

# Self-organization during reactive fluid flow in a porous medium

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**Abstract.** When a reactive fluid circulates inside a porous medium it can dissolve some minerals if equilibrium is not reached and modify the porosity and permeability. The positive feedback between fluid transport and mineral dissolution lead to complex reaction front morphologies such as fingers. Our study is carried out with two objectives: 1) to evaluate experimentally these processes at a decimeter scale, 2) to compare the experiment to a numerical model of water-rock interaction. The experiment consists of a two-dimensional porous medium that allows for the dissolution of halite under an imposed fluid flow. The numerical code used solves the equations of reaction and transport in a porous medium. Both experiment and numerical simulation indicate the development of an instability whose propagation rate depends on the rate of water injection raised to a 2/3 power.

## Introduction

At a decimeter to kilometer scale, circulation of a reactive fluid in a porous medium can lead to a reaction-infiltration feedback loop. As a flow passes through a rock, one or more of the minerals may dissolve out and the porosity may increase, causing the permeability to increase [Ortoleva *et al.*, 1987; Hoefner and Fogler, 1988; Steefel and Lasaga, 1990; Daccord *et al.*, 1993a; Lichtner, 1996]. Porosity-permeability relations are not linear: a small change of porosity may induce a large permeability variation; and a large change of porosity may also induce a small change of permeability. However, as a consequence of a permeability increase, the flow focuses where permeability is higher (fig. 1) and the reaction front can become unstable for a fluid velocity greater than a critical velocity [Ortoleva *et al.*, 1987]. If the initial rock texture is perfectly uniform, the resulting reaction front stays planar. However, if slight non-uniformities are initially present, as in all natural rocks, enhancement of the porosity and the permeability occurs, and the initial unevenness of the front can be amplified, leading to a finger geometry when the flow is sufficiently rapid [Steefel and Lasaga, 1990]. This mechanism is an example of geochemical self-organization: from an initial homogeneous system emerges an organized pattern which is not the result of an imposed template, but the consequence of the physical and chemical processes in the system themselves [Ortoleva, 1994]. Wormhole-like dissolution holes in limestone [Daccord *et al.*, 1993a; Bazin *et al.*, 1996], kilometer-scale scalloping dolomitization front advancing in limestone, or formation of karsts are geological consequences of this flow instability [Ortoleva *et al.*, 1987].

In the case of acid injection in carbonates, a fractal geometry can emerge [Daccord *et al.*, 1993a].

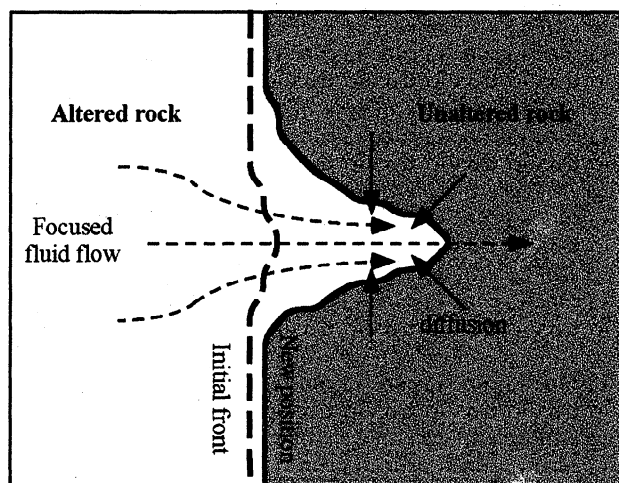
A positive feedback between reaction and flow amplifies the initial non-uniformities in the rock, but a negative feedback due to the diffusion of the soluble species inside the fluid phase prevents the finger from growing infinitely (fig. 1). The tendency of diffusion is to repress the unevenness of the reaction front. The mineral solutes, dissolved from the walls of the finger pattern, migrate to its tip through diffusion, pushing the fluid there towards saturation.

