Applied Geochemistry, Vol. 7, pp. 185–190, 1992
Printed in Great Britain

0883–2927/92 $5.00+.00
Pergamon Press Ltd

Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature

JANET GREENBERG and MASON TOMSON
Department of Environmental Science and Engineering, Rice University, Houston, TX 77251, U.S.A.

(*Received* 28 *May* 1991; *accepted in revised form* 27 *November* 1991)

Abstract—In this research, aqueous ferrous carbonate, $FeCO_3$, was studied in a batch reactor designed to maintain rigorously anoxic conditions in the absence of reducing agents. The precipitation kinetics were measured from 27 to 80°C and were found to be approximately 100 times slower than any measured precipitation rate previously reported for a 2:2 sparingly soluble salt. Dissolution kinetics results are reported at 26 and 60°C. Solubility product constant measurements are reported from 25 to 94°C. Statistical analyses and application of the Nielsen theory of surface reaction rates suggest that the precipitation of ferrous carbonate is surface reaction rate limited with an Arrhenius activation energy of 108.3 kJ/mol. The dissolution of ferrous carbonate is probably also surface reaction rate limited.

INTRODUCTION

THE precipitation and dissolution kinetics of carbonate minerals such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), ankerite ($CaFe(CO_3)_2$) and siderite ($FeCO_3$) are of considerable importance to limnology, sedimentology, economic geology, water treatment and corrosion control. Calcite, or calcium carbonate, has received the greatest attention, but several researchers have suggested that siderite, or ferrous carbonate, and related Fe-containing minerals may be more important to industry and the natural sciences than is generally recognized (BURKE, 1984; SONTHEIMER *et al.*, 1981).

Probably the primary reason that ferrous carbonate precipitation and dissolution in aqueous solutions have received limited attention is the difficulty working with reduced Fe in the laboratory in the absence of reducing agent additives, many of which are surface active. In the present research, techniques developed for the production and maintenance of rigorously anoxic conditions in the absence of reducing agents have made possible the synthesis of ferrous carbonate seed for use in seeded growth kinetics experiments.

In the present research, the precipitation kinetics of ferrous carbonate were measured from 27 to 80°C using the highly reproducible method of seeded growth kinetics used by NANCOLLAS (1979; and references therein) and others. All experiments were performed using well-aged synthetic ferrous carbonate seed crystals. Results from two dissolution kinetics experiments are also reported. In addition, the thermodynamic solubility product was determined from 25 to 94°C.

EXPERIMENTAL METHODS

Preparation of deoxygenated water and $FeCO_3$ *seed*

To prepare deoxygenated water, tap deionized water, passed through an ion exchange column (Barnstead ultrapure, mixed-bed cartridge, No. D8902) for removal of ions and silicates, and an activated C column for removal of organics, was sparged with CO_2 gas in a 2-l flask. The CO_2 gas was "oxygen-free" grade (certified, Big Three Industries Inc., La Porte, Texas) and was passed over an oxygen scavenger trap (Big Three Oxygen Trap, model OT1 or OT3, 100 or 300 cc capacity) before use. The CO_2-sparged water was then allowed to reflux for several hours in a Fuchs reflux apparatus (Ace Glass, catalog 900, No. 6620) under a steady stream of CO_2.

To prepare ferrous carbonate seed, ~60 g of ferrous ammonium sulfate hexahydrate (certified A.C.S., Fisher Scientific Co.) and 25 g of sodium bicarbonate (A.C.S. specifications, Baker analyzed powder) were placed into a 500 ml round-bottomed Pyrex flask. The flask was evacuated of air and filled with CO_2 using a Firestone valve (Ace Glass, catalog 900, No. 8766), for several vacuum/purge cycles. Approximately 350 ml of deoxygenated water that had been cooled under CO_2 were then passed into the flask. All transfers of anoxic materials, such as the deoxygenated water, were made via three-way valves, which allowed for purging of the valves themselves before water, gas, or seed slurry was passed through them. The reaction that took place produced a white to light grey solid, ferrous carbonate. The $FeCO_3$ seeds were settled and washed several times with deoxygenated water to remove sodium and ammonium sulfate. The final rinse contained <1 mg/l SO_4^{2-}.

