SEEDED GROWTH OF CALCIUM-CONTAINING SCALE FORMING MINERALS

Zahid Amjad, PhD
Noveon, Inc. (formerly BFGoodrich Performance Materials)
9911 Brecksville Road
Cleveland, Ohio 44141 USA

ABSTRACT

The conventional seeded growth technique has been used to study the influence of solution pH in the range 2.8 to 8.8 on the crystal growth of calcium sulfate dihydrate ($CaSO_4.2H_2O$, gypsum) from stable supersaturated solutions in the presence of polyacrylic acids. Results indicate that at a constant solution pH, crystal growth of gypsum in the presence of polyacrylic acid is preceeded by an initial slow growth reaction, hereafter called induction period, following which crystal growth of gypsum proceeds with a rate close to that in pure solution. Kinetic data collected as a function of solution pH in the range 2.8 to 8.6 suggest that solution pH has a marked effect on the induction period. The observed dependence of induction period on solution pH may be explained in terms of the degree of ionization of polyacrylic acid. The influence of commonly encountered scales as nucleators for gypsum growth has also been investigated using the conventional seeded growth technique. Kinetic data of this study indicate that $CaCO_3$ is an effective nucleator. Results on the influence of several products on the $CaCO_3$ induced gypsum crystal growth show marked dependence on product composition. In the case of calcium phosphate crystal growth, the constant composition technique has been used to study the influence of crystal growth inhibitors. A simple Langmuir adsorption model has been proposed to account for the marked inhibitory influence exhibited by an acrylic acid-based copolymer.

INTRODUCTION

Deposition of calcium containing mineral scales on heat exchanger, reverse osmosis membrane, and equipment surfaces is a persistent and an expensive problem

in industrial water systems, desalination systems, and secondary oil recovery operations utilizing water flooding techniques. The scales consist primarily of carbonates, sulfates, hydroxides, phosphates, and silicates of alkaline earth metals, particularly calcium, magnesium and barium. The problem of scale formation is intensified at higher temperatures because of the peculiar inverse temperature-solubility characteristics of these minerals in 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.

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. Now because of the associated toxicity problems of chromates, inorganic orthophosphates compounds are commonly used as chromate replacements. However, the use of phosphate compounds has led to the formation of highly insoluble calcium phosphate scales.

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 tertiary sewage treatment plant effluent), and the use of organic phosphonate scale and corrosion inhibitors which degrade to orthophosphate. Increased orthophosphate levels, combined with alkaline operating conditions, can lead to the formation of highly insoluble calcium phosphate scale deposits which are frequently attributed to hydroxyapatite [$Ca_5(PO_4)OH$ or HAP]. However, in cooling water systems it is not HAP which is initially formed, but instead a precursor phase is obtained which is widely known as amorphous calcium phosphate. The formation of other precursor phases, i.e., calcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$ or DCPD) and octacalcium phosphate [$Ca_4H(PO_4)_3$ or OCP] have also been reported to be formed during the precipitation of calcium phosphate.[4-6]

Materials which have gained acceptance in water treatment applications include polyacrylates, polymethacrylates, polymaleics, acrylic and maleic acid-based copolymers, sulfonated polystyrene, polyphosphates, and phosphonates. The influence of these inhibitors on scale forming minerals such as calcium carbonate, calcium sulfate, calcium phosphates, and barium sulfate has been the subject of numerous investigations. Results of these crystal growth studies suggest that the influence of these additives as crystal growth inhibitors may be explained by considering the adsorption of inhibitor molecules either generally on all crystal faces reducing the rate of crystallization to zero, or on selective faces, leading to a change in morphology of the developing scale crystals. Polymeric type inhibitors, such as polyacrylic acid and acrylic acid-based copolymers, usually fall into the latter catagory.

Several studies have been reported pertaining to the influence of solution pH on the performance of polymeric and non-polymeric inhibitors on the crystal growth of sparingly soluble salts. Recently Griffiths et al.[7] have shown that the performance of phosphonic acids as $CaSO_4 \cdot 2H_2O$ crystal growth inhibitors improves with increasing pH, and have attributed this performance to an increase in the degree of deprotonation. Leung and Nancollas,[8] using seeded growth technique, arrived at similar conclusions after studying the effect of benzene polycarboxylic acids on the crystal growth of $BaSO_4$. Recently Sheehan and Nancollas[9] examined the affect of pH in the 6 to 9 range on the growth rate of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) in the presence of polyacrylate. Recently there has been much interest in the inhibitory effect of polymeric carboxylic acids as crystal growth inhibitors for sparingly soluble salts.[10-12] Therefore, the present work focused on the use of a conventional seeded growth method to investigate the influence of solution pH and nature of seed

crystals on the crystal growth of $CaSO_4 \cdot 2H_2O$, in the presence of homo- and co-polymers of acrylic acid. In addition, the constant composition technique, in which the chemical potential of the solution species is kept constant by the stoichiometric addition of reactants, was used to study the influence of polymeric inhibitors on the crystal growth of calcium phosphate. The advantages of using the constant composition technique to evaluate inhibitor effectiveness as crystal growth inhibitors have been discussed previously.[12,13]