## Theoretical Approach

In a porous medium where a fluid circulates with a constant velocity and where the dissolving mineral is NaCl for example, the concentration  $c$  of  $\text{Na}^+$  or  $\text{Cl}^-$  is taken to obey the equation [Chen and Ortoleva, 1990]:

$$\frac{\partial(\phi c)}{\partial t} = \nabla(\phi D_h(\phi) \nabla c + \kappa(\phi) c \nabla p) - \phi A_\phi k(c - K) \quad (1)$$

where  $\phi$  is the porosity,  $\kappa$  the permeability coefficient (dependent on porosity) divided by the viscosity of the fluid,  $p$  the fluid pressure,  $D_h$  the coefficient of dispersion ( $\text{cm}^2/\text{s}$ ),  $A_\phi$  is the reactive surface of the rock ( $\text{cm}^2/\text{cm}^3$  of rock),  $k$  the kinetic constant for dissolution/precipitation ( $\text{cm/s}$ ), and  $K$  the equilibrium concentration. In Eqn. (1) the first right hand term represents mechanical and molecular dispersion, the second one the transport of fluid, and the third one the reaction of dissolution/precipitation between the fluid and the mineral. The variation of the concentration with time depends on these three terms. Darcy's law makes the link between the fluid pressure and the flow velocity  $v$  ( $\text{cm/s}$ ):



**Figure 1.** Feedback reaction-transport instability mechanism. An initial bump in a dissolution front is amplified because of flow focusing. Reactive fluid concentrates in the bump; porosity and permeability are locally increased so that the bump is extended. The diffusion prevents the instability to grow infinitely [after Ortoleva *et al.*, 1987].

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$$\phi v = -\kappa(\phi)\nabla p \quad (2)$$

The model is completed with a relation of conservation of water that yields the fluid pressure, the grain growth dissolution, and the dynamics of the porosity [Ortoleva, 1994]. To compare the effects due to the reaction rate, the diffusion, and the flow in Eqn. 1, it is convenient to use non-dimensional parameters. Thus the conservation of solute mass depends on two parameters, that are strongly scale dependent, namely the Peclet and Damkohler numbers. The Peclet number measures the relative importance of the advective and dispersive fluxes:

$$P_e = \frac{v_{inj} l^*}{D_h} = \frac{\text{flow velocity}}{\text{dispersion velocity}} \quad (3)$$

where  $l^*$  is the length scale of the considered process (cm),  $v_{inj}$  the flow rate of injection (cm/s), and  $D_h$  the coefficient of dispersion [Steefel and Lasaga, 1990]. The expression of the characteristic length is still debated. Daccord *et al.* [1993] have defined a Peclet number at a microscopic scale, where  $l^*$  represents the pore size and  $D_h$  is the coefficient of diffusion. On the contrary, Steefel and Lasaga [1990] defines the Peclet number at a macroscopic scale, and  $l^*$  is the size of the considered system. Steefel and Lasaga [1990] give the theoretical critical Peclet number,  $Pe_{crit}$ , above which destabilization of the dissolution front occurs:

$$Pe_{crit} = \frac{\pi(3 - \Gamma)(1 + \Gamma)}{2(1 - \Gamma)} \quad (4)$$

where  $\Gamma$  is the quantity  $\phi_o k_o / \phi_f k_f$ ,  $k$  is the permeability and  $\phi$  the porosity, and the subscripts  $o$  and  $f$  refer to the initial and final medium properties.

The Damkohler number is useful to compare the kinetics of reaction to the flow rate at a given length scale

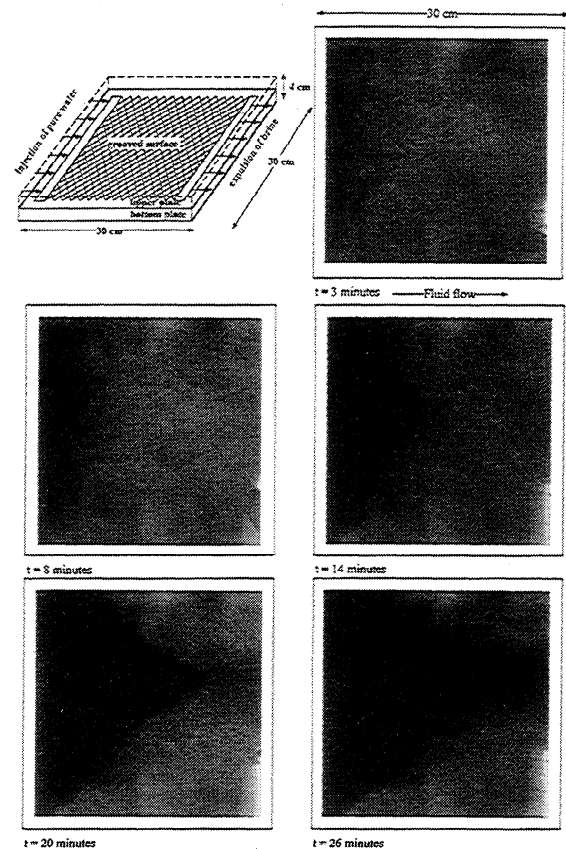
$$Da = \frac{A_\phi k l^*}{v_{inj}} = \frac{l^* / v_{inj}}{1 / A_\phi k} = \frac{\text{transit time}}{\text{reaction time}} \quad (5)$$

