

Minimum hydrochemical conditions allowing limestone cave development

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Abstract. Early theoretical investigations into initiation of limestone cave development suggested that water entering small fractures approaches saturation within a short distance and thus appeared to be unable to produce much further enlargement of these fractures. The answer to this problem seems to be White's (1977) "kinetic trigger" idea, emphasizing the precipitous drop in dissolution rates as equilibrium is approached. However, minimum conditions of flow rate, passage geometry, and initial CO₂ concentration may exist, below which the waters will so nearly achieve saturation that caves will be unable to develop. Modeling results indicate that under geologically reasonable PCO₂ and head gradient values, the minimum initial aperture widths in which caves will develop is of the order of 100 μm. Initial apertures wider than about 500 μm will form passages very easily, even under low head gradients. There will thus be strong differential selection among initial flow paths with regard to cavern passage development.

Introduction

One of the earliest theoretical efforts to study initiation of conduits within karst aquifers was made by Weyl [1958], who coupled calcite dissolution kinetics with laminar flow hydrodynamics. He assumed that diffusion of reaction products was the rate-limiting kinetic step, and calculated a "penetration length" for water entering initial fractures. This described the length that water can flow before reaching a given high level of saturation and which seemed very short compared to the observed lengths of natural cavernous conduits. Weyl's analysis showed that penetration lengths under what he considered natural conditions of fractures would be on the scale of millimeters to meters. Howard [1964] suggested that the first stages of initiation could be enhanced by local acid production, by either bacterially assisted oxidation of organic material [Murray and Love, 1929; Imbt, 1950] or sulfide minerals. Based on theoretical treatment and results of solution experiments, Howard [1964], and Howard and Howard [1967] also concluded that the solution process was not very accurately represented by Weyl's [1958] model of one limiting component. Curl's [1965] work stressed the slowness of CO₂ hydration as a potential limiting step, offering longer penetration lengths. Other suggested mechanisms addressing the problem of short penetration lengths include convergence of flow, addition of fresh solutions, and enhanced solution ability due to mixing of waters of differing composition, or "Mischungskorrosion" [Bögli, 1964; Howard, 1966; Runnells, 1969; Dreybrodt, 1981a]. Atkinson [1968] speculated that diurnal rock movements as a result of Earth tides or temperature fluctuations (as detected and measured by Davis [1968] in a

California cave) could pump undersaturated fluids in small fractures, thereby increasing early dissolution rates.

The drop in dissolution rates that accompanies close approach to equilibrium has since been recognized to be an important part of the conduit development process in what White [1977] called the "kinetic trigger." The key point of this idea is that upon approaching equilibrium, dissolution rates drop significantly. Although the waters are now slower to dissolve the passage walls, they can extend much greater distances into the conduit, in many cases to the exit, without becoming fully saturated. Since the downgradient section of the conduit is still enlarging, even if slowly, flow velocities within the conduit increase through time and relatively undersaturated (rapidly dissolving) waters can reach farther and farther downgradient until they occupy the entire conduit. Dreybrodt [1990] suggested that an initiation phase of conduit development could be measured as the time necessary for the relatively undersaturated waters to occupy the entire conduit and termed this the "breakthrough time."

Although White's [1977] concept of the kinetic trigger seems to have provided a sufficient mechanism to overcome the very short penetration lengths that concerned earlier investigators, there still must be minimum initial conditions for conduit development, below which the waters at work forming them will approach so close to saturation as to be unable to effectively enlarge the conduit within any realistic geologic time.

A series of model simulations was performed to investigate the minimum conditions. Starting with very small initial apertures for which "numerical saturation" was achieved during the growth of a developing conduit, subsequent simulations starting with larger and larger apertures were run. In this way, the minimum aperture at which conduit growth is successfully achieved was determined as a function of head gradient for various conduit lengths and initial PCO₂ values. Although theoretically saturation is approached only asymptotically by any of the kinetic processes considered by the model, finite residence times within model

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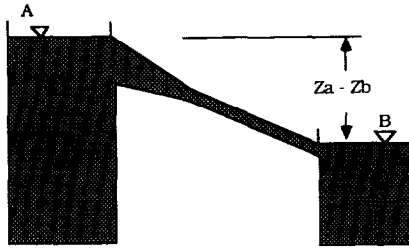


Figure 1. Schematic diagram of physical model formulation.

elements permit saturation to be achieved numerically. The relationship between these two approaches to saturation is discussed below.

Model Structure

Problem Formulation

A schematic diagram of the physical situation simulated by the model is shown in Figure 1 and consists of a circular cross-section conduit in limestone with static reservoirs of differing head at the entrance and exit. Although a rectangular fracture geometry might have been more representative, certain empirical elements of mass transfer theory for turbulent flow are currently unavailable for these geometries. *Buhmann and Dreybrodt* [1985] suggested that variations of cross-section geometry should introduce only a small difference in results. Conceptually, such a circular conduit can represent an intersection between a joint and bedding plane, which will provide a flow path of less resistance than either of the fractures alone.

