reaction mixtures were filtered (0.22 micrometer, Millipore Corporation, MA) and the filtrate analyzed for calcium and phosphate ions to verify the constancy (within 1%) of the concentrations. Crystallization rates were determined from the rates of addition of mixed titrants and corrected for surface area changes.<sup>10</sup> Table 1 lists the additives studied in this investigation.

#### 4. RESULTS AND DISCUSSION

The solution supersaturation was computed by accounting for the mass balance equations for total calcium and phosphate and electroneutrality conditions by successive approximations for ionic strength using the method described previously.<sup>10</sup> The driving force for the crystallization of HAP is the change in Gibbs free energy ( $\Delta G$ ) for going from the supersaturated solution to equilibrium:

$$\Delta G = - (RT/n) \ln (IP/K_{so}) \quad (1)$$

where IP is the ionic activity product,  $K_{so}$  the value of IP at equilibrium, and R, T, and n are the ideal gas constant, absolute temperature, and the number of ions in the unit formula of the calcium phosphate phases (for HAP  $n = 9$ ), respectively. The  $\Delta G$  values obtained using Equation 1 for various calcium phosphate phases indicate the thermodynamic stability of the experimental solutions compared to solutions in thermodynamic equilibrium with that particular phase. Positive  $\Delta G$  values represent undersaturated solutions and negative  $\Delta G$  values represent solutions supersaturated with respect to the solid phase under consideration. Table 2 summarizes the experimental conditions used and the results of typical crystal growth experiments made in the presence and absence of inhibitors.

By conducting a series of crystal growth experiments in the presence of varying concentrations of FA, it is possible to describe the concentration--performance relationship for FA (Figure 2). HAP growth rate decreases with increasing fulvic acid concentration.

Table 2. Crystallization of HAP on HAP-seed crystals in the presence of inhibitors

Exp	Inhibitor	Inhibitor conc., ppm	Rate of HAP crystal growth, $\times 10^3$ mole min <sup>-1</sup> m <sup>-2</sup>
10.	none	0.0	14.3
12.	none	0.0	13.6
13.	none	0.0	14.9
14.	FA	0.25	11.5
15.	FA	0.33	10.6
16.	FA	0.50	9.4
17.	FA	0.50	8.7
18.	FA	0.70	6.5
19.	FA	1.00	4.0
20.	FA	1.25	2.8
27.	TA	0.50	11.8
28.	TA	1.0	8.9
29.	TA	2.0	4.5
30.	TA	3.0	2.5
31.	TA	4.0	1.6
32.	SA	1.0	13.8
33.	SA	5.0	14.5
34.	BHCA	0.50	8.0
35.	BTCA	1.00	14.2
36.	BTCA	5.00	14.8
37.	PAA	0.25	8.0
38.	PAA	0.33	6.1
39.	PAA	0.50	3.5
40.	PAA	0.60	1.2
41.	PAA	1.00	0.7

<sup>a</sup>Initial conditions :  $T_{Ca}$  (total solution calcium concentration) = 0.500 mM,  $T_{phos}$  (total solution phosphate concentration) = 0.300 mM, pH 7.40, 37 °C

KCl = 7.00 mM, Titrant 1: CaCl<sub>2</sub> = 8.00 mM, Titrant 2 : KH<sub>2</sub>PO<sub>4</sub> = 4.80 mM + KOH = 9.91 mM.  $\Delta G$  (kJ mol<sup>-1</sup>) HAP, - 52.6; OCP, -10.2; DCPD +4.02

Interestingly, a fulvic acid concentration as low as 0.25 ppm significantly reduces the crystal growth rate of HAP. The rate data in Figure 2 also show that increasing the FA concentration from 0.25 to 1 ppm results in a significant decrease in growth rate, respectively. It is worth noting that a further increase in the inhibitor concentration to 1.25 ppm decreased the growth rate by about 80%.

In view of the above results indicating that fulvic acid exhibits strong inhibitory activity for HAP crystal growth, additional experiments were performed with TA (Table 2). The marked inhibition of HAP crystallization by TA is clearly seen in the plots of moles of HAP grown as a function of time during several of these experiments (Figure 3). For example, in the presence of 1 ppm TA the rate of HAP growth rate is reduced by 38% and