The prepared seed was heated in an oil bath at 70–90°C for several days to mature the solid particles into sharp crystals. SEM and light microscopy were attempted on portions of the seed slurry. There was considerable difficulty in preparing crystals for SEM examination due to sensitivity to oxidation. Using a light microscope, crystals could be observed for a few seconds before apparent surface oxidation. Both SEM and light microscopy studies suggested that initially spherical particles matured into sharpedged crystals by the end of one week of heating. Using the light microscope, about thirty crystals were measured and the average width was 1.5 ± 0.1 μm. The measured sedimentation velocity was consistent with this size range. Assuming that the crystals were cubes and using the density of siderite, the corresponding surface area was calculated to be 1.05 ± 0.09 m^2/g. The same batch of slurry was used in all kinetic experiments reported herein. Therefore, any error in the specific surface area will linearly affect the absolute rate calculations, but not the activation energies. The measured solubility of the seed in water (see Results and Discussion section) is characteristic of ferrous carbonate, and X-ray diffraction analysis confirmed the seed material is ferrous carbonate with no significant impurities. Immediate reaction of the solid with the atmosphere limited extensive examination, such as a conventional BET analysis.

Reaction vessel, sampling, and analytical method

The high-pressure glass reactor used in kinetics and solubility experiments is a modification of a Chemco 1000 ml glass stirred reactor. The vessel has a No. 316 stainless steel lid into which threaded ports were tapped for all of the necessary fittings for sampling ports, a thermometer, water and $FeCO_3$ seed addition, and gas entry. In preliminary experiments, in addition to the sampling of reaction solution, progress of the reaction was also monitored with a high pressure pH electrode ±0.01 pH units (Markson, model No. 987) and a modified conductivity cell (YSI model No. 3401 used in conjunction with YSI S-C-T meter model 33), which were placed into threaded ports in the vessel lid. An O-ring seals the lid to the reaction vessel. The vessel was stirred with a teflon stirring bar and heated in an oil bath on a Corning Hot Plate Stirrer (model PC-351). Temperature was maintained to within ~1°C. The stirring rate was sufficient to keep all solid particles suspended in the solution.

The 1,10-phenanthroline spectrophotometric method (Vogel, 1989) was used for all Fe measurements. A Varian 146 UV/vis spectrophotometer was used at 515 nm with matched 1 cm cuvettes. The standard deviation of the calibration was <1%.

Each sampling assembly consisted of an ⅛″ OD × 9″ long 316 stainless steel tube in a Cajon Ultra-Torr® bulkhead fitting. The fitting could be finger-tightened to seal its internal O-ring to the tube or loosened to allow movement of the tube up and down through the O-ring seal without opening the vessel to the atmosphere. Outside the vessel at the end of each tube were a two-way valve (Anspec Company, Ann Arbor, MI, H8453 Omnifit valve with tefzel key), a filter (Gelman Sciences Acrodisc, disposal filter assembly, No. 4192, 0.2 mm), and a 10 ml syringe with a stop at ~8 ml. To collect a filtered sample, the tube was lowered into the solution and the two-way valve opened. The pressure in the reaction vessel forced the syringe plunger up to the preset stop. The valve was then closed, the tube raised above the solution, and the syringe removed from the sampling assembly. The filtered solution in the syringe was transferred to a tared vial containing 1,10-phenanthroline solution for weighting and analysis of total dissolved Fe. It required ~10 s, or less, to collect a sample.

