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This paper presents a study of how various solution conditions (i.e., iron concentration, calcite supersaturation, pH, alkalinity, seed surface area, and ionic strength) influence the effectiveness of both ferrous (Fe(II)) and ferric (Fe(III)) ions as inhibitors of the growth of calcite, a common scale-forming mineral. It shows that when Fe(II) concentrations greater than 8×10^{-5} M or Fe(III) concentrations greater than 5×10^{-6} M are used, calcite growth is completely inhibited. Lesser concentrations of iron cause the calcite growth process to slow, and also cause growth to almost stop at a calcium concentration which is still significantly higher than the calcium concentration which would be in equilibrium with calcite seeds in the absence of iron. The extent of growth inhibition depends on the iron to seed ratio; a larger ratio results in increased growth inhibition. Lower supersaturations require less iron for the same extent of growth inhibition. Decreasing the alkalinity greatly reduces the inhibiting effectiveness of Fe(III); the inhibiting effectiveness of Fe(II) is also reduced at lower alkalinity but to a lesser extent. Fe(III) inhibits calcite growth more effectively at pH 7 than at pH 8; for Fe(II), studies of the effect of pH were inconclusive because very fast oxidation occurs at pH values greater than 7. Changes in ionic strength have only negligible effects. At the experimental conditions studied, Fe(III) is a much better inhibitior than Fe(II). However, adding oxygen to a solution that contains Fe(II) results in a dramatic increase in growth inhibition, so much so that the inhibition is even better than that observed on adding the same amount of iron directly as Fe(III).

Introduction

In a paper[1] describing research whose initial purpose was to investigate magnetic water treatment devices, we reported that both ferrous (Fe(II)) and ferric (Fe(III)) ions inhibit the growth of calcite, the most prevalent form of calcium carbonate. The buildup of scale deposits in water handling equipment is a serious problem encountered in many industrial processes. These scales are usually composed of calcium salts such as phosphates, sulfate hydrates, and carbonate polymorphs[2,3] with calcite as the most common scale-forming mineral.

Although inhibitors of calcium carbonate crystallization play a major role in fields ranging from scale prevention to biomineralization, the mechanisms of calcite growth inhibition by metal cations in general are not well understood. A few studies have examined the effect of iron on calcite growth. Meyer[4] investigated the inhibiting effects of 34 different cationic and anionic impurities on the growth rate of calcite. Of all the cationic additives investigated, Fe(II) caused the strongest decrease in calcite growth rate under the experimental conditions of his study. He reported that a concentration of only 10^{-8} M Fe(II) was sufficient to cause a 20% reduction in the growth rate of calcite. In a study of Fe(II) incorporation into calcite, Dromgoole[5] reported that $FeCl_2$ concentrations above 10^{-4} M produced such a strong reduction in the growth rate of calcite seeds that they could not obtain sufficient amounts of overgrowth for analysis.

To obtain more insight into the growth-inhibiting mechanism of iron, a systematic study of how solution conditions such as iron concentration, $CaCO_3$ supersaturation, pH, alkalinity, surface area, and ionic strength

influence the effectiveness of Fe(II) and Fe(III) as calcite growth inhibitors has been carried out.

Materials and Methods

Apparatus and Materials. All experiments were performed in a 250-mL Teflon reactor with a fitted Teflon lid. This reactor is identical to that shown in Figure 3 in our previous paper.[1] A N_2/CO_2 gas mixture was continuously bubbled through the solution, thus keeping constant both the pH and the desired carbonate concentration. To prevent the oxidation of Fe(II), the oxygen concentration in the gas mixture was reduced to extremely low levels by adding low concentrations of hydrogen to this gas mixture and then passing it through a tube containing copper turnings maintained at about 400 °C. Before entering the reactor, the gas was saturated with water. The gases used were Linde prepurified grade N_2, anaerobic grade CO_2, and prepurified grade H_2.

The reacting solution was stirred by a 1-in. cylindrical Teflon-coated stir bar. The stirrer speed (800 rpm) was sufficiently high to avoid diffusion limitations arising from the transport of ions or CO_2 through the bulk solution. A constant temperature was maintained by submerging the reaction vessel in a water bath thermostated at 25.0 ± 0.1 °C. pH was measured to a precision of 0.01 pH unit using a Fisher Accu-pHast MicroProbe glass body combination electrode and a Fisher Accumet 805MP pH meter. (The pH electrode was standardized daily at pH 7.00 and at pH 10.00 using certified Fisher buffer solutions.) Ca^{2+} activity was measured using an Orion calcium ion selective electrode and a Ag/AgCl reference electrode. Both pH and Ca^{2+} activities were monitored continuously throughout the growth measurements by a two-channel strip chart recorder.

The calcium electrode was calibrated in a sodium bicarbonate solution at each of the bicarbonate concentrations and pH's of the solutions used in the experiments. The millivolts vs log Ca^{2+} plot is quite linear in the log Ca^{2+} region between -2.3 and -3.7 (where Ca^{2+} is the concentration of free calcium ions in moles per liter). For smaller log Ca^{2+}, the slope of this line decreases slightly with decreasing calcium concentration. In the log Ca^{2+} region between -3.5 and -5, a polynomial fit (second or third order) was used to relate millivolts to log Ca^{2+}. At pH 7.00 and 0.15 equiv/L alkalinity, the slope of the calcium electrode is 28.8 mV/log Ca^{2+} (for log Ca^{2+} values between -2.3 and -3.7). This value represents the average of measurements of the slope of the electrode in five different solutions: in pure bicarbonate solution at 0.15 M ionic

(1) Herzog, R. E.; Shi, Q.; Patil, J. N.; Katz, J. L. *Langmuir* 1989, 5, 861-867.
(2) Nancollas, G. H. *Adv. Colloid Interface Sci.* 1979, 10, 215-252.
(3) Elloit, M. N. *Scale Control by Threshold Treatment*; Process Technology Division; UKAEA Research Group; Atomic Energy Research Establishment; Harwell: Berkshire, U.K., 1969; AERE-R5696.
(4) Meyer, H. J. *J. Cryst. Growth* 1984, 66, 639-646.
(5) Dromgoole, E. L.; Walter, L. M. *Chem. Geol.* 1990, 81, 311-336.

strength, in pure bicarbonate solution at 0.15 M ionic strength in the presence of oxygen, in the same solution but with 8×10^{-5} M ferrous chloride (no oxygen), in the same solution but with 7×10^{-6} M ferric chloride, or in pure bicarbonate at 0.3 M ionic strength (attained by adding NaCl). These five values differ by less than 0.3 mV/log Ca^{2+} from the mean. However, electrodes drift in potential with time. Repeated calibration measurements showed that the slope remained constant; only the intercept changed. To correct for this drift, the intercept of the log Ca^{2+} vs millivolts curve was adjusted for each run using the measured millivolt reading when a known amount of calcium chloride was added to the solution. During growth measurements a few calcite seeds attached to the membrane of the calcium electrode. To determine whether these could lead to erroneous measurements, the solution was decanted to a different beaker and the membrane was carefully cleaned by immersion in diluted hydrochloric acid (pH 1), rinsed with deionized water, and then used to remeasure the calcium concentration. The potential differences between the original solution (i.e., with seeds present and a few attached to the membrane) and the same solution (at the same stirring speed and CO_2 concentration but almost no seeds) were measured on two occasions. In one case there was no difference, and in another the difference was 0.5 mV, suggesting that the presence of seeds on the membrane of the electrode was not a problem.

