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THE INHIBITION OF CALCIUM CARBONATE FORMATION IN AQUEOUS SUPERSATURATED SOLUTIONS. SPONTANEOUS PRECIPITATION AND SEEDED CRYSTAL GROWTH

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ABSTRACT

The influence of the presence of humic, fulvic, and polyacrylic acid on the nucleation and crystal growth of calcium carbonate in aqueous supersaturated solutions was investigated in batch reactors at 25°C and pH = 8.50. The nucleation of calcium carbonate was investigated by free drift methods, and the crystal growth was investigated with seeded crystal growth experiments at constant supersaturation. In all cases calcite was found to form exclusively, and the presence of all tested compounds at

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concentrations between 0.1 – 1.0 ppm prolonged the induction time preceding the spontaneous formation of calcite. Humic acid at concentration up to 0.5 ppm inhibited the growth of calcite seeds up to 95% and polyacrylic acid at concentrations up to 0.1 ppm gave the same degree of inhibition. Polyacrylic acid was found to be stronger inhibitor. A concentration of 0.25 ppm of polyacrylic acid completely stopped crystal growth of calcite. Humic acid at concentration 1.0 ppm completely stopped crystal growth of calcite seed crystals. The retardation was explained by the adsorption of the polyelectrolytes onto the active growth sites of the crystals. Application of a Langmuir-type adsorption model on the kinetics data obtained in the presence of the inhibitors tested yielded a higher affinity constant of polyacrylic acid for the calcite seed crystals.

INTRODUCTION

The formation of deposits of alkaline earth insoluble salts is a serious problem in installations where untreated natural waters are used, such as in geothermal energy exploitation, in secondary oil production by waterflooding, cooling towers, production of tap water by reverse osmosis etc.[1,2] The formation of these deposits reduces heat transfer and the internal diameter of pipes, increases the operating pressure of pumps, and enhances the probability of corrosion damage. In many cases, the removal of deposits leads to discontinuous operation of the installations, resulting in higher operation costs.

Calcium carbonate is one of the most commonly encountered scale deposits and occurs in different crystalline forms : calcite, aragonite, vaterite, calcium carbonate monohydrate and calcium carbonate hexahydrate. Calcite, the thermodynamically most stable polymorph of calcium carbonate, forms armoring, hard mineral deposits. Precipitation and stabilization of calcium carbonate polymorphs depend on solution conditions, i.e. level of supersaturation, pH, temperature, pressure, and the concentration and chemical structure of additives.[1,3]

Numerous methods have been applied to inhibit calcium carbonate formation.[4] The most promising approach is addition of water soluble polyelectrolytes.[5-8] Water-soluble compounds (polyelectrolytes, phosphonates) prevent calcium carbonate formation even at very low concentrations (< 1 ppm) and are cost effective scale inhibitors. In several cases, the presence of polyelectrolyte and phosphonate crystal growth inhibitors may cause significant modifications of the crystal habit, reducing their ability to adhere on the surfaces. The main disadvantage of polyelectrolytes (polyacrylates, polymaleates and their copolymers) and phosphonates is their low biodegradability. As a result these compounds contribute to environmental pollution. Phosphonates decompose at high temperatures and release phosphate ions which may cause the formation of calcium phosphates scale. In the last decade there has been a need for "green inhibitors" (i.e. environmentally friendly) to control mineral scale formation. Humic and fulvic acids, commonly found in the natural environment, are polymeric molecules with molecular weights ranging from a few hundreds to several thousands. These acids predominantly contain phenolic and carboxylic acid functional groups and behave as negatively charged colloids or anionic polyelectrolytes in natural waters.[9] Fulvic and humic acids inhibit hydroxyapatite (HAP) and calcium phosphate dihydrate (DCPD) formation.[10,11] Presented here are the effects of two natural polyelectrolytes, humic and fulvic acids (Suwannee River) and one synthetic polyelectrolyte, polyacrylic acid, on the precipitation of calcium carbonate from labile and metastable supersaturated aqueous solutions.

EXPERIMENTAL

Two types of experiments are reported in the present investigation: a) spontaneous precipitation experiments at variable supersaturation conditions, and b) seeded growth experiments at sustained supersaturation conditions. All experiments were done in a batch-type, magnetically-stirred glass reactor, thermostatted by water at constant temperature circulated through a water jacket. The temperature in all experiments was kept at 25.0 ± 0.1°C. The stock solutions were prepared from crystalline, reagent grade chemicals (Merck, pro analisi) dissolved in triply distilled, CO_2-free water and were filtered through membrane filters (0.2 μm, Millipore). Calcium chloride and sodium chloride stock solutions were standardized by atomic absorption spectroscopy (Perkin Elmer, AAnalyst 300). The sodium bicarbonate and sodium carbonate solutions were prepared fresh for each experiment. Solids were dried at 105°C overnight followed by dissolution in triply distilled water. The fulvic acid and humic acid stock solutions were prepared by exact weighing the amounts of the respective solids. Polyacrylic acid stock solution was prepared with dilution of appropriate volume of its concentrated solution. The molecular weight of the polyacrylic acid used for the experiments was 2100 (the use of trade names in this report is for identification purposes only and does not constitute endorsement by the USGS).