Solubility and kinetics experimental method

The precipitation kinetics of ferrous carbonate were studied through a series of "free drift" dissolution followed by precipitation experiments from 25 to 94°C. The particular experimental method described below was chosen because numerous previous attempts at producing a stable supersaturated ferrous carbonate solution by addition of reagents to reach the metastable limit (as has been done by Nancollas (1979), Kazmierczak *et al.* (1982), and others) failed, probably because of oxidation caused by oxygen present in the solutions and apparatus. In this study, a supersaturated solution for seeded-growth precipitation was created by transferring an excess of $FeCO_3$ seed slurry under CO_2 pressure to ~750 ml of rigorously deoxygenated water in the reaction vessel. The vessel was pressurized to ~207 kPa (30 psig) partial pressure of CO_2 to promote dissolution of the $FeCO_3$ seed. When dissolution equilibrium was reached, as evidenced by steady aqueous Fe concentrations over time, samples were taken and measured for calculation of the thermodynamic solubility product. To induce precipitation the pH was raised by opening an exit valve to lower the CO_2 pressure to <35 kPa (<5 psig). This pressure change was found by trial-and-error to create a pH differential adequate to yield precipitation rates measurable within short time periods at the supersaturation ratios used. The exit valve remained open with a positive purge of CO_2 across the solution during the precipitation. Samples were withdrawn periodically until the solution Fe reached steady state. The exit valve could then be closed and the vessel repressurized to ~207 kPa (~30 psig) CO_2 to monitor dissolution.

Inherent in the precipitation and dissolution kinetics experimental method used in this research was exchange of CO_2 into and out of the solution. Also, in the precipitation experiments, the slow flow of CO_2 across the reaction solution caused a slight evaporative water loss through the open valve on the reaction vessel.

CO_2 *exchange*. When the CO_2 pressure was reduced to initiate precipitation, the solution bubbled vigorously, or "flashed", and rapidly released the excess CO_2. To test the effect of this phenomenon upon the solution Fe concentration, CO_2 exchange experiments were run at room temperature with only CO_2 and water (without $FeCO_3$), at the same stirring rate used in $FeCO_3$ experiments. Measurements of pH during these experiments indicated that CO_2 de-gassing is complete within ~2 min, with the solution pH at 99% of its final expected value within 30–40 s. This time is negligible within the precipitation reaction time frame reported here. For calculation of the precipitation reaction rate constant, the "time zero" value for total aqueous Fe was taken a few minutes into the experiment to avoid using data affected by the CO_2 exchange.

The dissolution reactions were initiated by the reverse process, the absorption of CO_2. However, experiments showed that the confining and release of the internal vessel pressure were not truly opposite processes. Measurements of pH showed that CO_2 absorption, a film-diffusion limited process, is essentially complete within 20–30 min at room temperature under 207 kPa (30 psig) CO_2. The pH changed <0.001 pH unit per minute after the first 16 min of CO_2 absorption, and the change in pH per minute continued to decrease thereafter. Therefore, data points at the beginning of the experiments (during CO_2 absorption) were omitted from the statistical analysis.

Evaporation of reaction solution during precipitation. The amount of reaction solution that evaporated through the open valve on the reaction vessel during precipitation depended upon the rate of flow of CO_2 across the solution and the temperature of the reaction solution. Evaporation was minimized in these experiments by allowing a full CO_2 flow rate for 5 min after the exit was opened, to allow for adequate gas exchange, and then reducing the flow for the duration of the experiment. In preliminary experiments, after the initial CO_2 pressure (~207 kPa, 30 psig) had been released to atmospheric pressure, the exit of the vessel was again closed under 35 kPa (5 psig) CO_2. Discoloration was often observed on the solid $FeCO_3$. The cause of this discoloration is uncertain, but when a slight flow of CO_2 gas

Table 1. Equilibrium data used to calculate siderite solubility products at various temperatures

Temperature (°C)	Equilibrium Total-Fe (mM)	P-CO_2 (atm-absolute)
25	2.221	3.014
43	1.510	2.952
62	1.133	2.830
83	0.776	2.592
94	0.621	2.476

was maintained throughout the precipitation experiment, the growing seed retained its original light color. Therefore, a slight flow of CO_2 gas was maintained in all precipitation experiments, except for the experiment at 27°C. It was shown by measuring the flow of CO_2 gas through the system and assuming it was saturated with water vapor that the increase in concentration from evaporation was negligibly small in all data. In the 27°C experiment, in which the precipitation rate was very slow (days), the exit was re-closed to prevent significant evaporation during the lengthy experiment. No discoloration was observed.

RESULTS AND DISCUSSION

Solubility vs temperature

Speciation calculations were based upon the equations and equilibrium constants presented in Nordstrom *et al.* (1990), activity coefficients from the Davies equation, and the charge and mass balances of species in solution. These constants and equations were incorporated into a FORTRAN program to predict solubility product constants (K_{sp}) from measured equilibrium total aqueous Fe concentrations and the P_{CO_2} (Table 1). Experimental K_{sp} values were determined in this work from 25 to 94°C, and are presented in Table 2, column 2.