Solutions were prepared using 18-MΩ water obtained by purifying tap water by reverse osmosis followed by passage through a charcoal filter and two ion exchange resin beds. All chemicals were reagent grade. The concentration of the $NaHCO_3$ buffer was 0.15 M (except as noted). In those cases when lower concentrations of $NaHCO_3$ were used, the solution ionic strength was kept fixed at 0.15 M by the addition of NaCl. $CaCl_2$ solutions were prepared using $CaCl_2 \cdot 2H_2O$. Buffer solutions and $CaCl_2$ solutions were filtered through 0.22-micrometer nylon filter membranes to remove dust and other insoluble matter and stored in polyethylene flasks sealed with parafilm. These solutions were replaced frequently. Fe(II) and Fe(III) solutions were prepared immediately before use in a Teflon flask using $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$, respectively.

The seed material was Mallinckrodt reagent grade calcite. The specific surface area was found by single-point BET analysis to be 0.32 m²/g. The average edge length was found by scanning electron microscopy to be 10 μm. X-ray diffraction patterns confirmed that the crystal samples were calcite; no aragonite was detectable.[6]

The reagents used in the assay for iron were 0.01 M bathophenanthroline (4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, disodium salt (GFS Chemicals)); sodium acetate (10% solution), Fe free (GFS Chemicals); hydroxylammonium chloride (10% solution), Fe free (GFS Chemicals); and hydrochloric acid (1 N), Fe free (GFS Chemicals).

Crystal Growth Experiments. In each experiment, 100 mL of a $NaHCO_3$/NaCl buffer solution was added to the reaction vessel and sparged by a N_2/CO_2/H_2 gas stream (the flow rate was about 2 mL/s). Five to ten minutes after equilibrium was reached (equilibrium was assumed when the pH reading became constant with time, about 15–25 min after gas bubbling began), the appropriate amount of 0.1 M $CaCl_2$ was added such that the solution became saturated with respect to calcite. Following the addition of $CaCl_2$, 1.0 mL of freshly prepared Fe(II) or Fe(III) solution at the concentration appropriate to achieve the desired total iron concentration was added. Then 0.5 g of calcite seeds was added with a polystyrene pipet by suspending the crystals in a small volume of solution withdrawn from the reactor. The calcite was allowed to interact with the iron for 30 min, and then by quickly adding more 0.1 M $CaCl_2$ (the volume added was always less than 7% of the total solution volume), the solution was made supersaturated with respect to calcite, and precipitation began (except when the iron concentration was sufficiently high). No further additions of calcium were made. Thus, as the calcite crystals grew, the driving force for calcite growth, i.e., the calcium concentration, decreased with time. (This procedure is called

the free drift method.[7] The resulting decrease in Ca^{2+} activity was monitored until Ca^{2+} activity became almost constant with time.

Initiating calcite growth by quickly adding a small volume of relatively concentrated calcium chloride solution produces a small region of very high supersaturation for a small length of time, which might induce secondary nucleation. In a following paper we show that the rate constant is directly proportional to the seed loading (in the absence of iron) which means that no significant amount of secondary nucleation occurs. Initiating calcite growth (in the absence of iron) by adding the same amount of seeds to a solution which already is supersaturated resulted in essentially the same rate constant. This gives further evidence that secondary nucleation does not occur and also shows that no increase in seed surface area occurs due to a possible grinding of the seeds by the stirring bar.

The sodium concentration and the CO_2 partial pressure in a pure carbonate system determine the pH and the carbonate and bicarbonate concentrations via electroneutrality conditions; it makes no difference whether the sodium is added as $NaHCO_3$, as Na_2CO_3, or as NaOH. However, sodium added as sodium chloride does not affect electroneutrality conditions since the electrical charges of the sodium and the chloride ions cancel each other. In this study sodium bicarbonate concentrations were chosen sufficiently large (0.15 M) that changes in pH and carbonate concentration due to calcite precipitation were negligble (usually the pH changed by less than 0.03 pH unit). Furthermore, varying the sodium concentration enabled us to vary pH while keeping the Ca^{2+} to CO_3^{2-} ratio constant, or to vary Ca^{2+}, CO_3^{2-}, and HCO_3^- concentrations while keeping the pH constant.

A variable which is frequently used in the water treatment literature is alkalinity (Alk). As defined by Stumm and Morgan,[8] alkalinity is the quantity of strong acid per liter which one would have to add to the solution to obtain a pH equal to that in a solution in which the only carbonic species are H_2CO_3 and dissolved CO_2, and where the sum of their concentrations, conventionally denoted as [H_2CO_3*], is equal to the sum of the concentrations of all carbonic species in the actual solution. Thus, alkalinity is defined as

$$Alk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

Electroneutrality of the solution requires that (for the experiments desccribed in this paper) the alkalinity be equal to the concentration of the sodium which is added as sodium *bicarbonate*. The reported alkalinities are *initial* values for the solution, i.e., before addition of any calcium or iron salts. Initial alkalinity is a convenient parameter to use to label solution conditions. However, it is not used to calculate solution speciation; these are calculated in a computer program using electroneutrality conditions, and include the effects of calcium and iron addition.

The base case solution condition for all experiments is an initial calcite supersaturation[9] of 7, a pH of 7.00, an alkalinity of 0.15 eqiv/L, a seed loading of 5.0 g/L, and an ionic strength of 0.15 M. Deviations from these conditions are indicated.

Assay for Iron. Bathophenanthroline forms a strong, intensely colored red complex with Fe^{2+} ions whose intensity can be quantified at Fe(II) concentrations down to 10^{-7} M.[10,11] Fe(III) can be reduced to Fe(II) using hydroxylammonium chloride as the reducing agent, and thus also quantified with bathophenanthroline.

(6) Many experimental details are described more extensively in Herzog, R. E. Ph.D. Dissertation, The Johns Hopkins University, Baltimore, 1991, a copy of which is available from University Microfilms. It includes scanning electron micrographs of these crystals.

(7) Zhang, J.-W.; Nancollas, G. H. *Reviews in Mineralogy*; Mineralogical Society of America: Washington, DC, 1990; Vol. 23, pp 365–396.

(8) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; 2nd ed.; Wiley-Interscience: New York, 1981; p 185.

(9) Supersaturation is the ratio of the calcite ion-activity product (IAP) to the thermodynamic solubility product IAP/K_{s0} = [Ca^{2+}]·[CO_3^{2-}]/[Ca^{2+}]$_{eq}$[CO_3^{2-}]$_{eq}$; since the continuous bubbling of CO_2 and the high alkalinity keep the carbonate concentration ([CO_3^{2-}]) very constant, this concentration is almost identical to the equilibrium carbonate concentration and (to high accuracy) cancels in this ratio. Thus, by supersaturation we mean the ratio of the concentration of free Ca^{2+} in the actual solution to that which it would have if the *total* calcium concentration were lowered until the solution was in equilibrium.

