Magnetic Water Treatment: The Effect of Iron on Calcium Carbonate Nucleation and Growth

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Magnetic water treatment devices have been used for many years to prevent scale, primarily $CaCO_3$, from depositing in pipes and boilers. This treatment technique remains controversial, mostly because there is not an accepted scientific explanation for how the devices might work—if indeed they work at all. We have investigated several mechanisms via which magnetic water treatment devices could conceivably work. All involve iron as a key intermediate. Experiments were conducted to test the hypothesis that a particular crystal form of ferric hydroxide effectively induces the heterogeneous nucleation of $CaCO_3$, thus providing competitive sites for $CaCO_3$ precipitation and significantly reducing the amount of scale being deposited. We find that this mechanism is unlikely since none of the seven different synthetic ferric hydroxides tested was an effective heterogeneous nucleator of $CaCO_3$. However, we found that trace concentrations of Fe^{2+} strongly inhibit calcite growth but not aragonite growth and that trace concentrations of Fe^{2+} also inhibit the transformation of aragonite into calcite. A similar effect was observed with Fe^{3+} but to a lesser degree. These experimental results suggest that magnetic water treatment devices may be effective only to the extent that they cause an increase in the Fe^{2+} concentration in treated water and that the Fe^{2+}, in turn, inhibits scale buildup.

Introduction

The buildup of scale deposites inside cooling water pipes and boilers is a costly problem in many industrial processes. Scales are typically formed by materials which become less soluble with increasing temperature and are therefore usually found in water-handling equipment in which the water is heated. Such scale deposits significantly reduce heat-transfer efficiency and can lead to partial or even complete blockage of water flow passages.[1] Once scale deposits are formed, they can be removed by various methods, ranging from washing the pipes and boiler walls with acid to actually chipping away the scale with a chisel; however, it is best to prevent scale precipitation in the first place.

Several techniques are commonly used to prevent or control scale buildup. One of the most controversial scale prevention methods is magnetic water treatment. Magnetic water treatment consists of passing water through a strong permanent magnet installed in or on a feed pipeline. Later, when the water is heated in a heat exchanger or a boiler, it presumably loses its tendency to deposit hard scale on the hot surfaces. The deposits that do form are reported to have a loose, nonadhering texture and to be easy to remove. Several hours may elapse between the time when the water is exposed to the magnetic water treatment device and the time when it is heated, yet it is claimed that the devices are still effective in preventing scale. This phenomenon is called the "memory effect".[2,3]

Manufacturers of these devices admit that they are not always effective. Furthermore, research groups that have evaluated magnetic water treatment devices in a controlled setting have concluded that the technique has no effect on scale deposition.[4,5] Despite general skepticism about whether or not magnetic water treatment works, the devices have been on the market for about 60 years, continue to be manufactured by many companies, and are popular. A number of researchers have suggested possible mechanisms to explain how magnetic water treatment might act to reduce scale buildup in pipes. One is that a magnetic field somehow alters the properties of water.[6] This idea has been exhaustively examined, and no theoretical or experimental work has been able to substantiate it.[7,8] Another is that a magnetic field directly affects precipitation of scale-forming salts.[9] This mechanism is unlikely for two reasons. First, the energy of interaction between a magnetic field of a few thousand gauss and a single diamagnetic ion (such as Ca^{2+}) is several orders of magnitude smaller than kT. Thus, any magnetic field effects would be negligible compared to effects due to molecular collisions. Second, if it were possible for a magnetic field to influence scale precipitation directly, the water would have to be supersaturated with respect to the scale at the time of exposure to the magnetic field. In most installations, this is not the case; the magnetic water treatment device is placed upstream of heating equipment, at a place where the water may be *under*saturated with respect to the scale. The water becomes supersaturated later, upon heating.

Since calcium carbonate is the most common scale-forming mineral, many studies have focussed on magnetic field effects on $CaCO_3$ precipitation. When $CaCO_3$ precipitates out of solution onto the surface of a heat exchanger or boiler, it is usually as a mixture of calcite and aragonite. Calcite grows in masses of rhombohedral crystals (see Figure 1), whereas aragonite grows in loose bundles of needlelike crystals (see Figure 2). The predominance of one crystalline phase over the other depends on conditions such as pH, temperature, nature of the metal

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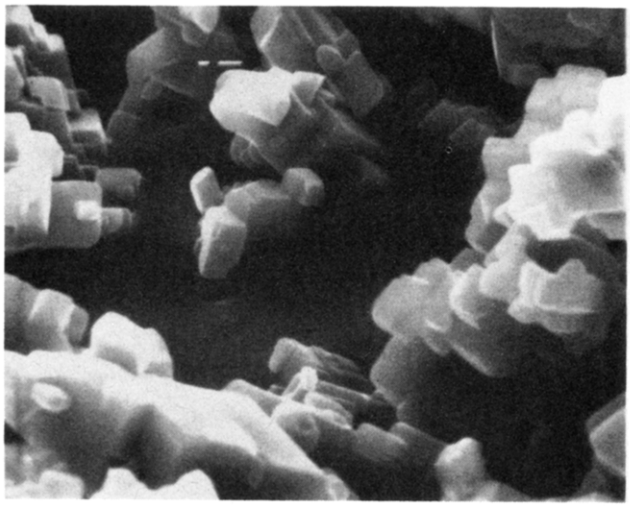

Figure 1. Scanning electron micrograph of synthetic calcite crystals, magnified 4700×.