User input allows selection of the initial geometry of the conduit including length, initial aperture, wall roughness, and elevation difference between reservoirs. Longitudinal variations in aperture may be included if desired. The problem is to determine, for geologically reasonable conditions, rates of passage growth by calcite dissolution in $\text{CO}_2/\text{H}_2\text{O}$ solutions. These rates vary as functions of both time and position along the conduit's length. Initial PCO_2 and temperature of the water entering the conduit at the upstream end are the chemical conditions supplied to the model. Full details and mathematical development of the model can be found in the work by *Groves* [1993].

The solution is subject to a number of physical and chemical simplifying assumptions. The fluid within the system is incompressible, with constant density and viscosity, and subject to negligible buoyancy forces. Flow is fully developed, in a steady state with respect to time, and the velocity component in the downstream direction (u) is much larger than that in the lateral direction (v). In addition (in cylindrical coordinates),

$$\frac{\partial u}{\partial r} \gg \frac{\partial u}{\partial x}, \frac{\partial v}{\partial r}, \frac{\partial v}{\partial x} \quad (1)$$

where x and r are downstream and radial coordinate axes, respectively. Concentration gradients affecting mass transfer in a direction normal to the conduit wall are assumed to be much steeper than those in the downstream direction, and a sharp transition between laminar and turbulent conditions is assumed to take place at a Reynolds number of 2300. In

rough pipes like those modeled in this project, the transition to turbulent flow can actually begin at lower Reynolds numbers [*White*, 1988], but an appropriate convection correlation describing mass transfer in turbulent flow that has been shown to be valid for Reynolds numbers below 2300 is currently unavailable [*Gnielinski*, 1976]. This should have minimal effect on results, since these runs designed to identify limiting conditions to conduit growth take place in very small conduits at low velocities, thus with low Reynolds numbers. Intergranular porosity within the aquifer is assumed to be negligible, with all flow within well-defined fractures.

Thermodynamic and kinetic expressions within the program consider the $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$ system only. Foreign ions have been shown to influence surface reaction rates, especially as equilibrium is approached, and the reader is referred to papers by *Berner and Morse* [1974], *Buhmann and Dreybrodt* [1987], and *Svensson and Dreybrodt* [1992] for further details on these effects. In general, foreign ions tend to lower surface reaction rates, such that conduits larger than those predicted by our calculations to be of minimal size for successful development may be unable to form into passages in the presence of rate-inhibiting ions. Thus initial fractures with aperture widths smaller than the minimum sizes that we predict will be unable to form into cave passages, but in some cases larger initial fractures may be required.

We also ascribe limited influence to ion pair formation.

General Model Format

We begin (Figure 2) by dividing the conduit into a number of elements of varying length that discretize the problem in space. Element lengths are calculated using a logistic equation [*Hall and Day*, 1977] that results in very short elements near the conduit's entrance (10^{-4} m), where solution rates are very rapid, and longer ones toward the exit (maximum length of 2 m). Discharge through the conduit is calculated and then used to determine velocity and residence time for the through-flowing water in each element.

Initially, water from the upstream reservoir is brought into the first element. A rate of calcite dissolution ($\text{ML}^{-2}\text{T}^{-1}$) is determined based on flow and chemical conditions; then this rate is multiplied by the surface area and residence time for the element to determine the appropriate amount of calcite to transfer from the passage walls into the water. The water's chemistry then reflects the additional calcite that has been added. The resulting final water composition for the first element becomes the input condition for the second, and the process is repeated down the conduit. It is during this process that saturation is identified if it occurs. Because the conduits are divided into elements with finite lengths, it is possible that the addition of new calcium within an element will bring the solution composition to or beyond the equilibrium value. If this happens, the dissolution rate will reach zero, and thus no additional conduit enlargement will be possible. We define this event as "numerical saturation."

At the end of a complete trip down the conduit a dissolution rate for each element will have been determined that varies along the conduit's length as a function of water chemistry. The program then dissolves the passage walls for a user-specified time step, the diameter of each element enlarging by an amount that reflects the dissolution rate