where  $v_{inj}$  and  $l^*$  are the same as for the Peclet number. When the Damkohler number is much greater than 1, the rate of the chemical reaction is larger than the rate at which the fluid is transported and the solution remains close to equilibrium. In this case, dissolution occurs in all the rock and the reaction front is diffuse and not razor sharp. In contrast, when the Damkohler number is smaller than 1, the reaction rate cannot keep up with the flow and local disequilibrium occurs [Steefel and Lasaga, 1990].

## Experimental Apparatus and Method

To study the fingering effect, a synthetic two-dimensional porous medium was built. It consists of two Plexiglas plates; one is flat, the other contains a 30 by 30 cm network of grooves on its top surface. The grooves have a squared section of 1 mm by 1 mm, and are separated by 5 mm; they cut each other with an angle of 90° and they make an angle of 45° with the flow direction (fig. 2). The flat plate covers the grooved surface of the other Plexiglas plate. The transparency of the Plexiglas allows camera use during the experiment.

We fill the grooves with sieved sodium chloride with a grain size in the range of 100 to 300  $\mu\text{m}$ . Pure water is injected on one side of the grooved plate with a peristaltic pump, the opposite side of the plate is left free, at atmospheric pressure. The following scenario emerges from the experiment: pure water is injected on one side of the Plexiglas plate, it cir-

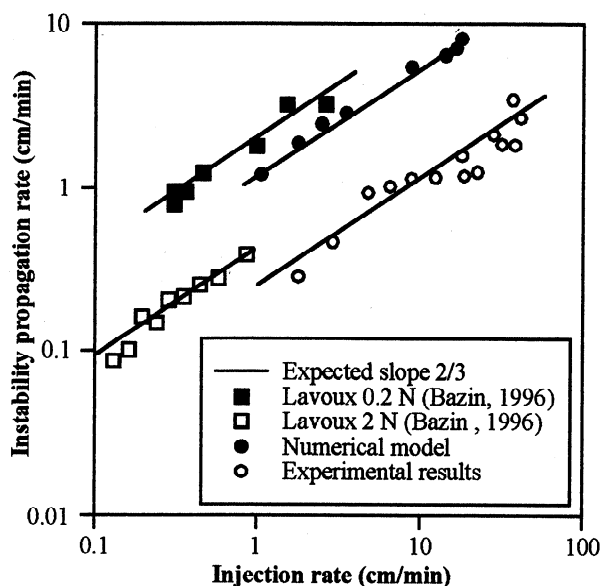


**Figure 2.** Experimental results of dissolution finger pattern. Grooves filled with salt appear in white whereas empty grooves and Plexiglas inert matrix are dark-gray colored. The dissolution front does not stay linear. Many instabilities (see at time  $t = 14$  minutes) may develop but only one crosses the system (see at time  $t = 26$  minutes). In this experiment, the injection velocity is 3.9 cm/min.

culates between the two plates inside the grooves and dissolves the salt, without any transport of the grains. The brine exists on the opposite side of the plate. During water circulation, the porosity of the system, filled grooves plus Plexiglas, increases from an initial estimated value of 25% (volume of the voids inside the salt divided by total volume) to a final value of 47% (volume of the grooves divided by total volume), when all the salt has dissolved, leaving empty grooves. The experimental apparatus is quite specific and does not model a real compacted rock but more a granular rock in which fluid circulation can occur.