EXPERIMENTAL PROCEDURES

Conventional Seeded Crystal Growth

The crystal growth of $CaSO_4 \cdot 2H_2O$ on seed crystals of $CaSO_4 \cdot 2H_2O$ and $CaCO_3$ was studied using the conventional seeded growth technique. The growth experiments were performed in a double-walled water jacketed beaker containing 120 ml of a $CaSO_4$ metastable solution. The metastable solution was prepared by carefully combining equimolar quantities of $CaCl_2$ and Na_2SO_4 such that the final $CaSO_4$ solution would be 3.45×10^{-2}M. Solution pH was controlled by the addition of buffers at a total conjugate acid/base concentration of 2.0×10^{-3}M, a concentration at which the influence of the buffering components on the rate of crystal growth was proved to be negligible. Crystal growth was initiated in these supersaturated solutions by the addition of a known weight of seed crystals and the reaction was monitored by analyzing aliquots of the filtered (0.22 um filter paper) solution for calcium by EDTA titrations.

Constant Composition Seeded Growth

Constant composition experiments were conducted by preparing a supersaturated solution of calcium phosphate in a double walled glass cell maintained at constant temperature. The crystal growth reaction was initiated by the addition of a known amount of seed crystals and a specific ion electrode was used to control the addition of stoichiometric amount of reactant solution from mechanically coupled burets. During the growth reaction samples were withdrawn, filtered (0.22 um filter paper) and the filtrate analyzed for the ionic constituents. The rate of crystal growth was calculated from the monitored rate of solutions addition. The effectiveness of the inhibitor was then assessed by comparing the rate of crystal growth in the presence and absence of inhibitor.

RESULTS AND DISCUSSION

Calcium Sulfate

Descriptions of the inhibitors and the experimental conditions used in this study are summarized in Table 1 and 2, respectively. The typical curves for calcium concentrations against time are shown in Figure 1. It can be seen that the growth of $CaSO_4 \cdot 2H_2O$ takes place immediately upon the addition of gypsum seed crystals to the metastable supersaturated solutions. The rate of crystal growth on $CaSO_4 \cdot 2H_2O$ from supersaturated solutions containing equivalent concentration of ions has been found to follow an equation of the form

$$-dTCa/dt = ks \ (TCa - T_eCa)^2 \qquad (1)$$

where TCa and T_e are the molar concentrations of calcium ion at time t and at equilibrium, respectively. Figure 2 illustrates the linearity of the plots of the integrated form of Equation 1. Reproducibility is shown by the agreement between the results of experiments 6 and 8 respectively. Results of experiments 6 and 10 in Table 2 indicate tha the rate of crystallization is directly proportional to the amount of seed crystals added initially. This confirms that crystallization occurred only on the added seed material. without any secondary nucleation or spontaneous precipitation.

Performance as a Function of pH

Studies were made of the rate of crystal growth of $CaSO_4 \cdot 2H_2O$ at 25°C and pH values from 2.8 to 8.6 in buffered calcium sulfate supersaturated solutions. Typical plots of the data plotted according to the integrated form of Equation 1 are shown in Figure 3. Rate data summarized in Table 2 show that in the pH 2.8 to 8.6 range and in the absence of inhibitor, second-order rate constant is independent of solution pH. Results presented in Table 2 for seeded growth experiments conducted in buffered solution show that rate constants are within ± 7% of that in the unbuffered solution. This suggests that buffering components at a total conjugate acid/base concentration of $2.0 \times 10^{-3}M$ does not significantly affect the rate of crystal growth of calcium sulfate dihydrate.

Results of crystal growth experiments made in the presence of polyacrylic acids are summarized in Table 2. Typical growth curves at pH 7.0 in the presence of a 5,000 M_w polyacrylare (PAA-5M) are illustrated in Figure 4. It can be seen that crystallization reaction in the presence of 0.22 mg/L of PAA-5M is preceded by an initial slow reaction, hereafter called induction period, of 195 min after which time the rate commences with a measurable rate. Representative plots of the integrated form of Equation 1 in the presence of varying concentration of PAA-5M shown in Figure 5 demonstrate the validity of this rate equation in interpreting the results in the presence of polymer. As shown in Table 2, the rate of crystal growth following the induction period has very little correlation with the concentration of polymer.

The influence of pH on the effect of several phosphonic acids as $CaSO_4 \cdot 2H_2O$ crystal growth inhibitors has been recently studied using a seeded growth technique.[7] 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 acids, the degree of deprotonation should, as is the case for 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 inhibitor molecules towards the crystal surface should also be influenced by the solution pH due to the dissociation of the carboxylic acid group.