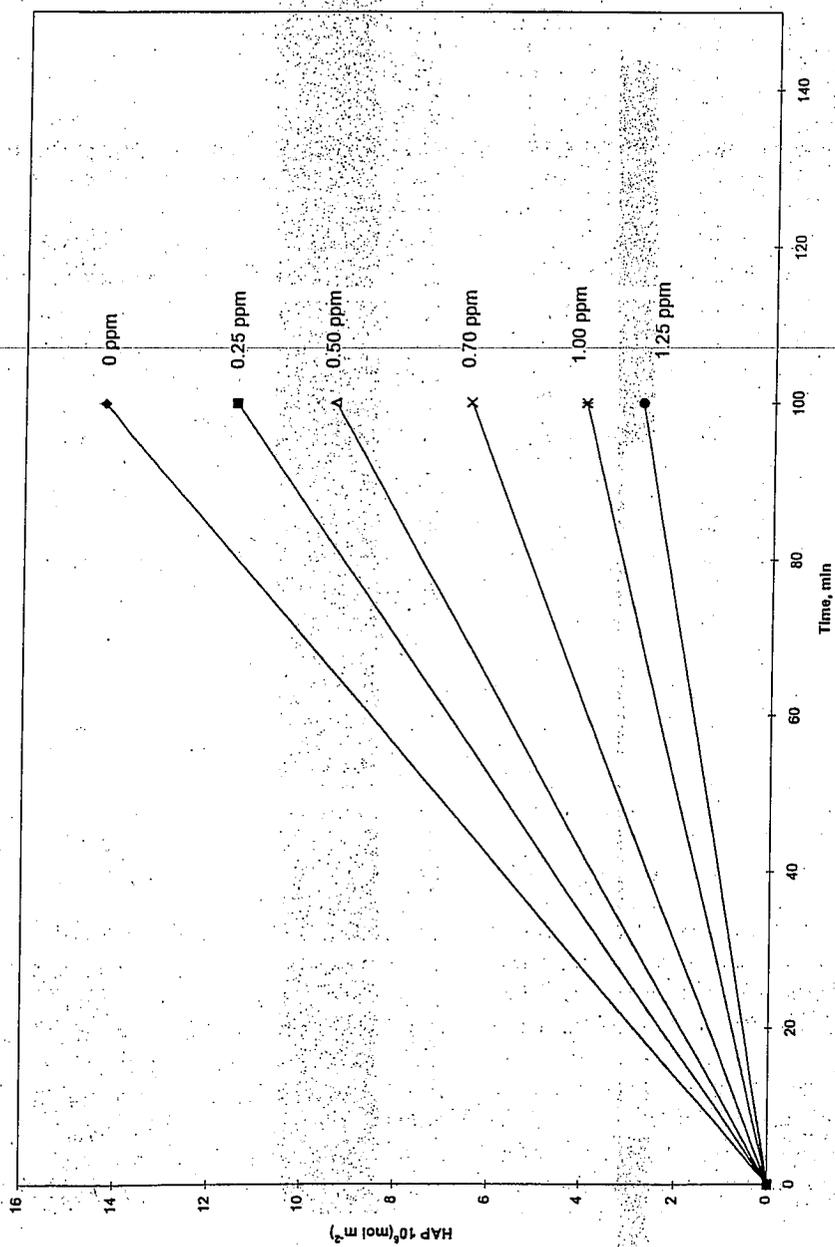


Figure 2. Crystal growth of hydroxyapatite onto hydroxyapatite seed crystals at constant supersaturation. Plots of amount of hydroxyapatite formed as a function of time in the presence of various concentrations of fulvic acid (FA).

