#### PHILOSOPHICAL TRANSACTIONS A

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# Review

**Cite this article:** De Wit A. 2016 Chemo-hydrodynamic patterns in porous media. *Phil. Trans. R. Soc. A* **374**: 20150419. http://dx.doi.org/10.1098/rsta.2015.0419

Accepted: 24 July 2016

One contribution of 12 to a theme issue 'Energy and the subsurface'.

#### Subject Areas:

environmental chemistry, physical chemistry, geochemistry, environmental engineering, chemical physics, fluid mechanics

#### Keywords:

fingering, oil recovery, pollution decontamination, CO<sub>2</sub> sequestration, CO<sub>2</sub> mineralization

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# Chemo-hydrodynamic patterns in porous media

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Chemical reactions can interplay with hydrodynamic flows to generate chemo-hydrodynamic instabilities affecting the spatio-temporal evolution of the concentration of the chemicals. We review here such instabilities for porous media flows. We describe the influence of chemical reactions on viscous fingering, buoyancy-driven fingering in miscible systems, convective dissolution as well as precipitation patterns. Implications for environmental systems are discussed.

This article is part of the themed issue 'Energy and the subsurface'.

### 1. Introduction

Oil recovery, pollution decontamination or CO<sub>2</sub> sequestration in soils are important environmental processes, in which hydrodynamic flows play a major role. Fluid mixing and enhanced dispersion can indeed emerge spontaneously during their implementation when the oil, the pollutant or CO<sub>2</sub> is displaced. In particular, several hydrodynamic instabilities can emerge because of gradients in density or viscosity [1]. As an example, a buoyancy-driven Rayleigh–Taylor instability can deform convectively a horizontal interface between two zones of different composition when the denser fluid lies on top of the less dense one in the gravity field. In the case of viscosity gradients, a viscous fingering (VF) instability can set in when the less viscous fluid displaces the more viscous one.

Chemical reactions are able to actively modify these hydrodynamic instabilities when changing the physical property of the fluid at the origin of the instability [2,3]. Gradients of concentration resulting from reaction– diffusion (RD) processes can then trigger gradients of density, viscosity or permeability. In turn, these can modify or even more strikingly induce hydrodynamic instabilities and convective flows. A highly nonlinear feedback between the chemical and hydrodynamic processes then takes place, which can be the source of complex reaction–diffusion–convection (RDC) dynamics.

We discuss here important applications in geological systems for which chemical reactions can play a crucial role to enhance or decrease convective flows. In this context, important questions are for instance: (i) Can a hydrodynamic instability optimize mixing and transport of chemicals in the porous matrix? (ii) As a corollary, can a chemical reaction control the properties of a given flow? Can it be used, for instance, to enhance or suppress convection and mixing due to a hydrodynamic instability? (iii) Are the properties of the RDC dynamics simply the addition of those of the underlying RD and hydrodynamic ones or are new synergetic nonlinear dynamics possible?

We review here some examples from our recent work in which these questions have been studied both experimentally and theoretically. We show the importance of taking chemical reactions into account to describe the properties of the chemo-hydrodynamic patterns and instabilities observed. Before doing so, let us first describe the experimental reactors and the typical RDC models used to study these systems.

#### 2. Experimental model systems

RDC dynamics can be conveniently studied experimentally at the laboratory scale using Hele-Shaw cells, i.e. two glass or Plexiglas plates separated by a thin gap (typically of the order of 0.1–0.5 mm) in which the dynamics takes place. The evolution of the flow velocity within these cells follows Darcy's law, i.e. the flow equation in porous media, provided the gap width is thin enough compared with the characteristic length of the dynamics [4,5]. The advantage of such reactors is that the dynamics is quasi-two-dimensional and easy to track through the transparent plates using a simple camera. Hele-Shaw cells are thus a popular tool to study hydrodynamic instabilities with or without reactions. The study of density-driven flow motions is made in vertical Hele-Shaw cells starting from an initially planar interface between two miscible or partially miscible liquid solutions (obtained, for instance, using a specific injection device [6]) or between a gas and a liquid. For VF and precipitation patterns, we use horizontal cells with injection either radially from the middle of the cell or linearly from one side of a rectangular cell. Video recording of the dynamics is made either by direct imaging of the patterns due to dyes or colour indicators or by indirect tracking of changes in refractive index by interferometric or Schlieren techniques [7]. Note that the use of colour indicators should be done with care, especially for buoyancy-driven flows, as they may affect the pattern in some cases [8–10].

