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Project Summary

Calcium Carbonate Dissolution Rate in Limestone Contactors

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The project summarized here investigated some of the parameters and relationships used to predict the performance of limestone contactors. The purpose of the project was to study the effect of limestone composition, especially the dolomite $[CaMg(CO_3)_2]$ and impurity content of the stone, on the kinetics of carbonate mineral dissolution and to determine the effect of temperature on the rate of dissolution. The rate of dissolution was determined by using a rotating disk apparatus and samples of limestone of varied composition.

The limestone samples included a white marble and a selection of sedimentary stones. The white marble contained a significant amount of silica (approximately 35%). The major mineral constituents of the sedimentary limestones ranged from approximately 100% calcite $(CaCO_3)$ to essentially pure dolomite. The approximate iron (Fe) content of the stones ranged from 15 to 377 mg Fe/100g and the approximate aluminum content (Al) from 1 to 134 mg Al/100g.

A heterogeneous reaction model for mineral dissolution effectively explained the results of the rotating disk experiments for all samples except the two with the highest dolomite content. The magnitude of the dissolution rate constant for fresh stone decreased by approximately 60% as the calcite content of the stone decreased from 0.92 to 0.09 g $CaCO_3$/g stone. The rate of dissolution of stones with a high dolomite content may have been enhanced by the presence of small amounts of calcite. The rate of solubilization of magnesium (Mg) was negligible in all samples except the two with the highest dolomite content (93 and 100 mass percent dolomite).

The overall dissolution rate constant decreased as the amount of calcium dissolved from the surface of the stone increased. For a given amount of calcium dissolved per unit area of stone surface, the magnitude of the percentage decrease in the dissolution rate constant increased as the iron and aluminum content of the stone increased. The effect of sample aging on the rate of dissolution was lowest when the weighted sum of the iron and aluminum content of the stone was less than about 10 mg/g. The weighted sum is equal to the aluminum content in mg Al/g plus 0.30 times the iron content in mg Fe/g. The presence of silica as the principal impurity in the white marble seemed to reduce the effective (calcite) surface area of the stone in proportion to the mass of silica in the sample, but it did not appear to affect the dissolution rate of the calcite surface.

The dissolution rate constant for calcite increased with increasing temperature, from 0.38×10^{-3} cm/s at 5°C to 2.80×10^{-3} cm/s at 25°C. The apparent activation energy was 101±8 kJ/mol for the surface reaction rate constant and

17±0.3 kJ/mol for the mass transfer rate constant in the heterogeneous reaction model.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at the back).

Background

A limestone contactor is a treatment device in which water flows through and dissolves carbonate minerals (typically calcium carbonate) from a packed bed of crushed limestone. Dissolution of calcium carbonate (under a closed-to-atmospheric-carbon dioxide condition) increases the pH, alkalinity, and dissolved inorganic carbon concentration of the water and depletes the amount of calcium carbonate in the bed. Limestone contactors are simple, low-cost devices, which usually require minimal maintenance and are, therefore, especially suitable for small water supplies.

In an earlier study (Letterman et al., 1987), limestone contactors effectively reduced the dissolution of corrosion byproducts, such as lead, copper, and zinc, from piping system surfaces. A mathematical model related the depth of limestone needed to reach the desired effluent water chemistry to the influent water chemistry, the limestone particle size and shape, the limestone bed porosity, and the temperature and superficial velocity of the water. Limited field experiments showed that contactor performance decreases as the water temperature decreases.

Another study (Haddad, 1986) monitored the long-term operation of a contactor containing somewhat impure, high-calcium limestone. Here, the author concluded that as the calcium carbonate dissolved, the rate of dissolution decreased because relatively insoluble impurities formed a residue layer. As the thickness of this layer increased, the rate of transport of calcium ion from the calcium carbonate surface to the bulk solution decreased, and, thus, contactor performance decreased with time.

Field experiments have shown (Letterman et al., 1987) that the temperature of the water flowing through a limestone contactor can affect its performance. For a given set of design and operating conditions, contactor performance tends to decrease with decreasing temperature. One of the objectives of this study was to obtain a better understanding of this relationship.

