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Chemical Dissolution of a Porous Medium by a Reactive Fluid

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Chemical dissolution of a two-dimensional porous medium by a reactive fluid which produces fractal patterns is studied. A new model is proposed that introduces a *cumulative* erosion process which broadens the branches of the cluster and gives structures very similar to the experimental ones. Diffusion-limited aggregation is a limiting case of this model. An interpretation of the evolution of the injection pressure with time which yields the fractal dimension is also presented, and agrees with the experimental results.

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It has been known for a long time that injection of a reactive fluid into a soluble porous medium yields very ramified dissolution patterns. In nature, the networks of caves in calcareous regions are macroscopic results of such processes. Acids are routinely injected into oil-bearing rocks and similar patterns are thought to occur. At present, there is no clear understanding of the physical basis of the patterns formed by chemical dissolution processes.

The physical phenomenon of the formation of dissolution patterns (DP) involves the flow of a liquid in a porous medium *coupled* with a chemical reaction.[1,2] Although qualitative 1D models[3] have been proposed, there are no quantitative models for the actual DP observed. In this Letter, I present experimental results on a simple 2D system and develop a new model that provides a quantitative description of the DP.

The essential idea of my experiments is to take advantage of the property of plaster of being slightly soluble in pure water. Thus I pumped water into the center of the model and observed a "breakdown" of the porous plaster medium (Fig. 1). I used 2D radial geometries,[4] the sample consisting of a thin disk (thickness $b = 1$ mm and radius $R_{\text{ext}} = 125$ mm) of pure plaster held between two transparent plates. Plaster was made by mixing 10 parts of water with 11 parts of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. After setting, the medium was very homogeneous[5] and had a porosity of 60% porous and a permeability of 60 μm^2.

Initially, the plaster was fully saturated (in chemical equilibrium) with water with a concentration in calcium sulphate $c_0 = 13$ mm. At time $t = 0$, pure water (viscosity μ and concentration in calcium sulphate $c = 0$) was injected at constant flow rate Q at the center of the disk, displacing the saturated water and subsequently dissolving some of the plaster. Good images of the final DP were obtained by injection of a low-melting-point alloy (Wood's metal) into the dried plaster sample. After cooling, the plaster was dissolved. Figure 1 shows three patterns obtained for different flow rates but same time. At low flow rate, the branches are broader and the number of ramifications decreases.

At first glance, the 2D radial structures obtained are very similar to other experimental growth patterns associated with the model of diffusion-limited aggregation[6] (DLA): dielectric breakdown,[7] electrodeposited metal leaves,[8] viscous fingering,[9] or diffusion-limited polymerization.[10] This analogy can be understood by comparison with viscous fingering in a porous medium. The velocity

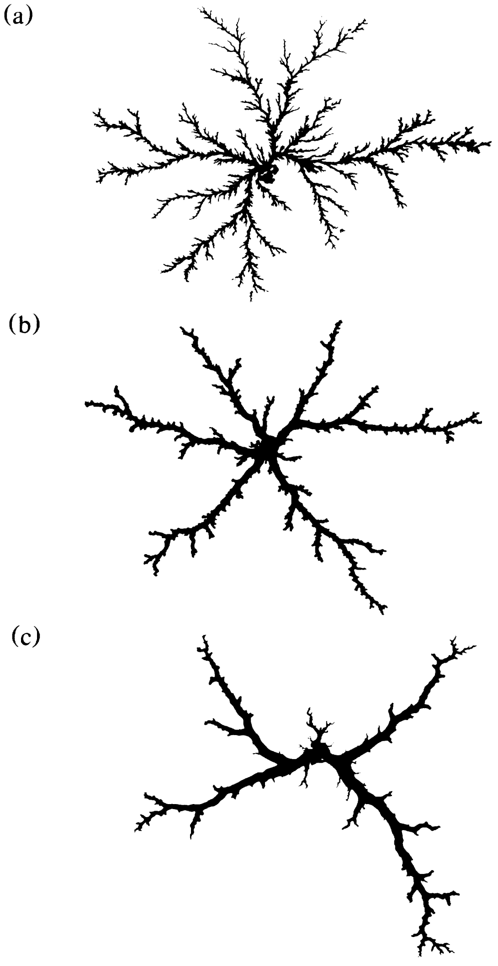

FIG. 1. Photographs of 2D radial experiments stopped after 4 h and performed at different injection rates. (a) 48 cm^3/h. (b) 4 cm^3/h. (c) 2 cm^3/h.