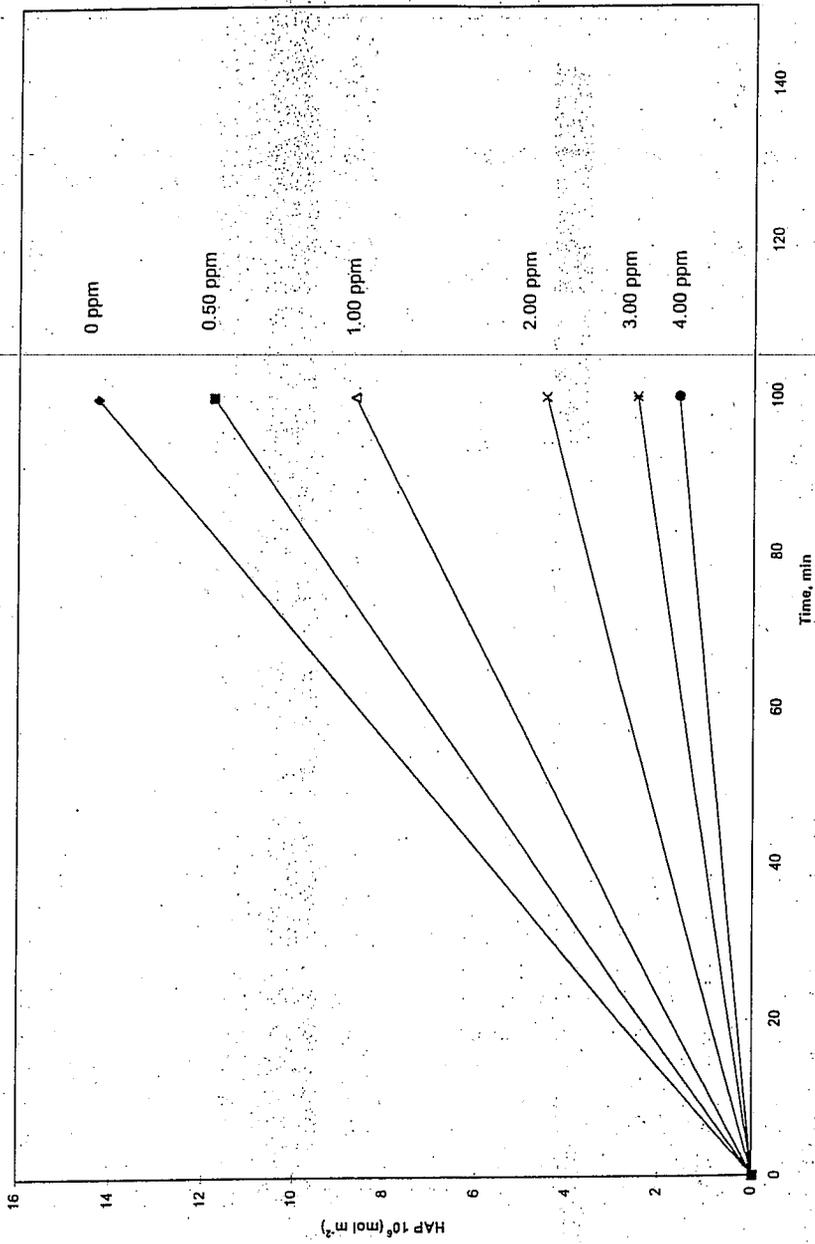


Figure 3. Crystal growth of hydroxyapatite onto hydroxyapatite seed crystals at constant supersaturation in the presence of varying concentrations of tannic acid (TA).

lecular weight poly(acrylic acid). The results of these experiments are summarized in Table 2. Amounts of HAP formed in solutions of constant supersaturation versus time profiles for varying concentrations of poly(acrylic acid), PAA, are shown in Figure 4. The data shown in Figure 4 indicates that PAA is an effective HAP growth inhibitor. Figure 5 shows the competitive inhibition data for SA, TA, FA, and BHCA at 0.5 ppm. The data indicates that BHCA (highly anionic compound) exhibits superior performance compared to SA, TA, and FA. Growth rates obtained in the presence of 1 ppm inhibitor concentration for PAA, BHCA, FA, and TA are  $\ll 1$ , 2.9, 6.8, and 10.4 ( $10^8 \text{ mole min}^{-1} \text{ m}^{-2}$ ), respectively. It is worth noting that, under similar experimental conditions, BTCA did not exhibit any inhibitory activity (Table 2). Based on this inhibition data (Table 2 and Figure 6), the ranking in terms of inhibitor efficacy is:

$$\text{PAA} > \text{BHCA} > \text{FA} > \text{TA} \gg \text{BTCA}, \text{SA} = \text{control (no additive)}.$$

The kinetic data clearly suggests that overall ionic charge of the additive plays a key role in influencing the growth rate. This is consistent with previous observations that the best inhibitors for  $\text{BaSO}_4$  precipitation were those that imparted the most negative electrophoretic mobility to the  $\text{BaSO}_4$  particles.<sup>20</sup> Similar observations have been reported in kinetic studies involving the effect of polycarboxylic acids on the crystallization of dicalcium phosphate dihydrate<sup>21</sup> and calcium carbonate.<sup>22</sup>

Polymeric and non-polymeric inhibitors play an important role in several industrial and biological processes where precipitation of sparingly soluble salts must be prevented. To explain the influence of inhibitors on the crystal growth and dissolution of sparingly soluble salts, various mechanisms have been proposed, including: a) inhibitor adsorption on the crystal surface, either generally or at the active sites, b) inhibitor formation of stable solution complexes with calcium, thus reducing solution supersaturation, and c) supersaturation decrease due to increased solubility resulting from increased ionic strength. Under the experimental conditions employed in the present study, however, the decrease in rate of crystallization must be attributed to surface adsorption rather than to an increase in ionic strength of the supersaturated solution in the presence of inhibitor. Inhibitors concentration is orders of magnitude smaller than a concentration that would give rise to significant changes in ionic strength or to simple calcium-inhibitor complex formation. The percentage of calcium complexed, even at the highest inhibitor concentration, accounts for less than 4% of total calcium concentration in solution (M. Reddy, unpublished results).

