Influence of Porosity on Rayleigh-Taylor Instabilities in Reaction-Diffusion Systems

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We analyze the effect of porosity in a porous medium on hydrodynamic instabilities in reaction-diffusion fronts. We use an experimental device to create an effective two-dimensional porous medium which is vertically orientated. In this system the molecular diffusion coefficients and the acid autocatalysis of the chlorite-tetrathionate reaction satisfy the appropriate conditions to produce a chemical front that advances through the cell leading to the products overlaying the reactants. The reactants have a lower density than the products and therefore a buoyantly unstable front develops. To evaluate the influence of the porosity on the formation and propagation of such instabilities, media with different porosities were used in the experiments. The amplitude of the instability is found to reduce as the porosity of the medium is decreased. For sufficiently small porosity, the instability can almost disappear leading to a planar front.

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Hydrodynamic deformations of the interface between fluids in motion, as well as those originating from the induced flux of the front between two chemical solutions initially at rest, are frequently found in reservoir engineering, chemical and pharmaceutical engineering, metallurgy, and biochemistry.

The spatial and temporal dynamics can be very complex under the influence of phenomena such as viscosity, density and surface tension variations, and chemical reactions. The interface between the two fluids becomes unstable and "fingers" appear at the interface where the fluid with greater mobility [1–3] invades the other one.

In spite of the importance of these phenomena in industrial processes [4], the fingering of spatially extended chemical fronts has just recently been carefully studied [5–10]. The autocatalytic reaction of chlorite-tetrathionate presents a complex kinetics, because both its stoichiometry and products change according to the relative concentrations of the reactants. The oxidation of tetrathionate as a consequence of chlorite, in a slight excess of the latter, is catalyzed by the hydrogen ion, which is a product of the reaction, presenting a known stoichiometry [11,12].

This research is motivated by the interest of understanding and controlling the chemohydrodynamical instabilities, based on the importance of this knowledge in industry and the environmental sciences. The objective of our work is to study the relationship between the chemical reaction and the hydrodynamics of the Rayleigh-Taylor instability by means of chemical autocatalysis inside a porous medium. In particular we will study the effect of the porosity defined as $\phi = \text{void volume}/\text{total volume}$.

To our knowledge this is the first experimental study with a predesigned two-dimensional porous medium created using a photographic engraving technique. This technique creates a heterogeneous media with tortuous paths in which the porosity can be accurately varied, thus providing a closer representation of a real porous medium. Previously known works involving inhomogeneous media involve either plates engraved with straight parallel channels [13,14] or built with microspheres [15,16], which greatly limit the design of the media under study. An important result of our work is that the instabilities found in these systems can even disappear if the chemical front travels in a porous medium of sufficiently small porosity.

We built a device consisting of a Hele-Shaw (HS) cell made of two Plexiglas plates of 20 cm × 20 cm × 1 cm each with a transparent photopolymer placed between the plates. The photopolymer has been photographically engraved from numerically generated patterns to create an effective two-dimensional porous medium.

A code was written to generate the pattern used for engraving the photopolymer [Fig. 1(a)]. For simplicity, here we used circular cylinders of equal diameters, arranged perpendicularly to the plates, as obstacles (a different shape can be employed). The predefined diameter, as well as the number of cylinders and the minimum separation, determines the desired porosity. With this image we built a mask, which we used to engrave the photopolymer.

The masks created were given a border of 2 cm so that the resulting pattern was generated inside a 16 cm × 16 cm square. The mask thickness was unaltered by the process and thus equaled the original thickness of the polymer to retain chemical solutions and maintain the separation distance of the Plexiglas plates. The porous medium, generated inside the square, illustrated by white dots in Figs. 1(a) and 1(b), had a narrow region of 0.9 mm in depth where the fluid could pass through.