(10) Blair, D.; Diehl, H. *Talanta* 1961, *7*, 163–174.

(11) Lee, G. F.; Stumm, W. *J. Am. Water Works Assoc.* 1960, *52*, 1567.

Table I. Equilibria and Equilibrium Constants

reaction	log K^{16}	ref
$H_2O \rightleftharpoons H^+ + OH^-$	−14.00	17
$CO_2 + H_2O \rightleftharpoons H_2CO_3^*$	−1.47	18
$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$	−6.35	18
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	−10.33	18
$CaHCO_3^+ \rightleftharpoons Ca^{2+} HCO_3^-$	−1.26	19
$CaCO_3°(aq) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	−3.15	19
$CaOH^+ \rightleftharpoons Ca^{2+} + OH^-$	−1.30	19
$FeHCO_3^+ \rightleftharpoons Fe^{2+} + HCO_3^-$	−1.10	19
$FeCO_3°(aq) \rightleftharpoons Fe^{2+} + CO_3^{2-}$	−4.73	20
$FeOH^+ \rightleftharpoons Fe^{2+} + OH^-$	−4.60	19
$CaCO_3(s)$ (calcite) $\rightleftharpoons Ca^{2+} + CO_3^{2-}$	−8.48	19
$FeCO_3(s)$ (siderite) $\rightleftharpoons Fe^{2+} + CO_3^{2-}$	−10.20	19
$FeOH^{2+} \rightleftharpoons Fe^{3+} + OH^-$	−11.81	17
$Fe(OH)_2^+ \rightleftharpoons Fe^{3+} + 2OH^-$	−23.3	19
$Fe(OH)_3°(aq) \rightleftharpoons Fe^{3+} + 3OH^-$	>−30	17
$Fe(OH)_4^- \rightleftharpoons Fe^{3+} + 4OH^-$	−34.4	17
$Fe(OH)_3(am) \rightleftharpoons Fe^{3+} + 3OH^-$	−42.7	21

Iron concentrations were measured using a colorimetric assay similar to a standard procedure.[12] For determination of Fe(II) and Fe(III), a 2.0-mL sample was added to 1.0 mL of HCl of appropriate molarity to give a pH of 1.0 ± 0.1; 0.60 mL of 10% hydroxylammonium chloride was added to reduce Fe(III) to Fe(II); 0.60 mL of 10% sodium acetate buffer was added, resulting in a pH of 3.8 ± 0.1; then 0.45 mL of 0.01 M bathophenanthroline was added, resulting in a pH of 4.0 ± 0.2. Solutions were vigorously vortex-stirred after the addition of each reagent. A standard curve of [Fe]$_{tot}$ (total iron concentration) versus absorbance was used to determine [Fe]$_{tot}$ and [Fe(II)]$_{tot}$ (total Fe(II) concentration) in unknown samples. [Fe(III)]$_{tot}$ (total Fe(III) concentration) was determined as the difference between [Fe]$_{tot}$ and [Fe(II)]$_{tot}$. (The assay for [Fe(II)]$_{tot}$ was made by using diluted HCl instead of hydroxylammonium chloride.) Less than 15 min after adding the bathophenanthroline, the absorbance of the resulting red solution was measured at 533 mm with a Perkin-Elmer Lambda 3B UV/vis spectrophotometer.

Data Analysis. A computer program was used to compute chemical speciation based on known NaHCO₃ and CaCl₂ concentrations and pH values. Activity coefficients were calculated using the Davies equation.[13] The equilibria and equilibrium constants used to compute CaCO₃, FeCO₃, and Fe(OH)₃ solubility are given in Table I.

The following first-order growth rate expression was used to model calcite growth:

$$R = -dC/dt = K(C - C_f) \quad (1)$$

where C is the concentration of calcium, C_f is the value this concentration reaches after a sufficiently long time[14] (in the absence of iron, C_f is equal to C_{eq}, the equilibrium concentration), and where K is the growth rate constant. This equation is easily obtained from a growth rate expression for calcite growth proposed by Nancollas and Reddy:[15]

$$-d[Ca^{2+}]/dt = K'([Ca^{2+}][CO_3^{2-}] - K_{sp}/\gamma_2^2) \quad (2)$$

where K_{sp} is the solubility product of calcite, γ_2 is the activity coefficient for divalent ions, [Ca^{2+}] is the free calcium concentration, and [CO_3^{2-}] is the carbonate concentration. Since the carbonate concentration and the ionic strength are almost

constant during the crystal growth experiment, the carbonate concentration equals the equilibrium carbonate concentration ([$CO_3^{2-}]_{eq}$) and $K_{sp}/\gamma_2^2 = [Ca^{2+}]_{eq}[CO_3^{2-}]_{eq}$; thus, [$CO_3^{2-}]_{eq}$ can be incorporated into the rate constant, and one obtains eq 1. By integrating eq 1 from 0 to t, one obtains

$$\ln(C - C_f) = -Kt + \ln(C_i - C_f) \quad (3)$$

where C_i is the initial calcium concentration. The values for K, the growth rate constant, reported here were obtained by fitting the measured calcium concentrations to this equation. All calcium concentrations reported here are free calcium concentrations.

Results

All calcite growth measurements made in the absence of iron, and almost all measurements made in the presence of iron were accurately fit assuming a reaction order of 1. (Higher order growth rate expressions, i.e., $R = K(C - C_f)^n$ with $n = 2$ or $n = 3$, did not fit the data.) A reaction order of 1 suggests that either adsorption of iron onto the calcite surface or ion diffusion through the boundary layer of the seeds is the growth-limiting step.[7]

There are two measures of inhibition by iron: its effect on the growth rate and its effect on the concentration of calcium that one can have in "equilibrium" with calcite seeds. Iron reduces the growth rate, resulting in a slowing of the precipitation process. This effect is quantified by changes in the growth rate constant and can be expressed as % reduction $\equiv (1 - K/K_0) \times 100\%$, where K_0 is the growth rate constant under conditions which are identical except for the absence of any iron. Iron also increases the "equilibrium" Ca^{2+} concentration; i.e., the measured concentration[22] after a long time in the presence of calcite seeds is higher than it would be in the absence of iron (see Figure 1). This elevation in "equilibrium" calcium concentration is another measure of calcite growth inhibition by iron. This effect is quantified as the difference between final calcium concentration in the presence of iron, C_f, and that in the absence of iron, C_{eq}, i.e., % inhibition $\equiv (C_f - C_{eq})/(C_i - C_{eq}) \times 100\%$ (C_f and C_i are measured values; C_{eq} is calculated).

Effect of Iron Concentration. Parts a and b of Figure 1 illustrate calcite growth inhibition by Fe(II) and Fe(III), respectively, using the base case solution conditions defined at the end of the Crystal Growth Experiments subsection. At these conditions Fe(III) performs better than Fe(II) as an inhibitor; the Fe(III) concentration necessary for *total* calcite growth inhibition is 5×10^{-6} M, and for Fe(II) it is 8×10^{-5} M. As is apparent from Figure 1, growth inhibition increases with increasing iron concentration. Fe(II) concentrations of 2×10^{-5} and 5×10^{-5} M resulted in inhibitions of 4 and 44% (and 53 and 88% reductions in growth rate), respectively; 2×10^{-6} and 3×10^{-6} M Fe(III) concentrations resulted in inhibitions of 2 and 8% (and 51 and 76% reductions in growth rate), respectively. (At these conditions, $C_{eq} = 1.9 \times 10^{-4}$ M and $K_0 = 0.49$ min^{-1}.)