After injection of pure water, a front of salt dissolution moves from left to right (fig. 2). At low flow rate, the dissolution front should be approximately flat and compact, whereas at high flow rate it destabilizes to a finger geometry [Ortoleva *et al.*, 1987; Daccord *et al.*, 1993a, 1993b]. The feedback that allows the destabilization of the initially planar reaction front is due to the dependence of the permeability on the fraction of salt within the system. Finger pattern grows and one or two fingers may develop. In fact, it appears that, in each experiment, one finger dominates and crosses the Plexiglas plate (fig. 2). The width and growth rate of the finger depend on the rate of water injection. The injection velocity,  $v_{inj}$ , is defined by

$$v_{inj} = \frac{Q}{\phi_o S} \quad (6)$$



**Figure 3.** Effect of injection rate on the finger propagation rate. The solid lines correspond to the expected behavior with a slope equal to  $2/3$ . At high flow rate, the slope of the experiments and the numerical model is  $2/3$ , in agreement with experiments of matrix acidizing done on Lavoux limestone with 0.2 and 2 N acid fraction [Bazin et al., 1996].

where  $Q$  is the flow rate of water injected ( $\text{cm}^3/\text{s}$ ),  $\phi_0$  the initial porosity of the system (25 %), and  $S$  the surface area of the injection front ( $3 \text{ cm}^2$ ). In the different experiments,  $Q$  varies from 1 to  $40 \text{ cm}^3/\text{min}$ , so the interstitial velocity ranges from 1.3 to  $53.3 \text{ cm/min}$ .

The dispersion coefficient,  $D_h$ , used to calculate the Peclet number depends mainly on advection in our experiment because diffusion velocity is always much slower than advection velocity. The coefficient of diffusion in a free fluid, at  $25^\circ \text{C}$ , is  $2.10^{-5} \text{ cm}^2/\text{s}$  [Nakashima, 1995], whereas the coefficient of advection in our experiment (injection rate times the space between two grooves, i. e.  $0.5 \text{ cm}$ ) is much bigger and ranges from 0.0083 to  $0.33 \text{ cm}^2/\text{s}$ . Therefore  $D_h$  is estimated to be equal to the advection coefficient and vary only with injection rate. The kinetic constant  $k$  is equal to  $4 \times 10^{-5} \text{ cm/s}$  [Alkattan, 1996]. Based on grain size and geometry,  $A_\phi$  is estimated to be equal to  $3.5 \text{ cm}^2/\text{cm}^3$  of rock. The length scale  $l^*$  in Eqns. (3) and (5) is taken to be 30 cm, the width of the grooved surface of our experimental apparatus and numerical model. Then the macroscopic Peclet number (Eqn. 3) is equal to 60 (it does not vary with flow rate because in all our experiments, diffusion is much slower than advection). The critical Peclet number (Eqn. 4) is estimated to be equal to 6.3 ( $k_o/k_f$  is estimated to be 0.33 and  $\phi_o/\phi_f$  is equal to  $0.25/0.47$ ). It is smaller than the Peclet number of our experiment and, therefore, destabilization of the front can occur. The Damkohler number (Eqn. 5) ranges from 0.25 to 0.0063. The Damkohler number is smaller than 1, thus the reaction rate is slower than the flow rate and the fluid is not in equilibrium with the rock. Therefore disequilibrium can exist over appreciable distances into the salt-bearing zone.

We observe that for all the injection rates we have tested, the diffusion cannot repress the unevenness of the front because the dissolution is limited by the mass-transfer from the surface of the grains of salt to the free fluid (fig. 2). After a

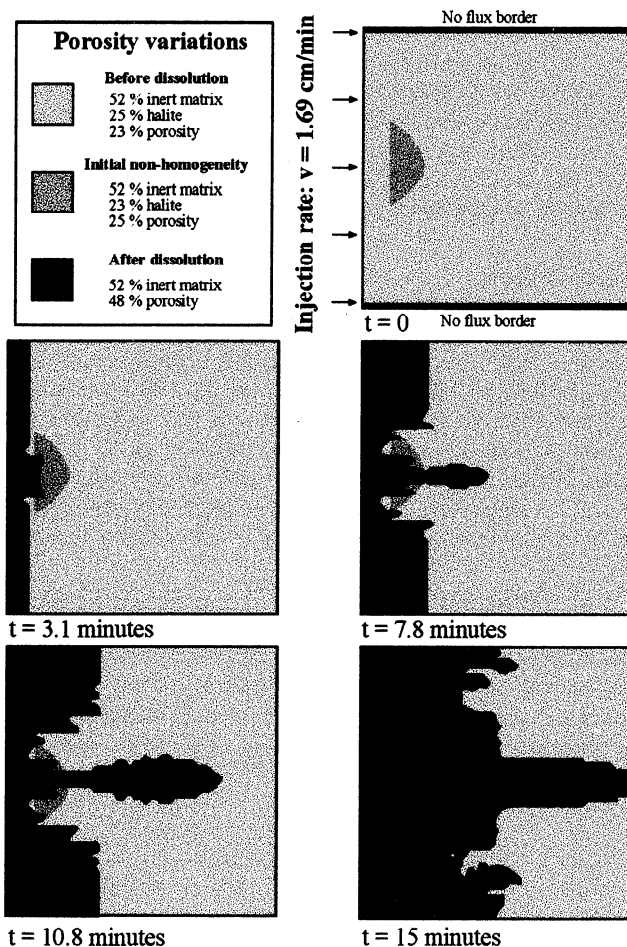
small period of initiation, the propagation rate of the finger is constant. Even if many bumps may develop at the beginning, one dominates and crosses the apparatus. We have observed that the finger has a larger diameter at low flow rate; whereas a higher flow rate produces a thinner finger.