This innovative method allowed us to simulate a two-dimensional porous medium. Previously, a set of spherical obstacles was used to simulate it [15,16]. This arrangement, when used as a monolayer in order to get a 2D porous medium, is naturally of hexagonal structure. This

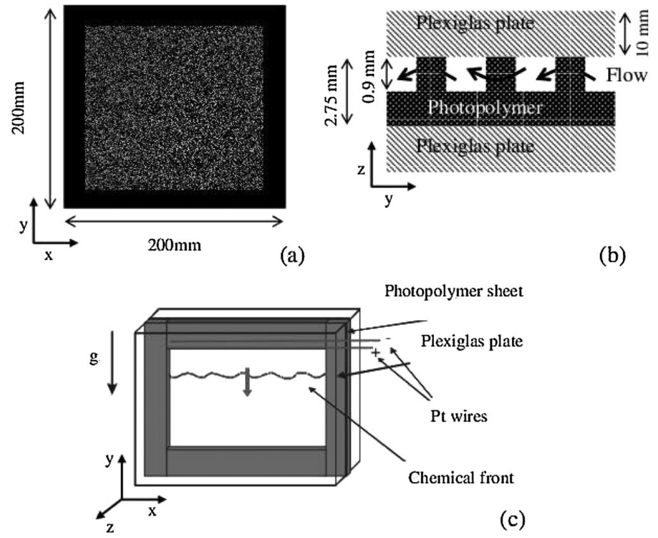

FIG. 1. (a) A schematic diagram of a two-dimensional porous medium formed using a photopolymer sheet (photographically engraved). The white regions correspond to flow channels. (b) Schematic representation of the medium. (c) Schematic representation of the container of porous media. The Pt wires that trigger the reaction are illustrated.

is caused by the presence of the parallel plates that constitutes the Hele-Shaw cell. Their influence forbids the possibility to obtain a random pattern of obstacles. There is a way to get some randomness with spheres by adding several layers of them, but it reduces the likeness of the arrangement to be a two-dimensional system, and induces difficulties in the visualization of the phenomenon under study.

This method could also be used to test the theoretical prediction of the works of De Wit and Homsy [17,18] on heterogeneous porous media. Their results could not yet be tested experimentally as far we know. For example, in some cases the anisotropy of the experimental porous medium employed makes it difficult to compare against the mentioned works.

Our experiments, based on previous studies concerning the influence of the temperature over the instabilities of the reaction front [10], were conducted at a temperature of (10.0 ± 0.1) °C. At this temperature, the amplitude and the wavelength of the instability at the interface are larger than the size of the pores. To achieve this thermal condition, the cell is placed into a thermal bath at a constant temperature. We employed a Cole Parmer refrigerator model Polystat, and the temperature was measured with a Fluke II K-52 thermometer and a type-K thermocouple.

In order to initiate the reaction it is necessary to apply a small voltage. This is done with the help of two platinum electrodes placed near the top of the cell, where a 4 V voltage is applied for a few seconds. This way of initiating the reaction causes, as a consequence of the autocatalysis, the front to descend and so the products will lie above the reactants. Because the former are heavier than the latter, a series of fingers will appear.

We took into account the importance of visually distinguishing the products from the reactants in order to analyze the images. To accomplish these objectives and based on previous works [10,19–21], we use bromophenol blue as a pH indicator which dyes the alkaline solution (reactant) with a blue color, and with a yellow one the acid solution (product). We also used the following reactant concentrations: $[\mathrm{S_4O_6^{2-}}] = 0.005M$, $[\mathrm{ClO_2^-}] = 0.020M$, and $[\text{bromophenol blue}] = 1$ g/l. To neutralize the acid character of the pH indicator we add a small quantity of NaOH with a concentration of $0.001M$. Through this work, we used analytical grade chemicals of high purity—Sigma-Aldrich-Fluka—to prepare the reactants, except the sodium chlorite which had a purity of 80%. We also employed AlphaQ ultrapure water.

The images obtained were stored and processed with in-house computer codes, in order to obtain the interface position and the length of the mixing zone as a function of time. To determine the mixing zone, the code finds the front shape of every image. Then it calculates the region along the vertical axis [Fig. 1(c)], where the average acid concentration lies between 5% and 95%. The length of this region is what we call the length of the mixing zone.

As a first experiment to study the effect of the porous media on the hydrodynamic instabilities, we carried out a series of experiments in which the employed photopolymer possessed two different zones: one smooth, a Hele-Shaw cell, and another including circular cylindrical obstacles that constitute a porous medium (PM) (Fig. 2). In this case the instability was initiated in the HS and then, after being developed there, the fingers enter the PM.