#### 3. Theoretical modelling

To support experiments or predict new dynamics, theoretical studies of RDC models expressing mass and momentum balance are needed. By considering an incompressible flow in a porous medium or Hele-Shaw cell, the flow velocity evolution can be described by Darcy's law,

$$\boldsymbol{\nabla}p = -\frac{\mu}{\kappa}\boldsymbol{u} + \rho \boldsymbol{g},\tag{3.1}$$

where *g* is the gravitational acceleration,  $\rho$  is density, *p* is the pressure field, *u* is the velocity vector,  $\mu$  is the viscosity and  $\kappa$  is the permeability. To describe the chemo-hydrodynamic coupling, these equations for the velocity field are coupled to RDC equations for the evolution of concentrations  $c_i$  of species *i*,

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i + f(\{c_j\}), \tag{3.2}$$

where  $D_i$  is the diffusion coefficient of species *i*, and  $f(\{c_j\})$  are the kinetic terms. The coupling between these mass and momentum transport equations is obtained by state equations expressing the dependence of the physical property of the solution at the source of the instability on

local concentrations. As an example, for buoyancy-driven density fingering, we assume that the solutions are diluted. In that case, under the Boussinesq approximation [1], the density  $\rho$  is considered constant except in the gravity force term  $\rho g$ , where it is taken to vary with concentration as

$$\rho = \rho_o \left[ 1 + \sum_i \alpha_i c_i \right], \tag{3.3}$$

where  $\rho_0$  is the density of the solvent and  $\alpha_i = (1/\rho_0)(\partial \rho/\partial c_i)$  is the solutal expansion coefficient of species *i*. For VF, it is rather the viscosity  $\mu$  in (3.1) that changes with composition [4], whereas precipitation patterns can be studied assuming that the permeability  $\kappa$  varies with the concentration of the precipitate [11,12]. The mobility expressing the capacity of a fluid to flow through a given system is proportional to the ratio  $\kappa/\mu$ . For buoyancy flows, it is proportional to the local density. In some cases, thermal effects can be added as well by letting  $\rho$  and  $\mu$  change with temperature and adding to the model an RDC equation like (3.2) for the temperature. In larger Hele-Shaw cells or full three-dimensional tanks, Stokes or Navier–Stokes equations have to be used instead of Darcy's law.

These RDC models can be used to numerically compute linear stability analysis, providing typical dispersion curves giving the growth rate  $\sigma$  of the instability as a function of its wavenumber q. Such  $\sigma = \sigma(q)$  functions give information on the characteristic onset time of an instability as well as the characteristic wavelength of the spatial patterns to be observed. The difficulty of linear stability analysis is that the base state profiles, the stability of which is analysed, are usually space- and time-dependent in RDC problems. The linear stability analysis can be complemented by full numerical simulations of the coupled nonlinear equations (3). Let us now review progress in the analysis of reactive flows in various cases.

#### 4. Reactive viscous fingering

VF is a hydrodynamic instability occurring when a less viscous fluid displaces a more viscous one in a porous medium. This instability has been much studied in petroleum engineering because it typically occurs when some given fluid (for instance, water or  $CO_2$ ) is injected into oil reservoirs to displace the more viscous oil [4]. Because of the fingering instability, the initially planar interface between the two fluids deforms into fingers. This is detrimental to the oil recovery efficiency because it enhances mixing of oil with the injected fluid. Control of this viscous instability is thus of tantamount importance, as its suppression or even reduction by only a few per cent could have huge economic impacts in terms of recovery costs. Similarly, VF enhances spreading of viscous pollutants in soils when advected by underground flows for instance. Recently, VF has also attracted renewed interest, as it occurs during  $CO_2$  injection into oils or saline aquifers [13–15]. There, again, it is crucial to understand how this instability controls the enhanced spreading of the  $CO_2$  plume in the porous matrix.