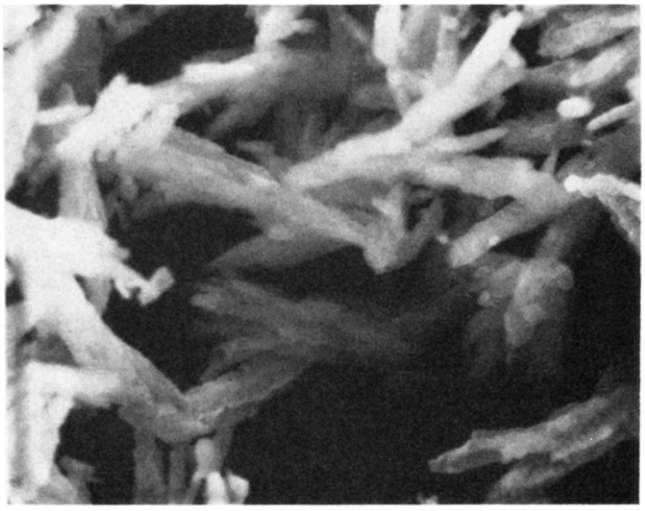

Figure 2. Scanning electron micrograph of synthetic aragonite crystals, magnified 6700×.

substrate, and ions present.[10] Calcite is thermodynamically stable relative to aragonite, but aragonite often is the first phase to precipitate out of solution—particularly at elevated temperatures such as those encountered in a boiler or a heat exchanger. Over time, aragonite may recrystallize into calcite.[11] This recrystallization, in addition to the natural ripening and growth of existing calcite crystals, makes scale deposits cement together to form hard, compact, crystalline encrustations.

Ellingsen and Kristiansen[12] measured rates of $CaCO_3$ precipitation from samples of Norwegian ground water that had first been exposed to a magnetic field and then deliberately made supersaturated with respect to $CaCO_3$ by subsequent addition of $Ca(OH)_2$. They observed that $CaCO_3$ precipitated more readily in the samples that were exposed to progressively stronger magnetic fields. As mentioned earlier, it is very unlikely that the magnetic field acted directly on the $CaCO_3$; however, Ellingsen's work is consistent with several plausible mechanisms which involve the interaction of $CaCO_3$ with an intermediate substance. Because it is found in most waters and because it is able to interact strongly with magnetic fields, we chose to investigate a number of mechanisms which involve iron as the key substance in magnetic water treatment.

The first mechanism investigated was that magnetic water treatment devices promote formation of a large number of ferric hydroxide crystals of a particular crystalline form. These tiny, insoluble, ferric hydroxide seed crystals are then carried along with the water to a boiler or heat exchanger, where the water is heated. Since $CaCO_3$ becomes less soluble with increasing temperature, the hot water becomes supersaturated with respect to $CaCO_3$, and $CaCO_3$ precipitates. The ferric hydroxide seed crystals in the bulk water provide sites for heterogeneous nucleation of $CaCO_3$—sites which compete with equipment walls. Thus, these ferric hydroxide seeds remove from solution much of the $CaCO_3$ which would ordinarily deposit on the walls of the hot water handling equipment.

Such a mechanism is physically appealing and furthermore is consistent with observations reported by manufacturers of magnetic water treatment devices. The "memory effect" is explained by the formation of stable, insoluble, ferric hydroxide crystals. Reports that the scale deposits which do form appear as a nonadherent sludge are also consistent with the mechanism described above.

There are several ways in which a magnetic field could produce ferric hydroxide of a particular form. The following mechanism was proposed by Zubarev.[13] Since ferric hydroxide is extremely insoluble near neutral pH (its solubility is only about 10^{-17} M Fe^{3+} at pH 7), slight changes in the water's pH could cause the water to become highly supersaturated with respect to ferric hydroxide. The result could be the nucleation of a large number of submicroscopic, amorphous, ferric hydroxide gel particles. Upon exposure to a magnetic field, these amorphous ferric hydroxide particles would crystallize into geothite (α-FeOOH). Zubarev argued that since goethite is isomorphic with aragonite (one of the common $CaCO_3$ polymorphs), the goethite particles would provide extremely effective sites for heterogeneous nucleation of $CaCO_3$. We conducted a number of experiments to determine if a strong magnetic field caused an amorphous-to-crystalline phase transition in ferric hydroxide but observed no effect. Furthermore, it has been reported that so-called "amorphous" ferric hydroxide is actually microcrystalline and already occupies an energy minimum,[14] making it unlikely that a magnetic field could alter its structure. However, there are other ways in which a magnetic field could influence crystalline ferric hydroxide formation.

Ferric hydroxide can exist in several different crystalline forms, depending on the conditions which led to its precipitation in the first place.[15] Various pathways of formation are followed during the oxidation of ferrous iron (Fe^{2+}) and during the hydrolysis of ferric iron (Fe^{3+}). A sequence of nucleation events occurs during the formation of the ferric hydroxide end products. Sometimes, metastable intermediate compounds called "green rusts" or "green solution complexes" are nucleated. These compounds are precursors for minerals like magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3).