Experimental Materials, Apparatus, and Methods

Limestones

The study was conducted using 13 samples of limestone including a white marble (sample WM) from a quarry in Proctor, VT, a sedimentary limestone (sample SL) from a quarry near Boonville, NY, Black River limestone (sample BR) from a quarry near Watertown, NY, and 10 samples (samples A-J) from a dolomite quarry near York, PA.

A sample of each stone was powdered and dissolved in concentrated hydrochloric acid. Dilutions of this solution were used to determine the calcium, magnesium, iron, and aluminum content of the stone with a direct current plasma spectrometer and an atomic absorption spectrophotometer. For a number of the samples, some translucent material, probably quartz, remained after 2 days of dissolution. The measured calcium and magnesium content of the samples was used to estimate the calcite, dolomite, and insoluble residue content of the samples. In these calculations the magnesium was assumed, based on x-ray diffraction and thin-section photomicrography results, to be associated only with dolomite.

The results of these calculations and the measured iron and aluminum values are listed in Table 1. In several cases, where the sum of the calcite and dolomite fractions was slightly greater than 100g/100g of stone, the insoluble residue content was set equal to zero.

Samples WM, SL and BR as well as a number of the samples from the York dolomite quarry (samples A, B, D, E and F) are high calcium content limestones. Other York samples (samples C, G, H, and I) are predominately dolomite, and sample J is essentially pure dolomite.

The WM sample had the highest insoluble residue content (36 g/100g) but

relatively low amounts of iron and aluminum (34 mg Al/100g and 71 mg Fe/100g of stone). It is very likely that the insoluble residue in this sample is quartz. Sample I, from York, had the highest amount of iron (377 mg Fe/100g) and sample H had the highest amount of aluminum (134 mg Al/100g).

The stone disks used in the rotating disk apparatus were prepared by cutting 3.10- or 2.45-cm-diameter, cylindrical cores from pieces of rock collected at the quarries. Each core was cut into a number of 3-mm-thick disks using a rock saw. The disk faces were smoothed and polished on a lapwheel with a silicon carbide abrasive. The back face and edge of the disks were coated with plastic so that only the polished face was available for dissolution. Each disk was mounted in a Teflon-coated[1] brass holder (Figure 1). Between dissolution rate experiments, each stone sample was "aged" by controlled dissolution in dilute acid solution. The cumulative amount of calcium and magnesium dissolved during aging was determined by measuring their concentrations in the dilute acid solution.
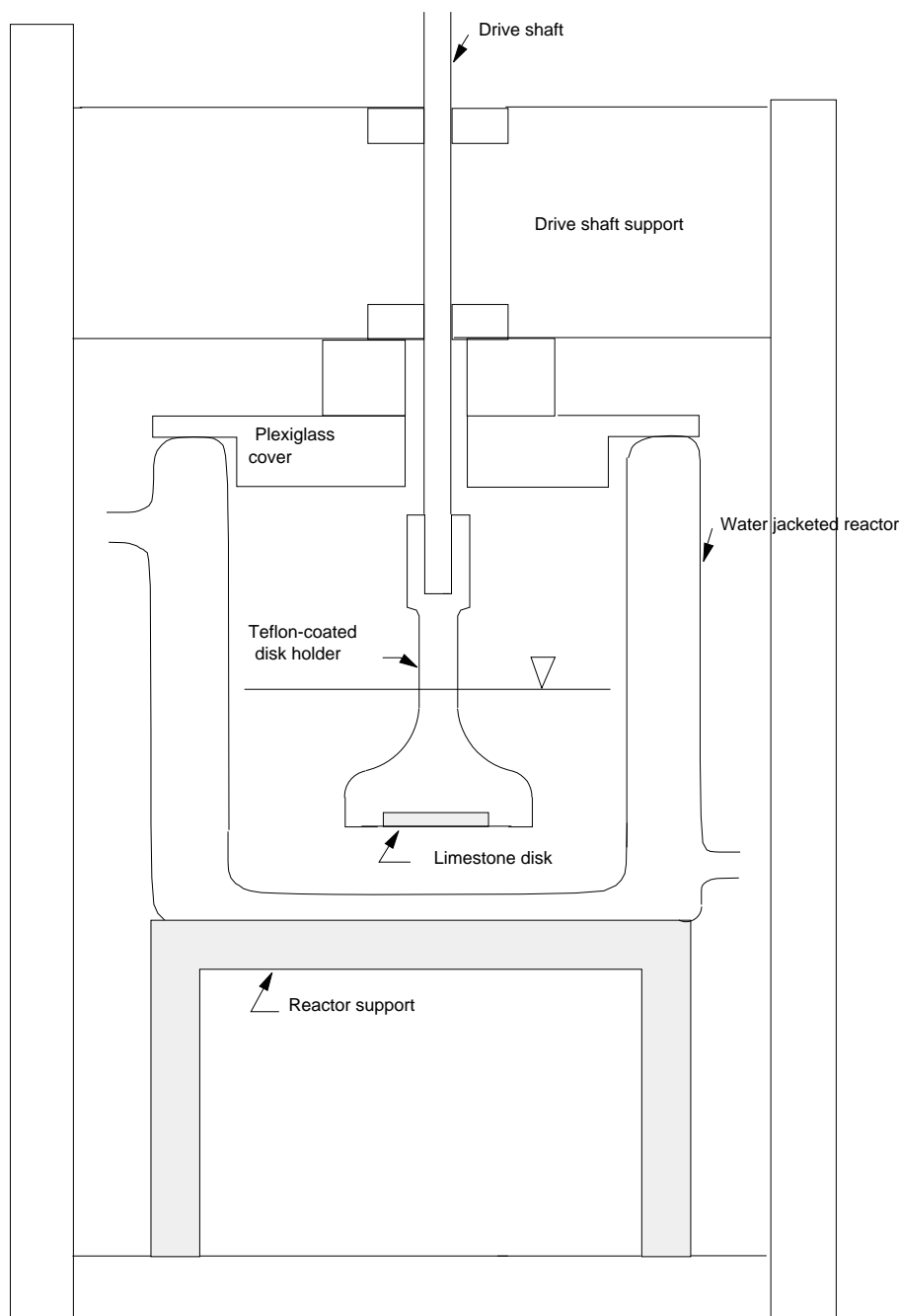
Rotating Disk Apparatus