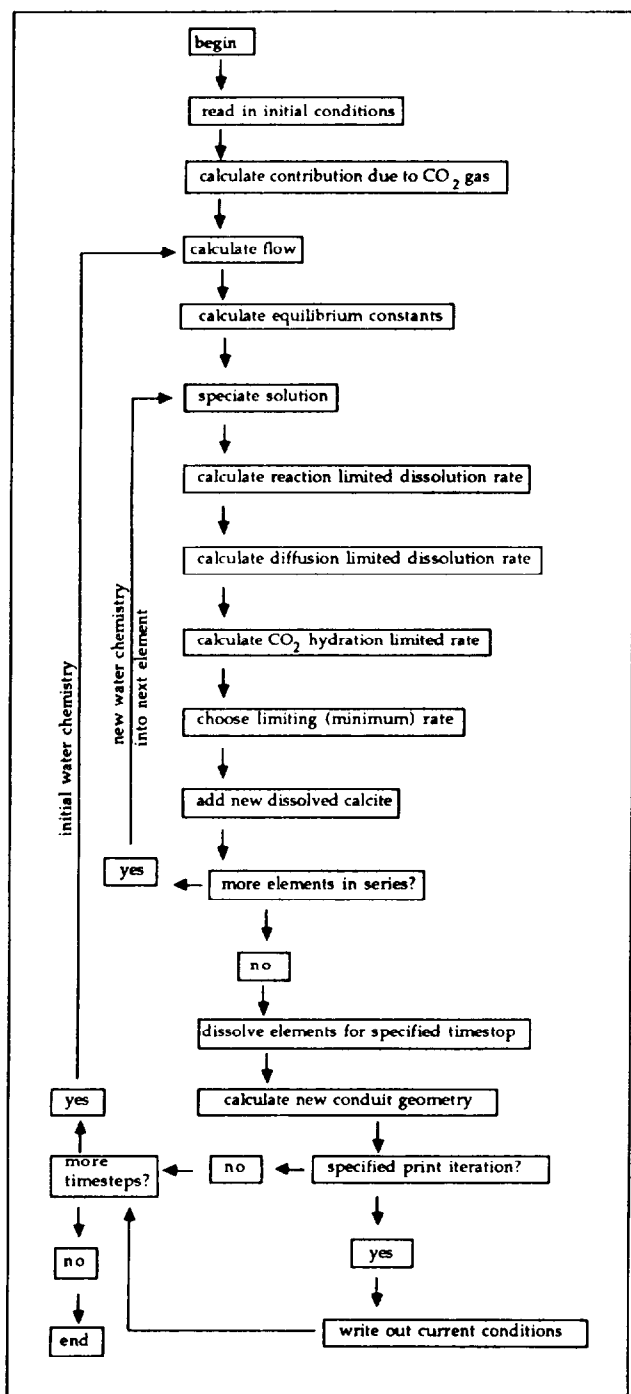


Figure 2. General organizational chart for simulation program.

determined for that point along the conduit. Thus at the end of the dissolving process, each element has a unique size.

The process is then repeated from the beginning, and a new discharge is calculated that takes into account the varying apertures along the conduit. This is then used to calculate new velocities and residence times, and a new slug of fresh solution begins a trip through the system. Because of the new geometry the rate of chemical change as the new water flows along the conduit will be different than that for the first trip, as will the dissolution rates at any point along

the conduit. In this way the problem is discretized in time. The process continues until either the conduit reaches a specified maximum diameter, or a specified number of iterations have occurred.

Flow Model

We use a one-dimensional form of the energy equation that is expressed in terms of energy losses due to friction of the fluid against the pipe walls. We assume that pipe diameter varies gradually, so that there are negligible energy losses due to expansions and contractions. Assuming that no mechanical work is being performed on the system, the energy equation may be expressed as [Granger, 1985]

$$z_a - z_b = \left(\frac{\bar{V}_1^2}{2g} \right) \left(\sum c_i f_i \frac{L_i}{D_i} \right) \quad (2)$$

where

- z_a elevation of the upstream reservoir, L ;
- z_b elevation of the downstream reservoir, L ;
- \bar{V}_1 mean fluid velocity in the first element, LT^{-1} ;
- g gravitational acceleration constant, LT^{-2} ;
- c_i factor relating the velocity of the i th element to that of the first element, dimensionless;
- f_i element friction factor, dimensionless;
- L_i element length, L ;
- D_i element diameter, L .

Equation (2) is valid for both laminar and turbulent flows; however, the friction factor f_i for turbulent flow is a function of both surface roughness and Reynolds number (Re_D) and thus must be obtained iteratively. The program does this with a lookup table based on the *Moody* [1944] diagram. Once f_i is obtained, (2) can be solved for the velocity and discharge of the first element. Velocities within other elements are determined using continuity.

Kinetics of Calcite Dissolution

Rates of calcite dissolution within an element are a function of both chemical and flow conditions. The model recognizes three potential limiting conditions: the rate of dissolution reactions at the mineral surface, mass transfer of reaction products between the mineral surface and bulk fluid, and reactions involving the dissolution and distribution of CO_2 gas in water. The model identifies the limiting step for any set of chemical and flow conditions by calculating three independent dissolution rates, each assuming a different rate-limiting step, and choosing the minimum calculated rate of the three, since these steps occur sequentially.

The program first calculates a dissolution rate assuming surface reaction rate kinetic control. A number of expressions have been developed to predict this rate based on theoretical and experimental evidence, and the program contains options for those of *Plummer et al.* [1978], *Dreybrodt* [1990], and *Palmer* [1991], with user selection of the desired model before a simulation begins.

The experimental data of *Plummer and Wigley* [1976] showed that as equilibrium is approached, a rapid decline in dissolution rates occurs. While *Plummer et al.*'s [1978] rate expression provides the most comprehensive detail concerning elementary steps of the dissolution process, it tends to overpredict rates close to equilibrium. *Dreybrodt* [1990] applied a fourth-order rate law close to equilibrium based on

linear regression of *Plummer and Wigley's* [1976] data. In *Dreybrodt's* [1990] model the fourth-order law takes effect at 90% saturation. At this level of saturation an abrupt drop in rates occurs as the fourth-order rate takes effect.