Previous investigations of the influence of both polymeric and non-polymeric inhibitors have shown that the reduction in the rates of crystal growth and dissolution of sparingly soluble salts by inhibitory anions follow a Langmuir adsorption model. If the adsorbed inhibitor at concentration  $[B]$  covers a fraction  $(A)$  of the total available surface, then the rate of adsorption may be expressed as  $k_1[B](1-A)$  and the rate of desorption as  $k_2A$ , where  $k_1$  and  $k_2$  are the corresponding rate constants. At equilibrium, then:

$$R / (R - R_i) = 1 + (k_2 / k_1) [B] \quad (2)$$

where  $R$  and  $R_i$  are the growth rate constants in the absence and presence of inhibitors, respectively. According to Equation 2, a plot of  $R / (R - R_i)$  against  $[B]^{-1}$  should give a straight line. Such plots for fulvic acid and tannic acid are shown in Figure 7. The data in Figure 7 suggest that crystal growth of HAP is completely inhibited, i.e.,  $\sim 1$  at a concentration of 1.3 and 3.9 ppm for FA and TA, respectively, which may be compared with 0.65 ppm obtained for PAA. Table 3 summarizes the concentrations needed for complete inhi-

multiscale

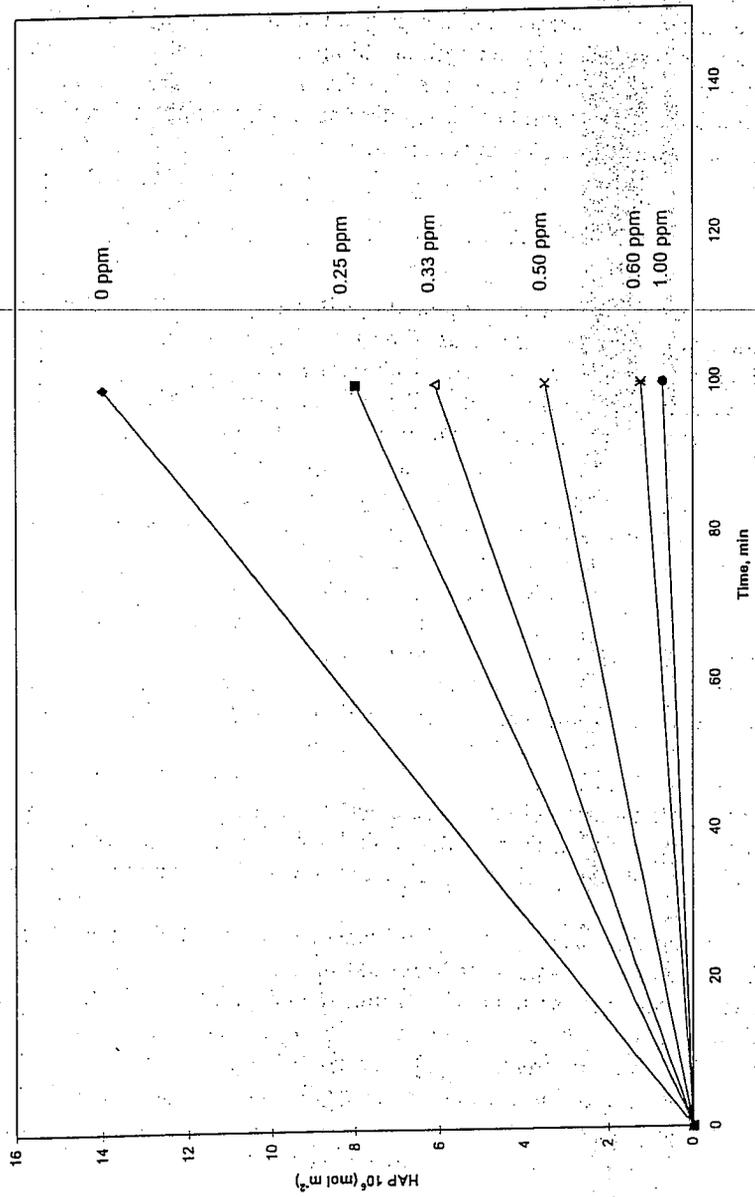


Figure 4. Hydroxyapatite crystal growth onto hydroxyapatite seed crystals at constant supersaturation in the presence of various additives at 0.5 ppm concentration.