The effect of the solution pH on the crystal growth of $CaSO_4 \cdot 2H_2O$ in the presence of PAA-5M was studied using the seeded growth technique. The results presented in Table 2 indicate that at constant temperature and polymer concentration (0.22 mg/L), the induction time is strongly dependent upon solution pH. For example, the induction times obsevred at various pH's were as follows:

pH	2.8	3.4	5.2	7.0	8.6
Induction time (min)	0	150	180	195	190

Data in Table 2 demonstrate the ineffectiveness (induction time < 2 min) of PAA-5M at pH 2.8 and at 0.22 and 1.0 mg/L polymer concentrations. It should be noted that under similar experimental conditions and at pH 7.0, induction times observed for PAA-5M at 0.22 and 1.0 mg/L were 195 and > 1200 min, respectively. The poor inhibitory perfcrmance exhibited by PAA-5M at pH 2.8 may be explained due to insignificant deprotonation of carboxylic acid group at this pH value.

As shonw in Table 2, the induction times observed for PAA-5M at 0.22 mg/L are 0, 150, 180 min. at pH 2.8, 3.4, and 5.2, respectively. However, no significant increases in induction times were observed upon raising the solution pH from 5.2 to 7 to 8.

Mixed Scales

The formation of mixed scales through the growth of one crystal face upon another is a common occurance which demands a matching of the atomic dimensions of one or more commonly occurring faces of each component. Some deposits require an epitaxial relationship, while in other cases heterogeneous nucleation of the second phase can take place on the surface of almost any substrate. The use of finely divided barium sulfate and calcium carbonate has been proposed as an effective method for limiting calcium sulfate scale formation.[14]

Although gypsum scale formation is usually modelled in the laboratory by studying the crystallization of $CaSO_4 \cdot 2H_2O$ on gypsum crystals, it is quite possible that the scaling process may involve the nucleation of gypsum on other crystalline phases which might be present or which might form preferentially. Thus under certain conditions other scale forming minerals such as calcium carbonate, barium sulfate, calcium fluoride, etc., may be first formed scale at surfaces such as those encountered in the field even though the bulk of the observed scale consists of calcium sulfate. Studies have been initiated regarding the growth of calcium sulfate on these substrates from stable supersaturated solutions of calcium sulfate. The results of preliminary experiments are shown in Figure 6 in which the calcium concentration is plotted against time following the addition of calcium carbonate seed material. It can be seen that, following an induction period of approximately ∽140 min, calcium sulfate dihydrate crystal growth (confirmed by x-ray analysis) occurs on $CaCO_3$ seed crystal. The data suggest that $CaCO_3$ is an effective nucleator for gypsum. Figure 6 presents a comparison of the effect of several commercially available inhibitors (including PAA-5M, a patented[15-17] acrylic copolymer (AA/E), and a sulfonated styrene/maleic anhydride copolymer or SS/MA) on $CaCO_3$ induced crystal growth of gypsum. The ranking (from best to worst) of polymers based upon observed induction periods, using results of seeded growth experiments is as follows:

$$PAA-5M > AA/E > SS/MA \sim control$$

Calcium Phosphate

The constant composition technique employed in the present investigation has the important advantage of enabling the study of crystallization of calcium phosphate at controlled supersaturations in the absence and presence of inhibitors. Typical plots of the volume of titrant added, following the addition of DCPD seed crystals to stable supersaturated solutions, as a function of time are shown in Figure 7. The slopes of the lines in Figure 7 are used to calculate crystal growth rates expressed as mol of DCPD $min^{-1}m^{-2}$ of surface. It can be seen that crystal growth began immedaitely upon the addition of seed crystals. The excellent reproducibility is illustrated by the agreement between the results of experiments 60 and 61.

Figure 7 illustrates the influence of AA/E on the crystal growth of DCPD. The observed rate increase in the latter stages of the crystallization may be interpreted in terms of the depletion of the solution copolymer by adsorption on the growing DCPD surfaces. As shown in Figure 7, the rate of DCPD crystal growth strongly depends upon the concentration of AA/E. For example, rates of DCPD crystal growth at 0, 0.01, and 0.02 mg/L concentration are 18.2, 8.3, and 2.7×10^{-7} moles min^{-1}, respectively. It should be noted that at 1.5 mg/L of AA/E concentration crystal growth reaction was completely inhibited for 20 hours.

If the inhibition of crystal growth of scale forming mineral is due to surface adsorption at the active growth sites, some form of adsorption isotherm should be applicable. In many instances the Langmuir adsorption model, which was developed for the adsorption of ideal gases onto solid surfaces, has been used to describe, empir-

ically, the reduction in the crystal growth rates of many scale forming minerals for a variety of inhibitors. If the adsorbed inhibitor of concentration [A] covers a fraction of the total available surface, then the rate of adsorption may be expressed as $k_a[C](1-k_d)$ and the rate of desorption as k_d, where k_a and k_d, are the corresponding rate constant. At equilibrium it can be shown that

$$Ro/(Ro-Ri) = 1 + k_d/k_a[A] \qquad (2)$$

where R_o and R_i are the growth rate constant in the absence and presence of inhibitor, respectively. In Figure 8, $R_o/(R_o-R_i)$ is plotted against [A] and it is seen that Langmuir isotherm satisfactorily described the marked inhibitory effects of AA/E in terms of a monomolecular blocking layer of copolymer.