The reactor used in the rotating disk apparatus (Figure 1) was 14 cm in diameter and the clearance between the disk and the walls of the vessel was greater than 4 cm. The disk was centered about 3 cm above the bottom of the vessel, and its rotational speed was varied over the range 200 to 1200 rpm.

The reactor was constructed with double-glass walls. A water bath was used to circulate water between the walls to maintain the reactor contents at preselected temperatures in the range 4°

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[1] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1. *Estimated Major and Minor Constituents of the Stone Samples (g/100g)*

Stone ID	Calcite	Dolomite	Insoluble	Fe	Al
WM	64	1	35	0.071	0.034
SL	92	4	4	0.101	0.114
BR	99	2	0	0.019	0.044
A	89	16	0	0.024	0.012
B	92	4	4	0.029	0.001
C	17	68	15	0.189	0.093
D	79	18	3	0.040	0.037
E	71	29	0	0.041	0.025
F	89	9	2	0.015	0.005
G	23	59	18	0.294	0.129
H	38	53	9	0.154	0.134
I	9	93	0	0.377	0.032
J	0	100	0	0.189	0.010

Figure 1. *Schematic diagram of the rotating disk apparatus.*

grade (ACS Certified) chemicals were used (KCl, N/10 HCl). The background electrolyte was 0.079 M KCl.

Methods

A free-drift method, in which the pH was allowed to increase as the carbonate minerals dissolved from the stone, was used in all experiments. Experimental solutions (600 mL) were prepared as needed by adding potassium chloride and the required volume of acid to boiled water and then transferring this to the reactor.

