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SOLUTION OF LIMESTONE UNDER LAMINAR FLOW BETWEEN PARALLEL BOUNDARIES

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Introduction

Although the *equilibrium* relationships of the major chemical components of carbonate rocks with ground water are fairly well known, knowledge concerning the *kinetics* of dissolution of carbonate rocks is almost completely lacking. A few theoretical treatments of such kinetics under simplified assumptions have been offered by Weyl (1958), Howard (1964a), and Curl (1965), and a few simple kinetic experiments have been attempted by Weyl (1958) and Kaye (1957). However, these experiments were not directly comparable to the dissolution of carbonate rocks by ground water flowing through joints and conduits. The experiments reported below investigate solution kinetics under conditions approaching those of natural ground water flow through joints and fissures in carbonate rocks. The experiments were restricted to flow within parallel walls of limestone with narrow gap widths in the size range of small, natural fractures and openings; the experiments were designed to represent the initial stage of solution enlargement of small fractures and joints into caves and fissures. As I have pointed out previously (HOWARD, 1964a, p. 48), "the first stages of solution of a cavern are the most critical in its history, for the patterns of ground water flow through the cavern and the resulting pattern of its development are determined to a great extent by the beginnings of solution."

Experimental

Artificial "joint openings" were constructed by sawing blocks of limestone into rectangular pieces which were then lapped together and cemented with epoxy along two edges to a predetermined gap width, to form parallel openings having the dimensions given in Table 1. The solutions were constrained, by the cement edges, to flow along the long dimension of the blocks. The resulting cavity is described by coordinate axes, x , y , and z where x is the long dimension (length), y is the intermediate dimension (width), and z is the gap width (Figure 1). In the equation below, the variable x refers to the position along the path of flow, referred to an origin at the point of entry of fresh solutions into the block. In the experiments, the x and y dimensions were oriented in the horizontal plane.

Two types of limestone were used to construct the blocks described above. Blocks A through F were made from a very pure crystalline limestone, the "Tennessee Marble" of the Holston or Lenoir formations, and blocks G and H used a pure, black, organic-rich, cryptocrystalline limestone (Stones River formation, West Virginia). Both of these limestones were almost pure calcium carbonate, and yielded negligible concentrations of magnesium or other ions upon dissolution in the "ground waters" described below.

Because the gap width in all blocks was much smaller than the width of the opening ($z \ll y$), the effects of the boundary walls in the y -direction were neglected, and the measure of the discharge through the openings used in all calculations is the actual discharge divided by the y -dimension of the block, or discharge per unit width, Qy . The flow was slightly constricted at the ends of the blocks, but these effects were neglected. The hydraulic

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gradient, b , was computed by dividing the measured hydraulic head acting across the block by the length of the block.

All experiments were conducted within the laminar flow regime, as verified by the proportional relationship between discharge and hydraulic gradient. Under laminar flow the following formula (after PAO, 1961) describes the relationship between the discharge per unit width, Q_y (cc/cm sec), the hydraulic gradient, b , (dimensionless), and gap width, z (cm):

$$hz^3 = 1.17 \times 10^{-4} Q_y \quad (1)$$

In laminar flow, surface roughness does not affect the flow characteristics. However, it may affect solution kinetics. Surface roughness of the blocks was not measured, but the surfaces subjected to solution in the experiments were exposed to the dissolving action of carbonic acid prior to the actual experiments so that the surfaces would be characteristic of dissolving limestone.

Although the openings were constructed to approximate a specified gap width, the percentage error in the constructed openings was large for the smaller gap widths. Therefore, Equation 1 was used to obtain a more realistic *effective* gap width for each block, from observed relationships between discharge and hydraulic gradient. Because of the solution enlargement of the openings during the experiments, the gap widths did not remain constant. The values given in Table 1 are averages, but more precise figures are used in individual experiments. Because the gap width did not increase greatly during any one set of experiments on the same block under different hydraulic gradients, no appreciable error was introduced by considering the gap width to be a constant.

The "ground-water" solutions run through the blocks consisted of distilled water charged with a specified partial pressure of carbon dioxide at one atmosphere total pressure. In one set of experiments the partial pressure of carbon dioxide, pCO_2 , was one atmosphere. This partial pressure of CO_2 was selected to represent approximately the upper limit of dissolved CO_2 of natural waters. This is not unreasonable, because partial pressures of at least 0.15atm have been measured in soil water. The lower limit of CO_2 concentration in ground water should be approximately equal to the equilibrium value with respect to atmospheric $10^{-3.5}$ atm. The compressed air used to approximate this lower limit had a pCO_2 in the range from $10^{-2.3}$ to $10^{-3.2}$ atm, as estimated from limestone saturation experiments (see later discussion).

The concentration of dissolved calcium ion in the solutions was determined by titration with NaEDTA (RAINWATER AND THATCHER, 1960, p. 127-129), and concentration values are reported as parts-per-million (ppm) of calcium ion. The temperature of the dissolving solutions in all experiments varied from 21 to 24.5°C averaging about 23.5°C. Presentation and analysis of results is treated separately for the case of a pCO_2 of 1 atm and atmospheric CO_2 content.