CONCLUSIONS

The advantages of using conventional seeded growth and constant composition techniques for evaluating the effectiveness of inhibitors include the excellent reproducibility of the results and the fact that crystallization on surfaces already present in the system represents a model which is probably closer to field conditions than are beaker testing experiments. The results presented in this paper show that trace quantities of polyacrylate markedly affect the induction period following which crystallization of $CaSO_4 \cdot 2H_2O$ takes place at a rate almost independent of the concentration and the molecular weight of the polyacrylate. In addition, duration of the induction periods depends upon solution pH.

The data on epitaxial growth of $CaSO_4 \cdot 2H_2O$ using $CaCO_3$ seed material show $CaCO_3$ to be an effective nucleator for $CaSO_4 \cdot 2H_2O$ crystallization. In addition, a comparison of the effect of several inhibitors on $CaCO_3$ induced crystal growth of $CaSO_4 \cdot 2H_2O$ show the following ranking in order of decreasing effectiveness (left to right):

PAA-5M, AA/E, SS/MA, control

The results of constant composition experiments on DCPD seeded growth in the presence of calcium phosphate inhibitor (i.e., AA/E) have shown that only a small fraction of the total surface area of the crystals seed be covered by adsorbed molecule in order to reduce the rate of calcium phosphate scale formation virtually to zero. The simple Langmuir adsorption model describes the marked inhibitory influence of AA/E on DCPD crystal growth.

ACKNOWLEDGEMENTS

REFERENCES

1. G.H.Nancollas, CORROSION/87, Paper No. 327, NACE, Houston, TX. 1987.
2. R.W.Zuhl, Z.Amjad and W.F.Masler, Journal Cooling Tower Institute, 8, 41, (1987).
3. J.E.Hoots and G.A.Crucil, CORROSION/86, Paper No. 13, NACE, Houston, TX. 1986.
4. R.G.Varsanik, Materials Performance, 14, 16 (1975).
5. M.H.Salimi, J.C.Heughebaret and G.H.Nancollas, Langmuir 1, 119, (1985).
6. E.D.Eanes, I.H.Gillissen and A.S.Posner, Proc. Int. Conf. Cryst. Growth, 373, (1966).
7. D.W.Griffither, S.D.Roberts and S.T.Liu, Paper No. 7861, Int. Symp. Oil Field Geothermal Chem., Society of Petroleum Engineers, 1979.
8. W.H.Leung and G.H.Nancollas, J. Inorg. Nucl. Chem., 40, 187, (1978).

9. M.S.Sheehan and G.H.Nancollas, Invest. Urol., 17, 446, (1980).
10. Z.Amjad, Journal Colloid Interface Science, 117, 98, (1987).
11. J.C.Vogel and R.M.Frank, Journal Colloid Interface Science, 83, 26, (1981).
12. Z.Amjad, Langmuir, 3, 224, (1987).
13. P.G.Koutsoukos, Z.Amjad, M.B.Tomson, and G.H.Nancollas, Journal American Chemical Society, 102, 1533, (1980).
14. K.R.Frohner and H.Panahandeh, Desalination, 16, 261 (1975).
15. W.F.Masler, III and Z.Amjad, U.S. Patent 4,499,002, February 12, 1985.
16. W.F.Masler, III and Z.Amjad, U.S.Patent 4,566,974, January 28, 1986.
17. W.F.Masler, III and Z.Amjad, U.S.Patent 4,639,490, January 27, 1987.

Table 1
Commercially Available Products Evaluated

Description	Acronym
Patented Acrylic Copolymer*	AA/E
Sulfonated Styrene/Maleic Anhydride Copolymer	SS/MA
Acrylic Acid/2-Acrylamido-2-Methylpropane Sulfonic Acid Copolymer	AA/SA
2,000 M_w Polyacrylate**	PAA-2M
5,000 M_w Polyacrylate**	PAA-5M
Hydroxyethane 1, 1-Diphosphonic Acid	HEDP

* See reference Nos. 15, 16, & 17.
** A Good-Rite[R] K-700 polymer available from The BFGoodrich Company.
Good-Rite[R] is a registered trademark of The BFGoodrich Company.

Table 2
Kinetic Data for Calcium Sulfate Dihydrate Crystal
Growth in the Presence of Polymers
$TCaSO_4 = 3.45 \times 10^{-2}$ M   25°C

| Experiment No.	Polymer	Dosage(mg/L)	Seed(mg)	pH	Induction Time (min)	$10ksM^{-1}min^{-1}$
6	None	0	190	5.5[a]	0	5.48
10	None	0	350	5.5[a]	0	10.6
5	None	0	185	5.5[a]	0	5.35
8	None	0	195	2.8	0	4.55
9	PAA-5M	0.22	190	2.8	0	4.82
11	PAA-5M	0.60	188	2.6	0	4.69
10	PAA-5M	1.00	192	2.8	0	4.91
16	None	0	190	3.4	0	5.25
18	PAA-5M	0.22	192	3.4	150	5.75
12	None	0	189	5.2	0	5.58
13	PAA-5M	0.22	194	5.2	180	5.95
14	None	0	192	6.4	0	5.65
15	PAA-5M	0.22	192	6.4	170	5.83
20	None	0	190	7.0	0	5.45
21	PAA-5M	0.22	189	7.0	195	5.75
24	PAA-5M	0.40	192	7.0	480	6.01
25	PAA-5M	1.00	191	7.0	> 1,200	---
22	PAA-2M	0.22	193	7.0	420	5.82
26	None	0	190	7.8	0	5.73
27	PAA-5M	0.22	190	7.8	190	5.92
28	None	0	194	8.6	0	5.87
30	PAA-5M	0.22	192	8.6	200	5.62