Palmer [1991] derived an expression that gives a rate of solution wall retreat for a conduit expressed in terms of distance from thermodynamic equilibrium, based on the experimental data of *Plummer and Wigley* [1976] and *Plummer et al.* [1978]:

$$S = \frac{31.56k_1(1 - C/C_s)^{n_1}}{\rho_r} \quad (3)$$

where

- S rate of conduit wall retreat, LT^{-1} ;
- k_1 temperature dependent, experimentally derived coefficient, $ML^{-2}T^{-1}$;
- n_1 reaction order far from equilibrium, dimensionless;
- C bulk fluid calcium concentration, ML^{-3} ;
- C_s saturation calcium concentration, ML^{-3} ;
- ρ_r rock density, ML^{-3} .

The coefficient k_1 varies as a function of temperature and PCO_2 and has values of 1.5–2.2. While *Palmer's* rate law lacks the kinetic detail of the *Plummer et al.* [1978] expression, it appears to agree better with the experimental data of *Plummer and Wigley* [1976] and *Plummer et al.* [1978] in the region close to equilibrium [*Palmer, 1991*] (note his Figures 9 and 10). As saturation is approached, the observed drop in rates is modeled by a change in k and n values, such that the rate becomes

$$S = \frac{31.56k_2(1 - C/C_s)^{n_2}}{\rho_r} \quad (4)$$

where n_2 varies between 3 and 6 (A. N. *Palmer*, personal communication, 1991), but is generally near 4, and

$$k_2 = k_1[1 - (C/C_s)_T]^{n_1 - n_2} \quad (5)$$

where $(C/C_s)_T$ is the saturation level (dimensionless) at which the higher-order rate takes effect and varies from 0.6 to 0.9 as a function of temperature and PCO_2 . Our model incorporates *Palmer's* rate law by rearranging (3) and (4) so that rates are expressed in $ML^{-2}T^{-1}$ (as they are in the expressions of *Plummer et al.* [1978] and *Dreybrodt* [1990]), so that

$$\text{rate} = k_x(C/C_s)^{n_x} \quad (6)$$

where x is 1 or 2, depending on distance from equilibrium. *Palmer's* [1991] expression was used to determine surface reaction rates in all simulations discussed in this paper.

Several improvements in *Palmer's* rate expression over previous efforts are apparent: the model recognizes that both lower- and higher-order reaction orders vary as functions of input conditions, and calculation of k_2 results in a smooth transition in rates as the higher-order rate takes effect. In addition, expressing the distance from equilibrium in the dimensionless form (C/C_s) rather than $(C_s - C)$ eliminates complications in the units of k as the reaction order changes.

Our model next determines a potential calcite dissolution rate assuming kinetic mass transfer control. The rate of mass transfer of Ca^{2+} from the mineral surface is given by [*Incropera and Dewitt, 1985*]

$$R = h_m(Ca_{\text{surf}}^{2+} - Ca_{\text{bulk}}^{2+}), \quad (7)$$

where

- R dissolution rate, $ML^{-2}T$;
- Ca_{surf}^{2+} calcium concentration at the mineral surface, ML^{-3} ;
- Ca_{bulk}^{2+} mean calcium concentration across the element cross section, ML^{-3} ;
- h_m convective mass transfer coefficient, dimensionless.

Ca_{bulk}^{2+} is given as the input calcium concentration for water into a given element, and Ca_{surf}^{2+} is determined by thermodynamic equilibrium.

The central task, as in any such mass transfer problem, is to determine an appropriate value for the convection coefficient h_m . For circular cross section pipes, this value can be obtained using the dimensionless Sherwood number (Sh_D), where

$$h_m = \frac{Sh_D D}{\delta} \quad (8)$$

where D is the conduit diameter (L) and δ is the diffusion coefficient for calcium in water (L^2T^{-1}). For fully developed laminar flow in circular cross section conduits, assuming constant surface concentration (as is assumed along the length of a single element), Sh_D has been shown to have a constant value of 3.66 [*Kays and Crawford, 1980*].

For turbulent flow in circular cross section conduits, Sh_D can be found using the convection correlation of *Gnielinski* [1976]:

$$Sh_D = \frac{(f/8)(Re_D - 1000)Sc}{1 + 12.7(f/8)^{1/2}(Sc^{2/3} - 1)} \quad (9)$$

where f is the flow friction factor, Re_D is the dimensionless Reynolds number, and Sc is the Schmidt number (dimensionless), where

$$Sc = \frac{\nu}{\delta} \quad (10)$$

where ν is the fluid kinematic viscosity in L^2T^{-1} . The *Gnielinski* [1976] expression has been shown to be valid for $Re_D = 2300-10^6$, and for $Sc = 0.6-10^5$. A Schmidt number for diffusion of calcium ion in water at typical groundwater temperatures is approximately 10^3 , within the valid range. Re_D values for larger conduits could, however, exceed 10^6 , so caution must be used in interpretations for which these conditions occur.