The calcite seed crystals were prepared by slow mixing of calcium chloride and sodium carbonate solutions at 70°C.[12] The crystalline solid was aged for one week under continuous stirring, filtered, washed with saturated calcium carbonate solution, and dried. The final solid was characterized by physicochemical methods including powder x-ray diffraction (XRD, Philips PW 1840), scanning electron microscopy (SEM, JEOL JSM 5200) and by specific surface area measurements (GEMINI, Micromeritics). The powder x-ray diffraction pattern of the crystalline calcite preparation coincided with that of the respective reference material.[13] The specific surface area of the seed crystals was determined by a multiple point method BET and was found equal to 0.30 m^2/g.

The total volume of supersaturated solutions was 500 ml. The supersaturated working solutions were prepared in the reaction vessel by careful and rapid mixing equal volumes (250 ml) of calcium chloride and sodium bicarbonate solutions under continuous stirring. In all experiments the total calcium was equal to the total carbonate concentration. The ionic strength of the supersaturated solutions was adjusted by the addition of appropriate volume of concentrated sodium chloride stock solution. For the crystal growth experiments in the presence of fulvic and humic acids, the appropriate volume of respective additive stock solution was added in the working solution. The solution pH was adjusted to 8.50 by the slow addition of 0.10 M standard sodium hydroxide solution (Merck, Titrisol). The solution pH was measured by a combination glass/Ag-AgCl pair of electrodes (Ingold), standardized before and after each experiment with NBS buffer solutions (7.413 and 9.180 at 25°C).[14] The working solutions were stirred by a magnetic stirrer with a Teflon coated stirring bar. A schematic representation of the constant composition experimental setup is shown in Figure 1.

In all experiments the precipitation of calcium carbonate resulted in the decrease of the solution pH due to proton release concomitant with the solid formation according to the reaction:

$$Ca^{2+} + xH_2CO_3 + yHCO_3^- + zCO_3^{2-} \Leftrightarrow CaCO_{3(s)} + uH^+ \qquad (1)$$

where x,y,z and u are stoichiometric coefficients.

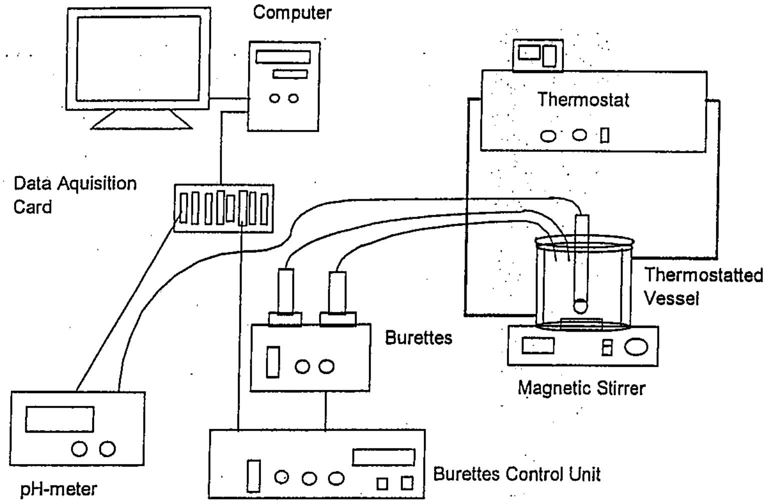

Figure 1. Experimental apparatus for the investigation of spontaneous precipitation and seeded crystal growth kinetics of calcium carbonate.

In the case of spontaneous precipitation experiments, the supersaturated solutions were initially stable. Initial total calcium concentration in spontaneous precipitation experiments was equal to 5.0 mM. The decrease of pH was monitored by a pH-meter, connected to a personal computer. Throughout the course of the spontaneous precipitation experiments, the pH of the working solution as a function of time was recorded and the collected data were stored in the computer for further analysis. The end of precipitation was verified by pH-constancy following initial pH drop. Solutions were filtered and the collected solids were dried overnight at 70°C for further characterization. The precipitation rates were determined from the pH variation as a function of time using curve-fitting software.

For seeded growth experiments, the working solutions were stable for periods exceeding 24h and were supersaturated with respect to all calcium carbonate polymorphs. The initial total calcium concentration in the seeded growth experiments was equal to 2.0 mM. One or two hours following pH adjustment in the working solutions, a precisely weighed amount of calcite crystals (ca. 20mg) was introduced in the supersaturated solutions and the precipitation started immediately. A pH drop as small as 0.005 pH units triggered the addition of titrant solutions from two mechanically coupled syringes of a computer controlled titrator through the appropriate software. Throughout the course of the seeded growth experiments, the pH of the working solution and the added volume of titrants as a function of time were recorded and stored in the computer for further analysis. The titrant solutions in the two burettes consisted of calcium chloride (titrant A) and a mixture of sodium carbonate, sodium bicarbonate, and an additive as appropriate (titrant B). The supersaturated working solution contained sufficient concentration of sodium chloride (inert electrolyte) so as to maintain the solution ionic strength during titrants addition. The titrant solutions were prepared so as to have the following composition :

Titrant A : $(10C_I + 2C_I)$ M $CaCl_2$
Titrant B : $10C_I$ (M) Na_2CO_3 + $2C_I$ (M) $NaHCO_3$ + $2C_{IN}$ (M)

where C_l and C_{IN} are the total calcium and tested additive concentrations in the working solution respectively. The concentration of the additive included in titrant B was twice its concentration in the working solution. This accounted for dilution caused by titrant addition. The amounts of total calcium and total carbonate in the titrants solutions were calculated according to the stoichiometry (1:1) of the precipitating calcium carbonate.