u of a fluid of viscosity μ in a porous medium of permeability k is proportional to the pressure gradient: $\mathbf{u} = -M\,\mathrm{grad}P$. Here $M = k/\mu$ is the mobility and P the pressure field. During the displacement of a viscous fluid by a nonviscous one, viscous fingering occurs as a result of the very sharp increase of mobility when a small perturbation appears at the interface between the fluids. In the present case, the injected reactive fluid and the saturating nonreactive fluid have the same viscosity but, at the interface (the *reactive* front), the permeability jumps from a low value in the porous medium to a quasi-infinite value in the etched channels. Furthermore, the incompressibility of the injected water which leads to a Laplace equation and the boundary conditions (constant pressure in the dissolved channels and at the boundary of the model) are similar to the case of viscous fingering which has been shown to be described by DLA.[9,11] Thus, we might expect DLA to model these unstable dissolution patterns.

A unique feature of my model is that it accounts for the chemical etching by including a *cumulative* effect based upon the real mechanism. This dissolution growth model leads to patterns very similar to the experiments. It can also be used to calculate the evolution of macroscopic variables with time, such as the injection pressure. The assumptions required to build the model are the three basic assumption of DLA (flow law obeying a Laplace equation, constant pressure on the boundaries, and random growth) plus another one describing the chemical dissolution which we shall discuss now.

The etching which causes the branch enlargement is a *diffusion-limited* process. This means that the chemical reaction between pure water and plaster occurs instantaneously and that the overall kinetics is limited by the removal of the dissolution products from the solid-liquid interface both by molecular diffusion and by convection (when the fluid is moving). Thus, the rate of etching is a function of the velocity of the fluid. The branches where the velocity is high are etched more rapidly, which increases their permeability and consequently the velocity. On the other hand, in the branches with low velocities the water becomes rapidly saturated and hence nonreactive: They cannot grow any more and will keep their sizes until the end. This mechanism is reminiscent of unstable fronts, where the development of a few large fingers inhibits the growth of smaller neighboring fingers (the screening effect).

We can model the enlargement of one branch by the enlargement of a straight tube in which flows a reactive fluid at a constant velocity. If we assume a dissolution kinetics limited by molecular diffusion, a first approximation of the increase of the local radius ρ at a fixed point versus time t is given by solution of the diffusion equation in a capillary. We get the relation $\rho \sim t^{3/4}$ for long times.[12] For constant flow rate, the total volume V is proportional to time and the evolution of the radius is $\rho \sim V^{3/4}$. This law ignores the finite solubility of the medium in the fluid and assumes a constant velocity through the channel (the thickness of the etching must be small in comparison with the radius). The main idea of my model is to keep track of the cumulative volume V which flows through a channel by means of a counter m and subsequently to compute the actual branch radius. The structure is generated in the following way:

(1) With each particle of the cluster are associated two counters. The first counter will contain its distance l from the seed particle, walking along the branches (the chemical length[13]), while the second counter is used to count the number of particles m sticking on the "downstream portion" of the cluster.

(2) The first counter is set when the particle sticks to the cluster, assigning it the l of the particle it is stuck on plus 1.

(3) Now, we walk toward the seed along the branch (we just have to find the adjacent particle the l of which is equal to the one on which we are, minus 1) incrementing the m of each particle by one unity, until we reach the seed.

(4) The process is iterated by our allowing another particle to diffuse randomly from far away.

(5) At the end of the simulation, the counter m of each particle contains exactly the mass of the downstream branches, and it is this value which is used.

In the first approach, I used a simple law $\rho = bm^{\beta}$ (assuming $V \sim m$) with β chosen to represent the physical process studied ($\beta = \frac{3}{4}$ with the previously described assumption). This computer-generated structure is now visualized by plotting on each particle position a disk of radius proportional to the local channel radius ρ. In addition, we can plot only the points which represent a large enough radius, higher than a critical value ρ_c. This cutoff simulates the limited resolution of the actual experimental system. Figure 2 displays two structures obtained for different values of the parameters. Of course, it may happen that a branch is wide enough to hide small neighboring ones: This is similar to the experiments in which the radii of the channels become larger than the grain size and then extend over several pores which could have been previously partially etched.

As a variation of the previous model, I computed the local radius increase at each time step, instead of incrementing m (step 3 in the above algorithm). I chose different growth laws, taking into account the local radius and flow rate, but the appearance of the final patterns did not change significantly [Fig. 2(c)].