The temperature dependence of the solubility product constants was fitted to the following equation as suggested by Nordstrom *et al.* (1990), using rigorous nonlinear least squares regression (Wentworth, 1965a,b; Systat, 1990):

$$\log K_{sp} = a + bT + c/T + d\log T \qquad (1)$$

with T in degrees Kelvin. Using the data in Table 1 along with the carbonate and water equilibria from Nordstrom *et al.* (1990), the following result was obtained:

Table 2. Negative logarithm of the solubility product of ferrous carbonate. The data in Table 1 were used for the calculation

Temperature (°C)	pK_{sp} Experimental	pK_{sp} eqn 2
25	10.765	10.780
43	10.935	10.898
62	11.032	11.061
83	11.251	11.281
94	11.416	11.412

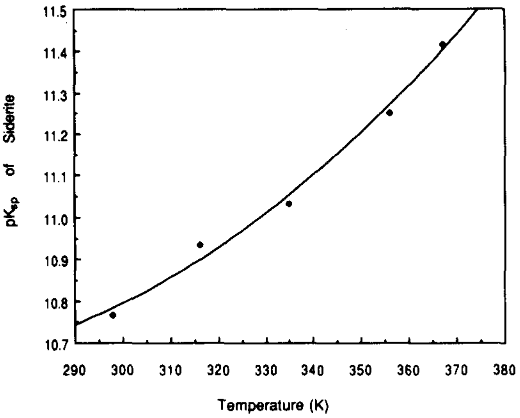

Fig. 1. Plot of pK_{sp} of siderite vs temperature (K). Smooth curve is least squares curve fit using eqn 2 and points are experimentally derived.

$$\log K_{sp} = -59.2385 - 0.041377T - 2.1963/T + 24.5724\log(T) \qquad (2)$$

with a corrected squared correlation coefficient of 0.995 (see Fig. 1). From eqn 2, the standard enthalpy change for dissolution at 25°C is calculated to be $\Delta H^0 = -9.46 \pm 2$ kJ/mol or -2.26 ± 0.5 kcal/mol. Calculated pK_{sp} values using eqn 2 are tabulated in column 3 of Table 2. The standard error in the pK_{sp} values is approximately ±0.01 log unit. The 25°C values of $pK_{sp} = 10.780$ and $\Delta H_r^0 = -2.26$ kcal/mol compare favorably with the values reported by Nordstrom *et al.* (1990) of $pK_{sp} = 10.45$ and 10.89, and of $\Delta H_r^0 = -2.48$ kcal/mol.

Precipitation kinetics

After numerous preliminary experiments to establish appropriate experimental conditions, seeded growth precipitation kinetics were measured at 27, 57, 58.5, 75 and 76°C (Table 3, except 75°C as noted below). The kinetics of ferrous carbonate precipitation at room temperature (see Fig. 2) were found to be approximately 100 times slower than any measured precipitation rate previously reported for a 2:2 sparingly soluble salt (Nielsen, 1986). A summary of the experimental conditions is presented in Table 4 for each temperature. The $FeCO_3$ seed material remained light grey to white in all but one case, the experiment at 75°C, as noted in Table 4.

The following equation was used to analyze the concentration vs time precipitation data (Nancollas, 1979):

$$dFe_t/dt = -k(Fe_t - Fe_{eq})^x \qquad (3)$$

in which Fe_t is the total dissolved Fe concentration at time t(M); t is time (seconds); x is called the reaction order, typically equal to 2 for a number of sparingly soluble salts (Kazmierczak *et al.*, 1981); k is the precipitation reaction rate constant ($M^{-1}\cdot s^{-1}$ for

Table 3. Precipitation kinetics data. Data in this table were curve fitted using eqn 6 to obtain the rate constants reported in Table 4