During the course of seeded growth experiments, samples were withdrawn and filtered through membrane filters (0.2 μm). The filtrates were analyzed for total calcium by atomic absorption spectroscopy in order to confirm the constancy of the solution composition. In all seeded growth experiments, analysis showed that the total calcium concentration remained constant to within ±2%. Working solutions at the end of each experiment were filtered and the solids were dried for further analysis.

In seeded growth experiments, the precipitation rates were determined from the traces of the titrant volume added as a function of time, using curve-fitting software. The rates of calcium carbonate formation were normalized for the seed crystal total surface area as follows:

$$R_g = \frac{dV}{dt}\frac{C_t}{A_t}\,(\text{mol.min}^{-1}.\text{m}^{-2}) \qquad (2)$$

where dV/dt is the rate of titrant addition of concentration C_t (mol/l) ($=10C_l$) and A_t is the total surface area of the added calcite seed crystals.

RESULTS AND DISCUSSION

Characterization of the Precipitated Solids

In all experiments, both at constant and decreasing supersaturation conditions, calcite was the only calcium carbonate phase found. Calcite is the thermodynamically most stable polymorph of calcium carbonate and its formation was favored by the experimental conditions. The identification of solid precipitates was done by XRD and SEM analysis. The XRD spectrum of spontaneously precipitated solid in the presence of humic acid and the reference spectral lines of calcite from the JCPDS database[13] are shown in Figure 2. There is a close correlation between the reflections of the spectra. Calcite was also formed under the same conditions with fulvic and polyacrylic acids.

A typical scanning electron micrograph of calcite seed crystals grown in the presence of fulvic acid is shown in Figure 3. As may be seen, the presence of fulvic acid did not cause any appreciable morphological changes in the characteristic rhombohedral shape of the calcite crystals formed in the absence of additives. Results were the same for the growth of calcite crystals in the presence of humic and polyacrylic acids.

Spontaneous Precipitation Experiments

The inhibition of the crystal growth rates relative to the absence of additives was expressed by the relative inhibition defined as :

$$\text{Relative Inhibition (\%)} = \frac{R_0 - R_i}{R_0} \text{x} 100 \qquad (3)$$

where R_0 and R_i are the calcite crystal growth rates measured in the absence and in the presence of the additives respectively. The experimental conditions for the calcium carbonate spontaneous formation, the induction times, and the relative inhibition obtained in the presence of the tested compounds are summarized in Table 1.

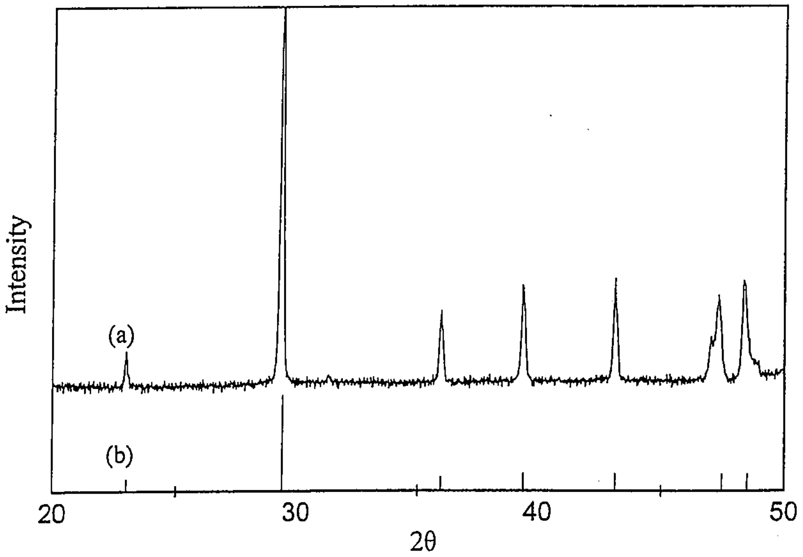

Figure 2. Powder x-ray diffraction spectrum (a) for calcium carbonate formed in the presence of humic acid at decreasing supersaturation and (b) the reference spectrum of calcite from JCPDS database (Card No. 05-0586).