The inhibiting effect of Fe(III) increases dramatically over a small concentration range; 2×10^{-6} M FeCl₃ results in a small but clearly discernible growth inhibition whereas 5×10^{-6} M FeCl₃ is sufficient to inhibit calcite growth almost completely. The inhibiting effect of Fe(II) also increases from little to total over a small concentration range; 2×10^{-5} M FeCl₂ inhibits calcite growth to only a small extent whereas 8×10^{-5} M results in complete growth inhibition.

(12) *The Iron Reagents*. GFS technical bulletin; G. Frederick Smith Chemical Co.; Columbus, OH, 1987; Section III.

(13) See ref 8, p 135.

(14) C_f is a fitted parameter. Usually its value is equal or very close to the measured value of C_f.

(15) Nancollas, G. H.; Reddy, M. M. *J. Colloid Interface Sci.* 1971, 37, 824–830.

(16) All log K values are for $T = 25$ °C and $I \rightarrow 0$.

(17) See ref 8, p 241.

(18) Lippmann, F. *Sedimentary Carbonate Minerals*; Springer-Verlag: New York, 1973.

(19) Smith, R. M.; Martell, A. E. *Critical Stability Constants. Inorganic Complexes*; Plenum: New York, 1989; Vol. 6.

(20) Fouillac, C.; Criaud, A. *Geochem. J.* 1984, 18, 297.

(21) Sillen, L. G.; Martell, A. E. *Stability Constant*; Special Publications No. 17; Chemical Society: London, 1964.
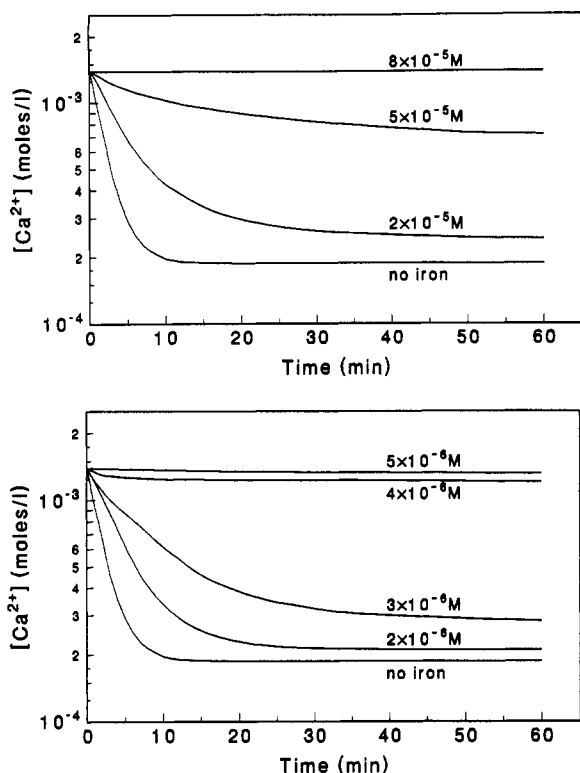
(22) Note that this increase in "equilibrium" concentration is not due to electrode error. Calibration measurements (made in the absence of calcite seeds) showed that the Ca^{2+} concentrations measured by the calcium electrode were not affected by the presence of either ferrous or ferric iron.

Figure 1. (a, top) Ca^{2+} concentrations in the presence of calcite seeds at various initial $FeCl_2$ concentrations. (b, bottom) Ca^{2+} concentrations in the presence of calcite seeds at various initial $FeCl_3$ concentrations.
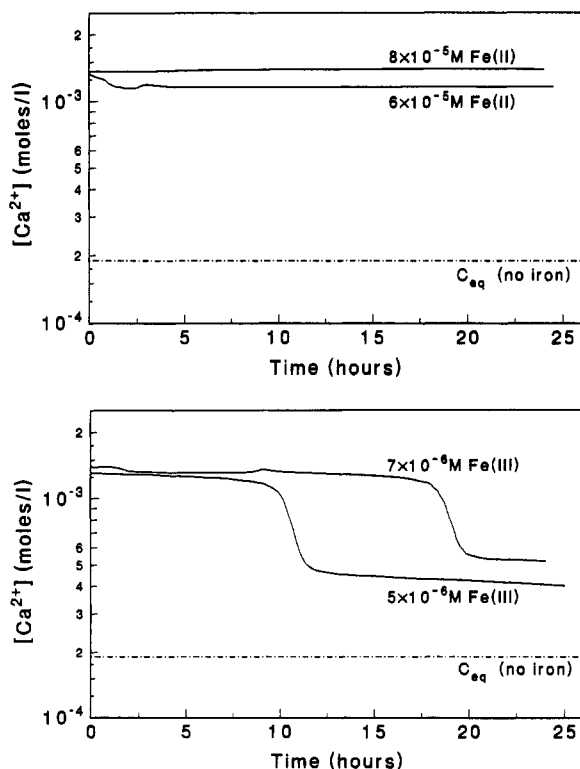

Figure 2. (a, top) Calcite growth inhibition by Fe(II) over an extended length of time. (b, bottom) Calcite growth inhibition by Fe(III) over an extended length of time.

Parts a and b of Figure 2 show calcite growth inhibition by Fe(II) and Fe(III), respectively, over an extended length of time for two different iron concentrations. Figure 2b shows that Fe(III) at a concentration of 5×10^{-6} M inhibits calcite growth almost completely for about 8 h (and that
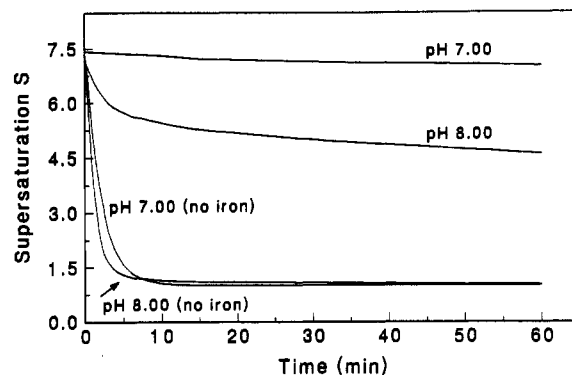

Figure 3. Effect of the presence of 5×10^{-6} M $FeCl_3$ on calcite growth at pH 7.00 and 8.00.
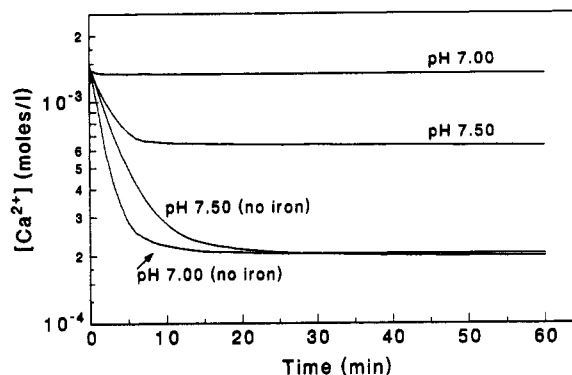

Figure 4. Effect of the presence of 1×10^{-5} M $FeCl_3$ on calcite growth at pH 7.00 and 7.50 (Ca^{2+}/CO_3^{2-} ratio = 1, S = 9).