A calcite dissolution rate is then calculated assuming kinetic control by CO_2 hydration, which has been recognized as the slow step among the homogeneous reactions involving dissolution of CO_2 gas in water [*Kern, 1960; Dreybrodt, 1981b*]. The model uses an expression derived by *Dreybrodt* [1981b]:

$$R = k_{CO_2}[CO_2] \left(\frac{V}{A} \right) \quad (11)$$

where

- k_{CO_2} equilibrium constant for dissolution of CO_2 gas in water [*Kern, 1960*], T^{-1} ;

- [CO₂] CO₂ concentration, ML^{-3} ;
 V solution volume, L^3 ;
 A surface area of mineral/water contact, L^2 .

Since all three kinetic steps must occur to dissolve limestone, the limiting condition and the overall solution rate are given by the minimum calculated rate for the local conditions.

By incorporating elements of the kinetic expressions discussed above, this model gives the most comprehensive description of the dissolution process available with existing information. *Plummer et al.*'s [1978] model gives the most mechanistically detailed rate law of those available, but assumes reaction-limited kinetics (at the pH values of karst waters), and tends to overpredict rates close to equilibrium. While *Palmer's* [1991] work provides a smooth transition to higher-order dissolution rates as equilibrium is approached, it also assumes reaction rate-limited kinetics. *Dreybrodt's* [1990] expression contains a term that accounts for the possibility that diffusion may limit dissolution rates, but the transition between low- and high-order kinetics is very abrupt and occurs at an arbitrary saturation state. The model presented in this paper combines existing expressions to overcome each of these problems, in addition to considering the rate of CO₂ hydration as another possible limiting step.

Model Validation

A number of laboratory experiments by other investigators have been designed to study rates of calcite dissolution under conditions that replicate those during early development of karst aquifers. *Rauch and White* [1977] drilled holes in limestone blocks of varying lithology and circulated CO₂-H₂O solutions with a constant PCO₂ near 1 atm through the blocks. The solutions were sampled hourly, and by measuring the evolution of pH, calcium, and bicarbonate, rates of calcite dissolution were calculated.

Several of these experimental runs were simulated using our model, concentrating on those drilled in blocks of Valentine limestone, an Ordovician limestone collected at Union Furnace, Pennsylvania. Starting with water at the temperature and PCO₂ of the experimental conditions, the model was configured to simulate dissolution by water flowing through 0.635-cm conduits that were the length of the blocks used in the run. At the end of each trip through the blocks the dissolved calcite was added to a reservoir of 3.5 L, the total amount of solution used in the experiments; then the program brought the solution back to the original PCO₂. This replicated the fixed PCO₂ (open system) conditions of the experiments. This process was then repeated for subsequent circulations through the blocks. At the end of each hour of (experimental) time elapsed since the beginning of the run, the program printed out the present calcium and bicarbonate concentrations, as well as pH. Separate runs modeled diffusion-controlled kinetics, and reaction-controlled kinetics using the *Plummer et al.* [1978] and *Palmer* [1991] expressions. Runs using the CO₂ hydration-limiting model were made as well and are discussed below.

A modification of the diffusion theory necessary for this simulation was to correct for the fact that concentration boundary layers were not fully developed within the short length of these drilled conduits. Increased diffusion rates that occur under laminar flow conditions within the not fully developed region can be calculated using the correlation of *Hausen* [1943]:

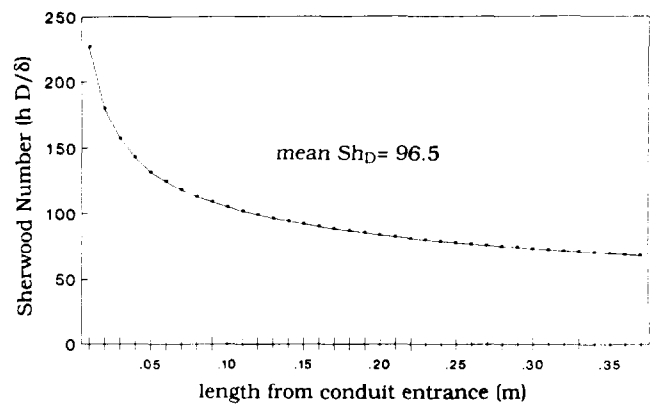


Figure 3. Calculated values of Sh_D as a function of length from the entrance to conduits of *Rauch and White* [1977].

$$Sh_D \cong 3.66 + \frac{0.0668/\lambda}{1 + 0.04/\lambda^{2/3}} \quad (12)$$

where

$$\lambda = \frac{x/D}{Re_D Sc} \quad (13)$$

where x is the length from the conduit entrance (L) and Sc is the dimensionless Schmidt number. This expression is based on a curve fit for the limiting case where Sc becomes very large, as in this case where ion diffusivity values are much smaller than those for the viscosity of water at typical karst water temperatures. The result of this boundary layer behavior is that values of Sh_D (and thus mass transfer by diffusion) are much larger than the fully developed flow value of 3.66 (Figure 3). The mean value of Sh_D over the length of the conduits used in the laboratory experiment was calculated and used in the simulations.