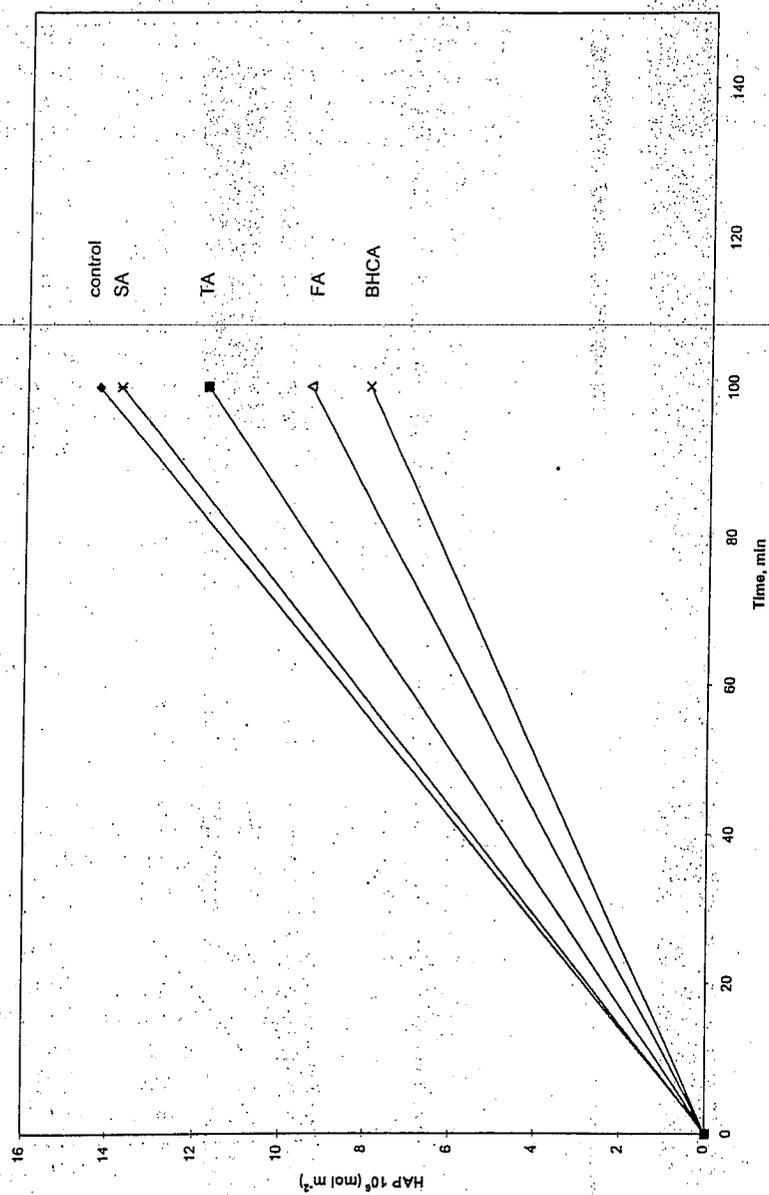


Figure 5. Hydroxyapatite crystal growth onto hydroxyapatite seed crystals at constant supersaturation in the presence of various additives and poly (acrylic acid) (PAC), (SA concentration = 1 ppm, all others are 0.5 ppm).