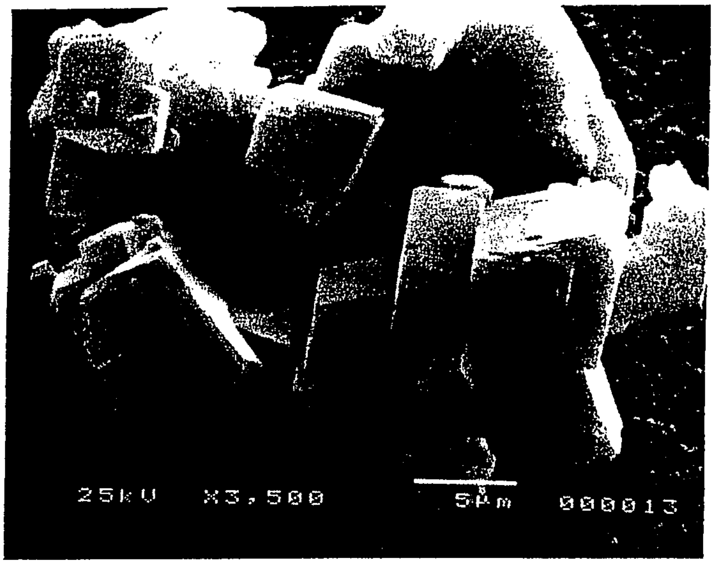

Figure 3. Scanning electron micrograph of calcite seed crystals grown in the presence of fulvic acid at conditions of sustained supersaturation.

As may be seen in Table 1, the induction time for the spontaneous precipitation of calcite in the presence of humic, fulvic, and polyacrylic acids was found to depend strongly on their concentration. It should be noted that polyacrylic acid was tested at higher supersaturations than humic and fulvic acids. This was done because polyacrylic acid at a concentration of 0.1 ppm gave significantly higher induction time (11515 s) than humic (1066 s) and fulvic (809 s) acids at the same initial calcium concentration (5.0 mM). The dependence of induction time on the concentration of humic, fulvic, and polyacrylic acids is shown in Figure 4. The influence of the additive's concentration on induction times was found to be stronger for polyacrylic acid than for humic and fulvic acids, although polyacrylic acid was tested at higher supersaturations. As may be seen in Figure 4, humic acid was more effective than fulvic acid at concentrations higher than 0.2 ppm. For concentrations exceeding 0.2 ppm, humic acid gave longer induction times than with fulvic acid at the same initial concentration. The difference in the behaviour in the presence of the three additives tested may be explained by the fact that polyacrylic acid adsorbs more strongly on the surface of the newly formed calcite seed nuclei and crystals at pH = 8.50 and blocks more effectively the active growth sites than humic and fulvic acids. The difference between humic and fulvic acids may also be due to the different adsorption behaviour exhibited by these acids. Adsorption of the additives on the crystals surface is influenced by the molecular charge density, the size and the type of functional groups of the molecule, the ratio of ionizable to non-ionizable groups, pH, and the ionic strength of aqueous media.[14]

Table 1. Spontaneous precipitation of calcium carbonate from aqueous solutions in the presence of humic, fulvic and polyacrylic (PAA) acids at 25°C and pH = 8.50. Initial conditions, induction times, and relative inhibition.

Exp. #	Additive	Concentration / ppm	Induction Time / s	% Relative Inhibition
1	Blank-1	0	176	-
2	Humic Acid	0.1	1066	53.2
3	Humic Acid	0.2	1723	81.2
4	Humic Acid	0.3	5940	87.5
5	Humic Acid	0.4	8164	92.7
6	Humic Acid	0.5	11355	95.3
7	Fulvic Acid	0.1	809	48.6
8	Fulvic Acid	0.2	2338	71.3
9	Fulvic Acid	0.3	2921	75.9
10	Fulvic Acid	0.4	3585	81.5
11	Fulvic Acid	0.5	5442	85.1
12	PAA	0.1	11515	-
13	Blank-2	0	102	-
14	PAA	0.1	1199	83.1
15	PAA	0.125	1631	87.1
16	PAA	0.15	2443	91.1
17	PAA	0.175	3857	93.7
18	PAA	0.2	9400	96.3
19	PAA	0.225	11651	98.3
20	PAA	0.25	Complete Inhibition	100

Blank-1 : Total Calcium = Total Carbonate = 5.00×10^{-3} M, Total Sodium Nitrate = 5.00×10^{-2} M.
Blank-2 : Total Calcium = Total Carbonate = 6.00×10^{-3} M, Total Sodium Nitrate = 6.00×10^{-2} M.

The concentrations of humic, fulvic, and polyacrylic acids in spontaneous precipitation experiments were significantly lower than the initial calcium concentration. The concentrations of the additives did not decrease to any significant extent the solution supersaturation with respect to calcite due to complex formation of the respective anions with the free calcium ions. This fact suggested that the inhibition of these compounds were caused by preferential adsorption at the active growth sites of the new nuclei and of the seed crystals. Similar behaviour has been reported for water soluble polymeric compounds[8,15] and for organophosphorus compounds.[16]

The results of the relative inhibition in the presence of the humic, fulvic, and polyacrylic acids as a function of their concentration are shown in Figure 5. The percent inhibition of each additive tested was found to depend strongly on the respective additive concentration. As may be seen in Figure 5, polyacrylic acid gave significantly higher relative inhibition than humic and fulvic acids at the same concentration. Polyacrylic acid at a concentration of 0.25 ppm resulted in a complete stop of calcium carbonate precipitation while humic and fulvic acids at 0.30 ppm gave relative inhibition 87.5 and 75.9% respectively. Humic acid gave higher relative inhibition than fulvic acid for the same concentration at all tested concentrations. This trend was also observed at the induction time dependence on the additive concentration at the same conditions. For concentrations higher than 0.2 ppm, there is tendency for a linear increase of the additive effectiveness while at higher additive concentrations the tendency to reach a plateau of the relative inhibition is higher.