Results of calculated versus experimental calcium concentrations using a variety of reaction-limited kinetic models are shown in Figure 4. The simulation using the *Palmer* [1991] rate law, with his k_1 value for impure limestone, shows the closest agreement with the experimental data. The overall results also suggest that reaction rates limit dissolution under these conditions, since these are the slowest of the rates. Diffusion rates are very high due to poorly developed concentration boundary layers. In addition, the Reynolds number describing the flow under the experimental conditions is 1850, which is in the poorly characterized "critical zone" between laminar and turbulent flow. Under these conditions the model calculates diffusion under laminar flow conditions, when transport may in fact be enhanced from that predicted by theory. It should be noted that at the pH values typical of karst waters, the reaction-limiting models are assumed to be independent of flow conditions, since they assume that transport from the surface is rapid, and thus are not affected by the experimental flow conditions as are the diffusion results. Runs performed using the model for CO₂ hydration-limiting kinetics reached equilibrium within a short distance into the first pass through the blocks. The rates predicted from this model are far higher than those for the other models, suggesting that CO₂ hydration is not limiting in these cases.

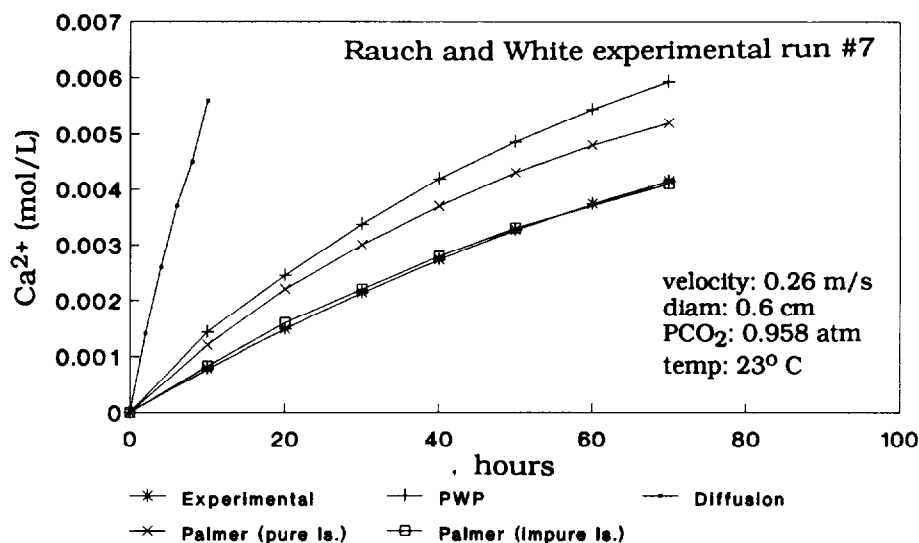


Figure 4. Experimental versus simulated results of run 7 of *Rauch and White* [1977] for calcium concentrations through time.

Comparisons of calculated versus experimental bicarbonate concentrations showed similar agreement to that for calcium data. Results from other runs comparing *Rauch and White's* [1977] experimental data from very pure limestones (runs 8, 12, and 20) also yielded similar results.

One area of potential difficulty in applying the model to experimental conditions is characterization of the actual surface area of mineral/water contact within the experimental systems. The model assumes smooth geometric surfaces, where the actual rock surface areas may contain surface roughness elements leading to higher values. *Anbeek* [1992] has suggested that surface areas of naturally weathered mineral surfaces may be dramatically higher than the hypothetical smooth surface enveloping the actual surface. Machined rock surfaces, as in the interiors of the drilled holes of the *Rauch and White* [1977] experiments, will likely be smoother than naturally weathered surfaces. Just how smooth, however, these surfaces are remains unclear.

Porosity values for the limestones used in the laboratory experiments were not reported. All of the systems studied by the simulations in this project, however, were from fine- to medium-grained micritic limestones of Paleozoic age, which typically have very low porosities. Any deviations of surface areas from those assumed in the model as a result of voids are probably minimal.

Simulations

In order to investigate the magnitude of minimum conditions under which conduits will successfully develop, a series of runs was made. A set of representative initial conditions was selected ($t = 15^{\circ}\text{C}$, $\text{PCO}_2 = 0.03$ atm, closed conditions with respect to addition of CO_2 , hydraulic gradient of 2.0%); then all parameters except initial aperture width were held constant. Additional simulations were conducted with similar initial conditions, but steeper head gradients. Several sets of such simulations were conducted, over a range encompassing all geologically reasonable PCO_2 values (0.003–0.3 atm), and flow path lengths (10–10,000 m).

Results and Discussion

Results from a typical set of simulations with standard conditions but different head gradients are plotted in Figure 5, showing the time required for breakthrough to be achieved as a function of the hydraulic gradient acting across the conduit. Input conditions other than gradient are those listed above, and breakthrough is defined as the time required for low-order, rapid dissolution rates to become present along the entire length of the passage. As head gradient decreases, the time required for passage development increases. Development times increase dramatically as head decreases, approaching an apparent asymptote representing an essentially infinite breakthrough time at a limiting, or minimum, head. In one simulation very close to the limiting value (not plotted, since breakthrough was not achieved), passage growth was so slow that discharge had increased only a few percent after 10^{10} years. Minimum conditions thus occur, because as the limiting gradient is approached, the time required for passages to form approaches infinity.