During the pumping of the pure water, the injection pressure P_{inj} was also measured (with the external pressure as reference) and decreased linearly versus the logarithm of time. For understanding this physically, I used the notion of equivalent structure radius R_e defined from Darcy's law for radial flow,

$$P_{\mathrm{inj}} = (\mu Q/2\pi k b)\ln(R_{\mathrm{ext}}/R_e).$$

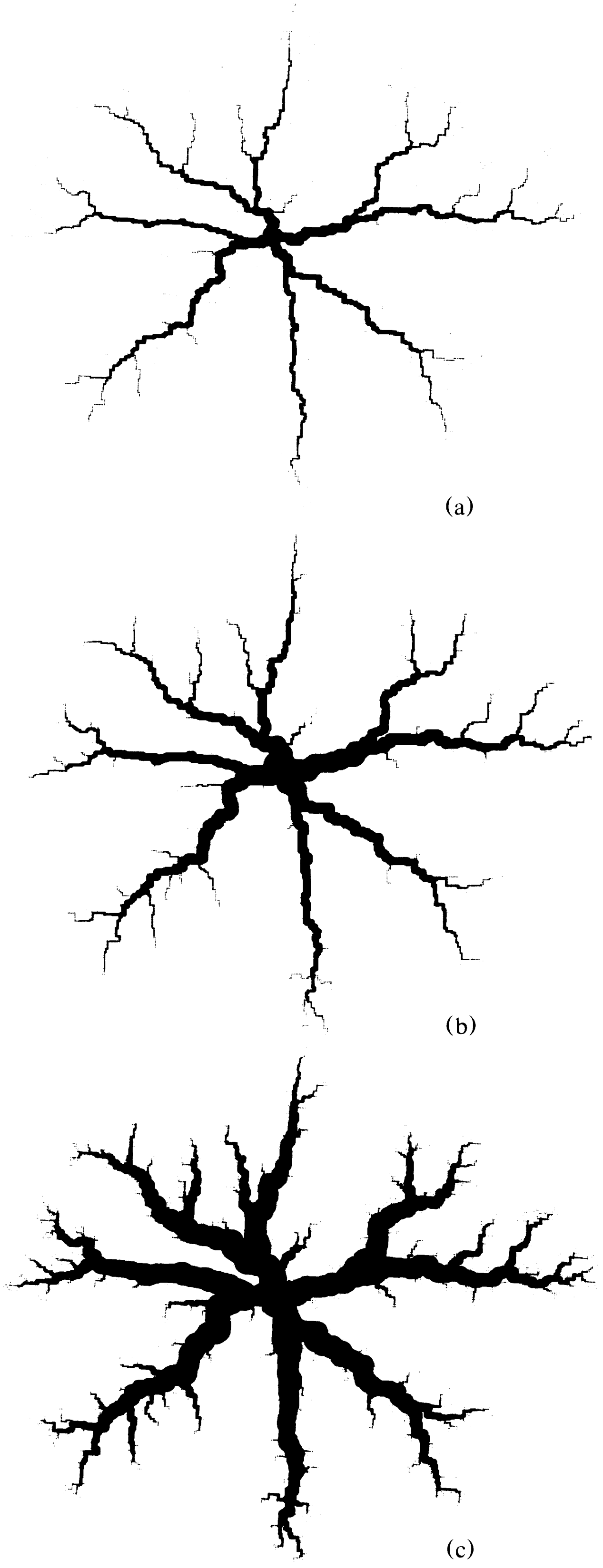

FIG. 2. (a) 10000-particle DLA cluster plotted while accounting for the cumulative effect according to the law $\rho = A(m/N)^{\beta}$ with $A=10$ lattice units, $\beta = \frac{3}{4}$, and $\rho_c = 0.01$ lattice unit. (b) Same cluster as in (a), but with $A=20$ and $\rho_c = 0.1$. (c) Same cluster as in (a) but the channel width is computed at each time step. $A=15$, $\rho_c = 0$.

Physically, R_e corresponds to the radius of the disk in which there is a negligible pressure drop. The fact that the experimental pressure decreases linearly versus the logarithm of time t indicates that R_e has the form

$$R_e = R_{\rm ext}(t/T)^{\alpha};$$

therefore

$$P_{\rm inj}/(\mu Q/2\pi kb) = -\alpha \ln t + {\rm const},$$

with T being a characteristic time. I found experimentally[4] that $\alpha = 0.7 \pm 0.1$, which is significantly different from the stable displacement case. Indeed, suppose the rock were dissolved uniformly (i.e., radially, in a circular way). Then, neglecting the pressure drop in the dissolved zone, we should get $R_e \sim \sqrt{t}$ and therefore $\alpha = 0.5$.