7×10^{-6} M inhibits for more than 17 h). Then the calcium concentration decreases rapidly to a new "equilibrium". At this second "equilibrium" level calcite growth is again almost completely inhibited. The Fe(II) studies (Figure 2a) do not show this decrease to lower "equilibrium" levels; in the presence of 6×10^{-5} M $FeCl_2$ the calcium concentration became constant after about 5 h and stayed constant for more than 19 h; in the presence of 8×10^{-5} M $FeCl_2$ it stayed constant for more than 24 h. Since measurements were terminated at these times, one cannot know whether a decrease ever would occur.

Our measurements of the amount of iron adsorbed onto calcite seeds are incomplete. They will be discussed in more detail in a following paper. However, we can say that typically about 10% of the added iron (ferrous and ferric) is adsorbed during the 30-min pre-exposure time.

Effect of pH. Figure 3 compares the inhibiting effect of 5×10^{-6} M $FeCl_3$ at pH 7.00 and pH 8.00, in solutions having an initial alkalinity and an initial supersaturation of 0.15 equiv/L and about 7, respectively. The results of these measurements suggest that Fe(III) is more effective at lower pH. However, changing the pH while keeping alkalinity constant is accomplished by changing the partial pressure of CO_2 and results in a change of the CO_3^{2-} concentration. Thus, to have the same initial supersaturation, one also has to change the initial Ca^{2+} concentration.

In order to produce a solution with the same Ca^{2+}/CO_3^{2-} ratio[23] (i.e., a solution with the same initial supersaturation and the same initial calcium concentration) at different pH values, solution alkalinity has to be changed. Figure 4 compares the inhibiting effect of 1×10^{-5} M $FeCl_3$ at pH 7.00 and at pH 7.50 in solutions having alkalinities of 0.15

(23) By the Ca^{2+}/CO_3^{2-} ratio we mean the ratio of the free calcium ion concentration to the free carbonate ion concentration in a solution that contains no iron and is in equilibrium with calcite seeds.
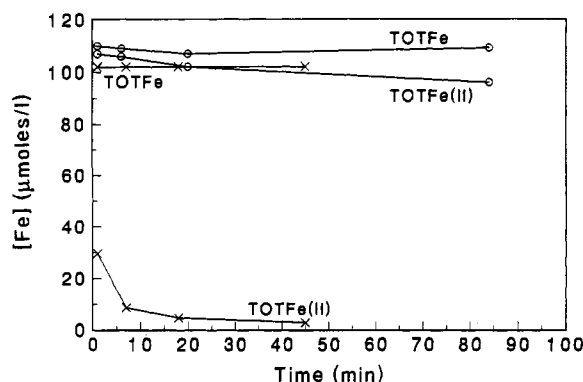
Figure 5. Oxidation of iron as a function of time: O, ferrous iron at pH 7.00; ×, ferrous iron at pH 8.24. ($[Fe]_{tot} = [Fe(II)]_{tot} + [Fe(III)]_{tot}$).

Figure 6. Effect of O_2 on calcite growth inhibition by Fe(II) (S = 9, seed loading 20 g/L).

and 0.05 equiv/L, respectively, and a Ca^{2+}/CO_3^{2-} ratio of 1. (These data were obtained without preexposing the calcite seeds to iron; other deviations from the base case set of conditions include a seed loading of 20.0 g/L (6.40 m^2/L) and an initial supersaturation of S = 9.) One again sees that lowering the pH increases the inhibition effectiveness of Fe(III). However, it is not possible to change the pH while keeping alkalinity *and* pCO_2 constant. Changing either one of these parameters will cause a change in the Ca^{2+}/CO_3^{2-} ratio or in the Ca^{2+}/HCO_3^- ratio, or in both, and it will also affect the surface charge of the calcite seeds. We have not yet sorted out the best way to use or combine these interrelated variables to describe the effectiveness of iron as a calcite growth inhibitor.

Our study of the influence that pH has on calcite growth inhibition by Fe(II) was inconclusive. Experimental difficulties were encountered because of the tendency for Fe(II) to oxidize in the presence of oxygen. Even though oxygen concentration was minimized by adding hydrogen to the feed gas and passing it through a bed of hot copper turnings, the very low oxygen concentration nonetheless present in the system was sufficient to promote oxidation at higher pH's. Figure 5 shows the concentration of Fe(II) as a function of time in pH 7.00 and in pH 8.24 sodium bicarbonate solutions (0.15 M) which were saturated with respect to calcite and contained no seeds (2.0-mL samples were removed at selected times and assayed for iron). It shows that the oxidation of Fe(II) as a function of time at pH 7.00 is very slow and can be ignored for the first few hours following the addition of $FeCl_2$. However, at pH 8.24 oxidation occurs rapidly, as it should since it is known that the oxidation rate increases as the square of the OH⁻ concentration.[24]

Effect of Added Oxygen. The effect of adding O_2 was a dramatic increase in the effectiveness of Fe(II) as a calcite growth inhibitor. As is shown in Figure 6, when solution conditions were such that the iron remained in the divalent form (i.e., pH 7.00, no O_2 added), 10^{-5} M Fe(II) was essentially ineffective; using a gas mixture that contained ~30% O_2, this same iron concentration caused much better calcite growth inhibition, even better than when the same amount of iron was added directly as Fe(III).[25]

Effect of Supersaturation. The initial calcite supersaturation has a strong influence on the extent of growth inhibition caused by a fixed initial iron concentration. Parts
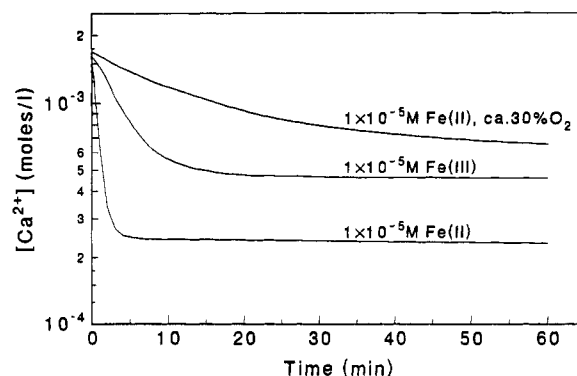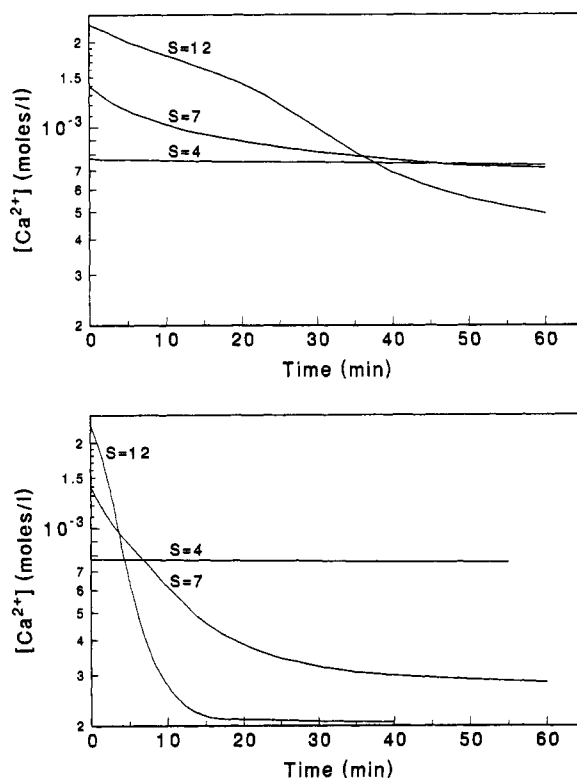