Each experiment began by raising the vessel and solution into place beneath the rotating disk and against the plexi-glass cover. Samples of solution (either 2- or 5-ml volume) were withdrawn from the vessel at 6 or 9 min intervals for a period of 1.5 hr with the use of an automatic pipette (1 to 5 ml). The samples were stored in polyurethane disposable test tubes at 4°C for no longer than 2 days before the ion concentrations were measured by atomic absorption spectrophotometry.
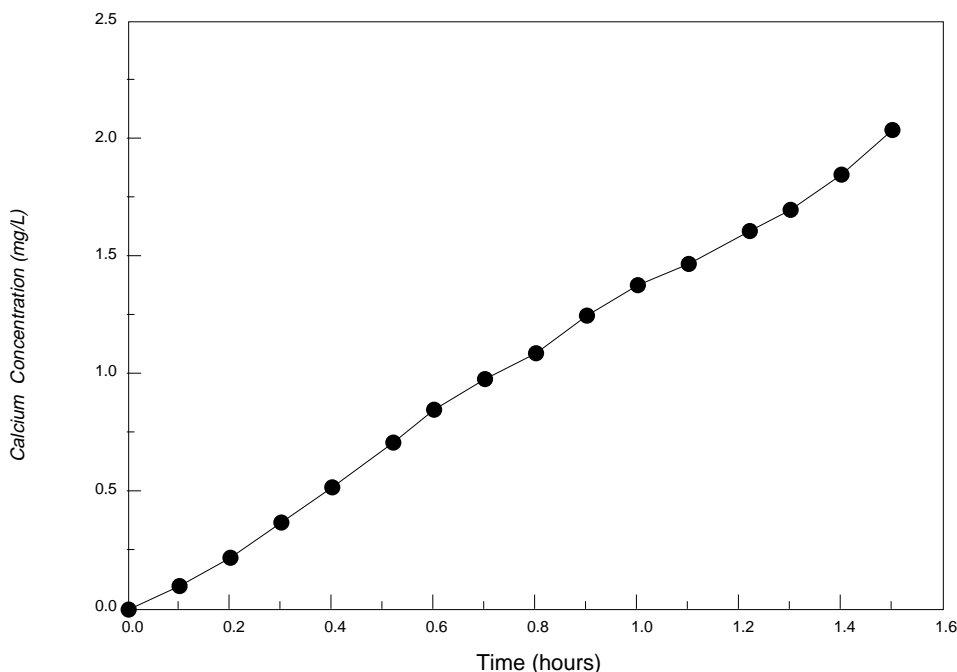
Experimental Results

The calcium concentration and pH change with time in a typical rotating disk experimental run are shown in Figures 2 and 3. In this example, the WM stone sample was used, the rotational speed was 600 rpm, and the initial acidity was 0.01 meq/L. At the end of the experiment the pH was 9.04 and the calcium concentration was about 2 mg/L. For an initial acidity of 0.01 meq/L and with no calcium in the solution at t = 0, the calculated equilibrium calcium concentration is 11.6 mg/L and the calculated equilibrium pH is 10.02.

The overall dissolution rate constant, k_o, was determined for each experimental run by using the measured calcium concentrations and, in some cases, the measured magnesium concentrations. For the stones that released negligible amounts of magnesium, the calcium concentrations (C_t) were substituted in the relationship,

$$M = \ln \{(C_{eq} - C_t)/(C_{eq} - C_o)\}(V_t/A) \qquad (1)$$

where C_{eq} and C_o are the equilibrium and initial calcium concentrations, respectively, and A is the surface area of the stone sample disk exposed to the solution. C_o was zero in all experiments. V_t is the volume of the solution in the rotating disk apparatus. For sample WM and samples A-J, the limestone disk was 3.6 cm in diameter and, therefore, A was 10.17 cm². For the 3.1-cm diameter SL sample and the 2.5-cm-diameter BR sample, A was 7.91 cm² and 4.71 cm², respectively.

to 25±0.2°C. The plexi-glass cover on the reactor had holes for inserting the rotating shaft, pH electrode, and wetted nitrogen inlet tube. Additional holes were provided for measuring the temperature and pipetting samples for the calcium measurement. The bulb of the pH electrode was located 1.5 cm from the rotating disk and 3 cm above the bottom of the vessel.