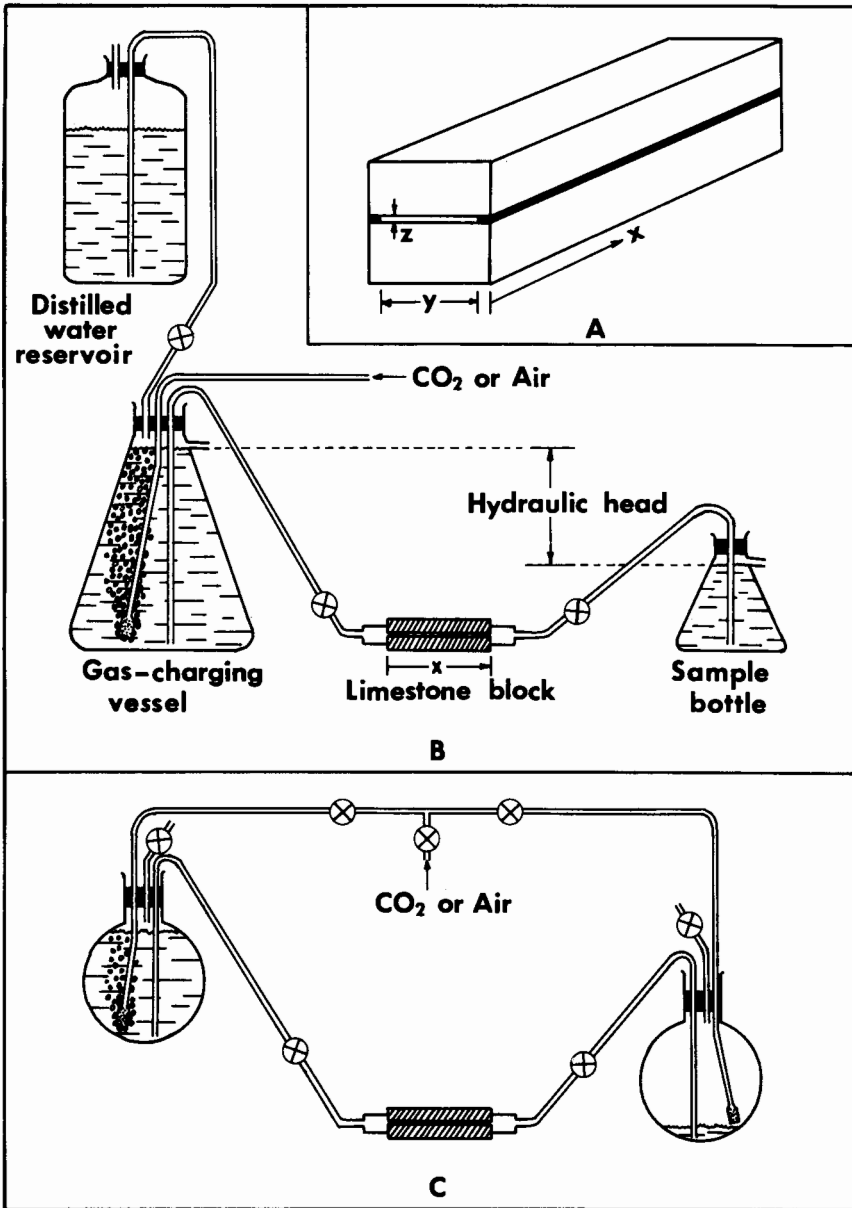


Figure 1. Experimental apparatus as described in text.

One atmosphere partial pressure of carbon dioxide: Two types of experiments were conducted at one atmosphere pCO₂. In the first of these, distilled water charged with carbon dioxide at one atm partial pressure was run through the various blocks as a closed system under different hydraulic gradients using the apparatus shown in Figure 1. In the second type of experiment, the "ground-water" solutions were repeatedly passed through the same block as a semi-closed system and sampled at intervals to find the functional dependence of the amount and rate of solution upon the total length of flow (Figure 1.)

In the first type of experiment, the concentration of calcium ion being discharged from the blocks was determined. The initial concentration of calcium ion was negligible. For each experiment the discharge was measured, and in some cases the hydraulic head also was measured. In cases where the hydraulic head was measured, the effective gap width of the blocks was computed by substitution into Equation 1. When the hydraulic head was too small to be measured, effective diameters were assumed from the calculations for known hydraulic heads. In such cases, Equation 1 was then used to calculate the hydraulic gradient.

For each experiment, computations were made of Qy , velocity, and residence time of the solutions within the blocks. These were plotted against ppm of calcium. It was found that, within the experimental error, all plots on a log-log scale relating ppm to Qy were parallel straight lines. However, the position of the lines for blocks of approximately the same gap width was dependent upon the length of the block. Plots for blocks of the same gap-width were made nearly coincident by plotting the parts-per-million increase of calcium ion per unit length of flow (ppm/x) versus Qy . The resulting plots described the family of curves

$$\frac{\text{ppm}}{x} = K Q_y^{-0.75} \tag{2}$$

where K is a constant. The experimental data are plotted in Figure 2 and values of K for the individual blocks are given in Table 1. The constant K may be calculated approximately from the following relationship:

$$K = 0.0956 z^{-0.2} \tag{3}$$

This equation should be assumed to be valid only over a range of gap width from about $10^{-2.5}$ cm to about 10^{-1} cm, the range of the experimental values.