the presence of various additives and poly (acrylic acid) (PAA), (SA concent-

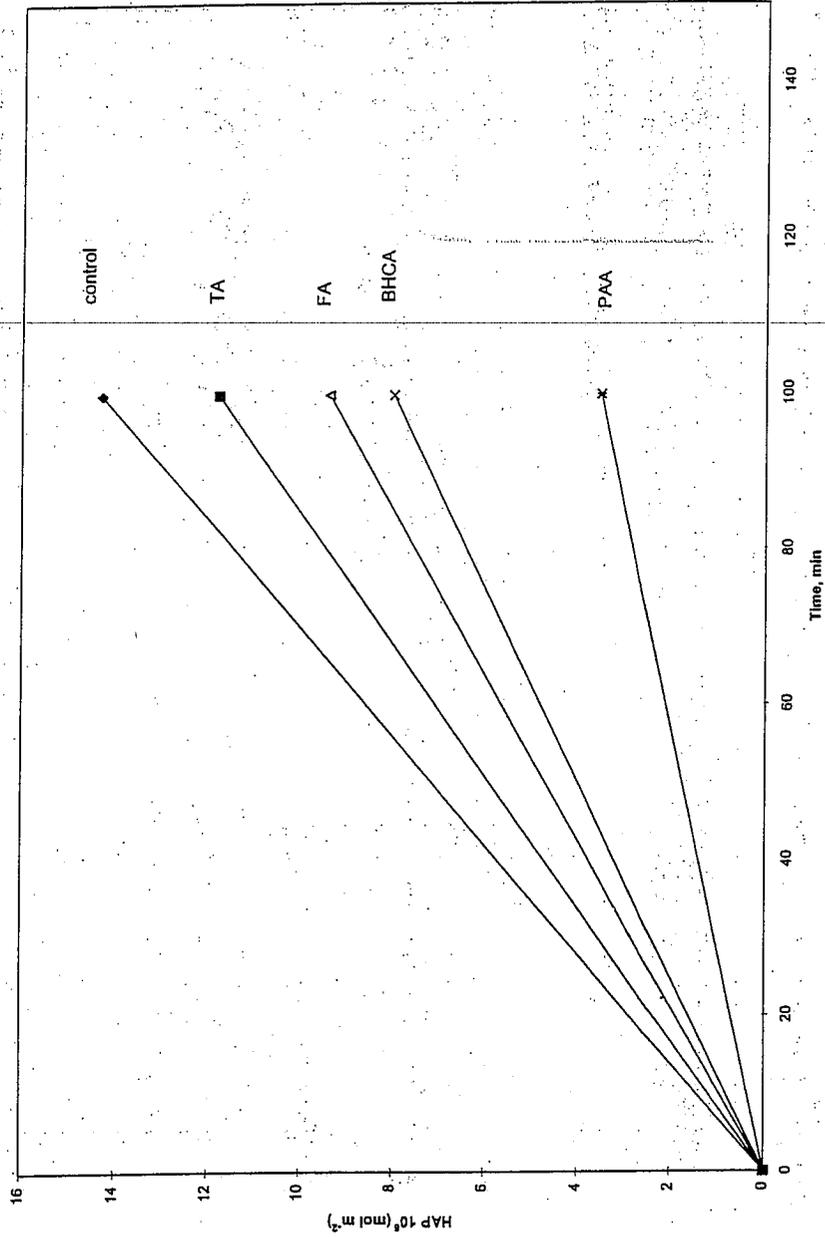


Figure 6. Hydroxyapatite crystal growth onto hydroxyapatite seed crystal at constant supersaturation in the presence of varying concentrations of poly (acrylic acid) (PAA).

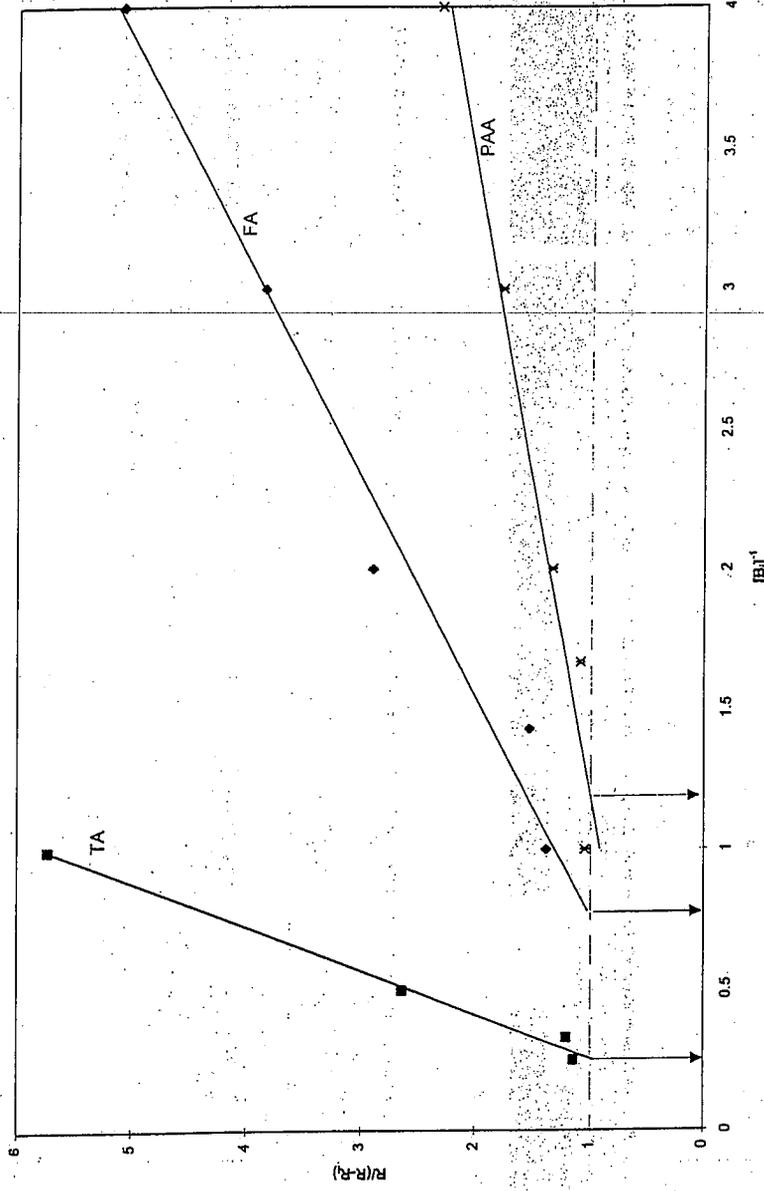


Figure 7. The Langmuir rate function for hydroxyapatite crystal growth onto hydroxyapatite seed crystals at constant supersaturation plotted as a function of the reciprocal fulvic acid (FA), tannic acid (TA), and poly(acrylic acid) (PAA) inhibitor concentrations.

Table 3. Comparative growth rate data on inhibitor performance as indicated by the inhibitor concentration needed to reduce the growth by 50% in the absence of inhibitor for HAP, DCPD, and calcite.

System	Inhibitor conc, ppm			Ref.
	FA	TA	PAA	
HAP	1.3	3.9	0.65	this study
DCPD	0.52	0.83	0.021	submitted for publication
Calcite	0.45	1.1		submitted for publication

hibition for HAP, DCPD, and calcite for FA, TA, and PAA. It is interesting to note that for all these systems the order of inhibitor effectiveness is the same, i.e., PAA > FA > TA.