a   unbuffered solution
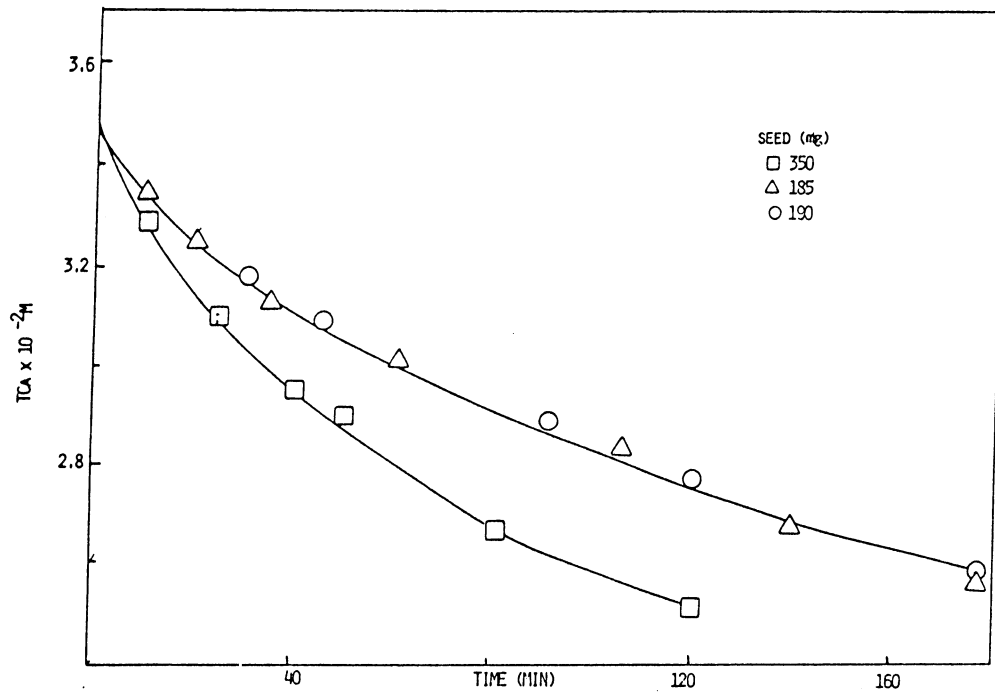
FIGURE 1 - The Effect of Seed Concentration on the Total Calcium vs. Time for Growth of Gypsum
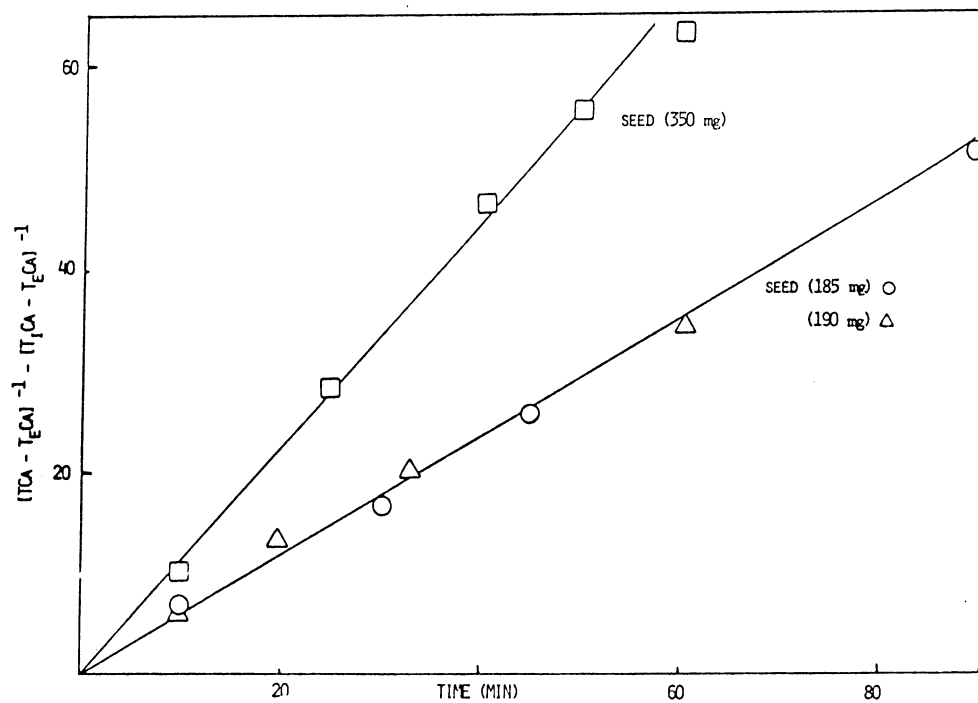