Many of the ferric hydroxide minerals differ from each other only subtly. An interesting example is the δ-FeOOH/δ'-FeOOH pair. Both compounds have identical crystal structure, but in δ-FeOOH, Fe^{3+} is arranged evenly on the octahedral sites of the crystal lattice, whereas in δ'-FeOOH, Fe^{3+} has a random arrangement. The result of the ordering of the Fe^{3+} in δ-FeOOH is that δ-FeOOH

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is strongly ferrimagnetic, but δ'-FeOOH is not.[16]

The preferred pathway of formation of ferric hydroxide is sensitive to O_2 concentration, iron concentration, pH, temperature, and ions present in solution. In such unstable systems, in which intermediate species are in equilibrium neither with their precursors nor successors, a strong magnetic field could perhaps influence the reaction pathway. The result could be the nucleation of a large number of crystals of a particular form of ferric hydroxide—a form not normally encountered at the system temperature, pH, etc., a crystalline form which would be an especially effective heterogeneous nucleator for calcium carbonate.

Yet another hypothesis concerns a corrosion process. Recently, there has been interest in determining the effects of magnetic fields on electrochemical reactions occurring at metal/solution interfaces. Fahidy[17] and Kelly[18] have conducted theoretical and experimental studies to examine whether or not an externally applied magnetic field can influence electrochemical processes occurring at the metal/solution interface and report positive results. In fact, Busch and co-workers[19] made carefully controlled experiments to determine if aqueous conducting solutions flowing through actual magnetic water treatment devices could give rise to significant induced voltages and currents. They reported positive results[20] and proposed that the corrosion of iron could be accelerated by a magnetic water treatment device. Again, in such a scenario, seed crystals of a particular form of insoluble ferric hydroxide might form as a result of exposure to the field and act as heterogeneous nuclei for $CaCO_3$.

To investigate these hypotheses, we undertook a research program that had two aspects. One was to determine which, if any, of the many ferric hydroxide minerals is an effective heterogeneous nucleator for $CaCO_3$; the other was to determine whether or not a magnetic field can promote the formation of this compound. This paper presents both of these aspects, but its major focus is on another mechanism, a mechanism that was suggested by an observation during these experiments.

We observed that adding very low concentrations of Fe^{2+} drastically decreases the rate of growth of calcite crystals but has little effect on the rate of growth of aragonite crystals. Our experiments also showed that trace amounts of Fe^{2+} strongly inhibit the natural transformation of aragonite into calcite.

The literature abounds with papers examining the effect of impurities such as Mg^{2+} ions and phosphonate scale inhibitors on $CaCO_3$ nucleation and growth. Marine geologists are interested in the role of Mg^{2+} in determining the composition and morphology of mollusk shells and marine rocks,[21,22] and engineers are interested in the interaction between phosphonate compounds and scale-forming minerals.[23] Less attention has focused on effects of iron impurities; however, a number of investigators have made observations related to those made in our laboratory. Rudert and Müller[10] reported that a higher aragonite/calcite ratio occurs in $CaCO_3$ scale that precipitates on steel piping than on any of the other materials they investigated (including copper, brass, PVC, aluminum, and zinc piping). Peters and Stevens[24] observed a preponderance of aragonite deposits on the surface of a crystallizer when trace amounts of $FeSO_4$ were present. Hasson and Bramson[25] reported a 40% decrease in the $CaCO_3$ scaling rate of a test heat exchanger when about 1.3 ppm of Fe^{2+} was present. Meyer[26] reported that the presence of only 10^{-8} M Fe^{2+} was sufficient to cause a twofold decrease in the initial growth rate of calcite from supersaturated solution.

As a result both of our experiments and of work done by other investigators, there is ample evidence to suggest that iron can reduce scale buildup by inhibiting calcite growth rather than by causing $CaCO_3$ to nucleate. It is not clear whether this phenomenon is linked to magnetic water treatment; perhaps magnetic water treatment devices are effective only to the extent that they increase the concentration of Fe^{2+} in the boiler water solution, and perhaps it is the Fe^{2+} which is responsible for inhibiting scale buildup.

Experimental Procedures and Results

All chemicals used in the preparation of seed crystals and solutions were Fisher reagent grade. All solutions were prepared using 18 MΩ deionized water. $NaHCO_3$ and $CaCl_2$ solutions were filtered through 0.22-μm Nylon filter membranes to remove as much dust and lint as possible. All glassware was Pyrex, washed with 1 M HCl, and repeatedly rinsed with 18 MΩ deionized water.

Calcite seed crystals were prepared by adding an excess of $CaCO_3$ powder to deionized water and allowing the mixture to digest for several months prior to use. Aragonite seed crystals were prepared by using the method of Wray and Daniels.[27] The resulting calcite and aragonite crystals were separated from their respective solutions by vacuum filtration through a 0.22-μm Nylon membrane, washed with 10 5-mL portions of acetone, air-dried, and placed in capped glass vials. Seeds from the *same* batches were used in all experiments. Scanning electron micrographs of these aragonite and calcite crystals are shown in Figure 1 and 2.

Slurries of calcite (or aragonite) seed crystals were prepared immediately before use in an experiment by suspending 0.050 g of the dry crystals in 1.0 mL of deionized water and injecting the entire volume of slurry into the reaction vessel with a micropipet.