The inverse of the slope of the straight line (Figure 7) is a measure of the sorption "affinity constant" of the inhibitor for HAP and may be useful for comparing the effect of various inhibitors. Because molecular weights of fulvic and tannic acids are not available for comparing the performance of various inhibitors, an arbitrary criterion was selected to determine the concentration of inhibitor that results in 50% reduction in growth rate ( $R_{0.5}$ ). Table 4 lists the concentration of a variety of inhibitors for HAP system taken from this report and other published investigations.

Comparison of  $R_{0.5}$  for various carboxyl- and/or hydroxy-containing additives reveals that the most effective inhibitor among these additives is poly(acrylic acid) and the additive which exhibits the least effectiveness is glycolic acid. This ranking of performance suggests that the inhibitory power strongly depends upon the ionic charge of the additive.

Among the phosphorus-containing additives, the best performance is observed for HEDP and PBTC. Phytic acid showed the poorest performance (by a factor of 50 less effective than HEDP).

Regarding the influence of metal ions, zinc ions are ten times more effective in inhibiting HAP crystal growth than magnesium ions. It is interesting to note that the inhibitory power of zinc is comparable to phosphonates which are considered to be the best inhibitors for HAP.

Table 4. Inhibitor concentration that reduces HAP growth rate onto HAP seed crystals at constant supersaturation to one half the inhibitor-free value (i.e.,  $R_{0.5}$ )

Inhibitor	Acronym	Inhibitor Conc.	
		ppm	Ref.
Fulvic acid	FA	1.3	this study
Tannic acid	TA	3.9	this study
Mellitic acid	MA	1.9	6
Citric acid	CA	11	4
Glycolic acid	GLA	38	7
Poly(acrylic acid)	PAA	0.65	this study
Pyrophosphate	PYP	0.18	4
Phytic acid	PA	5.8	23
Nitriilotri(methylene phosphonic acid)	NTMP	0.4	4
1-Hydroxyethylidene-1,1-diphosphonic acid	HEDP	0.12	4
2-phosphonobutane-1,2,4-tricarboxylic acid	PBTC	0.11	7
Hydroxyphosphono acetic acid	HPA	0.22	7
Magnesium	Mg	1.3	24
Zinc	Zn	0.13	25
Glucose	GL	5.9	26