FIGURE 2 - Gypsum Crystal Growth Kinetics*
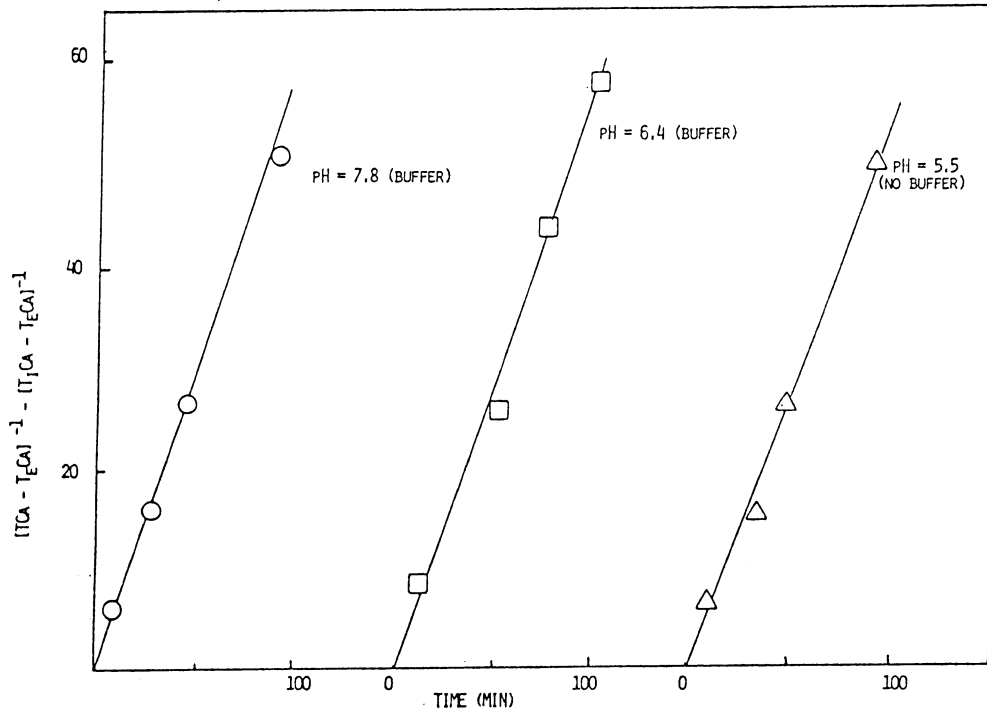*See Equation 1 in Paper, Page 3.

FIGURE 3 - Gypsum Growth Kinetics at Varying Solution pH.*
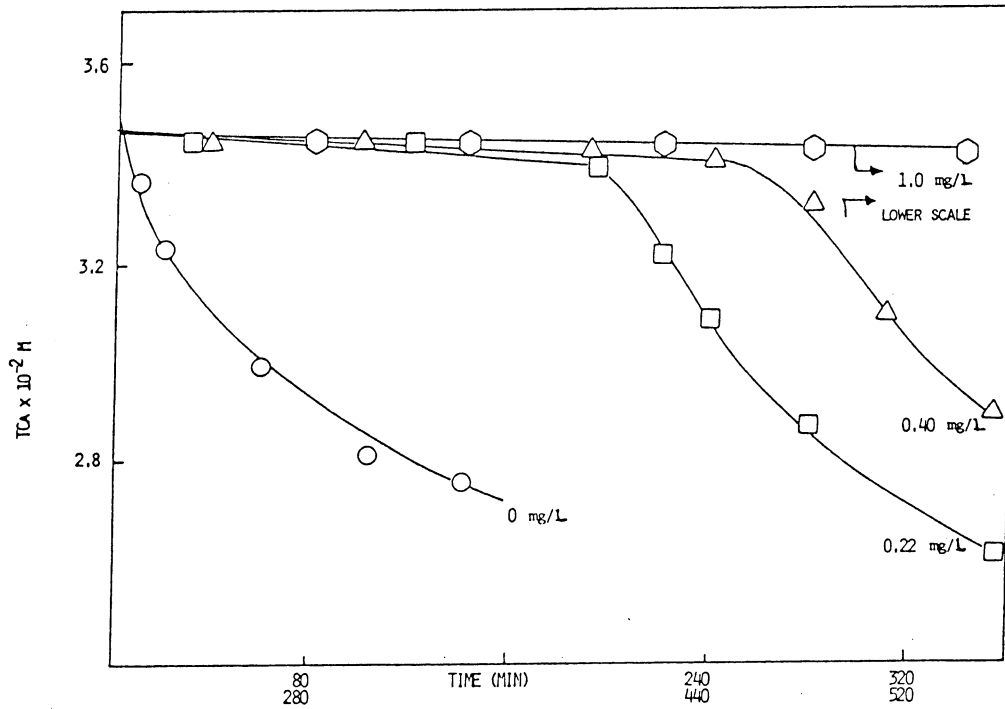*See Equation 1 in Paper, Page 3.