The reaction vessel was a 250-mL jacketed Pyrex beaker, connected to a circulating water bath thermostated at 25.0 ± 0.1 °C. For each experiment, after thorough cleaning, the beaker was filled with 100 mL of 0.15 M $NaHCO_3$ solution. (Using this $NaHCO_3$ concentration ensured that the solution's ionic strength remained essentially constant at 0.15 M, even upon addition of small amounts of other ionic species.) Then 3.6% CO_2 in N_2 was rapidly bubbled through it, causing the $NaHCO_3$ solution to equilibrate with this known partial pressure of CO_2. The solution was stirred at 450 rpm with a glass impeller. A Teflon cover, with holes drilled in it to support sensing electrodes, minimized gas exchange with the atmosphere.

The pH of the solutions was monitored continuously to a precision of 0.001 pH units by using a gel-filled combination pH electrode with automatic temperature com-

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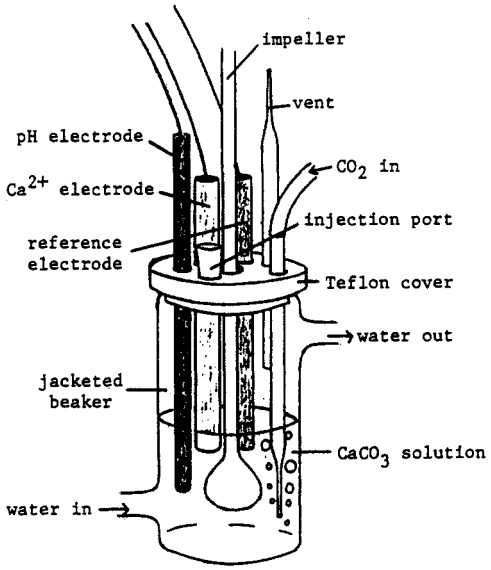

Figure 3. Sketch of reaction vessel used in crystal seeding experiments.

pensation and a Fisher Accumet 805MP pH meter connected to a strip chart recorder. Equilibrium between the $NaHCO_3$ solution and the CO_2 was confirmed by observing that the pH reading became constant with time. CO_2 bubbling was continued throughout the entire experiment. A sketch of the reaction vessel is shown in Figure 3.

Supersaturation with respect to $CaCO_3$ was accomplished by adding a small, known volume of 0.10 M $CaCl_2$ to the $NaHCO_3$ solution with a micrometer syringe. Ca^{2+} concentration was measured by using an Orion Ca^{2+} selective electrode and Ag/AgCl reference electrode and monitored continuously with a strip chart recorder. The Ca^{2+} electrode was calibrated by adding a series of known volumes of $CaCl_2$ solution with a micrometer syringe under conditions *identical* with those of the actual experiments.

The $CaCO_3$ supersaturations reported here are the ratio of the initial Ca^{2+} concentration to the equilibrium Ca^{2+} concentration, i.e.

$$S = [Ca^{2+}]/[Ca^{2+}]_{eq} \quad (1)$$

The equilibrium Ca^{2+} concentration was determined by seeding a supersaturated solution with a large number of calcite seeds and measuring the free Ca^{2+} concentration after it stopped decreasing with time.

Under the experimental conditions described above, the pH of the solutions remained constant at 8.30 during the entire course of an experiment. It varied briefly by 0.02 to 0.08 pH unit when $CaCl_2$ was added and then returned to within 0.01 pH unit of its original set point. It also varied briefly by no more than 0.02 pH unit upon seeding with calcite and then returned to the original set point (see Figure 4).

1. Effect of Ferric Hydroxide on $CaCO_3$ Nucleation and Growth. To test whether a particular form of ferric hydroxide is an especially effective heterogeneous nucleator of $CaCO_3$, a variety of ferric hydroxides were synthesized by using recipes from the literature. Many of these minerals are either naturally abundant or common corrosion products. Hematite (α-Fe_2O_3) and akaganéite (β-FeOOH) were synthesized by the method of Matijević and Scheiner,[15] goethite (α-FeOOH) by the method of Atkinson et al.,[28] lepidocrocite (γ-FeOOH) by the method of Bernal et al.,[29] δ-FeOOH by the method of Glemser and Gwinner,[30] and magnetite (Fe_3O_4) by the method of Feitknecht.[31] In addition, ferrihydrite, or "amorphous ferric hydroxide" ($Fe(OH)_3 \cdot nH_2O$), was prepared by using a modification of Duffy's method.[7] All of the iron hydroxide minerals were washed repeatedly with deionized water until the washes reached pH 7. To limit the crystal size range, the final wash was allowed to settle for 20 min and decanted. The supernate was then centrifuged at 3400 rpm for 1 h. The concentrated slurries at the bottoms of the centrifuge tubes were then collected for use as seed crystals. An estimate of the size range of the crystals in the slurry, calculated by using Stoke's law, was 0.08–5 μm in diameter.

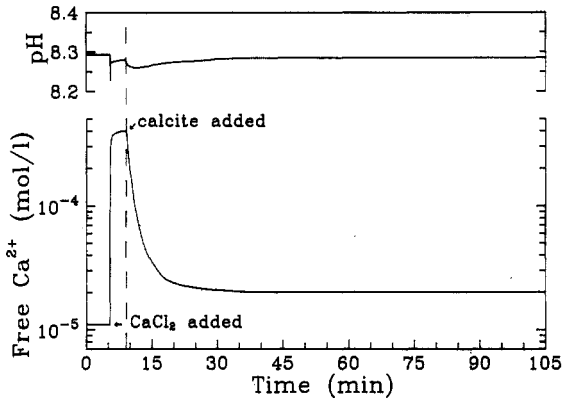

Figure 4. Tracing of chart recorder output, showing free Ca^{2+} concentration and pH with time.