27°C		57°C		58.5°C		76°C	
Time (h)	T-Fe (mM)	Time (h)	T-Fe (mM)	Time (h)	T-Fe (mM)	Time (h)	T-Fe (mM)
0	1.798	0	1.107	0	0.959	0	0.726
2	1.758	0.0833	1.048	0.0833	0.921	0.0250	0.651
4.78	1.735	0.250	0.982	0.2500	0.869	0.050	0.629
9.43	1.700	0.4167	0.948	0.4167	0.843	0.0833	0.610
23.43	1.643	0.6667	0.905	0.6667	0.822	0.1167	0.597
36.80	1.615	0.9167	0.894	0.9166	0.801	0.1500	0.588
49.67	1.613	1.417	0.874	1.4170	0.779		

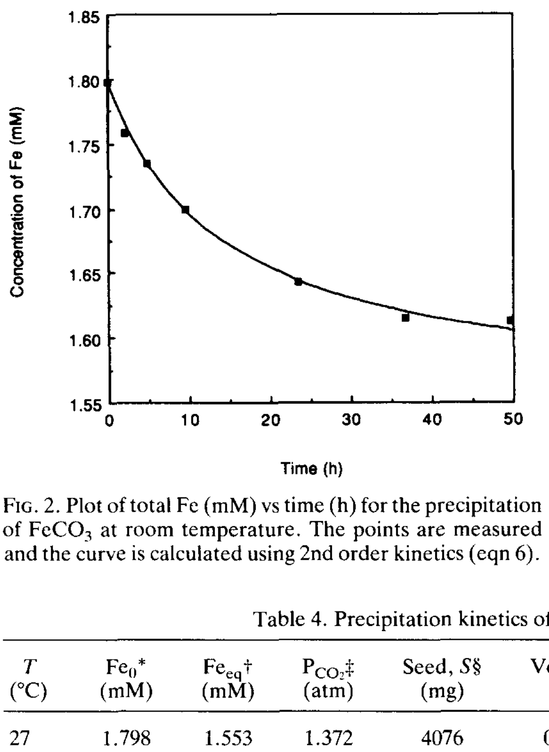

FIG. 2. Plot of total Fe (mM) vs time (h) for the precipitation of $FeCO_3$ at room temperature. The points are measured and the curve is calculated using 2nd order kinetics (eqn 6).

second order reactions); and Fe_{eq} is the expected total dissolved Fe concentration at equilibrium (M). To calculate a precipitation rate constant, k_p, that is independent of total seed surface area and reactor volume, the value of k in eqn 3 is multiplied by V (dm^3 or L), the solution volume, and divided by S (m^2), the seed surface area (KAZMIERCZAK *et al.*, 1982; LEVENSPIEL, 1972):

$$k_p = k(V/S). \qquad (4)$$

In preliminary experiments, a nonlinear curve fit was used in which all data could be combined as a function of temperature by substituting the Arrhenius equation for the precipitation rate constant:

$$k_p = A \exp(-E_a/RT) \qquad (5)$$

in which A is the preexponential factor and E_a is the activation energy (J/mol). The nonlinear methods converged to a reaction order of 2.0 ± 0.1.

The integrated form of eqn 3 with $x = 2$ is:

$$1/(Fe_0 - Fe_t) - 1/(Fe_0 - Fe_{eq}) = k_p(S/V)t \qquad (6)$$

Table 4. Precipitation kinetics of ferrous carbonate vs temperature

T (°C)	Fe_0* (mM)	Fe_{eq}† (mM)	P_{CO_2}‡ (atm)	Seed, S§ (mg)	Vol., V‖ (L)	k¶ (mM/s)	k_p** $L^2/(mol/m^2/s)$	k_p'†† $L^2/(mol/m^2/s)$
27	1.798	1.553	1.372	4076	0.495	8.17×10^{-5}	9.45×10^{-3}	391.8
57	1.107	0.813	1.068	5062	0.620	2.77×10^{-3}	0.323	9166.7
58.5	0.959	0.726	1.090	4768	0.580	2.76×10^{-3}	0.319	8328.5
75‡‡	0.809	0.452	0.823	3418	1.00	3.04×10^{-3}	0.847	17,261.6
76	0.726	0.554	0.734	5501	0.70	4.24×10^{-2}	5.14	104,477.0

*Fe_0 is the initial concentration of total Fe in solution that was used as the time zero value for the numerical analysis. See text for further detail.