FIGURE 4.- The Effect of Polymer Concentration (PAA-5M) on Total Calcium as a Function of Time.
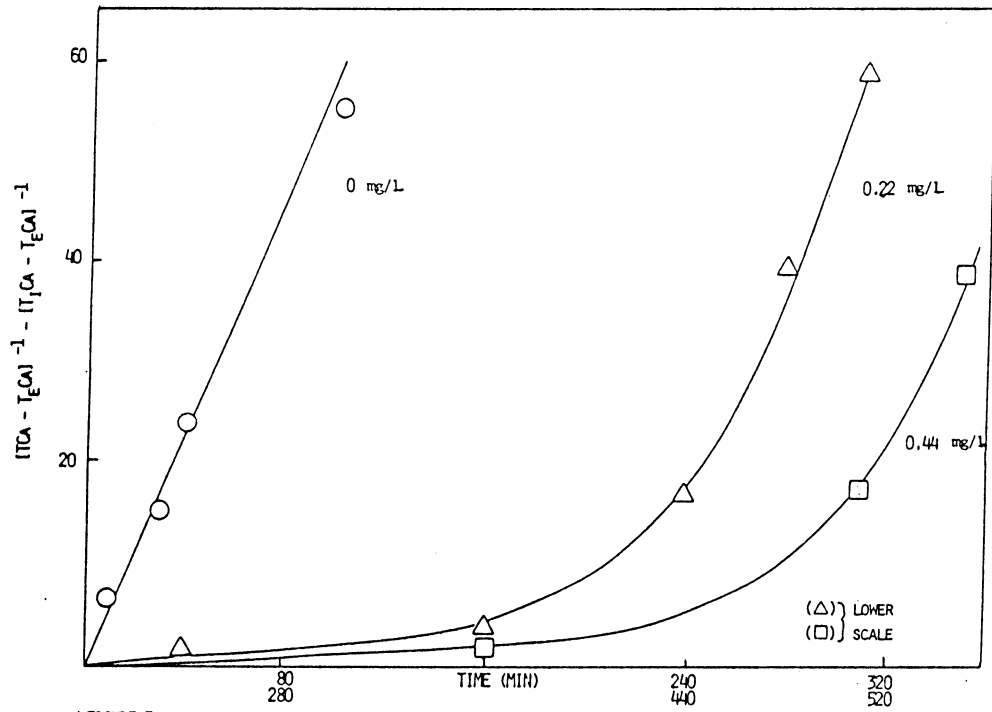
FIGURE 5 - GYPSUM GROWTH KINETICS AS A FUNCTION OF PAA-5M CONCENTRATION*
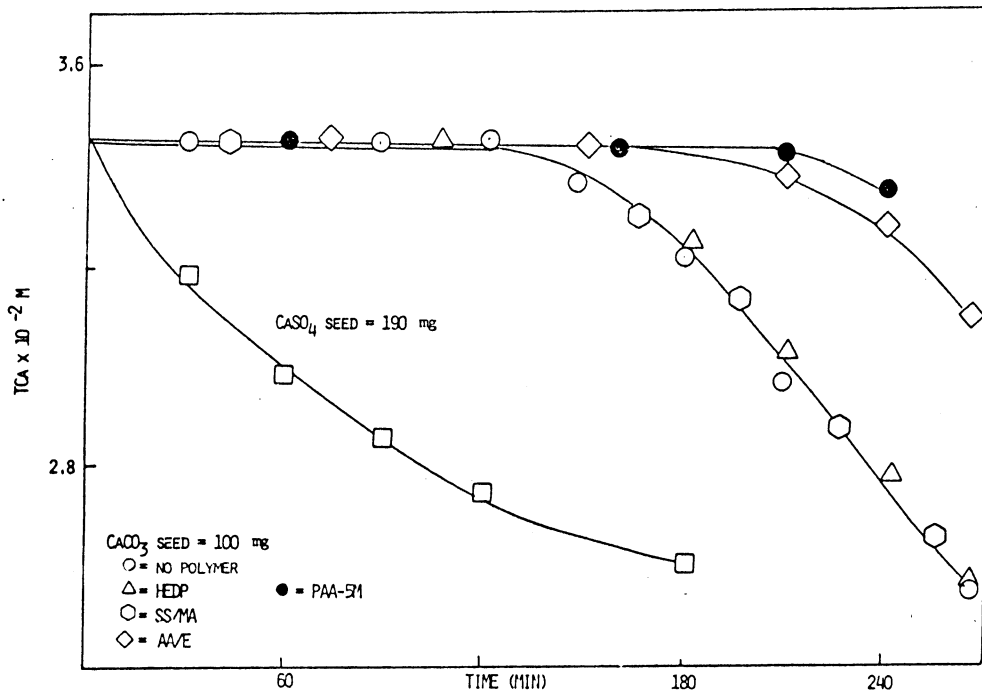*SEE EQUATION 1 IN PAPER, PAGE 3.