It is assumed that the measured inhibition was due to the adsorption of additive molecules at the active growth sites of the crystals to fit the kinetics data obtained from rate measurements. A Langmuir type kinetic model is used, in which it is assumed that the reduction of the rates of crystal growth is proportional to the coverage of the surface of the seed crystals by the additive molecules.[17] This model assumes monolayer coverage, lack of lateral interactions between adsorbate molecules, and energetically equivalent adsorption sites. The relationship between the rates of crystal growth in the presence and in the absence of additives with the additive concentration is given by the Equation (4):

$$\frac{R_0}{R_0 - R_i} = 1 + \frac{1}{bC} \qquad (4)$$

where C is the additive concentration and b is the affinity constant, being a measure of preferential affinity of the additive for the crystal surface. The above equation describes a linear relationship between the ratio $R_0/(R_0-R_I)$ and the inverse of additive concentration, 1/C. For concentrations higher than 0.2 ppm experimental data gave a satisfactory fit for the tested additives (Fig. 6). For humic and fulvic acids at concentrations lower than 0.2 ppm a second linear part was found. This was probably due to either the presence of active growth sites with different energy on the crystal surface or to the lack of validity of the Langmuir adsorption model over the entire concentration range. In contrast to humic and fulvic acids, polyacrylic acid did not give a second linear dependence.

According to the model described by Eq. (4) the intercept is expected to be equal to unity. For the polyacrylic and humic acids the value of the intercept was lower than 1. This value suggests complete inhibition at concentrations below the concentration corresponding to the complete coverage of crystal surface with a monolayer of polyacrylic and humic acids molecules.[18] The same behaviour has been reported for the crystal growth of several insoluble salts of the alkaline earth metals in the presence of

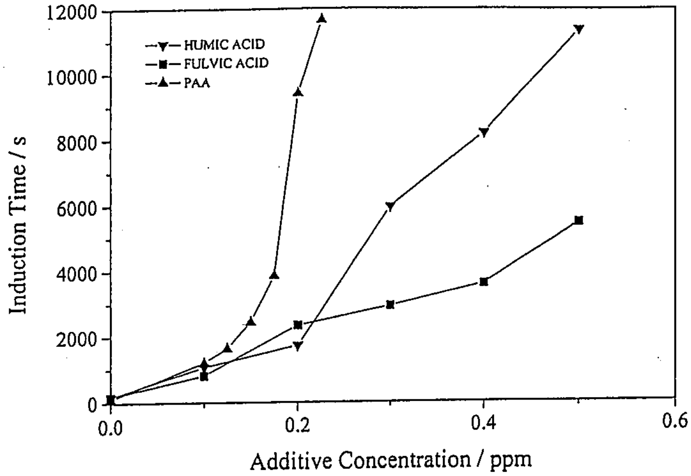

Figure 4. Dependence of the induction time preceding the spontaneous precipitation of calcium carbonate in aqueous solutions in the presence of humic, fulvic, and polyacrylic acids at pH = 8.50, 25°C.

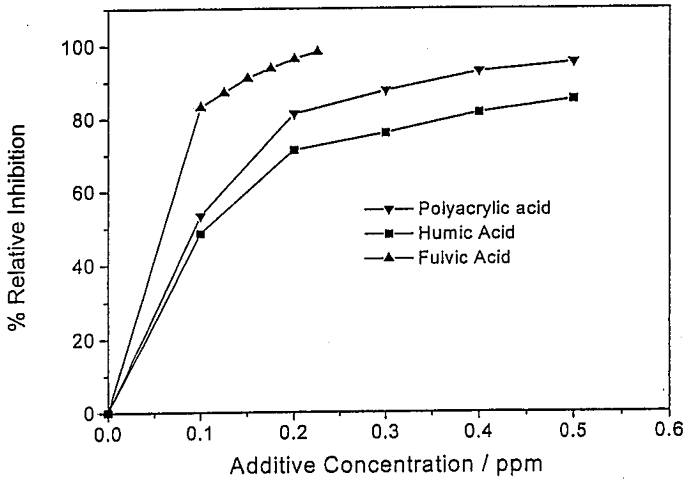

Figure 5. Dependence of the ratio R_i/R_0 on the humic, fulvic, and polyacrylic acids concentration for the spontaneous precipitation of calcium carbonate at pH = 8.50, 25°C.