All solutions used in the rotating disk experiments were made with distilled and deionized water that had been boiled for a few minutes, several hours before use, to remove carbon dioxide. Fisher analytical

Figure 2. *Calcium concentration in the rotating disk apparatus as a function of time: WM sample; w = 600 rpm and initial acidity of 0.01 meq/L.*
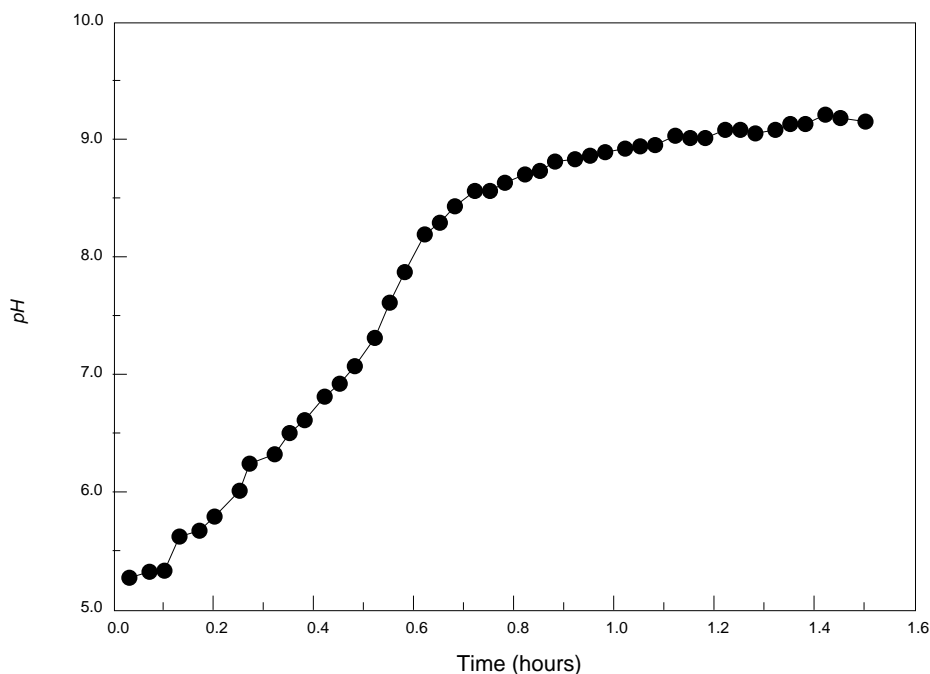
Figure 3. *pH versus time for the rotating disk experiment of Figure 2.*

The magnitude of C_{eq} was determined for each experimental run by using a chemical equilibrium model and effective solubility products determined for a number of the stone samples (Table 2). For the stone samples that were not included in the solubility product experiments, i.e., samples B, D, E, G, H and J, the average value of the effective solubility products (pK_{sp} = 8.81) for the samples from the same quarry was used. pK_{sp} = 8.35 was used for sample BR because of its similarity to sample SL.

Table 2. *Effective Solubility Products for Calcium Carbonate and Calcium-Magnesium Carbonate in Selected Limestone Samples.[*]*

Stone sample ID	Negative log of the effective solubility product
WM	8.20 ± 0.07
SL	8.35 ± 0.06
A	8.76 ± 0.09
C	8.72 ± 0.07
F	8.88 ± 0.05
I	8.89 ± 0.04

[*]Values are for 25°C and infinite dilution.

As samples were withdrawn during an experiment, the magnitude of V_t decreased. A value of V_t was calculated for each value of C_t using the relationship,

$$V_t = V_o - nv \qquad (2)$$

where V_o is the volume of the solution in the reactor at the start of the experiment, v is the volume of each sample withdrawn for the calcium and magnesium measurements, and n is the total number of samples withdrawn from the reactor up to that sample. In the dissolution rate experiments, V_o was 600 mL and v was either 2 or 5 mL.

A straight line was fitted to the M versus time points using the method of least squares (M is given by Equation 1). The slope of this line is equal to the overall dissolution rate constant.

Figure 4 is an M versus time plot for a fresh sample of WM stone. In this experiment, the disk rotational speed was 600 rpm, the water temperature was 25°C, and the initial acidity was 0.01 meq/L. The slope of the least squares line in Figure 4 yields an overall dissolution rate constant of 3.3×10^{-3} cm/s.