The relationship given by Equation 2 does not hold true for values of Qy greater than about $0.6\text{cm}^2/\text{sec}$ or ppm/x less than about 0.2. The relationship replacing (2) for values of Qy greater than, and ppm/x less than, the above values is approximately

$$\frac{\text{ppm}}{x} = 0.159 Q_y^{-0.4} \tag{4}$$

Few data points were taken in this region and the relationship must be considered tenuous. From experiments run under known hydraulic head and discharge, it was found that the transition found laminar to turbulent flow within the blocks began at a Qy of about $2.6\text{ cm}^2/\text{sec}$. It would thus appear that the transition between (2) and (4) is not associated

Block	Width (cm)	Length (cm)	Gap width (cm x 10 ⁻²)	K
A	2.34	6.43	0.50	0.200
B	2.36	6.43	1.2-1.4	0.225
C	1.71	12.54	1.3-2.4	0.205
D	1.37	6.18	2.8	0.196
E	1.70	12.70	5.1	0.158
F	2.58	12.50	8.9	0.133
G	2.10	13.25	1.2	0.210
H	1.63	13.25	8.9	0.159

TABLE 1. Block Dimensions and Experimental Values of the Constant K.

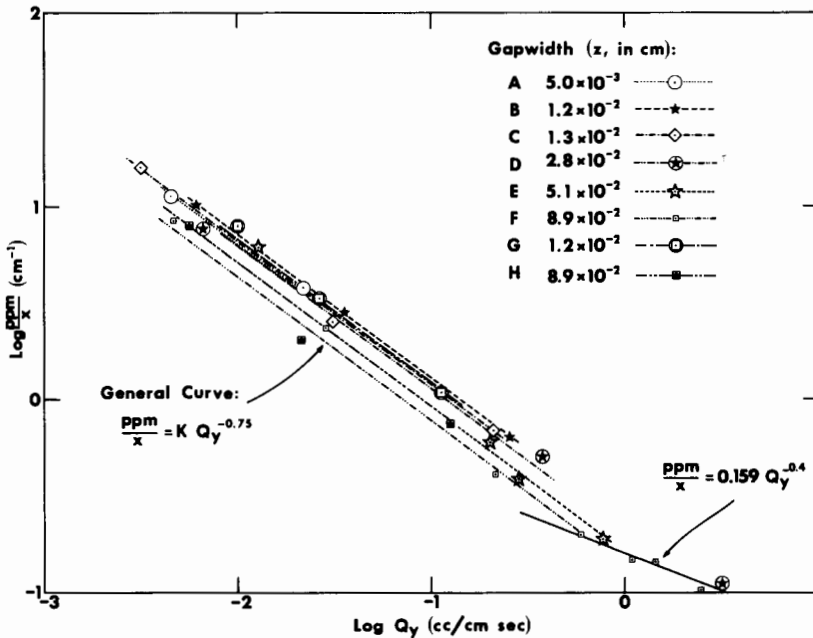


Figure 2. Relationship between $\log(\text{ppm}/x)$ and $\log Q_y$ for single-run experiments with $p\text{CO}_2 = 1 \text{ atm}$. Equations fitted to the experimental data are also shown.

with a change in flow regime. It may be that at a low concentration of dissolved calcite a different mechanism may be active, giving a higher rate of dissolution than would be expected from (2). A relationship similar to (4) was found for atmospheric CO_2 content (Equation 13), for which the calcium ion concentration was within the same range of values. On the other hand, the data do not rule out the possibility that higher velocity rather than higher concentration of calcium ion is the factor determining the transition from (2) to (4).

In the second type of experiment, run with a $p\text{CO}_2$ of 1 atm, the carbon dioxide charged water was successively run through the same block under an approximately constant hydraulic head. This experiment was run with block C, to investigate the dependence of rate of solution on length of flow for lengths greater than the longest of the individual blocks, about 13 cm. Under the experimental setup, the water was passed through the block with a falling head. Because of the high partial pressure of dissolved carbon dioxide, it was necessary to recharge the solution with carbon dioxide continuously except when passing through the block. Thus the experimental conditions could not exactly duplicate the closed system of continuous circulation over long distances. Additionally, the average hydraulic head decreased slightly as the experiment progressed, due to the removal of samples from the solution reservoir. Because of the large volume of solution passed through the block during each successive run (about 500 cc), the gap width of the block increased from about 1.7×10^{-2} to 2.5×10^{-2} cm during the course of the experiment. Therefore, the derived relationship given below must be considered approximate. The experimental dependence of ppm on the total length of flow is given by the points in Figure 3. Two of the points were selected as the basis for the fitting of an exponential decay curve

through the experimental points (solid line in Figure 3). It is evident that the fit of the curve to the data is quite good. The equation of this curve is

$$\text{ppm} = 235 [1 - \exp(-1.43 \times 10^{-2}x)], \quad (5)$$

where x is given in centimeters. The slope, or tangent, to this curve at any point is

$$\frac{d\text{ppm}}{dx} = 3.36 \exp(-1.43 \times 10^{-2}x) \quad (6)$$

In the following analysis, it is assumed that recirculation runs (in each of the blocks) would approach the same asymptote with a path describable by an exponential decay curve. Thus, in the general case Equations 5 and 6 become, respectively:

$$\text{ppm} = 235 [1 - \exp(-Cx)] , \quad (7)$$

and

$$\frac{d\text{ppm}}{dx} = 235 C \exp(-Cx) , \quad (8)$$

where C has a functional dependence upon hydraulic gradient and block diameter.