In this context, chemical reactions are important as they can change the viscosity of a solution and thus modify the viscous fingering instability [16–26]. We have recently classified theoretically the influence of an  $A + B \rightarrow C$  reaction [27] on fingering when a solution of A displaces a solution of B generating a product C of different viscosity [28–32]. We have shown that the reaction can influence, stabilize or, in some cases, even trigger VF. To do so, we compared experimentally the non-reactive displacement of polymers/water-miscible interfaces with the same displacement when a reactant is added in the aqueous phase and viscosity is changed *in situ* by a reaction. In particular, we use the viscosity dependence of some polymers on pH to modify the dynamics (figures 1–4).

We have, on the one hand, shown that reactions can induce fingering of an otherwise stable displacement of a more viscous solution injected into a less viscous one [31,32]. This occurs when the chemical reaction produces an extremum in the viscosity profile, in which a locally adverse mobility gradient can trigger fingering. In the case of a maximum (reaction increasing the viscosity, figure 2), fingers then develop at the back of the reaction zone where the polymer



**Figure 1.** Reaction-driven viscous fingering in a rectilinear geometry in the case of a reaction-induced local increase of viscosity. A viscous aqueous solution of polyacrylic acid displaces, from left to right, a less viscous aqueous dyed solution of NaOH in concentration (*a*) 0 M, no fingering is observed; (*b*) 0.01 M and (*c*) 0.02 M. The injection flow rate is 0.50 ml per minute, and time (from top to bottom) is 0, 75, 150 and 225 s. Courtesy of LA Riolfo [32].



**Figure 2.** Viscosity as a function of  $\eta = (x - x_o)/\sqrt{Dt}$  shown a given time after contact, where  $x_o$  is the initial position of the contact line and *D* is the diffusion coefficient of the polymer in water. The viscosity profile is reconstructed on the basis of experimentally measured viscosities in the case of miscible contact between a solution of polyacrylic acid and water containing increasing concentration of NaOH. The change of pH induces a change in viscosity of the polymer. Courtesy of LA Riolfo [32].

displaces the more viscous product generated by the reaction (figure 1). On the contrary, if the reaction decreases the viscosity below that of the displaced solution, then the adverse mobility gradient acts at the frontal part of the minimum in the viscosity profile, which triggers fingers



**Figure 3.** Reaction-driven viscous fingering in a rectilinear geometry in the case of a reaction-induced local decrease of viscosity. A viscous aqueous solution of sodium polyacrylate displaces, from left to right, a less viscous aqueous dyed solution of glycerol and HCl in concentration (*a*) 0 M, no fingering is observed; (*b*) 0.3 M and (*c*) 0.5 M. The injection flow rate is 0.50 ml per minute, and time (from top to bottom) is 0, 140, 280 and 360 s. Courtesy of LA Riolfo [32].





**Figure 4.** Temporal evolution of miscible viscous fingering. An aqueous solution of sodium polyacrylate is displaced radially by dyed water (top panels) and by a 0.5 M HCl and dyed aqueous solution (bottom panels). The reaction stabilizes the fingering instability. The pattern is shown from left to right when the fingers reach a radius of 18, 27 and 36 mm, respectively. The injection flow rate corresponds to a Péclet number  $Pe = 5.31 \times 10^2$ . Radius of field of view = 46 mm. Courtesy of LA Riolfo [32]. (Online version in colour.)

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extending ahead of the reaction zone (figure 3). Even more strikingly, reactions are also able, in some cases, to partly stabilize fingering (figure 4). These results show the power of reactions in enhancing, decreasing or localizing fingers. The amplitude of this effect can be controlled quantitatively, as the larger the concentrations, the more efficient the influence of chemistry. Such results pave the way for future studies of *in situ* chemical control and suppression of VF in porous media flows, which could be of tantamount economic importance.

#### 5. Reactive Rayleigh–Taylor and double-diffusive instabilities

Buoyancy-driven flows develop in the presence of an adverse density stratification in a gravity field, typically when a denser fluid lies on top of a less dense one. Gradients in density can be triggered by either thermal or solutal effects, but we focus here on the latter induced by gradients of concentrations of chemicals. A classical buoyancy-driven instability is the Rayleigh–Taylor instability occurring when a denser fluid overlies a less dense one across a horizontal contact line. The initially planar interface between the two fluids deforms then into so-called density fingers. In the course of time, these fingers grow on average the same distance up- and downwards with regard to the initial contact line position (figure 5, top left). Differential diffusion processes [33–38] can also destabilize an initially stable stratification of a less dense solution of A on top of a denser solution of B when the lower solute B diffuses faster than A, triggering double-diffusive (DD) fingers. These convective flows extend on average also to the same distance above and below the initial contact line (figure 5, top middle) [33,37]. A so-called diffusive-layer convection (DLC) mode can, on the other hand, also develop symmetrically around the contact line in the case of an initially stable density stratification when the upper solute A diffuses faster than B (figure 5, top right) [33,37,38].