†Fe_{eq} is the equilibrium concentration of total dissolved Fe calculated using eqn 6.

‡At all temperatures the total pressure was measured and the partial pressure of water was subtracted to obtain the partial pressure of CO_2.

§This is the quantity of $FeCO_3$ seed added to the reaction vessel. These values can be converted to units of m^2 by multiplying by the estimated surface area of the seed, 1.05 m^2/g, and dividing by 1000.

‖The volume of reaction solution is assumed to be constant in all experiments for the data points used in the statistical analysis. It is assumed to have been changed negligibly from evaporation and changed only 1–8% from sampling.

¶The second order experiment-specific rate constant, k, in units of (mM/s) was calculated from the specific experimental data using eqns 4 and 6.

**The second order experiment-independent rate constant, k_p, is obtained by multiplying k by the reaction volume, V, and by 1000 to convert from millimolar units to molar units, and dividing by the seed surface area, S. That is, $k_p = k(V/S)$ (LEVENSPIEL, 1972; KAZMIERCZAK *et al.*, 1982).

††This second order experiment-independent rate constant, k_p', is obtained from eqn 7.

‡‡As this experiment proceeded, the seed crystals turned dark red, indicating surface oxidation. Consequently, this datum was not included in further analyses.

Table 5. Dissolution kinetics of ferrous carbonate at 26 and 60°C

Experimental conditions					1st Order*		2nd Order†	
T (°C)	Fe_0‡ (mM)	V (L)	Seed, S§ (mg)	P_{CO_2}‖ (atm)	Fe_{eq} (mM)	k_d^{1st} (L/m²/s)	Fe_{eq} (mM)	k_d^{2nd} (L²/mol/m²/s)
26	1.601	0.750	5639	1.96	1.842	1.529×10^{-4}	1.961	0.0534
60	0.910	0.660	873	1.82	1.182	2.651×10^{-5}	1.281	0.343

*The rate law used was: $\ln[(Fe_{eq} - Fe_0)/(Fe_{eq} - Fe_t)] = kt$. Both Fe_{eq} and k were obtained via nonlinear least squares analysis. Then the value of $k_d^{1st} = k(V/S)$ was calculated with V in liters and S in m².

†The rate law used was: $1/(Fe - Fe_{eq}) - 1/(Fe_0 - Fe_{eq}) = kt$. Both Fe_{eq} and k were calculated using nonlinear least squares. Then $k_d^{2nd} = k(V/S)$ was calculated with V in liters and S in m².

‡Fe_0 is the concentration of total Fe in solution that was used as the time zero value for the numerical analysis. The value was taken after sufficient time had elapsed for CO_2 exchange to take place.

§This is the quantity of $FeCO_3$ seed added to the reaction vessel. These values can be converted to units of m² by multiplying by the estimated surface area of the seed, 1.05 m²/g, and dividing by 1000.

‖At all temperatures the total pressure was measured and the partial pressure of water was subtracted to obtain the partial pressure of CO_2.

in which Fe_0 is the initial total dissolved Fe concentration. For each experiment, both the precipitation rate constant, k_p, and the equilibrium Fe concentration, Fe_{eq}, were calculated for use in eqn 6 via a non linear least squares algorithm (DEMING, 1946; WENTWORTH, 1965a,b). This was done because small variations in the Fe_{eq} values calculated independently from the speciation program described above caused a large biased error in the calculated rate constant, k_p. However, when the Fe_{eq} values calculated via the nonlinear algorithm are compared with those calculated from the speciation program using the experimental partial pressures of CO_2 to calculate the ferrous carbonate ion activity products (K_{sp}), the root mean squared deviation between the two ion activity products is only 0.04 log unit. The calculated k_p and Fe_{eq} values for each temperature are listed in Table 4. Equation 6 reproduces the experimental observations in Table 3 with an average correlation coefficient of 0.998. Figure 2 shows the plot of measured aqueous total Fe concentration vs time for the 27°C experiment with the corresponding second order plot from eqn 6.