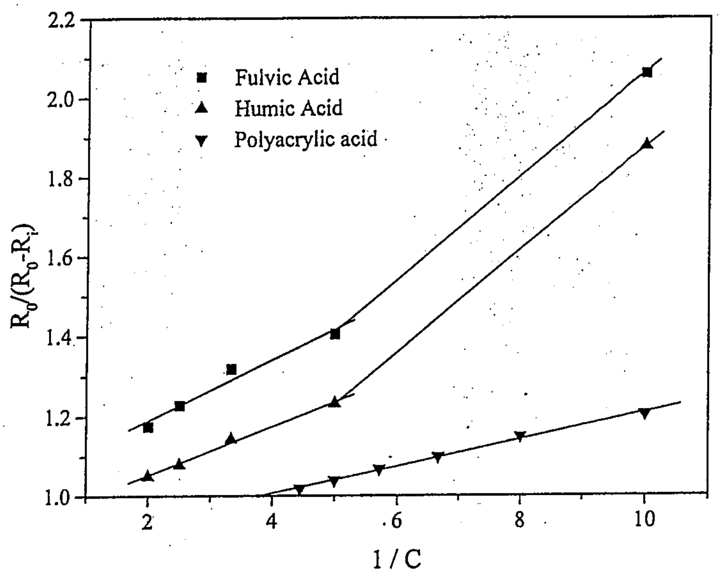

Figure 6. Fit of the kinetic results for the spontaneous precipitation of calcium carbonate in the presence of humic, fulvic, and polyacrylic acids at pH = 8.50, 25°C.

organophosphorus compounds.[2] For fulvic acid the intercept was found to be greater than 1. This suggested that complete inhibition is not possible and that the relative inhibition reaches a limiting value at certain additive concentration.

Seeded Growth Experiments

The seeded growth experiments for the evaluation of the effectiveness of polyacrylic, humic, and fulvic acids as precipitation inhibitors were done with stable supersaturated solutions. The experimental conditions for the seeded growth experiments and the relative inhibition obtained are summarized in Table 2. In all seeded growth experiments, overgrowth of calcium carbonate on calcite seed crystals started immediately after the addition of seed crystals without any induction times at all concentrations of tested additives.

The relative inhibition of calcium carbonate overgrowth on calcite seed crystals in the presence of humic, fulvic, and polyacrylic acids was found to depend strongly on their concentrations but to a different extent. The dependence of % relative inhibition on the tested additive concentration is shown in Figure 7. As may be seen in Figure 7, the polyacrylic acid gave higher relative inhibition than humic and fulvic acids for the same concentration. Also, the presence of polyacrylic acid resulted in the complete inhibition of calcium carbonate precipitation at concentrations exceeding 0.2 ppm. Similar results were obtained for humic acid which was found to be a more efficient inhibitor than fulvic acid. Humic acid completely inhibited calcium carbonate precipitation at concentrations higher than 0.8 ppm.

Table 2. Crystal growth of calcium carbonate on calcite seed crystals in the presence of humic, fulvic, and polyacrylic acid at 25°C and pH = 8.50. Initial conditions and relative inhibition.

Exp. #	Additive	Concentration / ppm	Relative Inhibition
1	Blank	0	-
2	Humic Acid	0.05	25.9
3	Humic Acid	0.1	56.4
4	Humic Acid	0.2	79.1
5	Humic Acid	0.3	89.3
6	Humic Acid	0.4	95.7
7	Humic Acid	0.5	96.9
8	Humic Acid	0.6	98.7
9	Humic Acid	0.8	99.1
10	Humic Acid	1.0	100
11	Fulvic Acid	0.1	12.5
12	Fulvic Acid	0.2	39.4
13	Fulvic Acid	0.3	59.3
14	Fulvic Acid	0.5	78.1
15	Fulvic Acid	1.0	85.9
16	Fulvic Acid	1.5	94.2
17	Fulvic Acid	2.0	94.4
18	PAA	0.05	90.0
19	PAA	0.1	97.5
20	PAA	0.15	96.9
21	PAA	0.2	98.5
22	PAA	0.25	100

Blank : Total Calcium = Total Carbonate = 2.00×10^{-3} M,
Total Sodium Chloride = 2.00×10^{-2} M.

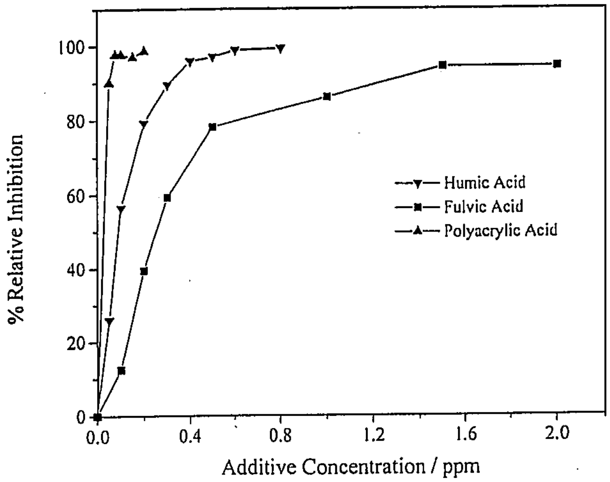

Figure 7. Dependence of the ratio R_i/R_0 on the humic, fulvic, and polyacrylic acids concentration for the calcium carbonate overgrowth on calcite seed crystals at pH = 8.50, 25°C.