For combinations of head gradient and aperture size below the minimum conditions, flow through the conduit is so slow that the finite residence time in each element permits saturation to be achieved numerically, although theoretically saturation is approached only asymptotically by any of the rate-limiting processes. This numerical saturation occurs in the first few elements even though the element lengths in this region are extremely short. Correspondingly, passage enlargement is confined to the first one or two elements, which grow unboundedly, further increasing residence times. Under these conditions the flow and dissolution model no longer adequately describe solutional processes near the entrance. However, it is reasonable to conclude that for gradient/aperture conditions below the threshold, dissolution of the limestone at the surface, or at the soil/limestone contact, will be more rapid than conduit development within joints or fissures.

Those conduits that had much smaller apertures than the threshold size for successful growth achieved numerical

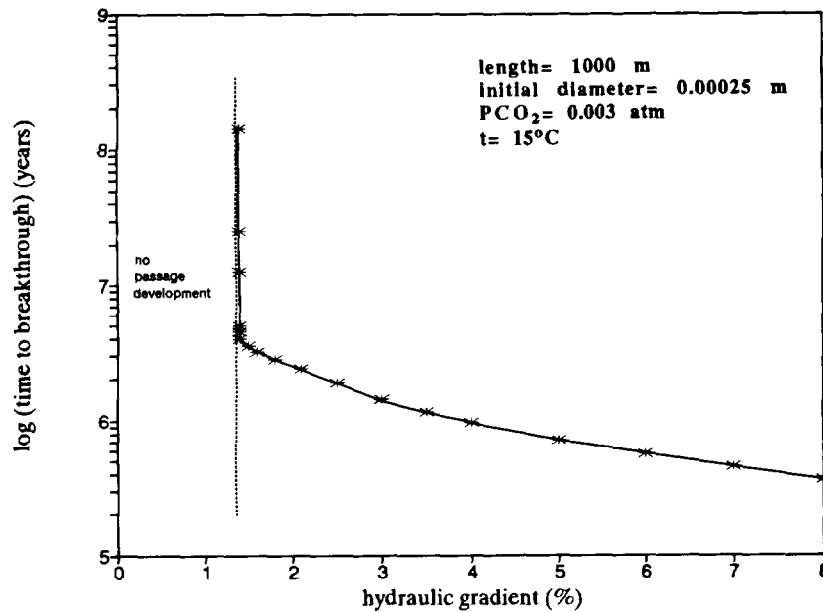


Figure 5. Required breakthrough times as a function of hydraulic gradient for standard conditions.

saturation very rapidly, generally during the passage of water through the unenlarged conduit. However, for runs with initial apertures just below the limiting case, up to hundreds or thousands of years would pass before the waters reached the numerical saturation. With increasing initial apertures or hydraulic gradients, a threshold is finally reached where continued growth is assured within geologically reasonable times. These values are plotted in Figures 6 and 7.

Results of these experiments indicate that under the influence of a wide range of PCO_2 and head gradient values, the minimum initial aperture of a typical 1000-m-long flow path in which conduits will be able to develop is of the order of 100–200 μm . This is the case even for waters with PCO_2 values as extreme as 0.3 atm, which is higher than any values

which could be expected to be found naturally within karst systems [Atkinson, 1977]. For these waters a conduit with an initial aperture of 100 μm required a head gradient of about 11%. For conduits with initial sizes smaller than this, required minimum head gradients rise dramatically.

The minimum conduit size required for conduit development by waters with an initial PCO_2 of 0.03 atm, a typical value for karst waters [Atkinson, 1977], is nearly independent of the initial length (Figure 7) for conduits between 10 and 10,000 m in length. Flow paths with initial apertures of less than 100–200 μm once again require very high head gradients to develop.

Waters with initial PCO_2 values of 0.03 atm are able to successfully develop conduits with initial apertures of about 500 μm , even under the influence of head gradients as low as

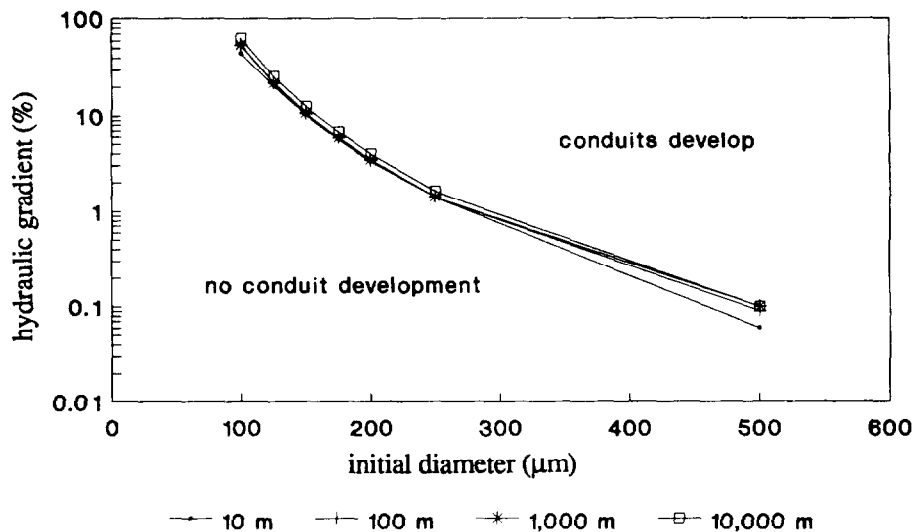


Figure 6. Predicted minimum initial diameters of successfully developing conduits as a function of head gradient for various lengths.