An Arrhenius activation energy, E_a = 108.3 kJ/mol, was calculated from the second order k_p values at various temperatures via eqn 5. The corresponding pre-exponential term, $A = 6.35 \times 10^{16}$. Standard deviation in calculation of the activation energy was 0.456. The large magnitude of the activation energy indicates that the ferrous carbonate precipitation rate is limited by the rate of reactions at the crystal surface, rather than by diffusion or mass transport in solution (NANCOLLAS, 1979).

Activity-based rate constants k'_p were also calculated using a FORTRAN program for a rearranged second order version of eqn 3 into a commonly used rate law (NANCOLLAS, 1979; GARSIDE, 1984):

$$dFe_t/dt = -k'_p(S/V)([\{Fe_t^{2+}\}\{CO_3^{2-}{}_t\}]^{1/2} - K_{sp}^{1/2})^2 \quad (7)$$

in which { } represents ion activities, k'_p is the precipitation rate constant (L²/mol/m²/s), and the remaining parameters are as defined above. The rate constants k'_p are listed in Table 4. The activation energy corresponding to the k'_p values in eqn 7 is E_a = 95.8 kJ/mol and $A' = 1.83 \times 10^{19}$, similar to the value obtained from k_p values in eqn 6. The difference arises from use of a speciation program to estimate the values of $\{Fe_t^{2+}\}$ and $\{CO_3^{2-}{}_t\}$. Standard deviation was 0.430.

Dissolution kinetics

Only two dissolution results are reported because of complications associated with the slow absorption of CO_2 across the gas–liquid interface. First and second order dissolution rate laws fit the data equally well due to the limited amount of data.

The following equation for dissolution corresponds to eqn 3 given above for precipitation:

$$dFe_t/dt = k(Fe_{eq} - Fe_t)^x \quad (8)$$

with the parameters as defined previously. Integrating this equation and substituting k_d (S/V) for k, in which k_d is the experiment-independent rate constant for dissolution, give the following first order empirical relation:

$$\ln[(Fe_{eq} - Fe_0)/(Fe_{eq} - Fe_t)] = k_d(S/V)t \quad (9)$$

and the following second order empirical relation:

$$1/(Fe_{eq} - Fe_t) - 1/(Fe_{eq} - Fe_0) = k_d(S/V)t. \quad (10)$$

A summary of the experimental conditions and the corresponding Fe_{eq} and first and second order rate constants are presented in Table 5 for each temperature. The dissolution rate constant, k_d, and the equilibrium Fe concentration, Fe_{eq}, were again calculated for use in eqn 8 via a nonlinear least squares algorithm (WENTWORTH, 1965a,b).

The Arrhenius activation energies calculated from the first and second order rate constants are 45.6 and 43.0 kJ/mol, respectively. Both activation energies are larger than the activation energy for diffusion in water, 20–25 kJ/mol (NANCOLLAS, 1979), suggesting that the dissolution is probably surface reaction rate limited. Because only two dissolution experiments were performed, the uncertainty in the activation energy is larger than that for the precipitation experiments. More work is needed to better define the dissolution kinetics.

Comparison to other research

The authors are able to locate only one report of research regarding the precipitation kinetics of an iron carbonate phase that can be used for comparison (WAJON *et al.*, 1985). Dissolved Fe concentrations vs time were reported for the precipitation of a calcium–siderite phase onto Ca- and Mg-containing carbonate minerals from 15 to 45°C. The authors reported tables of Fe concentration vs time, and their precipitation data are clearly a strong function of temperature, as reported herein. Sufficient information was not reported for calculation of a system-independent rate constant similar to k_p or k'_p.

NIELSEN (1986) developed a semi-empirical theory to calculate the initial precipitation rate for surface reaction rate limited materials from a knowledge of the metal ion dehydration rate, the ion pair formation constant, the solubility product constant, and the experimental supersaturation ratio. In this approach, it is assumed that the precipitation rate is primarily limited by the rate of metal ion dehydration on the growing crystal surface. Nielsen used this approach to calculate the precipitation rate for numerous sparingly soluble salts, such as calcium carbonate, calcium oxalate, calcium sulfate and barium sulfate. Considerable numerical detail is involved in the calculation and the reader is referred to NIELSEN (1986) and BODEK *et al.* (1988), and references therein, for further discussion and worked examples. Using the Nielsen approach, the initial precipitation rate of ferrous carbonate perpendicular to the crystal surface at 25°C is calculated to be 2.1×10^{-14} m/s, which is 100 times slower than any measured precipitation rate previously reported for a 2:2 sparingly soluble salt. At 27°C (Fig. 1), the initial experimental precipitation rate of $FeCO_3$ in this work is calculated to be 1.88×10^{-14} m/s, which is in excellent agreement with the theory developed by NIELSEN (1986).