Chemical reactions can drastically modify all these buoyancy-driven instabilities as shown both theoretically and experimentally [33,34,39–48]. As an example, the reaction is able to break the symmetry of the hydrodynamic patterns as seen in figure 5 in the case of a simple  $A + B \rightarrow C$  reaction [33]. Experiments are performed by replacing the salt and sugar solutions used in the non-reactive case by aqueous solutions of an acid (HCl) and a base (NaOH). Their respective density varies with the concentration of the chemicals. The Rayleigh–Taylor case is trivially obtained by putting the denser solution on top. The reactive DD equivalent features initially a less dense solution of NaOH above a denser solution of HCl, such that the species diffusing faster (the acid HCl here) is on the bottom. The DLC case starts with a less dense solution of HCl on top of the denser NaOH solution.

As said above, in the non-reactive cases, fingers extend on average the same distance above and below the initial contact line between the two solutions of different composition and hence different density. On the contrary, as seen in figure 5, all reactive equivalents feature asymmetric fingers extending only towards the top. This is related to the fact that the acid–base reaction consumes the acid A and the base B reactants to produce in the intermediate reaction zone the salt product C of different density. This breaks the symmetry of the underlying density profile, inducing a preferential direction growth of the fingers [33,34,40,43,44]. In this acid–base experiment, fingers extend towards the top. Moreover, in the course of time, when a lot of product C has been produced, secondary instabilities can set in between the pure reactant A above C and the zone of product C above the reactant B [33].

A general theoretical classification of all possible density profiles in the  $A + B \rightarrow C$  reactive case shows that the situation varies depending on the relative contribution of each species to the density profile (through their solutal expansion coefficient value) and on the ratio of diffusion coefficients [48]. The three-variable chemical system is thus much richer than the two-variable non-reactive equivalent.

In the case of vertical interfaces, as for instance at the vertical boundary between two domains of different composition, the reaction zone deforms convectively in the form of gravity currents with one or two vortices depending on the relative density of the product C versus that of the reactants A and B [49,50].



**Figure 5.** Comparison between buoyancy-driven patterns in a vertical Hele-Shaw cell due to a Rayleigh–Taylor (RT), doublediffusive (DD) or diffusive layer convection (DLC) instability in non-reactive (top line) and reactive (bottom line) cases. Field of view: 1.8 cm  $\times$  2.7 cm. Courtesy of L Lemaigre [33,34].

## 6. Convective dissolution in reactive solutions

Recently, increased interest in  $CO_2$  sequestration scenarios has further revived modelling on the effect of reactions on buoyancy-driven flows. In these sequestration techniques, the idea is to capture the  $CO_2$  at the exit of plants, inject it in its supercritical state into soils and trap it into oil fields, ancient coal mines or saline aquifers [51]. Aquifers are receiving special interest as they are largely spread out around the globe and could safely store a large amount of  $CO_2$  [52]. Moreover, once dissolved in the saline water, carbon dioxide could ideally react there with minerals present in the brine to be transformed into solid precipitates.

In the course of the sequestration process, the injected less dense  $CO_2$  rises up to the impermeable cap rock delimiting the aquifer, which leads locally to a stratification of less dense  $CO_2$  on top of salt water. Upon dissolution of  $CO_2$  in the lower aqueous host phase, a zone of denser water containing  $CO_2$  grows diffusively below the interface. After some time, convection sets in, whereby fingers of the denser  $CO_2$ -enriched water sink into the fresh water. This convective fingering illustrated in figure 6 is beneficial to the sequestration technique, as it enhances mixing and further dissolution of  $CO_2$  in the water. Understanding the optimum conditions for this convective capture and dissolution has generated a lot of modelling [54–61] and experimental [62–71] studies over the years. Indeed, owing to the difficulty of *in situ* studies, political decisions on future sequestration techniques rely heavily on theoretical predictions based on numerical simulations of the problem. To benchmark these models, quantitative comparison with experiments is of tantamount importance.