In Fig. 3 the advancing chemical front is shown at different times. The thick line represents the reaction front at the moment when the front enters the porous medium (time = 125 s). In Fig. 4 the amplitude of the mixing zone is shown as a function of time. From this figure it can clearly be seen that in a time interval from 125 to 140 s the mixing zone decreases, which corresponds to the moment when the instability crosses the interface between the regions HS and PM. The same effect is observed in Figs. 2 and 3. The same analysis can be performed in Fig. 4. It can be seen that the instability begins in the plain zone when the reaction starts and, as it advances, the instability develops and increases its amplitude. At the moment that the reaction front reaches the PM zone, it can be seen that the region occupied by the instability, the mixing zone, is considerably reduced.

The effect that the reduction of the porosity, and therefore the permeability, causes on the instability is in agreement with works carried out on Hele-Shaw cells with different plate separations "a" [22]. In these works the permeability, given by $a^2/12$, can only be modified by changing the separation distance. In this work, as a differ-

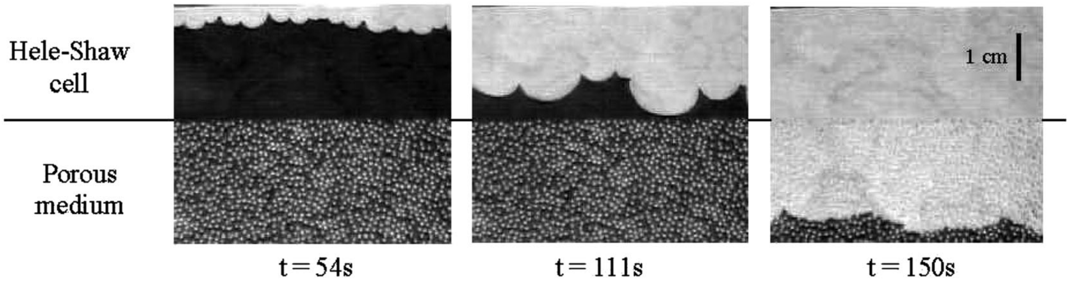

FIG. 2. Images of the experiment as the instability enters the porous medium. The white zone corresponds to the products, and the dark one to the reactants. The white dots in the lower zone are part of the porous medium.

ence from those previously cited, the permeability modification is induced by the presence of a porous media, which produces a region of lower permeability into the cell.

We also studied the variation of the wave number $k_{\max}$, corresponding to the mode with maximum spectral density power, both in the HS and in the PM. This was done through a Fourier analysis performed on the reaction front profile. We can see (Fig. 3) that at the beginning of the reaction $k_{\max} = (1.18 \pm 0.05)\ \mathrm{mm}^{-1}$ and then, just before entering the porous zone, it reduces to $k_{\max} = (0.64 \pm 0.05)\ \mathrm{mm}^{-1}$. A characteristic of these types of instabilities is that the fingers overlap as the instability evolves, and therefore the wave number decreases. We can also see a strong reduction of this parameter at the moment when the front enters the porous medium, as $k_{\max} = (0.19 \pm 0.04)\ \mathrm{mm}^{-1}$. This shows that this parameter is strongly influenced by the medium where the instability is developed, increasing the overlap between the fingers. This effect can be observed starting at $t = 125$ s, just when the front enters the porous medium.

We then observe that the wave number $k_{\max}$ decreases when the porosity reduces, which agrees with works on Hele-Shaw cells of different permeabilities [22], and also coincides with the statement that the permeability is proportional to the porosity [23–25].

In order to perform our study on the influence of the porosity on the formation and propagation of the instabilities, we conducted a series of experiments with PM of different porosities. We can see in Fig. 5 the mixing zone for different porosities ($\phi = 0.11, 0.27, 0.35$, and 0.89). At the beginning of the reaction, it is not easy to note the influence of the medium on the development of the instability, but the effect becomes clearer after 800 s. This happens because at early times the wave amplitude is of the order of the size of the pore (~1 mm).