My model allows us to predict this experimental behavior of the pressure versus time. Consider a disk of porous medium of radius $R_{\rm ext}$. By injecting a reactive fluid at the center, we get a dissolution structure described by the above model. We can distinguish three zones (Fig. 3). Close to the center, the channels are wide and the pressure drop is actually negligible (zone 1). At the periphery (zone 3), the plaster is still intact and the pressure varies radially according to Darcy's law: $P(r) \sim \ln(R_{\rm ext}/r)$. In the intermediate zone (zone 2), from $r = R_1$ to $r = R_f$, the flow is shared between the channels and the porous medium. In the limiting case where we can neglect this transition zone ($R_e = R_1 = R_f$), we have the trivial result $P_{\rm inj} \sim \ln(R_{\rm ext}/R_f)$. R_f corresponds to the growth region of the cluster, and so it scales[14,15] like the radius of gyration, $R_f \sim N^{1/D}$, N being the total mass of the cluster and D its fractal dimension; N is proportional to the time t, and the injection pressure varies like $-D^{-1}\ln t$. The experimental value $\alpha = 0.7 \pm 0.1$ agrees qualitatively with this simple approach.

However, we showed[4] that R_e is significantly smaller than R_f, which indicates that the transition zone actually exists. My model allows us to quantify its effect. I represent each portion of the actual pattern which is embedded in the porous medium by two media in parallel, a channel of radius $\rho(r)$ (in which I assume Poiseuille flow), and a piece of porous medium (in which I assume Darcy flow). A parameter B describing the relative permeability of the porous medium versus the channels is then naturally introduced as the ratio of the prefactors of the two flow laws. I first compute at a given time (for a given structure size R_f) the fraction ϕ of the total flow

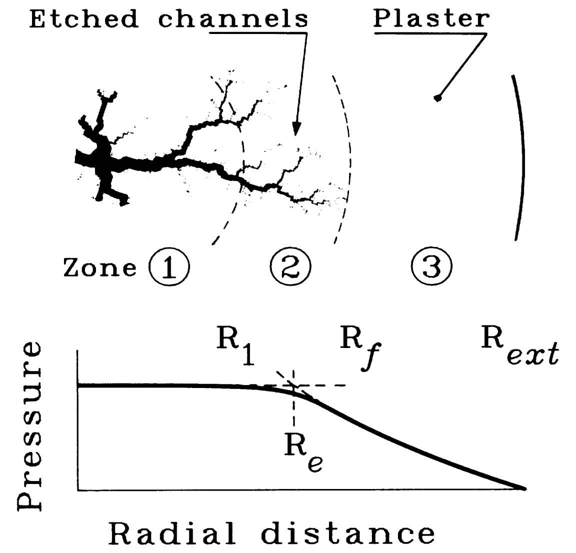

FIG. 3. Schematic representation of the different zones in a radial dissolution experiment and pressure profile (arbitrary units).

flowing in the channels, versus the distance r from the origin. The pressure profile $P(r)$ along a radius of the disk is then calculated by integration of Darcy's law from the periphery ($r=R_{\text{ext}}$), the flow rate being $Q(1-\phi)$. The plot of $P_{\text{inj}}=P(r=0)$ vs R_f (Fig. 4) displays a linear behavior in a wide range of values of B (the limiting case $R_1=R_f$ discussed above corresponds to $B=0$).

This model should be applicable to other physical processes displaying a cumulative effect, e.g., dielectric breakdown,[7] viscous fingering, and diffusion-limited polymerization.[10] Further support for the idea presented here comes from theoretical[16,17] and experimental[18] studies of viscous fingering when the viscosity ratio is large but not infinite. One finds an enlargement of the branches just as in Fig. 1.

In summary, I describe simple dissolution experiments yielding fractal structures, and develop a new model based on physical laws which produces patterns very similar to the experimental ones. This model is the first to describe *cumulative* effects in breakdown phenomena. In addition, I predict the behavior of the injection pressure versus time, in very good quantitative agreement with that observed experimentally.

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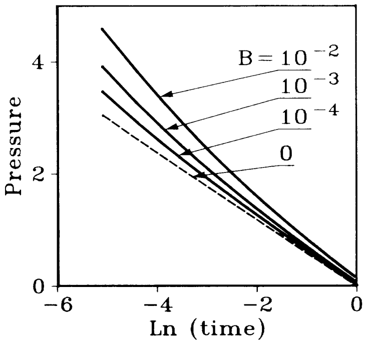

FIG. 4. Dimensionless injection pressure vs dimensionless time (t/T) predicted by my model in the case of finite values of the parameter B.

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[4] Elsewhere, we have undertaken a systematic study of different sample geometries [G. Daccord and R. Lenormand, Nature (London) (to be published)]. We found that the 2D radial patterns have a fractal dimension $D=1.6\pm0.1$.

[5] Indeed, if we imbibe a dried disk of plaster with saturated water, we get a perfectly circular front.

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