Figure 7. (a, top) Ca^{2+} concentration as a result of calcite growth in the presence of 5 × 10^{-5} M $FeCl_2$ at various initial calcite supersaturations. (b, bottom) Ca^{2+} concentration as a result of calcite growth in the presence of 3 × 10^{-6} M $FeCl_3$ at various initial calcite supersaturations.

a and b of Figure 7 show Ca^{2+} concentrations as a function of time for various supersaturations in the presence of iron. An initial Fe(II) concentrations of 5 × 10^{-5} M caused ~100, 44, and 8% inhibition and ~100, 88, and 86% reduction in growth rate when the initial calcite supersaturation were 4, 7, and 12, respectively (the reduction in growth rate for the S = 12 curve was calculated using only the data after time = 23 min). At the same initial supersaturation, an initial Fe(III) concentration of 3 × 10^{-6} M caused ~100, 8, and 1% inhibition and ~100, 76, and 16% reduction in growth rate.

Effect of Seed Loading. At an initial Fe(III) concentration of 5 × 10^{-6} M and a seed loading of 5.0 g/L (i.e., 1.60 m^2/L), calcite growth is ~100% inhibited (Figure 8b). The inhibition decreased to 5% when the seed loading was increased to 15.0 g/L (i.e., 4.80 m^2/L); the reduction in growth rate changed from ~100 to 66%. A similar effect was observed with ferrous ions; the inhibition caused by 7 × 10^{-5} M $FeCl_2$ decreased from 85 to 70% and the reduction in growth rate changed from ~100 to 92% when

(24) Sung, W.; Morgan, J. J. *Environ. Sci. Technol.* **1980**, *14*, 561–568.

(25) Solutions with seed loadings of 20.0 g/L (6.40 m^2/L) and initial supersaturations of S = 9 were used for these measurements. Note that each of these differences from the base case solution conditions will require an increase in iron concentration if one is to obtain the same % inhibition. A difference in experimental method also occurred; the seeds already had been in the saturated solution for 10–20 min when the iron was added.
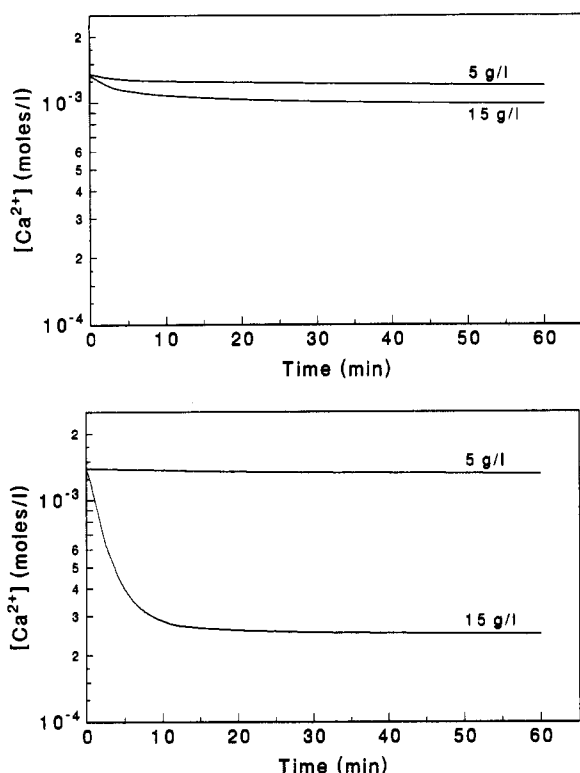
Figure 8. (a, top) Ca^{2+} concentration as a result of calcite growth in the presence of 7×10^{-5} M $FeCl_2$ at different seed loadings. (b, bottom) Ca^{2+} concentration as a result of calcite growth in the presence of 5×10^{-6} M $FeCl_3$ at different seed loadings.

Figure 9. (a, top) Calcite supersaturation as a result of calcite growth in the presence of 1×10^{-4} M $FeCl_2$ in 0.15 and 0.05 equiv/L alkalinity solutions. (b, bottom) Calcite supersaturation as a result of calcite growth in the presence of $FeCl_3$ in 0.15 and 0.05 equiv/L alkalinity solutions.

the seed loading was raised from 5.0 to 15.0 g/L. (The growth rate constant at a seed loading of 15 g/L in the absence of iron is $K_0 = 1.45$ min^{-1}.)

Effect of Alkalinity. The inhibiting effect of both ferric and ferrous ions is reduced when solution alkalinity is lowered. Figure 9a shows that, at a fixed pH of 7.00 and a fixed initial supersaturation of 7, a 3-fold decrease in alkalinity (from 0.15 to 0.05 equiv/L) greatly reduced the inhibition effectiveness of Fe(II). Figure 9b shows that for Fe(III) the effect is even stronger. Despite a 20-fold increase in iron concentration (from 5×10^{-6} to 1×10^{-4} M), the inhibition decreased from ~ 100 to 52%. (At an alkalinity of 0.05 equiv/L, $C_{eq} = 6 \times 10^{-4}$ M.) Note that the growth curves are plots of supersaturation versus time instead of Ca^{2+} concentration versus time; since the equilibrium Ca^{2+} concentration depends on solution alkalinity, this enables one to compare effects on a common basis.[26]