The effectiveness of these solid ferric hydroxide minerals as heterogeneous nuclei for $CaCO_3$ was tested by adding several drops of a particular type of ferric hydroxide slurry (or a mixture of several slurries) to a supersaturated $CaCO_3$ solution and monitoring the free Ca^{2+} concentration over time. Enough ferric hydroxide was added to make the solutions visibly turbid. The $CaCO_3$ supersaturation used for these experiments was 25 and was obtained by adding 0.40 mL of 0.10 M $CaCl_2$ to 100 mL of 0.15 M $NaHCO_3$.

In the absence of any seed nuclei, solutions at this supersaturation usually remain stable for more than 4 h; upon addition of large numbers of extremely effective nuclei (e.g., calcite seeds), a very rapid decrease in free Ca^{2+} concentration occurs, indicating growth on the seeds. (This is shown in Figure 4—a tracing of an actual chart recorder output in which calcite seeds were used.)

The result was that *none* of the solid ferric hydroxide minerals which we synthesized caused a significant decrease in free Ca^{2+} concentration when introduced into the supersaturated $CaCO_3$ solutions. However, scratching the side of the glass reaction vessel with a glass stirring rod did cause the free Ca^{2+} concentration to decrease with time. Adding ground silica had the same effect, indicating that tiny bits of silica are significantly better as heterogeneous nuclei than are goethite, hematite, or any of the other ferric hydroxides under investigation.

When calcite seeds were introduced into supersaturated $CaCO_3$ solutions that also contained ferric hydroxide particles, rapid decreases in free Ca^{2+} concentration occurred. The rates of $CaCO_3$ precipitation were approximately the same as those in solutions that contained no iron. This demonstrated that growth on calcite seeds is neither induced nor significantly inhibited by any of the ferric hydroxide minerals under investigation.

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As mentioned earlier, most of the ferric hydroxide minerals that were synthesized are either common corrosion products or naturally abundant. During the formation of these compounds, several metastable intermediate complexes are produced—"green rusts", for example. Under the appropriate conditions, a magnetic field could perhaps alter the pathway of formation of ferric hydroxide—the result being the nucleation of a compound that strongly affects nucleation and growth of $CaCO_3$.

2. Effect of Oxidation Intermediates on $CaCO_3$ Nucleation and Growth. To test whether intermediates or end products formed during the oxidation of Fe^{2+} to Fe^{3+} in the presence of a magnetic field can be effective heterogeneous nuclei for $CaCO_3$, the reaction vessel was placed between the pole faces of a Model V-4004 Varian electromagnet. A magnet current of 3 A and a pole face separation of 3 in. resulted in a field strength of 3.75 kG (as measured with a Model 4048 F. W. Bell Gaussmeter). This field could be zeroed out (to less than 5 G—a negligible field since the magnetic field of the earth is about 0.5 G) by repeatedly reversing the current polarity while gradually lowering the current.

The experiments were similar to those described in the previous section; 1.0 mL of a freshly prepared 0.010 M $FeSO_4$ solution was added to 100 mL of 0.15 M $NaHCO_3$ in the jacketed reaction vessel. This resulted in a total Fe^{2+} concentration of about 5.6 ppm (mg/L)—a concentration not atypical for ground water.[32] Since the volume of $FeSO_4$ added was only 1% of the total solution volume, no significant dilution occurred upon its addition nor were the CO_2 equilibria affected. The CO_2 gas mixture that was bubbled through the solution contained 3.6% CO_2, 23% O_2, and the balance N_2. As oxidation of the Fe^{2+} proceeded, the solution took on an orange tint as colloidal ferric hydroxide formed.

About 1 h after addition of the $FeSO_4$, sufficient $CaCl_2$ was added to result in a $CaCO_3$ supersaturation of 25. No decrease in free Ca^{2+} concentration was observed, even after about 2 h. Sufficient extra $CaCl_2$ was then added to increase the $CaCO_3$ supersaturation to 60. Still, no detectable decrease in free Ca^{2+} concentration occurred within the next hour. Finally, calcite seeds were introduced. Normally, upon addition of calcite to a supersaturated $CaCO_3$ solution, the free Ca^{2+} concentration rapidly decreases with time, but in this case the free Ca^{2+} concentration did not decrease. It appeared that the precipitation of $CaCO_3$ was strongly inhibited by the iron.

By systematically removing, one at a time, the possible causes of this inhibition, e.g., the magnetic field, the O_2 (to minimize the concentration of trivalent iron species), and the SO_4^{2-} anion ($FeCl_2$ was substituted for $FeSO_4$), we determined that Fe^{2+} was the species responsible for inhibiting calcite growth. The following sections describe experiments which show that trace amounts of Fe^{2+} inhibit calcite growth, but not aragonite growth, and that trace amounts of Fe^{2+} inhibit the recrystallization of aragonite into calcite. Experiments also show that Fe^{3+} inhibits calcite growth but not to the extent observed with Fe^{2+}.

3. Effect of Fe^{2+} on Calcite and Aragonite Growth. The technique used to examine the effect of Fe^{2+} on calcite and aragonite growth was similar to the procedure used to determine the effect of solid ferric hydroxide on $CaCO_3$ nucleation and growth. As in previous experiments, all experiments were conducted at 25 °C, at a solution pH of 8.30, and at a solution ionic strength of 0.15 M.