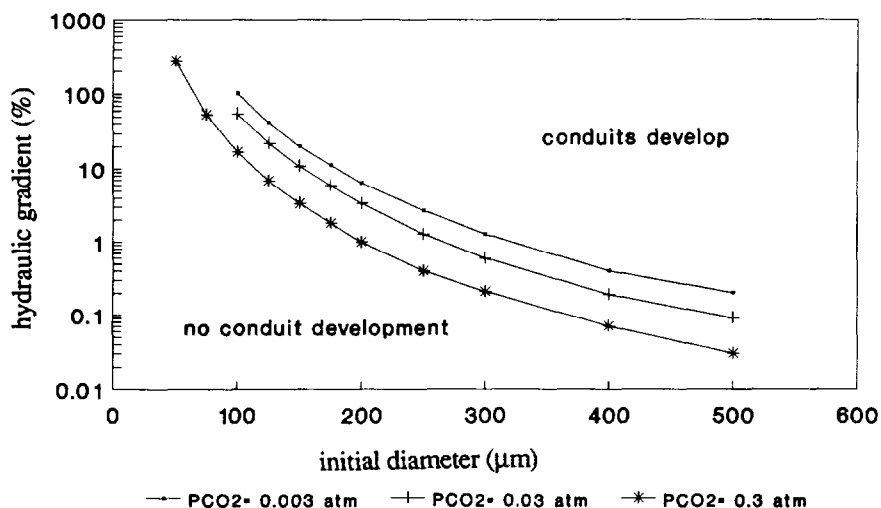


Figure 7. Predicted minimum initial diameters of successfully developing conduits as a function of head gradient for various initial PCO_2 values.

0.1%. This means that there is but a factor of perhaps 3–5 between the initial apertures of flow paths that cannot form conduits because of their small size and those in which conduits will form easily. Thus selective enlargement of certain passages, possibly at the expense of others, may be a strong function of initial size. *Motyka and Wilk* [1984] investigated Triassic limestones in Poland and found 200 μm to be the most frequent value of fissure widths [*Dreybrodt*, 1990]. The most frequent measured fractures within Hungarian carbonates were slightly smaller [*Böcker*, 1969], and some fracture widths larger than 1 mm were found. Assuming that these values are representative of fractured limestones, one could expect that some fractures that exceed widths of a few hundred micrometers (and thus are able to develop into conduits) would be present.

Some application of these results to an understanding of the large-scale morphology of cave systems can be made by considering the classic work of *Ford and Ewers* [1978] who used a parameter they called “fissure frequency” to distinguish conduits that form along deep flow lines from those that develop at or near the water table. According to this model, deep “bathypneatic” caves, typified by caves within the Sierra el Abra of central Mexico, require a body of rock that is essentially fracture-free except for the master fracture set that has guided deep initial solution. It is not clear, however, what kind of structural situation might result in such a configuration. Our modeling results suggest that perhaps the fissure distribution is a more appropriate measure than fissure frequency and that many small fissures might exist that will not permit the eventual growth of conduits.

Dreybrodt [1990] modeled breakthrough times under a wide variety of hydrochemical conditions. Several runs were made with our program to compare calculated breakthrough times with similar initial conditions (using *Palmer's* [1991] model for reaction-limited kinetics), and in general, ours were longer, up to about an order of magnitude. Several differences in the models are apparent and may be responsible for the longer breakthrough times, including (1) the saturation states at which the two models predict that higher-order kinetics should begin to limit dissolution, (2) the

order of the higher-order reaction, and (3) initial conduit geometries (circular versus rectangular apertures).

Conclusions

Although *White's* [1977] kinetic trigger mechanism provides a means for developing cave systems to overcome what were earlier thought to be prohibitively short penetration lengths, there still exists a minimum set of conditions which will permit conduits to form, below which the waters at work forming them will essentially reach saturation before appreciable penetration into the aquifer. We have calculated limiting conditions of gradient, flow length, and initial PCO_2 below which caves will not successfully develop in a finite time. Results indicate that under realistic head gradients and PCO_2 values, the minimum initial aperture of potential flow paths in which conduits will develop is of the order of 100 μm . Using typical soil PCO_2 values, initial flow paths larger than about 500 μm form passages very easily, even under very low head gradients. Observed distributions within fractured limestones [*Böcker*, 1969; *Motyka and Wilk*, 1984] suggest that fracture widths range from less than 100 μm to more than 500 μm . These results indicate that selective enlargement of certain passages within incipient karst aquifers may be a strong function of initial size.

A mainframe version of the FORTRAN code used in this project can be obtained by contacting the authors.

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