Effect of Ionic Strength. The effect of ionic strength on calcite growth inhibition by Fe(II) and Fe(III) was studied by comparing measurements at $I = 0.15$ M to those at $I = 0.30$ M (ionic strength was adjusted by adding NaCl). Changing the ionic strength causes changes in activity coefficients and thus changes in values of the equilibrium concentrations of calcium and carbonate. Appropriate changes in calcium and CO_2 concentrations therefore were made to keep both the initial supersaturation and the pH at their standard values of 7. Doubling the ionic strength had essentially no effect on growth inhibition by Fe(III), as also was the case for measurements made in the absence of iron. For Fe(II) at a concentration of 2×10^{-5} M
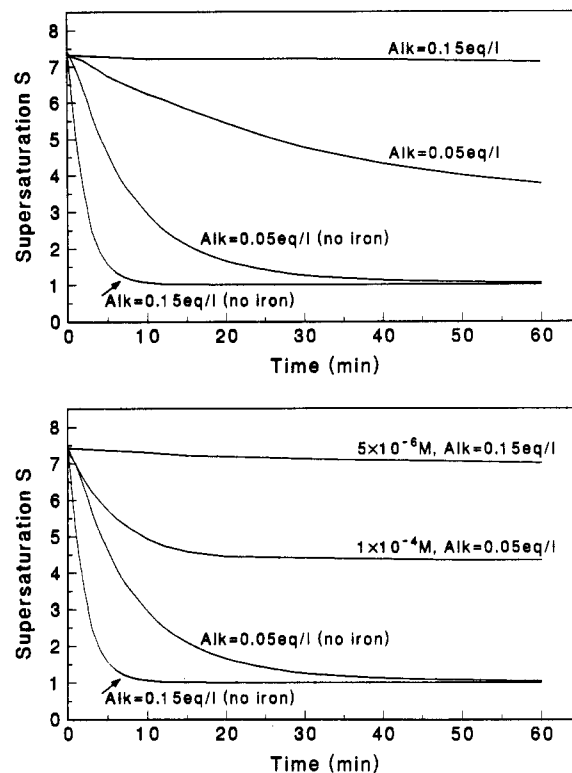
essentially no change in % inhibition occurred. However, at an Fe(II) concentration of 5×10^{-5} M the % inhibition did increase from 44 to 90% when the ionic strength was doubled. Variations in ionic strength do occur during an experiment because the calcium concentration in decreasing. Nonetheless, since they always are less than 2%, even for Fe(II), these variations in ionic strength have negligible effects on calcite inhibition.

Dependence on the Experimental Method. Calcite growth inhibition by iron depends on the experimental method. Adding first the seeds and then the iron to the reactor solution results in less growth inhibition than adding seeds to a solution that already contains a uniform iron concentration. In the former case, at the time the iron is added to the solution some seeds are exposed to a relatively high iron concentration while most of the seeds are exposed to much smaller concentrations. This can result in nonuniform adsorption of iron onto the seeds, which may be the reason for the less effective growth inhibition.

If the calcite seeds are not pre-exposed to iron for a sufficient length of time before the solution is made supersaturated with respect to $CaCO_3$, inhibition effectiveness is decreased. Measurements made using preexposure times of 0, 15, 30, and 60 min showed that 30 min was sufficient for growth inhibition to become independent of preexposure time. Unless otherwise indicated, all experiments reported here had 30 min of exposure of the calcite seeds to iron before supersaturation.

Calcite growth measurements made in the presence of Fe(III) were usually very reproducible. However, calcite growth measurements made in the presence of Fe(II) were somewhat less reproducible. The variability of results may be due to the very high sensitivity of Fe(II) to traces of oxygen. Although precautions were taken to remove as

(26) Although solution conditions were chosen to avoid a significant change in pH during calcite precipitation, this was not possible at an alkalinity of 0.05 equiv/L. The pH changed from 7.00 to 6.86 as calcite precipitation progressed. This change in pH certainly influenced the precipitation process and also increased the equilibrium calcium concentration from 6×10^{-4} to 8×10^{-4} M.

much oxygen as possible, it is not likely that the solution was totally free of it. Furthermore, during the preparation of the iron solution, dissolved Fe(II) is exposed to laboratory air for a short period of time. Small variations in the experimental procedure could cause the amounts of Fe(II) which oxidize to Fe(III) to be different, and thus be the cause of the observed differences in growth curves under otherwise identical conditions.

Discussion

Calcite seeds have sites on the seed surface at which calcium and carbonate ions incorporate into the crystalline lattice, resulting in the growth of the seeds. According to commonly accepted crystal growth theory, there are basically three energetically different kinds of sites: kinks, steps, and terraces.[27] Crystal growth takes place as a successive sequence of the following steps: (1) diffusion of lattice ions from the bulk solution to the crystal surface; (2) adsorption onto the crystal surface on kink, step, or terrace sites; (3) two-dimensional surface diffusion of the adsorbed lattice ion toward an energetically favorable step site; (4) one-dimensional surface diffusion toward an energetically favorable kink site; (5) attachment at the kink by dehydration of the ion (and the site) and thus incorporation of the ion into the crystal lattice. Partial dehydration of the lattice ion may also occur in steps 2–4. Crystal growth can be inhibited by adsorption of ions or molecules that are not lattice ions but are present in solution, usually in trace concentrations (called "poisons").[28] These ions or molecules adsorbed onto growth sites, somehow (energetically and/or sterically) preventing the lattice ions themselves from adsorbing onto growth sites. At moderate supersaturations, i.e., when surface nucleation can be excluded, crystal growth is completely inhibited by a monolayer coverage of all steps. As long as steps are only partly covered by the poison, growth will occur but at a decreased rate.[28] Kink sites are energetically more favored because the lattice ion is attached at three sides to the surface. These sites are "active" even at saturation, and they are the ones which determine the equilibrium concentration; these sites are also the ones most readily blocked by poisons. Parts a and b of Figure 1 showed that increasing the iron concentration causes growth to be increasingly inhibited. At low iron concentrations, most of the kink sites and a fraction of the steps are blocked, resulting in a reduced rate of calcite growth. At higher iron concentrations, almost all kink sites and a larger fraction of the steps are blocked, and the calcite growth rate is further reduced. At sufficiently high iron concentrations, all kink and step sites are blocked, and no growth occurs.

Increasing the supersaturation increases the number of active growth sites; i.e., it increases the number of kinks. With increasing supersaturation any particular site has an increasing probability of being occupied by a lattice ion. It also has an increasing probability that two neighboring sites on a step become occupied, resulting in formation of two new kink sites. Thus, a low iron concentration, sufficient to block most of the kinks and a fraction of the step sites, will inhibit calcite growth effectively only at supersaturations low enough that the probability of creating new kinks is very small and low enough that the fraction of unblocked kink sites also is very small. With increasing supersaturation, the probability that new kinks are created at locations on the steps which are not blocked by iron increases, and the crystals
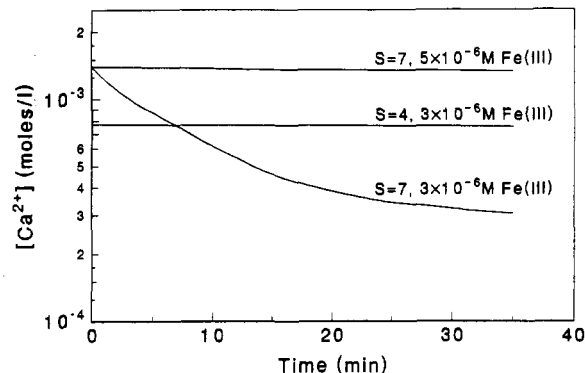

Figure 10. Iron concentrations needed to inhibit calcite growth at two different initial supersaturations.

grow. Our results support this view. Parts a an b of Figure 7 show that iron concentrations of 5×10^{-5} M $FeCl_2$ or 3×10^{-6} M $FeCl_3$ were sufficient to block all growth sites which are active at a supersaturation of 4. Figure 10 shows that, for ferric ions, raising the supersaturation of 7 causes some sites to activate, but increasing the Fe(III) concentration to 5×10^{-6} M is sufficient to block these sites, even at a supersaturation of 7. Furthermore, the number of active growth sites is proportional to the surface area of the seed material. Therefore, as the seed loading is increased, a concentration of iron which results in almost total growth inhibition at low seed loadings will inhibit growth only to a lesser extent. This effect is shown in Figure 8.