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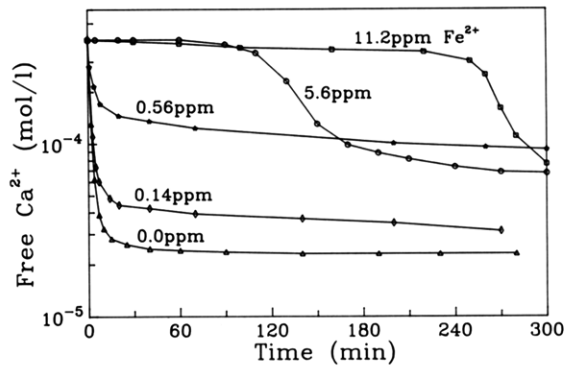

Figure 5. Effect of varying amounts of Fe^{2+} on calcite growth at a $CaCO_3$ supersaturation of 25.

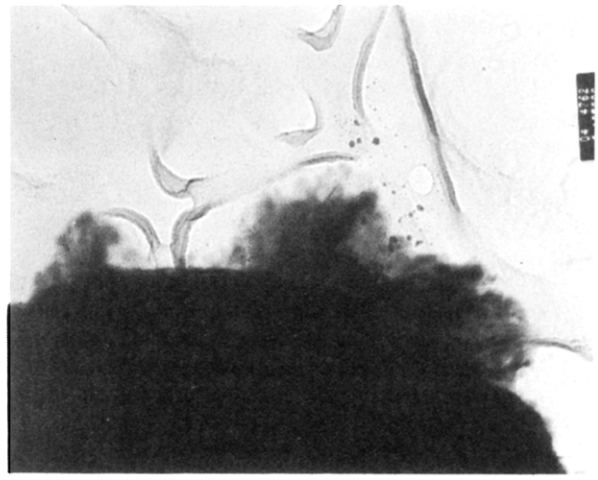

Figure 6. Transmission electron micrograph showing iron-rich surface percipitate on calcite seed crystals. Sample was removed during an experiment to determine the effect of 5.6 ppm Fe^{2+} on calcite growth.

Fresh solutions of $FeSO_4$ were prepared immediately before use in the experiments. An $FeSO_4$ solution of appropriate concentration (1.0 mL) was added to the $NaHCO_3$ solution shortly before addition of $CaCl_2$. After addition of $CaCl_2$ (causing $CaCO_3$ supersaturation), a slurry of either calcite or aragonite seeds was added and the resulting decrease in free Ca^{2+} concentration continuously monitored. Total Fe^{2+} concentrations ranged from 0.0 to 56 ppm.

Figure 5 shows the effect of varying amounts of Fe^{2+} on the growth rate of *calcite* from a solution at a $CaCO_3$ supersaturation of 25. These measurements show that Fe^{2+}, at concentrations of 5.6 ppm and above, *very strongly inhibits* the initial growth rate of calcite. Lower Fe^{2+} concentrations appear to retard the rate at which the free Ca^{2+} concentration approaches its equilibrium value but do not strongly influence the initial growth rates.

Chemical speciation was obtained by solving the chemical equilibrium relations with a computer program called MINEQL[33] with tabulated thermodynamic solubility data. Results of these calculations gave an equilibrium solubility of $FeCO_3$ of about 0.1 ppm Fe^{2+}. Since a concentration of 5.6 ppm Fe^{2+} was used, this meant that the system was highly supersaturated with respect to $FeCO_3$ and suggested that calcite growth is inhibited by precipitation of $FeCO_3$ on the calcite surface. Indeed, upon examination of a small sample of the reaction suspension from one of the experiments with a transmission electron microscope, a partial

(33) Westall, J. C.; Zachary, J. L.; Morel, F. M. M. Technical Note No. 18, Dept. of Civil Engineering, MIT, Cambridge 1976.

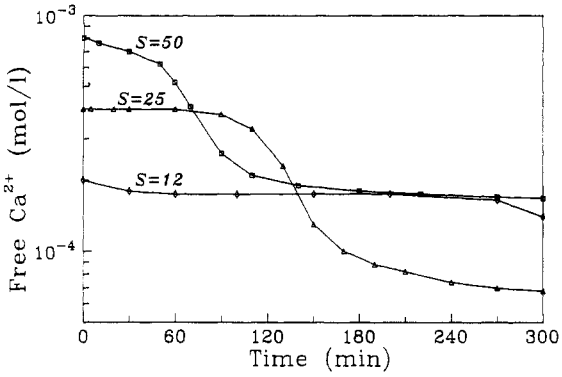

Figure 7. Effect of 5.6 ppm Fe^{2+} on calcite growth at varying $CaCO_3$ supersaturations.

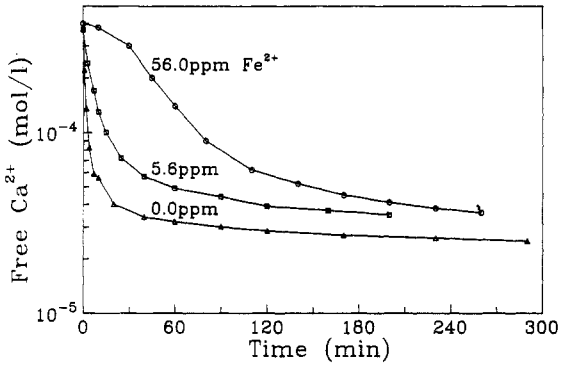

Figure 8. Effect of varying amounts of Fe^{2+} on aragonite growth at a $CaCO_3$ supersaturation of 25.

coating of an iron-rich material on the surfaces of the calcite seeds was observed. This can be seen in Figure 6. The large, black region at the bottom is a calcite crystal; the fainter, dark gray regions are iron-rich deposits.