Acknowledgements—The authors gratefully acknowledge the support of the Gas Research Institute under contract No. 5088-212-1717, but in no way does this work constitute an endorsement by GRI of any products or views contained herein. In addition, the work was supported by Exxon Chemical Co., Texaco Inc., Chevron Oil Field Research Inc., Conoco Inc., Arco Oil and Gas Co., Zapata Corporation, Champion Chemicals Inc., Welchem Inc., and Ciba-Geigy. Likewise, the supporting companies in no way endorse the products or views contained herein. The manuscript preparation by Kathy Pradia was appreciated.

Editorial handling: J. L. Bischoff.

REFERENCES

BODEK I., LYMAN W. J., REEHL W. F. and ROSENBLATT D. H. (eds) (1988) *Environmental Inorganic Chemistry*. Pergamon Press.

BURKE P. A. (1984) Synopsis: recent progress in the understanding of CO_2 corrosion. In *Advances in CO_2 Corrosion*, Vol. 1, NACE Corrosion/83 Symposium, (eds R. H. HAUSLER and H. P. GODARD), pp. 3–9. National Association of Corrosion Engineers.

DEMING W. E. (1946) *Statistical Adjustment of Data*. John Wiley and Sons.

GARSIDE J. (1984) Advances in characterization of crystal growth. In *Advances in Crystallization from Solutions* (ed. G. R. YOUNGQUIST), AIChE Symposium Series. American Institute of Chemical Engineers.

KAZMIERCZAK T. F., SCHUTTRINGER E., TOMAZIC B. and NANCOLLAS G. H. (1981) Controlled composition studies of calcium carbonate and sulfate crystal growth. *Croatica Chemica Acta* **54**, 277–287.

KAZMIERCZAK T. F., TOMSON M. B. and NANCOLLAS G. H. (1982) Crystal growth of calcium carbonate: a controlled composition kinetic study. *J. phys. Chem.* **86**, 103–107.

LEVENSPIEL O. (1972) *Chemical Reaction Engineering*. John Wiley and Sons.

NANCOLLAS G. H. (1979) The growth of crystals in solution. *Adv. Colloid Interface Sci.* **10**, 215–252.

NIELSEN, A. E. (1986) Mechanisms and rate laws in electrolyte crystal growth from aqueous solution. Division of Environmental Chemistry and the Division of Geochemistry, 190th Meeting of the American Chemical Society, Chicago, IL, September 8–13, 1985. *J. Crystal. Growth* **67**, 600.

NORDSTROM D. K., PLUMMER L. N., LANGMUIR D., BUSENBERG E., MAY H. M., JONES B. F. and PARKHURST D. L. (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. In *Chemical Modeling of Aqueous Systems II* (eds C. MELCHIOR and R. L. BASSETT). *ACS Symposium Series* **416**, 398–413.

SONTHEIMER H., KOLLE W. and SNOEYINK V. (1981) The siderite model of the formation of corrosion resistant scales. *J. Am. Water Works Assoc.* **73**, 572–579.

SYSTAT (1990) Systat, version 3.2. Systat, Inc. Evanston, Illinois.

VOGEL A. (1989) *Textbook of Quantitative Chemical Analysis*. Bath Press.

WAJON J. E., HO G.-E. and MURPHY P. J. (1985) Rate of precipitation of ferrous iron and formation of mixed iron–calcium carbonates by naturally occurring carbonate materials. *Water Res.* **19**, 831–837.

WENTWORTH W. E. (1965a) Rigorous least squares adjustment. Applications to some non-linear equations, I. *J. Chem. Education* **42**, 96–103.

WENTWORTH W. E. (1965b) Rigorous least squares adjustment. Application to some non-linear equations, II. *J. Chem. Education* **42**, 162–167.