## REFERENCES

- Gaffar A and Moreno EC, "Evaluation of 2-Phosphono- in butane 1,2,4-Tricarboxylate as a Crystal Growth Inhibitor *in vitro* and *in vivo*", *J Den Res*, 1985;64:6-11.
- Amjad Z, "Constant Composition Study of the Crystal Growth of Dicalcium Phosphate Dihydrate. The Influence of Polyphosphates, phosphonates, and Phytate", *Can J Chem*, 1988;66:2181-2187.
- Meyer JL and Nancollas GH, "The Influence of Multidentate Organic Phosphonates on the Crystal Growth of Hydroxyapatite", *J Crystal Growth*, 1973;13:295-303.
- Amjad Z, "The Influence of Polyphosphates, Phosphonates, and Poly(carboxylic acids) on the Crystal Growth of Hydroxyapatite", *Langmuir* 1987;3:1063-1069.
- Nancollas GH and Tomson MB, "The Precipitation of Biological Minerals", *Faraday Discussion Chem Soc*, 1976;61:176-183.
- Amjad Z, "The Influence of Mellitic Acid on the Crystal Growth of Hydroxyapatite" In *Adsorption on and Surface Chemistry of Hydroxyapatite*, D.N. Misra (Ed.) Plenum Press, New York, 1984.
- Amjad Z, "Inhibition of Hydroxyapatite Crystal Growth by Phosphonated Hydroxy Carboxylic Acids, Non-Phosphonated Hydroxy Carboxylic Acids, and Poly (Acrylic Acid)", *Phos Res Bull*, 1997;7:1-16.
- Amjad Z, "Evaluation of Phosphono-, Alpha hydroxy Carboxylic, and Polycarboxylic acids as Dicalcium Phosphate Dihydrate Crystal Growth", In *Mineral Scale Formation and Inhibition*, Z. Amjad (Ed.), Plenum Press, New York, 1995.
- Smith BR and Alexander AE, "The Effect of Additives on the Process of Crystallization. II. Further Studies on Calcium Sulfate", *J Colloid Interface Sci.* 1970;34:81-90.
- Amjad Z, "Performance of Polymeric Additives as Hydroxyapatite Crystal Growth Inhibitors", *Phos Res Bull*, 1995;5:1-12.
- Amjad Z, "Constant Composition Study of Dicalcium Phosphate Dihydrate Crystal Growth in the Presence of Poly(acrylic acids)", *Langmuir*, 1989;5:1222-1225.
- Amjad Z, "Inhibition of Barium Sulfate Precipitation: Effects of Additives, Solution pH, and Supersaturation", *Water Treatment*, 1994;9:47-56.
- Amjad Z, "Inhibition of Calcium Fluoride Crystal Growth by Polyelectrolytes", *Langmuir*, 1991;7:2405-2408.
- Amjad Z, Pugh J, Zibrida J and Zuhl R, "Polymer Performance in Cooling Water: The Influence of Process Variables", *Materials Performance*, 1997;36(1):32-38.
- Shimabayashi S, Hashimoto N, Kawamura H and Uno T, "Formation of Hydroxyapatite in the Presence of Phosphorylated and Sulfated polymer in an Aqueous Phase", In *Mineral Scale Formation and Inhibition*, Z. Amjad (Ed.), Plenum Press, New York, 1995.
- Williams G and Sallis JD, "Structural Factors Influencing the Ability of Compounds to Inhibit Hydroxyapatite Formation", *Calcif Tissue Int*, 1982;34:169-177.
- Nystrom M, Ruohomaki K and Kaipia L, "Humic Acid as a Fouling Agent in Filtration", *Desalination*, 1996;106:79-87.
- Lacout JL, Koutsoukos PG, Rouquet N, and Freche M, "Effect of Humic Compounds on the Crystal Growth of Dicalcium Phosphate Dihydrate", *Agrochimica*, 1992;36:500-510.
- Leenheer JA, Wershaw RL, and Reddy MM, "Strong Acid, Carboxyl-Group Structures in Fulvic Acid from the Suwannee River, Georgia. I. Minor Structures". *Envir. Sci. Tech.*, 1995;29:393-398.
- Coffey MD, Paper No. SPE 5302, Inter. Symp. Oilfield, Soc. Pet. Eng., Dallas, Texas, 1975.
- Amjad Z, "The Inhibition of Dicalcium Phosphate Dihydrate Crystal Growth by Polycarboxylic Acids", *J. Colloid Interface Science*, 1987;117:98-103.
- Amjad Z, "Kinetic Study of the Seeded Growth of Calcium Carbonate in the Presence of Benzene Polycarboxylic Acids", *Langmuir*, 1987;3:224-228.
- Koutsoukos PG, Amjad Z, and Nancollas GH, "The influence of Phytate and Phosphonate on the Crystal Growth of Fluorapatite and Hydroxyapatite", *J. Colloid Interface Science*, 1981;83:599-605.
- Amjad Z, Koutsoukos PG and Nancollas GH, "The Crystallization of Hydroxyapatite and Fluorapatite in the Presence of Magnesium Ions", *J. Colloid Interface Science*, 1984;101:250-256.
- Dalpi M, Karayianni E and Koutsoukos PG, "Inhibition of Hydroxyapatite Formation in Aqueous solutions by Zinc and 1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane", *J. Chem. Soc. Farady Trans.*, 1993; 89:965-969.
- Dalas E and Koutsoukos PG, "The Effect of Glucose on the Crystallization of Hydroxyapatite in Aqueous Solutions", *J. Chem. Soc. Farady Trans.*, 1989;85:2465-2472.

Water Soluble Polymers  
Solution Properties and Applications

Edited by

Zahid Amjad

*The B.F. Goodrich Company  
Brecksville, Ohio*

Plenum Press • New York and London

Library of Congress Cataloging in Publication Data

Water soluble polymers: solution properties and applications / edited by Zahid Amjad.  
p. cm.

Proceedings of a Symposium on Water Soluble Polymers: Solution Properties and Applications held in Las Vegas, Nevada, September 7-11, 1997 at the 214th American Chemical Society National Meeting sponsored by the Division of Colloids and Surface Chemistry of the American Chemical Society.

Includes bibliographical references and index.

ISBN 0-306-45931-0

1. Water-soluble polymers—Congresses. 2. Water-soluble polymers—Industrial applications—Congresses. I. Amjad, Zahid. II. American Chemical Society. Division of Colloid and Surface Chemistry. III. American Chemical Society. Meeting (214th: 1997: Las Vegas, Nev.) IV. Symposium on Water Soluble Polymers: Solution Properties and Applications (1997: Las Vegas, Nev.)

QD382.W3W374 1998

547.70454—DC21

98-39451

CIP

Proceedings of a Symposium sponsored by the Colloid and Surface Chemistry Division of the American Chemical Society on Water Soluble Polymers: Solution Properties and Applications, held September 7-11, 1997, in Las Vegas, Nevada

ISBN 0-306-45931-0

© 1998 Plenum Press, New York  
A Division of Plenum Publishing Corporation  
233 Spring Street, New York, N.Y. 10013

<http://www.plenum.com>

10987654321

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Printed in the United States of America