As can be seen in Figure 5, the curves showing free Ca^{2+} concentration with time have pronounced sigmoidal shapes when 5.6 ppm and higher concentrations of Fe^{2+} are present. With increasing Fe^{2+} concentration, the time at which the inflection point occurs also increases. This suggests that the initial growth rate of calcite is strongly inhibited, because $FeCO_3$ forms as a surface precipitate, and until sufficient Fe^{2+} is consumed, Ca^{2+} cannot compete effectively for growth sites on the crystal. However, at very high $CaCO_3$ supersaturations, the system is overwhelmed with Ca^{2+}, and the Fe^{2+} loses its effectiveness in competing for growth sites on the calcite. This is demonstrated in Figure 7, in which the effect of 5.6 ppm Fe^{2+} on calcite growth is shown at $CaCO_3$ supersaturations ranging from 12 to 50. With increasing $CaCO_3$ supersaturation, the time at which the inflection occurs in the precipitation curves decreases. It should be mentioned that over time, whether or not Fe^{2+} is present, the free Ca^{2+} concentration gradually approaches a value close or equal to its equilibrium value. This indicates that $CaCO_3$ controls the solubility of the system and that Fe^{2+} affects only the kinetics of $CaCO_3$ precipitation.

The effect of Fe^{2+} on *aragonite* growth was very different from its effect on calcite growth. Results from experiments in which aragonite seeds were used are shown in Figure 8. Fe^{2+} concentrations ranged from 0 to 56 ppm, and all experiments were at a $CaCO_3$ supersaturation of 25. Figure 8 shows that a concentration of Fe^{2+} (5.6 ppm) which is sufficient to inhibit completely the initial growth rate of calcite only slightly affects aragonite growth. Even 56 ppm of Fe^{2+} (a 10-fold increase in Fe^{2+} concentration) does not significantly inhibit aragonite growth.

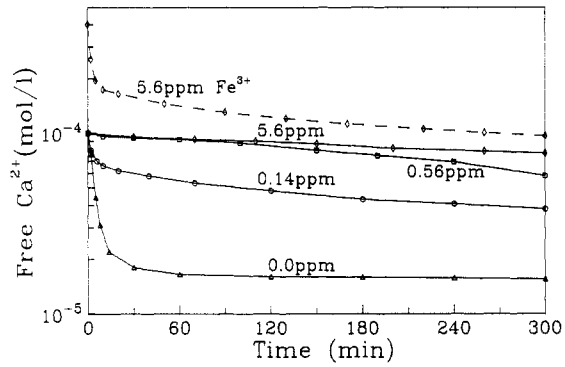

Figure 9. Effect of varying amounts of Fe^{3+} on calcite growth at a $CaCO_3$ supersaturation of 6, except for the dashed line, for which the supersaturation was 25.

Since these experiments show that Fe^{2+} preferentially inhibits calcite but not aragonite growth, they suggest that Fe^{2+} should also inhibit the spontaneous recrystallization of calcite from aragonite. We conducted recrystallization experiments to investigate this possibility (described below) and did obtain this result.

4. Effect of Fe^{3+} on Calcite Growth. Experiments to investigate the effect of Fe^{3+} on calcite growth were conducted in a manner identical with that described in the previous section. Instead of $FeSO_4$, $FeCl_3$ was used to prepare the iron solutions. Fe^{3+} at 5.6 ppm (the same concentration as the Fe^{2+} concentration that strongly inhibited the initial growth rate of calcite) showed a much weaker inhibiting effect on calcite growth. This same Fe^{3+} concentration (5.6 ppm) had no effect on aragonite growth.

By lowering the $CaCO_3$ supersaturation from 25 to 6, we were able to observe a fairly strong and reproducible inhibiting effect on calcite growth due to trace concentrations of Fe^{3+}. These results are shown in Figure 9. Because the effect of Fe^{2+} on calcite growth is much stronger than the effect of Fe^{3+}, attention was focused on determining how Fe^{2+} influences the transformation of aragonite to calcite.

5. Recrystallization of Aragonite to Calcite. The aragonite seeds used in these experiments were from the same batch as those used in the seeded growth experiments. The filtered aragonite mother liquor from the seed preparation had been set aside for use in these recrystallization experiments. The pH of the aragonite mother liquor was 8.1. To examine the effect of Fe^{2+} on the rate of recrystallization of aragonite into calcite, 0.150 g of dry aragonite crystals was added to each of 15 clean, dry, glass vials. To each of five of the vials was added 10.0 mL of aragonite mother liquor containing 10.0 ppm Fe^{2+}, to each of five other vials was added 10.0 mL of the aragonite mother liquor containing 1.0 ppm Fe^{2+}, and to the last five vials was added 10.0 mL of aragonite mother liquor containing no Fe^{2+} (controls). The vials were capped, placed in an ultrasonic bath for about 1 min to break up clumps of aragonite crystals and to disperse the slurry uniformly, and then placed in an oven thermostated at 53 ± 2 °C. A temperature of 53 °C was chosen because recrystallization would then occur in a reasonable amount of time (at 25 °C it can take from months to years).[21] Furthermore, 53 °C is closer to the temperature in a boiler or heat exchanger than is 25 °C.