Fulvic acid did not completely inhibit calcite crystal growth even at concentrations of 2 ppm, significantly higher than the concentration in which humic acid resulted in complete inhibition. Relative inhibition for fulvic acid reached a plateau. This was probably due to the stronger adsorption of polyacrylic and humic acid molecules on the active growth sites of the calcite seed crystals in comparison with fulvic acid at pH = 8.50. A linear dependence of the relative inhibition on the additive concentration was observed at concentrations higher than 0.4 ppm for humic acid and 0.5 ppm for fulvic acid. Thus, from the kinetic analysis according to the Langmuir model (Eq. (4)) a linear relationship between the ratio $R_0/(R_0-R_i)$ and the inverse of additive concentration, C, is predicted for concentrations higher than 0.4 ppm for humic acid and 0.5 ppm for fulvic acid respectively. Polyacrylic acid gave linear dependence between the ratio $R_0/(R_0-R_i)$ and the inverse of additive concentration, 1/C, at all concentrations. The same response was observed for the tested compounds in the spontaneous precipitation experiments. The analysis of the kinetic data obtained from the overgrowth of calcium carbonate on calcite seed crystals is shown in Figure 8. At concentrations lower than 0.4 ppm for humic acid and 0.5 ppm for fulvic acid, a second linear dependence was observed. Again this is probably due to either the presence of active growth sites with different energy at the calcite surface or to changes in the mode of adsorption with increasing surface concentration. At higher surface coverage, the structure of the molecules adsorbed on the mineral surfaces may change. The polyacrylic acid molecule is linear and simpler in structure than humic and fulvic acid molecules.

From the kinetic analysis (Eq. (4)), the value of the intercept for polyacrylic and humic acids was found to be lower than unity and for fulvic acid slightly higher than unity. This is in agreement with the variation of relative inhibition versus additive concentration (Figure 7).

The values of the affinity constants for humic, fulvic, and polyacrylic acids, as calculated from the kinetics analysis according to the Langmuir type model, are

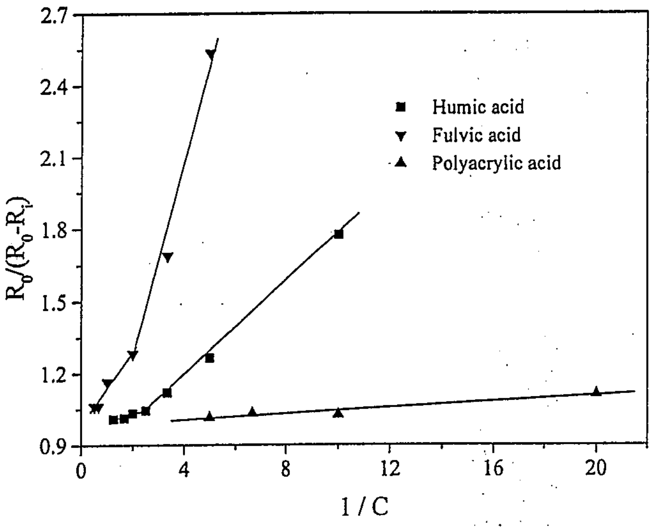

Figure 8. Fit of the kinetic results for the overgrowth of calcium carbonate on calcite seed crystals in the presence of humic, fulvic and polyacrylic acids at pH = 8.50, 25°C.

summarized in Table 3. The affinity constant for polyacrylic acid was significantly higher than affinity constants for humic and fulvic acid. The affinity constant for humic acid was higher than the affinity constant for fulvic acid. Additives may be arranged in the following order with respect to their affinity constants for calcite crystal growth :

Polyacrylic acid >> Humic Acid > Fulvic Acid

Polyacrylic and humic acids, which caused complete inhibition at lower concentrations than fulvic acid, yielded higher values of the affinity constant. The affinity constant of polyacrylic acid was significantly higher than the affinity constants of the organophosphorus compounds, BPDMI and ETMPA, which were reported to effectively inhibit the precipitation of calcium carbonate. Polyacrylic acid is more effective than these organophosphorus compounds because it gave the same results but at lower concentrations.[19-21]

Table 3. Affinity constants for the additive-calcite interface calculated from kinetics of crystal growth data according to the Langmuir model.

Additive	Affinity Constant
Humic Acid	1.9×10^7
Fulvic Acid	4.6×10^6
PAA	1.6×10^9
Mellitic Acid	2.0×10^6 (19)
Phosphate	5.9×10^7 (20)
BPDMI	1.6×10^7 (21)
ETMPA	1.0×10^7 (21)

BPDMI : 1,3-Bis[(1-phenyl-1-dihydroxyphosphonyl)-methyl]-2-imidazolidinone
ETMPA : Ethylenediamine-tetra-bis-methylene phosphonic acid

The affinity constant for humic acid was of the same order of magnitude as the affinity constants for the organophosphorus compounds. BPDMI and ETMPA gave the same relative inhibition at almost the same concentration and completely inhibited the precipitation of calcium carbonate at the same low concentration at which humic acid was tested.[21] In the contrast, the affinity constant of fulvic acid was lower (comparable to mellitic acid), and its inhibition efficiency was poorer than with polyacrylic and humic acids and BPDMI and ETMPA. The difference in effectiveness as precipitation inhibitors among polyacrylic, humic, and fulvic acids may be attributed to the characteristics of their molecules, such as the degree of ionization of their functional groups, their charge density at pH = 8.50, molecule size, stereochemical geometry, flexibility and to the ability for binding to more than one active growth sites by one molecule. The polyacrylic acid molecule is linear, fully ionizable at pH = 8.50, and more flexible for adsorption on crystal surface than humic and fulvic acids. The exact formulae for humic and fulvic acids are not known; thus it is very difficult to determine specific reasons for the better performance of humic acid as a precipitation inhibitor in comparison with fulvic acid.