This view of inhibition also is consistent with our preexposure time results. Since the number of terrace sites on a crystal surface is much larger than the number of step sites, which, in turn, is much larger than the number of kinks, when calcite seeds are introduced into a solution that contains iron, the iron at first mostly adsorbs onto terrace sites. But, step sites and kinks are stronger adsorbers (ions on a terrace are adsorbed to the seed surface at only one side, whereas they are adsorbed to the surface on two and three sides on steps and kinks, respectively). Thus, over time, more of the iron will migrate to these sites and, since these are the sites at which calcite growth (in the absence of surface nucleation) occurs, the inhibiting effectiveness of iron increases with time until adsorption equilibrium with the kink sites is achieved.

Inhibition by Fe(III) probably involves the interaction of colloidal $Fe(OH)_3$ particles with the calcite surfaces. Precipitation of colloidal $Fe(OH)_3$ particles is known to occur within the first minutes after ferric ions are added to a solution.[29] A rough calculation shows that the ratio of the number of colloidal ferric hydroxide particles to the number of calcite seeds is approximately 10^6. (This calculation assumes that the diameter of the colloidal Fe-$(OH)_3$ particles is about 10 Fe^{3+} ions, an estimate based on the results by Flynn[29]). Since the ratio of the number of $Fe(OH)_2^+$ ions (if in equilibrium with solid ferric hydroxide) to the number of calcite seeds is only about 10^2 (and this ratio is even smaller for the other ionic ferric species), it is much less likely that one of the ionic ferric species is the growth inhibitor. However, a related supplemental mechanism may be that colloidal iron hydroxide particles adsorb onto the calcite surface where they serve as a source of the appropriate ionic Fe(III) species, which is the true growth inhibitor.

Inhibition by Fe(II) is different. Fe^{2+} itself can form a carbonate mineral, siderite ($FeCO_3$), suggesting that Fe^{2+}

(27) Nancollas, G. H. *Adv. Colloid Interface Sci.* **1979**, *10*, 215–252.
(28) Sears, G. W. *J. Chem. Phys.* **1958**, *29* (No. 5), 1045–1048.

(29) Flynn, C. M. *Chem. Rev.* **1984**, *84* (No. 1), 30–41.

ions can adsorb readily onto surface carbonates. Fe^{2+} also forms complexes with carbonate and bicarbonate ions in solution.[30] It has been shown[31] that the $CaCO_3$ surface, if exposed to water, contains the functional groups $\equiv CO_3H$ and $\equiv CaOH$. These functional groups can interact with metal cations, resulting in the formation of a surface complex.[32] This suggests that inhibition by Fe(II) is caused by free Fe^{2+} complexing with surface-bound carbonate or bicarbonate ions.

Figure 6 shows that, in the presence of oxygen, Fe(II) is a better inhibitor than Fe(III), but in its absence Fe(II) is much less effective than Fe(III). Since the concentrations of the various Fe(II) species in solution are orders of magnitude larger than those of Fe(III), much more Fe-(II) is available for adsorption onto the calcite surface. When O_2 is added to the solution, Fe(II) can oxidize to Fe(III). Furthermore, it is known[33] that surface-bound Fe^{2+} oxidizes very readily, much faster than ferrous ions in solution. Since the surface-bound ion already is close to where its inhibiting action occurs, this may be a very effective delivery mechanism.

We reported in the previous paper[1] that Fe(II) is a much better calcite growth inhibitior than Fe(III), in apparent contradiction with the above. The reason for this difference is that pH 8.3 was used in that study. At that pH, the oxidation of Fe(II) to Fe(III) occurs very rapidly. Thus, even in the absence of added oxygen, the data reported previously actually refer to the in situ oxidation of Fe(II). This may well also be the case in the work of Meyer[4] mentioned in the Introduction since the pH in his study was about 8.4. His reported requirement of even lower iron concentrations than reported here is reasonable because both his supersaturation and his seed surface area were much smaller than those we used.

The large enthalpy of hydration of Fe(III) may be related to its efficacy as a calcite growth inhibitor. Lippmann[18] attributed the calcite growth inhibition by Mg^{2+} ions to the larger hydration enthalpy of magnesium in comparison to calcium. Adsorbed Mg^{2+} ions are shielded by a layer of water molecules which are more strongly bonded to magnesium than they are to calcium ($\Delta H^\circ_{hyd} = -473$ and -395 kcal/mol for Mg^{2+} and Ca^{2+}, respectively). He postulated that the carbonate ions are not able to remove the water molecules in order to adsorb onto the growth site, and as a result, these growth sites are blocked by magnesium. If valid, this explanation also may apply to the inhibiting effect of iron since the hydration enthalpies of Fe^{2+} and Fe^{3+} are significantly larger than that of Ca^{2+} ($\Delta H^\circ_{hyd} = -473, -1067,$ and -395 kcal/mol for Fe^{2+}, Fe^{3+}, and Ca^{2+}, respectively[34]).

Summary and Conclusions

Both Fe(II) and Fe(III) are very effective inhibitors of calcite growth. Complete calcite growth inhibition occurs with as little as 5×10^{-6} M $FeCl_3$, whereas about 8×10^{-5} M $FeCl_2$ is required to obtain the same result (solution conditions are an initial calcite supersaturation of 7, pH = 7.00, Alk = 0.15 equiv/L, seed loading 5.0 g/L, and $I = 0.15$ M). The inhibiting effectiveness of Fe(II) increases drastically in the presence of oxygen.

For either oxidation state of iron, the % inhibition increases sharply over a relatively narrow concentration range of iron. Better growth inhibition is observed at larger iron concentrations, smaller supersaturations, smaller seed loadings, and larger alkalinities. Fe(III) inhibits calcite growth better at lower pH values; the effect of pH on growth inhibition was inconclusive for Fe(II) because its very rapid oxidation at pH 8 made it likely that the observed inhibition was due to Fe(III). Variations in ionic strength have negligible effects on inhibition.

Calcite growth inhibition likely is caused by adsorption of an ionic iron species or, in the case of Fe(III), ferric ions or small colloidal ferric hydroxide particles onto the calcite surface. Adsorption of iron onto the calcite surface has two different effects on calcite growth: the growth rate is reduced, and a higher calcium concentration can exist in solution in "equilibrium" with calcite seeds. The presence of iron does not seem to affect the reaction order of calcite growth under the experimental conditions of this study.

(30) Singer, P. C.; Stumm, W. *J. Am. Water Works Assoc.* 1970, *62*, 198–202.

(31) Stipp, S. L.; Hochella, F. M., Jr. *Geochim. Cosmochim. Acta* 1991, *55*, (No. 6), 1723–1736.

(32) Stumm, W. *Chemistry of the Solid-Water Interface*; Wiley-Interscience: New York, 1992; p 57.

(33) See ref 32, Chapter 9.

(34) Noyes, R. M. *J. Am. Chem. Soc.* 1962, *84*, 513–522.