Effect of Insoluble Residue on the Dissolution Rate

The overall dissolution rate constant for fresh calcitic stones (stones with low dolomite content) tended to decrease as the
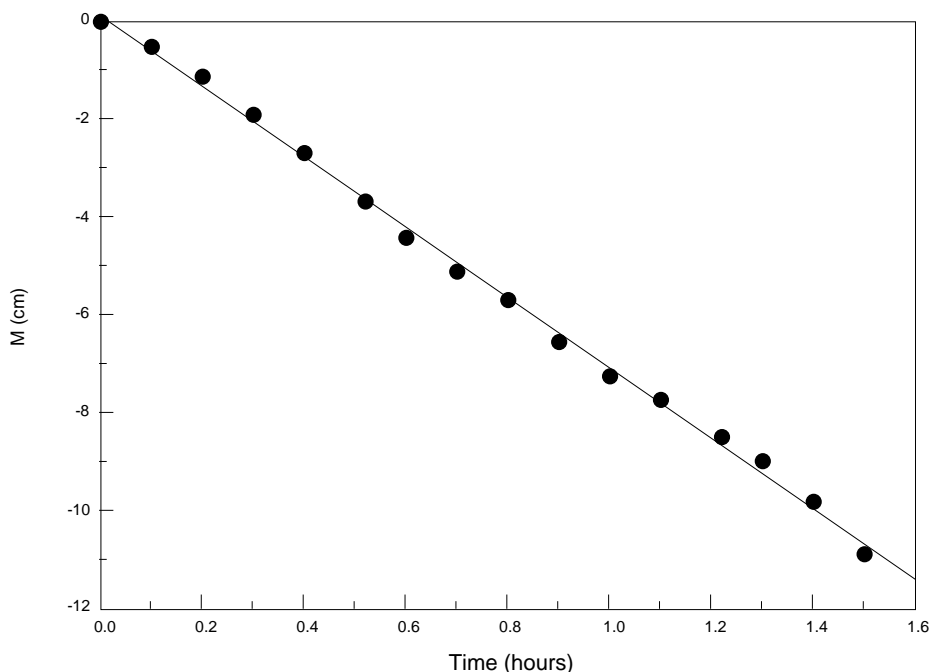
Figure 4. *Determination of the overall dissolution rate constant (ko) for the experiments of Figures 2 and 3 (ko = o.oo33 cm/s).*

estimated amount of insoluble residue in the stone increased. We concluded that the insoluble impurities reduced the area of calcite exposed to the solution. To test this hypothesis, we assumed that the area of exposed calcite is proportional to the mass percent of calcite in the stone. The rate constants were "corrected" for the residue content by dividing them by the mass percent of calcite in the stone. The results of this calculation, listed in the right-hand column of Table 3, show that this correction reduces the effect of the residue content on the overall dissolution rate constant.

The corrected overall dissolution rate constant for the coarse-grained WM sample (3.12×10^{-3} cm/s) is somewhat less

than the values of 3.51×10^{-3} and 3.75×10^{-3} cm/s for the fine-grained SL and BR samples.

Effect of Aluminum and Iron Content on the Dissolution Rate

We observed that the extent to which the dissolution of calcium from the stone surface reduced the overall dissolution rate constant depended on the aluminum and iron content of the stone.

Figure 5 shows the normalized overall dissolution rate constant (i.e., the measured value divided by the initial, fresh stone, value, k_o/k_{oi}) plotted versus the amount of calcium dissolved from the surface of the stone, Ca_d, for stones A through H. (The results for stones I and J were

also plotted but are not shown in Figure 5.) For stones C, I, G, and H, the overall dissolution rate constant decreased by more than 60% as the amount of calcium dissolved increased from 0 to 4 mg Ca/cm^2. For stones B, F, and J, the decrease was less than 30%.

Values of k_o/k_{oi} were interpolated from Figure 5 at $Ca_d = 2$ mg Ca/cm^2 and then listed in Table 4 in rank order, from the highest ($k_o/k_{oi} = 0.90$ for stone F) to the lowest ($k_o/k_{oi} = 0.23$ for stone G). The stones with the highest aluminum content (> 25 mg Al/100g of stone) had the greatest decrease in the overall dissolution rate constant for this amount of calcium dissolved. For several stones, especially stone I with $k_o/k_{oi} = 0.36$, the iron content seemed to be an additional factor.

Since both the iron and aluminum content of the stone seem to determine how sample aging affects the overall dissolution rate constant, a composite parameter that includes a weighted combination of the iron and aluminum concentrations ($aC_{Al} + bC_{Fe}$) was derived, where C_{Al} is the aluminum concentration in mg Al/100 g and C_{Fe} is the iron concentration in mg Fe/100 g. The highest linear correlation between k_o/k_{oi} and the Fe+Al parameter ($r^2 = 0.92$) was obtained with weighting factors a=1 and b=0.3, i.e., ($C_{Al} + 0.30 C_{Fe}$). The quantity k_o/k_{oi} and corresponding values of ($C_{Al} + 0.30 C_{Fe}$) are listed in Table 5.