We conclude that the development of the Rayleigh-Taylor instability in reaction-diffusion fronts is strongly influenced by the presence of the porous medium where the hydrodynamic instability takes place.

We observed that a reduction in the porosity causes a diminution of the amplitude of the instability (reduction of the mixing zone) and also a decrease of the main wave number. This could even lead to the disappearance of the hydrodynamical instability. The porous medium produces on the fluids an increment of the mixture, because the porous structure modifies the streamlines, twisting and splitting them. This causes a breaking of the classic pattern

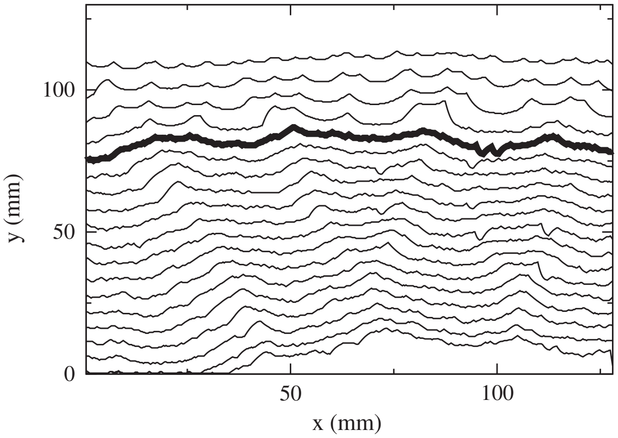

FIG. 3. Front profiles for different times at intervals $\Delta t = 25$ s. The thick line corresponds to the reaction front profile at the time when the front arrives at the porous medium.

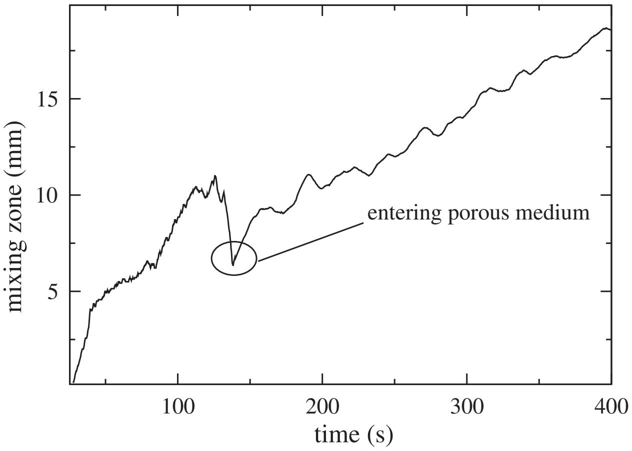

FIG. 4. Mixing zone as a function of time for HS and PM systems.

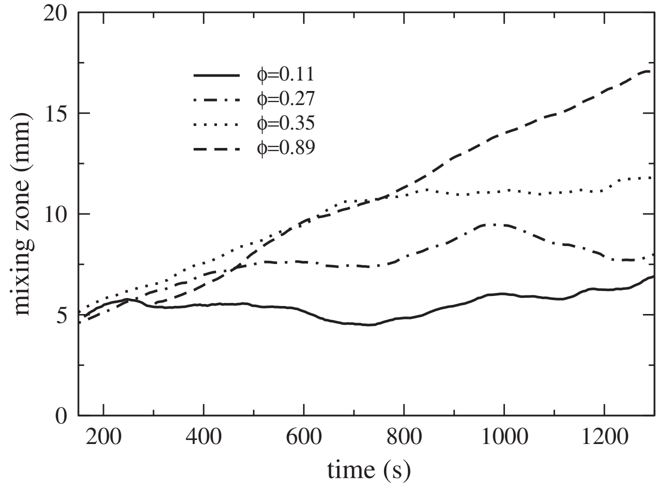

FIG. 5. Mixing zone for different porosities.

corresponding to these instabilities (fingering) and also a reduction of the main wave number $k_{\max}$. These effects lead to the formation of a planar front, which could not be obtained by the use of a Hele-Shaw cell, that possess neither the tortuosity nor the porosity of a porous medium.

Our results show that is important to know the properties of the medium where instabilities take place, in our case the porosity.

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