Because the exponential decay curve is nearly linear for very small values of the exponent, Equation 2 may be assumed to represent the relationship between ppm and x for very small values of x . Therefore, the value of Equation 8 for $x = 0.0$ can be equated with the derivative of Equation 2, giving

$$C = \frac{KQ_y^{-0.75}}{235} . \quad (9)$$

The coefficient C was introduced without specific reference to the actual experimental values of z , b , and Q_y in the experiment yielding Equation 5. As a check on the validity of the assumptions giving (7), (8), and (9), the block diameter used in the recirculation runs can be used to estimate the average hydraulic gradient during the runs. For the

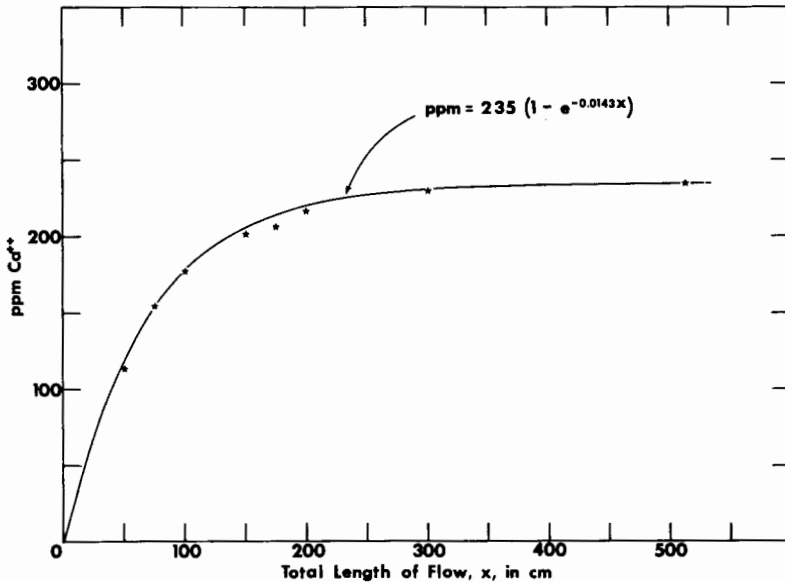


Figure 3. Experimental data and fitted curve showing the dependence of ppm of calcium ion to length of flow, x , in the recirculation experiment with $p\text{CO}_2 = 1$ atm.

recirculation experiment, the value of C was 1.43×10^{-2} . The average value of z during the experiment was about 2.2×10^{-2} cm. Using (9), Q_y may be found to be 2.37×10^{-2} cm²/sec. Because it took about 5 hours for 500cc of solution to pass through the block, this figure is quite reasonable. From (1) the average hydraulic gradient would be 0.26. The median hydraulic gradient during the runs was about 0.4, but the time average of the hydraulic gradient was probably very close to the value predicted by (9), inasmuch as the head and corresponding discharge decreased during the progression of each run.

The rate of increase of gap width may be equated with the rate of increase of calcium ion in solution by the equation

$$\frac{dz}{dt} = \frac{d\text{ppm}}{dx} \frac{100Q_y}{2.72 \times 40} 10^{-6}, \quad (10)$$

where 2.72 is the density of limestone, the ratio 100/40 corrects parts-per-million of calcium ion to the equivalent concentration of dissolved calcite, and the factor 10^{-6} converts parts-per-million to grams-per-cm³. The units of dz/dt are cm/sec. Equation 10 is valid for any point along the path of flow.

The final equation relating the rate of increase of gap width to the discharge and position along the path of flow relative to the origin is obtained by substitution of (8) and (9) into (10) to give

$$\frac{dz}{dt} = 9.2 \times 10^{-7} K Q_y^{0.25} \exp(-4.27 \times 10^{-3} K x Q_y^{-0.75}). \quad (11)$$

Equation 1 may be used to eliminate Q_y , giving

$$\frac{dz}{dt} = 8.85 \times 10^{-6} K z^{0.75} h^{0.25} \exp(-4.77 \times 10^{-6} K x z^{-2.25} h^{-0.75}). \quad (12)$$

These equations indicate that the rate of enlargement of the openings decreases in the direction of the flow. This means that after a finite time the walls of the conduit will no longer be parallel. Thus (11) and (12) are valid only during the initial stages of solution while the channel walls remain of essentially uniform gap width along the direction of flow. Also, (11) and (12) should not be assumed to be valid for values of Q_y greater than 0.7 cm²/sec or less than 3×10^{-3} cm²/sec, or for values of z outside of the experimental range of 5.0×10^{-3} to 10^{-1} cm.

In the above experiments CO₂ was introduced into the reacting solutions by bubbling the contents of a commercial cylinder of CO₂ through the solutions at one atmosphere pressure. The CO₂ in the gas cylinder was specified to be 99.5% pure, and should have equilibrated with the solutions to a partial pressure of essentially one atmosphere. The equilibrium constants given by Garrels and Christ (1965) predict an open system saturation value of calcium ion at 23.5°C of 400ppm for a pCO₂ of one atmosphere. The corresponding saturation value for water first equilibrated with respect to one atmosphere pCO₂ in the absence of limestone and then saturated with respect to limestone in the absence of a gas phase (closed system saturation) would be 318ppm. Experimental determination of open and closed system saturation with respect to limestone using CO₂ from the cylinder as described above and the "Tennessee Marble" yielded low equilibrium values of 305ppm and 256ppm, respectively. These values are consistent with a pCO₂ of $10^{-0.37}$ atm (0.47 atm) using the equilibrium constants of Garrels and Christ.