For each experiment, we have measured the rate at which the finger propagates. The finger advancement rate is observed to be proportional to the injection flow rate to a  $2/3$  power (fig. 3). These results are in agreement with experiments of acid injection in limestone [Bazin et al., 1996] where a wormhole propagates inside a limestone core because of acid dissolution.

## Numerical Model

A numerical model of water-rock interactions, CIRF.A, has been developed by Ortoleva et al. [1992] and is used here to study the coupling between reaction and transport in our experiment. This code allows the two-dimensional simulation of mass transfer, porosity and permeability changes, and reaction front induced by infiltration of reactive fluids in rocks; thus it is well adapted to model the experiment [Chen and Ortoleva [1990].

In the numerical model, a  $50 \times 50$  nodes grid represents the  $30 \times 30 \text{ cm}$  grooved surface of the experiment (fig. 4). Each



**Figure 4.** Numerical modeling of a dissolution front of halite. An initial porosity non-uniformity inside the rock creates an instability on the reaction front (see the porosity at time  $t = 0$ ). Planar at the beginning, the front becomes scalloped and one finger pattern develop. The finger grows and crosses the model. The conditions are similar as in the experiment (fig. 2).

node contains initially the same porosity (25%), salt fraction (22%), and inert matrix fraction (53%) as in the experiment. Physical parameters are the same as in the experiment (temperature, injection rate, fluid pressure, grain size). To initiate the unstable behavior, a slight porosity variation is put on the left of the model (see fig. 4 at  $t = 0$ ). Instead of a 25% porosity, some nodes have a 27% porosity. This small heterogeneity serves to initiate a small bump on the dissolution front.

When the fluid circulates from left to right, salt dissolves and a dissolution front moves from left to right. The width of the reaction zone is always very thin, and the reaction front is razor sharp. As in the experiment, an instability grows when reaching the initial porosity variation and traverses the system (fig. 4). In the numerical model, one finger initiates and can split in two branches, one of which ultimately dominates. This is the main difference with the experiment where only one finger propagates without splitting. As for the experiment, the finger propagation rate is estimated and found to be proportional to the injection flow rate raised to a  $2/3$  exponent (fig. 3). This factor  $2/3$  is explained through the circulation of a reactive fluid inside a capillary whose radius increases due to the dissolution of the walls but its theoretical interpretation is still discussed [Daccord *et al.*, 1993a, 1993b].

We observe a factor 3 to 5 between the finger propagation rate in the numerical model and in the experiment. We believe this difference could be associated with the fact that the dependence of permeability on porosity is stronger in the numerical model than observed in the experiment. Despite this difference, the overall behavior of the reaction-transport loop is described by the numerical model: instability of a planar front and development of a finger,  $2/3$  slope, and duration of the numerical experiment are in agreement with the experiment.

## Conclusions

Instability of a flow-driven reaction front occurs via a flow-focusing mechanism. We have studied experimentally the coupling between reaction and transport and found that it depends strongly on the imposed flow rate. The apparatus we used allows to test rigorously the numerical model for the same conditions (two-dimensions, identical physical and chemical parameters). As predicted by the theory, an experimental finger develops with the same behavior as the numerical model.

The reaction-transport instability shows that, if a rock is homogeneous at a considered scale, self-organization patterns can emerge through the reaction-infiltration feedback, and large initial non-uniformities (due to tectonic events or sedimentary features for example) are not required to create porosity variations and localized deformation in the upper crust.

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