According to the results in Table 5, the effect of iron and aluminum on the overall dissolution rate constant will be minimized if the quantity $C_{Al} + 0.30 C_{Fe}$ for the stone is less than about 10 mg/100g.

In a special experiment, the brownish residue layer that formed on the SL disk was scraped into concentrated nitric acid, ultrasonicated and the solution was analyzed for total soluble aluminum. The soluble aluminum expressed as the amount per area of disk was 0.97 μmoles/cm^2 (26 μg/cm^2). The scraped residue did not dissolve completely in acid which suggested the presence of alumino-silicates. The overall dissolution rate constant for the SL stone increased to 90% of its original value when the residue layer was scraped from the disk surface.

Conclusions and Recommendations

A heterogeneous reaction model for mineral dissolution, in which the rate of dissolution is controlled by a surface reaction and a cation mass transfer resistance acting in series, effectively explained the results of the rotating disk experiments for all samples except the two with the high-

Table 3. *Comparison of Experimental and Corrected Overall Dissolution Rate Constants (k_o)for Essentially Fresh Limestone Disks.[*]*

Stone	Mass % Calcite	Experimental $k_o \times 10^3$ (cm/s)	Corrected $k_o \times 10^3$ (cm/s)
Calcium dissolved in "aging" = 0.2 mg Ca/cm^2			
WM	64	1.99	3.12
SL	92	3.26	3.51
BR	100	3.75	3.75
Calcium dissolved in "aging" ≈ 0 mg Ca/cm^2			
B	92	4.39	4.77
F	89	3.46	3.89

[*]*Small amounts of calcium had been dissolved from samples WM, SL, and BR before the first rate constants were determined.*

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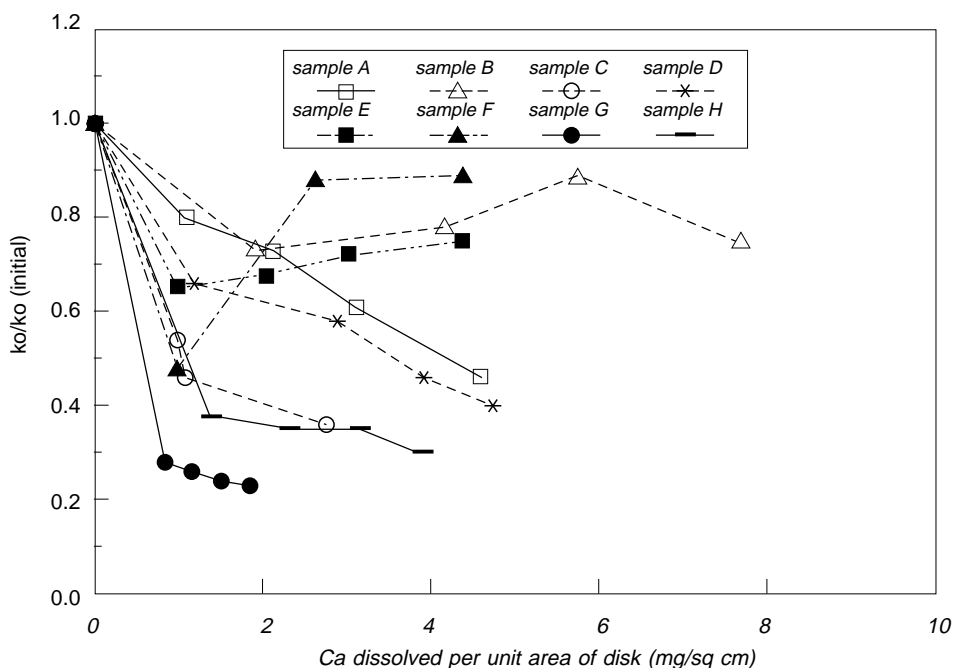
Figure 5. Effect of amount of calcium dissolved from disk surface on the fractional decrease in the overall dissolution rate constant.