Several factors might account for the lower experimental values relative to the theoretically-predicted values:

- 1) The various solutions may not have equilibrated completely with the carbon dioxide bubbling through the system.
- 2) The carbon dioxide may not have been as pure as specified.
- 3) Errors in the equilibrium constants may have been great enough to give the 24% error between predicted and experimental results.
- 4) The titration solutions may have had a standardization error of this magnitude.
- 5) Diffusional loss of CO₂ from the circulating solutions subsequent to recharging

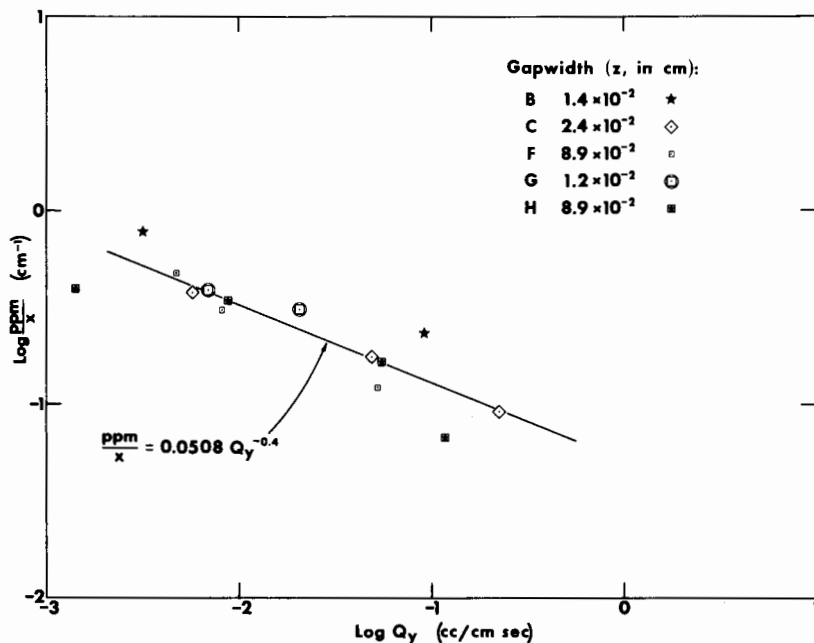


Figure 4. Relationship between $\log(\text{ppm}/x)$ and $\log Q_y$ for single-run experiments with $p\text{CO}_2 = 10^{-1.8}\text{atm}$. Equations fitted to the experimental data are also shown.

and while passing to and from the limestone blocks may have limited the amount of solution or caused reprecipitation of calcite within the apparatus.

6) The actual temperature during the experiments may have been a few degrees different from the measured temperatures.

7) Surface effects on the face of the dissolving limestone blocks may have limited the solubility of the limestone. Precipitation of organic material onto the limestone (cf. CHAVE, 1965) or presence of small concentrations of copper, lead, and other ions in the dissolving solutions (cf. TERJESSEN et al., 1960) have been suggested as inhibitory mechanisms in the solution of calcite. The organic material or inhibitory ions may have derived either from the distilled water or the dissolved limestone.

Factors 1 and 5 above would be expected to produce random errors changing from experiment to experiment. The consistency of both the saturation experiments and the circulation experiments argue against the importance of these factors. In addition, factor 5 does not account for the low value for the open system saturation. Saturation experiments with respect to atmospheric content of CO_2 predicted from the equilibrium relationships values of $p\text{CO}_2$ 2-10 times greater than "normal" atmospheric content. This renders less likely the importance of factors 3 and 4. The ease of obtaining nearly pure CO_2 and the manufacturer's purity specification reduce the probability of the importance of factor 2. Temperature effects upon solubility are likewise ruled out as the only contribution by the magnitude of the deviation between experimental and theoretical saturation values; temperature variation from 20°C to 25°C (encompassing the temperature range during the experiments) accounts for only a 10% change in the solubility of limestone.

Surface effects upon the dissolving limestone thus are the most suspect factor causing the discrepancy between experimental and theoretical saturation values. The asymptotic

concentration of 235ppm given by (5) for infinite path length of flow bears further upon this question.

The asymptotic calcium ion concentration of closed system circulation should be equal to the closed system saturation value, and for the recirculation apparatus used to approximate closed system circulation the asymptote should be greater, due to the recharging of the solutions with CO_2 before each recirculation. In actuality it was less. One difference between the saturation experiments and the recirculation experiment was the volume of dissolving water, being approximately 80cc for the saturation experiments and 500cc for the recirculation run. The difference between the asymptotic concentration and the closed system saturation would be explained by a surface inhibitory mechanism if the source of the inhibitant were the dissolving limestone and if the action of the inhibitant were proportional to its total quantity in the dissolving solutions relative to the surface area of dissolving limestone (as opposed to its concentration).

If surface effects are responsible for the experimental saturation anomalies, they should be relatively important at high concentrations of dissolved limestone (long path lengths of flow), and should have little effect at low concentrations of dissolved limestone.

Atmospheric partial pressure of carbon dioxide: The experiments for this case were run under conditions identical to those run with a partial pressure of 1atm of pCO_2 except that air from a compressor was bubbled through the water. Results were less consistent than for those with a pCO_2 of 1atm. Three possible reasons for this lie in the higher experimental errors at low concentrations of calcium ion, variations in the partial pressure of carbon dioxide in the compressed air, and introduction of variable quantities of acidic components into the solutions by the compressed air. Assuming that this third source of error was of negligible importance, the approximate partial pressure of CO_2 in the compressed air was estimated by open system saturation of air-charged water with limestone, using the equilibrium constants of Garrels and Christ (1965), giving a pCO_2 of $10^{-3.25}$ atm. A closed system saturation of air-charged water with limestone gave an estimated pCO_2 of $10^{-2.32}$ atm. These values are not unusual for laboratory air.