At selected times, a set of three vials (one containing 10.0 ppm Fe^{2+}, one containing 1.0 ppm Fe^{2+}, and one control) was removed from the oven, and the vials were lightly shaken to resuspend the settled crystals. The samples were washed from their vials with deionized water and collected by vacuum filtration onto 0.22-μm Nylon filter membranes.

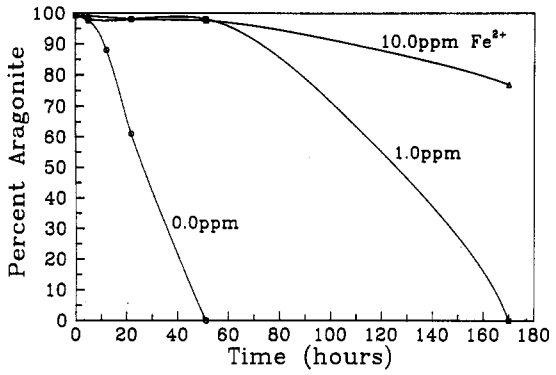

Figure 10. Effect of varying amounts of Fe^{2+} on the rate of recrystallization of aragonite into calcite. The temperature was 53 °C.

To dry the crystals, the samples were washed with a small amount of acetone. Precautions were taken to ensure that the entire crystal slurry was washed from its vial so that no preferential sampling of calcite or aragonite occurred. A small amount of each dried sample was resuspended in several drops of 200 proof ethanol, agitated in an ultrasonic bath for 5 s, and then placed dropwise onto a glass microscope slide for powder X-ray diffraction analysis.

X-ray diffraction measurements were made by using a Phillips Model XRG-3100 powder diffractometer with Cu Kα radiation. The method used to determine the relative weight percents of aragonite and calcite in the samples was essentially the same as the method developed by Davies and Hooper.[34] Figure 10 shows the percent of aragonite in the crystal slurries as a function of time, in the presence of 0.0, 1.0, and 10.0 ppm Fe^{2+}. It shows that 1.0 ppm Fe^{2+} strongly inhibits the rate of transformation of aragonite into calcite; 10.0 ppm Fe^{2+} inhibits this transformation even more strongly. Only after 170 h (over 6 days) was a significant amount of calcite detected in the samples that contained 10.0 ppm Fe^{2+}.

This experiment shows that Fe^{2+}, in trace concentrations, very effectively inhibits the transformation of aragonite to calcite, at near neutral pH and 53 °C.

Summary and Conclusions

A plausible mechanism explaining magnetic water treatment is the introduction of ferric hydroxide seed crystals into the water, thus providing sites for heterogeneous nucleation of $CaCO_3$—sites that compete with equipment walls. To investigate this mechanism, a large number of ferric hydroxide compounds were synthesized and tested for their effectiveness as heterogeneous nuclei for $CaCO_3$. However, *none* of the ferric hydroxide minerals investigated—goethite, hematite, lepidocrocite, akaganéite, magnetite, δ-FeOOH, or ferrihydrite—was particularly effective at inducing nucleation of $CaCO_3$ from supersaturated solution. In fact, silica particles were better heterogeneous nuclei for $CaCO_3$ than any of them.

During experiments to determine if any of the species produced during the oxidation of Fe^{2+} to Fe^{3+} in the presence of a magnetic field could induce $CaCO_3$ precipitation, we found that Fe^{2+} was an extremely good *inhibitor* of calcite growth. Although the precise mechanism whereby Fe^{2+} inhibits calcite growth is not known, experiments and calculations suggest that $FeCO_3$ precipitates onto the calcite surfaces, blocking growth sites, and thus reduces the rate at which Ca^{2+} is removed from solution as $CaCO_3$. A similar effect was observed with Fe^{3+}, but to a lesser degree. Since trace concentrations of Fe^{2+} inhibit calcite growth, experiments were conducted to determine the effect of Fe^{2+} on aragonite growth. The result was that Fe^{2+} had little or no inhibiting effect on aragonite growth.

These observations are consistent with our suggestion that Fe^{2+} can reduce scale buildup in pipes. Scale deposits usually contain both aragonite and calcite, but aragonite grows in bundles of long, neelde-shaped crystals that might be more easily removed from equipment walls (by conventional blow-down procedures) than the more tenacious calcite deposits. The natural dissolution of aragonite and its recrystallization into the thermodynamically stable calcite makes existing calcite scale even stronger. Recrystallization experiments show that in the presence of Fe^{2+}, the spontaneous transformation of aragonite to calcite is inhibited.

Our experimental observations may explain the reported action of magnetic water treatment devices as scale preventives. Magnetic water treatment devices could induce the liberation of iron into the water, and scale growth thus could be inhibited. This mechanism is both physically reasonable and consistent with all observations made in the field. However, whether and how passage of water through a magnetic water treatment device can result in liberation of the necessary iron to inhibit scale growth is still an open question.

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Registry No. $CaCO_3$, 471-34-1; Fe^{2+}, 15438-31-0; Fe^{3+}, 20074-52-6; calcite, 13397-26-7; aragonite, 14791-73-2; ferric hydroxide, 1309-33-7.

(34) Davies, T. T.; Hooper, P. R. *Mineral. Mag.* **1963**, *33*, 608.