Table 4. Effect of the Iron and Aluminum Content on the Fractional Decrease in the Overall Dissolution Rate Constant (k_o) at Ca_d = 2 mg Calcium Dissolved/sq cm of Limestone Surface.

Stone ID	% Calcite	$k_o \times 10^3$ * (cm/s)	k_d/k_{oi} +	Fe (mgFe/100g)	Al (mgAl/100g)
F	88.9	3.5	0.90	15	5
A	88.9	4.7	0.74	24	12
B	92.1	4.4	0.73	29	1
J	0	0.9	0.70	189	10
E	70.7	3.3	0.65	41	25
D	78.9	4.2	0.61	40	37
C	16.5	2.7	0.43	189	93
I	8.8	2.8	0.36	377	32
H	38.3	3.3	0.35	154	134
G	22.9	3.2	0.23	294	129

* Interpolated from Figure 5 at Ca_d = 2 mg Ca/cm². + k_{oi} = value when negligible Ca dissolved from the stone.

Table 5. Effect of the Weighted Sum of Iron and Aluminum in the Limestone on the Fractional Decrease in the Dissolution Rate Constant at 2 mg Calcium/sq cm of Limestone Surface.

Stone ID	C_{Al} + 0.30 C_{Fe}	k_d/k_{oi} * (mg/100 g)
F	0.90	10
A	0.74	19
B	0.73	10
J	0.70	67
E	0.65	37
D	0.61	49
C	0.43	149
I	0.36	145
H	0.35	180
J	0.23	217

*k_{oi} = value when negligible Ca dissolved from the stone.

est dolomite content. For calcite and the experimental conditions of this study, the surface reaction rate was relatively large and the rate of dissolution was essentially mass transfer controlled. The results show that a calcium ion diffusivity of 0.8 x 10⁻⁵ cm²/s (at 25°C, can be used in predicting the mass transfer resistance.

The stone samples with the highest calcite content and lowest dolomite content had the highest initial rates of dissolution. The magnitude of the overall dissolution rate constant for fresh stone decreased by approximately 60% as the calcite content of the stone decreased from 0.92 to 0.09 g $CaCO_3$/g stone. The rate of dissolution of stones with high dolomite content may be enhanced by the presence of small amounts of calcite. For example, the stone that was essentially pure dolomite had a dissolution rate constant that was 66% less than the constant for another dolomitic stone with approximately 9% calcite. When the high dolomite content samples were fresh, it appeared that the calcium carbonate component of the dolomite dissolved faster than the magnesium carbonate component. The rate of dissolution of magnesium was negligible in all samples except the high dolomite content samples (93 and 100 mass percent dolomite).

The overall dissolution rate constant decreased as the amount of calcium dissolved from the surface of the stone increased. Analysis of several stone surfaces, by scanning electron microscopy and x-ray energy spectroscopy, indicated that the density of calcium atoms on the surface of the stone decreased and the density of aluminum, silicon, and iron increased as calcium dissolved. For a given amount of calcium dissolved per unit area of stone surface, the magnitude of the decrease in the overall dissolution rate constant increased as the iron and aluminum content of the stone increased. The results suggest that the effect of sample aging on the rate of dissolution is a minimum if the weighted sum of the iron and aluminum content of the stone is less than about 10 mg/g. The weighted sum is equal to the aluminum content in mg Al/g plus 0.30 times the iron content in mg Fe/g. To minimize the negative effect of mineral dissolution and residue-layer buildup on the performance of a limestone contactor during long-term operation, the iron and aluminum content should be less than this weighted sum.

The presence of silica as the principal impurity in the white marble reduced the effective surface area of the calcite in proportion to the mass of silica in the sample but did not appear to cause a

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reduction in the dissolution rate of the calcite surface.

The dissolution rate of calcite increased with increasing temperature, from 0.38×10^{-3} cm/s at 5°C to 2.80×10^{-3} cm/s at 25°C. The apparent activation energy determined for the surface reaction rate constant in the heterogeneous reaction model was 101 ± 8 kJ/mol, a value that is significantly larger than literature values (46 to 63 kJ/mol). The apparent activation energy for the mass transfer rate constant was 17 ± 0.3 kJ/mol, which is consistent with values in the literature for mass transfer controlled kinetics.

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