Results of the single-run experiments with the various blocks under different hydraulic gradients are shown in Figure 4 as the relationship between Qy and ppm/x . An approximate relationship fitting these data is given by the equation of the line constructed in Figure 4:

$$\frac{\text{ppm}}{x} = 0.0508 Q_y^{-0.4} \quad (13)$$

A closed-system recirculation run was made for this partial pressure of CO_2 (Figure 5). Two exponential decay curves are shown in this figure. Neither curve fits the data as well as in the case of a pCO_2 of 1atm. The following relationship will be used in the mathematical development, with acknowledgement of the error in the approximation:

$$\text{ppm} = 8.20 [1 - \exp(-4.04 \times 10^{-2} x)] \quad (14)$$

Using (13) and (14) with the assumptions of identical asymptotes for all blocks and that all recirculation runs follow an exponential decay curve in ppm vs. length, the equivalents of (11) and (12) for the lower pCO_2 become

$$\frac{dz}{dt} = 4.68 \times 10^{-8} Q_y^{0.6} \exp(-6.2 \times 10^{-3} x Q_y^{-0.4}) \quad (15)$$

and

$$\frac{dz}{dt} = 8.32 \times 10^{-6} z^{1.8} h^{0.6} \exp(-1.66 \times 10^{-4} x h^{-0.4} z^{-1.2}) \quad (16)$$

respectively.

Discussion

The experimental results given in Equations 11, 12, 15 and 16 are similar in form to the theoretical derivation based upon mass-transfer theory given by Weyl (1958) and

to the simplified model treated by Howard (1964a). Weyl's equations are not in the functional form of the experimental equations, but may be changed to this form (see Appendix), giving

$$\frac{dz}{dt} = 5.40 \times 10^{-6} C_s z^{-1.0} \exp(-1.75 \times 10^{-8} x h^{-1.0} z^{-4.0}), \quad (17)$$

where C_s is the molar saturation (asymptotic) concentration of calcium ion. Note that the powers of hydraulic gradient and gap width differ significantly from those of (12) and (16), although the agreement is closest with (12). In addition, Weyl's derivation does not predict the observed differences in the form of the rate equations depending on the original concentration of CO_2 in solution. By use of (10), Equation 17 can be used to predict values of ppm of calcium ion given length of flow, discharge per unit width, hydraulic gradient, gap width, and the saturation concentration of calcium ion. These may then be compared to the experimental values of ppm as a test of the validity of Weyl's model. It was found that within the experimental range of Qy and z , Equation 17 predicted a much more rapid approach to saturation than was observed, with a greater discrepancy at lower values of Qy and z . Therefore, it would appear that the actual solution process is not very accurately represented by Weyl's diffusion model of one limiting component.

The rate equation given by Howard (1964a) in the present notation, is

$$\frac{dz}{dt} = M \exp(-Nxh^{-1.0} z^{-3.0}), \quad (18)$$

where M and N are unspecified constants. This model also shows a large discrepancy from the experimentally-derived equations.

The asymptotic approach to saturation of the solutions flowing through the joint openings means that little significant solution will occur after a finite length of flow. Weyl (1958) defines a "penetration distance" to an arbitrary degree of saturation which may be used to approximate the limit of significant solution along the path of flow. Weyl selected the penetration distance to 90% saturation as this measure. This penetration distance for

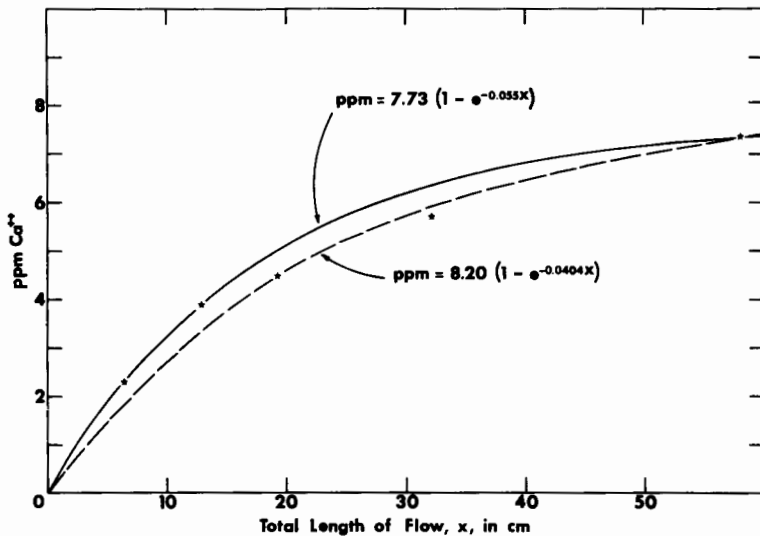


Figure 5. Experimental data and fitted curves showing the dependence of ppm of calcium ion to length of flow, x , in the recirculation experiment with $p\text{CO}_2 = 10^{-1.8}\text{atm}$.

a $p\text{CO}_2$ of 1atm within the range of conditions limiting the applicability of (11) and (12) is

$$x_{90} = 2.37 \times 10^6 h^{0.75} z^{2.25}, \quad (19)$$

and for a $p\text{CO}_2$ of $10^{-1.8}$ atm is

$$x_{90} = 1.39 \times 10^4 h^{0.40} z^{1.20}. \quad (20)$$

If the penetration distance is of the order of magnitude of, or larger than, the total length of flow of ground water in the natural joint, then enlargement of the original joints and fractures into cavern passages by virtue of solutional attack of the limestone by dissolved CO_2 should be expected. If the penetration distance is much shorter than the length of the unenlarged joints and fractures, then *this* mechanism cannot be responsible for the initial stages of development of any cavern passages.