CONCLUSIONS

In the present work it has been shown that the presence of humic, fulvic, and polyacrylic acid at very low concentrations can strongly inhibit nucleation and crystal growth of calcium carbonate from labile and metastable supersaturated aqueous solutions. Humic, fulvic, and polyacrylic acids did not affect the nature of the calcium carbonate phase formed, which in all cases was calcite. Polyacrylic and humic acids gave higher relative inhibition than fulvic acid at the same conditions. Polyacrylic and humic acids were found to completely inhibit the crystallization of calcium carbonate at very low concentrations while fulvic acid failed to yield complete inhibition even at significantly higher concentrations. The higher inhibition efficiency of polyacrylic acid in comparison with humic and fulvic acids is due to the larger extent of adsorption of polyacrylic acid molecules on calcite surface in our experimental conditions, as indicated by the higher affinity constant of polyacrylic acid molecules for calcite surface. Also, humic acid was more effective as a precipitation inhibitor than fulvic acid. The difference in inhibition efficiency between polyacrylic, humic, and fulvic acids may be attributed to their molecular characteristics.

REFERENCES

1. J.C. Cowan and D.J. Weintritt, *Water Formed Scale Deposits*, Gulf Publishing, Houston, Texas, 60 (1976).
2. Z. Amjad, "Kinetic Study of the seeded growth of Calcium Carbonate in the presence of Benzenepolycarboxylic Acids", Langmuir 3:224 (1987).
3. D. Wilson, 'Influence of molecular weight on selection and application of Polymeric Scale Inhibitors', Corrosion/94, Paper No. 48, NACE, Houston, Texas, (1994).
4. J. Glater, J.L. York and K.S. Campbell, "Scale Formation and Prevention", in : *Principles of Desalination,* K.S. Spiegler and A.D.K. Laird. ed., Academic Press, 627 (1980).
5. M.P.C. Weijnen and G.M. van Rosmalen, 'The influence of various polyelectrolytes on the precipitation of gypsum' Desalination, 54:239 (1985).
6. O.J. Vetter, 'An evaluation of scale inhibitors', J.Pet.Techn., 997 (1972).
7. Z. Amjad, 'Calcium Sulfate Dihydrate (Gypsum) scale formation on heat exchanger surfaces : The influence of Scale Inhibitors', J. Colloid Interface Sci. 123:523 (1988).
8. A.M. Carrier amd M.L. Standish, "Polymer mediated Crystal habit modification", in : *Mineral Scale Formation and Prevention.* Z. Amjad, ed., Plenum New York, 63 (1995).
9. Mortvedt, P.M. Giordano and W. L. Lindsay, "Micronutrients in Agriculture", American Society of Agronomy, Madison, Wiscosin, (1972).
10. J.L. Lacout, P.G. Koutsoukos, N. Rouquet and M. Freche, 'Effect of Humic compounds on the crystal growth of Dicalcium Phosphate Dihydrate', Agrochimica, 36:500 (1992).
11. Z. Amjad and M.M. Reddy, 'Influence of Humic compounds on the Crystal Growth of Hydroxyapatite', in : *Water Soluble Polymers : Solution, properties and applications*, Z. Amjad, ed., Plenum Publishing Co., N.Y. 77 (1998).
12. M.M. Reddy and G.H. Nancollas, 'The crystallization of Calcium Carbonate II. Calcite Growth mechanism', J. Colloid Interface Sci. 37, 824 (1971).
13. JCPDS ASTM Card No 05-0586
14. M.P.C. Weijnen, 'The influence of additives on the crystallization of Gypsum', Ph.D. Thesis, University of Delft, (1984).
15. A.E. Austin, J.F. Miller, D.A. Vaughan and J.F. Kircher, 'Chemical additives for calcium sulfate scale control', Desalination, 16:345 (1975).
16. C.W. Davies and G.H. Nancollas, 'The precipitation of Silver Chloride from aqueous solutions. Part III. Temperature Coefficients of Growth and Solutions', Trans.Faraday.Soc., 51:818 (1955).

17. G.H. Nancollas and S.J. Zawacki, 'Inhibitors of Crystallization and Dissolution', Industrial Crystallization 84:51 (1984).

18. W.H. Leung and G.H. Nancollas, 'Nitrilotri(methylenephosphonic acid) adsorption on Barium Sulfate crystals and its influence on crystal growth', J.Crystal Growth, 44:163 (1978).

19. E.K. Giannimaras and P.G. Koutsoukos, 'The crystallization of Calcite in the presence of Orthophosphate', J. Colloid Interface Sci. 116:423 (1987).

20. A.G. Xyla, J. Mikroyannidis, and P.G. Koutsoukos, 'The inhibition of Calcium Carbonate precipitation in aqueous media by Organophosphorus compounds', J. Colloid Interface Sci. 153:537 (1992).