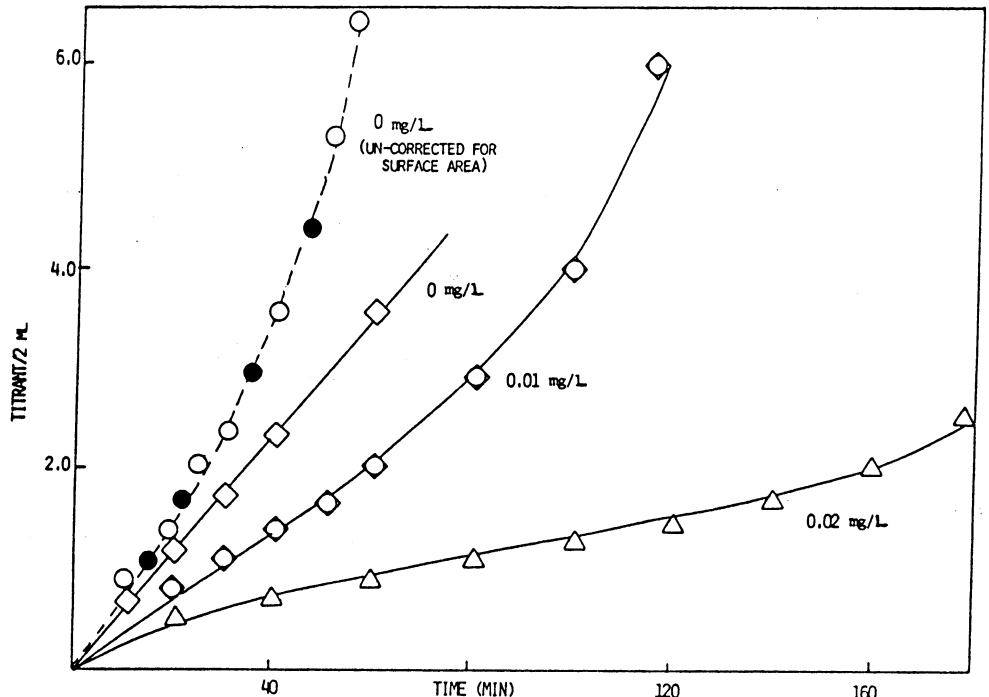FIGURE 6 - GYPSUM CRYSTAL GROWTH ON CALCITE SEED CRYSTALS IN THE PRESENCE OF VARIOUS INHIBITORS.

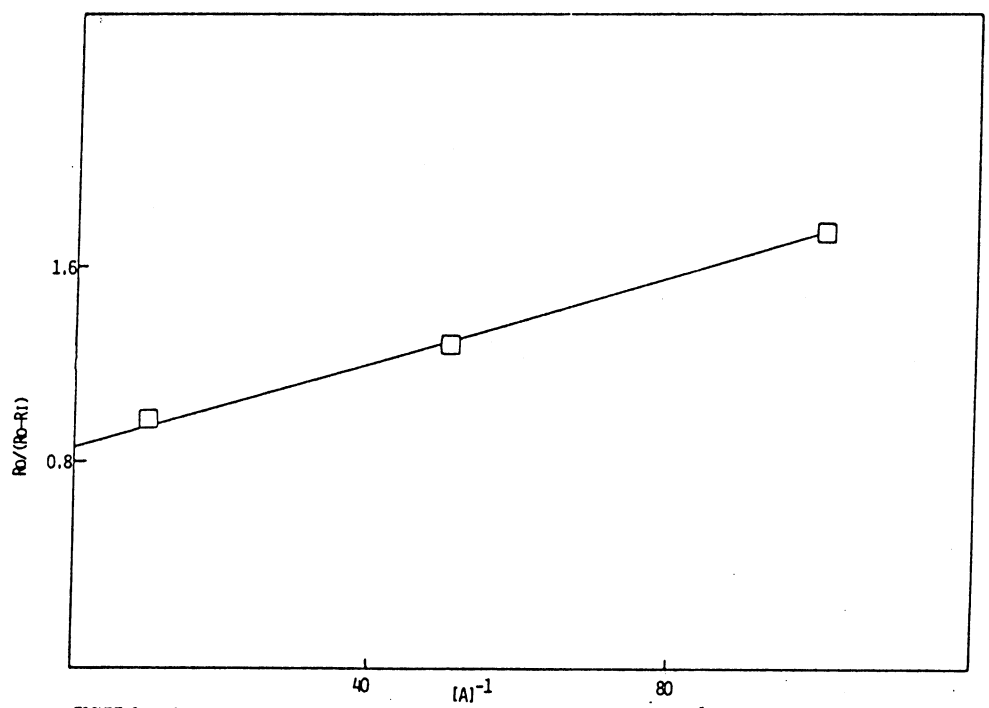FIGURE 7 - DCPD CRYSTAL GROWTH AT CONSTANT SUPERSATURATION IN THE PRESENCE OF AA/E. TITRANTS UPTAKE VS. TIME.

FIGURE 8 - DCPD CRYSTAL GROWTH IN THE PRESENCE OF AA/E. $R_0/(R_0-R_i)$ VS. $[A]^{-1}$