Length of the path of ground-water flow through limestone, original joint diameters, and hydraulic gradients through limestone vary greatly depending upon the stratigraphy, structure, and physiographic situation. Two hypothetical ground-water flow patterns will be introduced to test for the feasibility of joint enlargement by the mechanisms investigated in this paper. The first situation represents a favorable extreme for ground-water flow through limestone in which the path length of flow is assumed to be short (10m) and the hydraulic gradient is postulated to be high ($10^{-1.0}$). Assuming further that $p\text{CO}_2$ is 1 atm, the gap width of unenlarged joint that would give a penetration distance of 10m is 6.8×10^{-2} cm from the criterion of (19). Because natural joints and fractures under favorable circumstances might reach such a gap width, initiation of cavern development by solution attack by dissolved CO_2 is not unreasonable under favorable conditions of high hydraulic gradient and short distance of ground-water flow through limestone. On the other hand, under a less favorable hydraulic regime in which the hydraulic gradient is only 10^{-3} and the length of flow is 1000m, an original gap width of 0.89cm would be required to give a penetration distance of 1000m. Because such a gap width seems unlikely, the present mechanism alone could not account for the initial stages of cavern development under the assumed hydraulic regime.

In fact, cavern development does take place under hydraulic situations as extreme or more extreme than the "unfavorable" situation postulated above. Cavern development in the Black Hills of South Dakota, described by Howard (1964b), takes place under such low hydraulic gradients and long paths of subterranean flow. F. A. Swenson (personal communication) describes an artesian ground water system through limestone in South Dakota in which the hydraulic gradient is about 3×10^{-4} and the path of ground-water flow is about 240km. Swenson asserts that significant limestone solution is taking place at present and has taken place in the past along the length of this flow. Thus it would appear that mechanisms other than solution by virtue of original undersaturation with respect to CO_2 are active in cavern development in certain cases. Such mechanisms might include convergence of flow, addition of fresh solutions along the path of flow, *Mischungskorrosion* effects, addition of CO_2 or other acids along the path of flow, systematic changes of pressure or temperature along the path of flow, control of pH in the ground water by species other than those involving calcium and carbonate radicals.

Of the innumerable joints and fractures within limestone of karst areas only a few are ultimately enlarged to form cavern passages. Therefore, it is relevant to ask whether the mechanism discussed in this paper promotes differential enlargement of one initial fracture relative to another because of an initial advantage in fracture diameter or hydraulic gradient acting across it. In order for differential enlargement to occur, the ratio of the larger to the smaller passages being compared must increase with time. For this to be true, then the rate of change of the rate of increase of gap width with time, d^2z/dt^2 , must be a positive, increasing function of gap width. Equations 12 and 16 give complicated acceleration functions, in which it is impossible to tell by inspection whether or not the

Length of flow, x , (cm)	A			B		
	$z=10^{-3}$ cm	$z=10^{-2}$ cm	$z=10^{-1}$ cm	$z=10^{-3}$ cm	$z=10^{-2}$ cm	$z=10^{-1}$ cm
0	1.0×10^{-5}	3.6×10^{-6}	1.3×10^{-6}	6.0×10^{-6}	3.8×10^{-7}	2.4×10^{-6}
5	0	4.8×10^{-6}	1.3×10^{-6}	7.6×10^{-9}	3.4×10^{-7}	2.4×10^{-6}
10	0	5.2×10^{-6}	1.3×10^{-6}	4.4×10^{-10}	3.2×10^{-7}	2.4×10^{-6}
20	0	5.6×10^{-6}	1.3×10^{-6}	6.0×10^{-13}	2.5×10^{-7}	2.4×10^{-6}
50	0	4.0×10^{-6}	1.3×10^{-6}	0	1.1×10^{-7}	2.3×10^{-6}
100	0	1.3×10^{-6}	1.3×10^{-6}	0	2.1×10^{-8}	2.2×10^{-6}
200	0	8.0×10^{-8}	1.3×10^{-6}	0	6.0×10^{-10}	1.9×10^{-6}
500	0	4.4×10^{-12}	1.4×10^{-6}	0	5.6×10^{-15}	9.6×10^{-7}
1000	0	0	1.3×10^{-6}	0	0	4.8×10^{-7}

TABLE 2. Acceleration of Passage Gap Width, d^2z/dt^2 , for $h = 1$.

above criterion is met. Therefore numerical values of the acceleration functions of (12) and (16) are given in Table 2. In Table 2A the accelerations are given for an arbitrary hydraulic gradient and selected values of gap width and position along the path of flow for the case governed by (12). Similar numerical examples are given in Table 2B for accelerations derived from (16). In Table 2B the acceleration is at all points a positive, increasing function of passage diameter, indicating differential enlargement. In Table 2A, however, at the entrance region of the flow path the acceleration is a positive but decreasing function of passage diameter, indicating that all joints of different gap widths are competitive. Note that although the *acceleration* for the entrance region in Table 2A decreases with increasing gap width, (12) shows that the *rate* of increase of passage gap width increases with increasing gap width if the hydraulic gradient is constant. For points farther from the entrance region of the passage (large x), the inverse relationship between gap width and acceleration in Table 2A changes to a direct relationship, indicating that selective enlargement of originally larger joints will occur. This is related to the penetration distance discussed earlier.

A table similar to Table 2 might be made in which the gap width is assigned an arbitrary value and the hydraulic gradient is allowed to vary. This would show that in the entrance region no selective enlargement of passages with originally larger hydraulic head would occur, but that farther along the path of flow, the hydraulic gradient would become a selective factor in passage enlargement.

The presence of, or lack of, selective enlargement is a major determinant of the path of ground water flow and the pattern of the resultant caves. However, because the experiments reported in this paper are subject to refinement and enlargement to cover a greater range of hydro-chemical conditions, no inferences as to their significance in this respect are offered. A general discussion of the subject is given in HOWARD (1964a).

The experimental results presented in this paper are not regarded as definitive or conclusive, but rather indicative of the solution kinetics of the CO_2 -water-calcite system in the laminar flow regime. These experiments were conducted on a limited budget, but show the feasibility of experimental investigation under conditions approximating natural ground-water flow through limestone. A few suggestions are offered for possible enlargement of the experiments. Because the experiments described show little agreement with Weyl's mass-transfer theory of solutions kinetics, similar experiments might be run on gypsum blocks, whose solution chemistry is simpler than that of the carbonate system. Other carbonate rocks might be employed, to include 1) limestones with other physical and chemical characteristics and 2) dolomite. The experiments described might be enlarged to include a greater variety of gap widths, a greater range of CO_2 partial pressure and, finally, to admit both very slow and very rapid flows. A particular problem is encountered for very rapid flows, including flows in the turbulent flow regime, in that concentrations of dissolved calcium ion for a reasonable length of flow are very low, so that either more

sensitive analytical techniques would have to be employed or recirculation techniques would be required. Finally, the solution kinetics of passages with non-parallel walls might be investigated.

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APPENDIX — DERIVATION OF EQUATION (17)

Weyl (1958) defines the quantity C' , the fractional difference from saturation, as

$$C' = 1 - \frac{C}{C_s} \tag{1A}$$

where C is the concentration of solute and C_s is the saturation concentration of the solute. Weyl gives concentration in moles-per-liter, and the solute of interest is dissolved calcium carbonate. Because the author's concern is with the rate of change of concentration with length of flow, Equation 1A can be differentiated to give the following relationship:

$$\frac{dC}{dx} = -C_s \frac{dC'}{dx} \tag{2A}$$

The concentrations measured in this paper are average concentrations of the outflow, which Weyl distinguishes by bars (e.g., \bar{C} and \bar{C}'). Weyl's equation relating \bar{C}' to the variables of length of flow, gap width, and flow velocity is given as an infinite series. Because the series converges rapidly, only the coefficients for the first term will be used. Weyl's equation for laminar flow in parallel channels becomes, in the present notation

$$\bar{C}' = 0.98 \exp(-1.5 \times 10^{-4} x V^{-1} z^{-2}) \tag{3A}$$

where V is the average velocity through the channel. Because $Vz = Qy$, V may be eliminated from (3A), and Qy may be further eliminated by use of (1), giving

$$\bar{C}' = 0.98 \exp(-1.75 \times 10^{-8} x h^{-1} z^{-4}) \tag{4A}$$

Therefore, by differentiating,

$$\frac{d\bar{C}'}{dx} = -1.72 \times 10^{-8} h^{-1} z^{-4} \exp(-1.75 \times 10^{-8} x h^{-1} z^{-4}) \tag{5A}$$

The relationship between dz/dt and dC'/dx in molar concentrations is

$$\frac{dz}{dt} = \frac{10^{-1}}{2.72} \frac{d\bar{C}}{dx} \quad (6A)$$

From (5A), (6A), and (2A), $d\bar{C}'/dx$ can be related to dz/dt , and Qy can be eliminated using (1), giving Equation 17.



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A brief account, with hydrographs and tabulated data, of the failure of a reservoir located on Mesozoic limestone, near Konya, Turkey. The 28m-high earthfill dam was completed in 1950. Between February and April 1960 the reservoir held water, but by June it had completely drained, leaving a bottom containing circular, vertical sinkholes in the alluvium covering the limestone. —ALL

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More than 25% of this important volume of proceedings concerns karst hydrology. The papers are too numerous to be cited here. —JFQ

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An important review paper. Included is a map showing the distribution of carbonate rocks, a critical discussion of chemical and mechanical weathering and its topographic expression, and ground water hydrology. Three types of limestone terrain are described: youthful, covered by post-glacial marine landforms and sediments, and covered by glacial deposits. A periglacial limestone cycle of erosion is proposed. In the lively discussion of this paper, conflicting opinions were expressed concerning the abundance and age of solution cavities in large bodies of carbonate rock in permafrost regions. Several observations (unfortunately, not included) indicate that, contrary to Bird's opinion, large solution openings exist, transmit water, and are probably susceptible to continuing enlargement under present permafrost conditions. —JFQ

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The cave, approximately 40m long, is penetrated by salt water only during heavy seas. Its algal vegetation is largely dependent on the occurrence of fresh water seepage from the roof and walls.—JFQ

*Containing only technical books and articles in the karst sciences published in non-speleological journals. Contributions to this list, containing the complete reference citation are welcomed.