In this context, one should be cautious about the fact that some experiments visualize convective dissolution of  $CO_2$  due to colour indicators that track the pH changes associated with



**Figure 6.** Comparison between convective dissolution of gaseous  $CO_2$  in (*a*) pure water and (*b*) an aqueous solution of 0.01 M KOH contained in a vertical Hele-Shaw cell at time t = 13 min. Field of view: 8.6 cm  $\times$  2.5 cm. Courtesy of C Thomas [53].

the acidification inherent to dissolution of  $CO_2$  in water [40,63,64,67]. While this greatly helps in recording the dynamics, one should realize that the contours of the fingers imaged are pH isocurves specific to the colour indicator selected, which is not necessarily equivalent to the very contours of the  $CO_2$  fingers. Using pH indicators might thus sometimes provide an incorrect tracking of the convective zone, as shown recently using optical Schlieren techniques [10]. Other experiments have used miscible non-ideal mixing of liquids to mimic  $CO_2$  convective dissolution [57,72–75]. The characteristics of such a buoyancy-driven instability of a miscible interface are, however, not exactly equivalent to those of the partially miscible case of  $CO_2$  dissolving in water [53,76–80]. From a theoretical point of view, the main difference between this convective dissolution and the Rayleigh–Taylor instability of a miscible non-ideal stratification is that, with  $CO_2$ , we deal with a partially miscible system for which  $CO_2$  dissolves in water only with a finite solubility. The transfer from the upper component to the lower host phase is thus controlled by solubilization and not by diffusion. Quantitative extrapolation of  $CO_2$  mixing properties or dissolving fluxes by analysis of miscible non-ideal model systems should therefore be discussed with care.

We have recently introduced the two-layer stratification of a liquid ester on top of water as a good model system to study the convective dissolution of one liquid phase into another one [78]. Some esters indeed dissolve only with a finite solubility (which can vary depending on the ester chosen) in water. Starting from an initially statically stable stratification of the less dense ester on top of water, a convective dissolution process is observed with fingers that are similar to those observed in the  $CO_2$ /brine system. The advantage of ester–water stratification is its versatile use as a liquid–liquid system at room temperature and the possibility to vary chemical reactions in the host aqueous phase.

Chemical reactions are indeed of special interest in order to compute the amount of  $CO_2$  that can be dissolved in an aquifer [81,82]. It has already been shown that a reaction fixing  $CO_2$  to the porous matrix has a stabilizing effect on convection [83,84]. This is in a sense logical as this kind of reaction consumes the species at the origin of the convective instability. In the most general case, however, reactants are present in solution. Their concentration as well as that of the products of the reactions contribute as well to the density distribution that controls the buoyancy-driven instability. In that respect, we have shown that a general  $A + B \rightarrow C$  chemical reaction can control the convective dissolution of one component A into a host phase in which the reactant B is

dissolved [53,76,78,85]. From a theoretical point of view, we have classified the conditions for the controlled enhancement or slowing down of the convection in the case where all species have the same diffusion coefficients [76,85]. In short, the reaction is stabilizing when the product is less dense than the reactants, as shown experimentally in the case of an ester dissolving in an aqueous solution of NaOH [78]. The local decrease of density induced by the fact that the product is less dense creates a non-monotonic density profile [71,76,78,85,86] with a minimum that blocks the further progression of the fingers in the bulk of the host phase. On the contrary, a destabilizing effect can be obtained when the product has a sufficiently larger contribution to density than both reactants. We have experimentally demonstrated this case for dissolution of gaseous CO<sub>2</sub> into aqueous solutions of hydroxide bases (figure 6) [53,76]. A striking aspect of this control is the fact that the amplitude of the chemical stabilization or enhancement varies with the nature of the reactant in the host phase and with its concentration. As an example, convective fingers are more intense and appear earlier than in non-reactive systems as soon as CO<sub>2</sub> reacts with the hydroxide base to produce a denser salt. This effect is stronger for the series LiOH < NaOH < KOH < CsOH [53]. This effect can be understood on the basis of density profiles reconstructed using the respective solutal expansion and diffusion coefficients of each reactant and related product. These results show that chemical reactions should not be neglected when predicting theoretically the amount of  $CO_2$  that can be stored in a given aquifer and its shutdown time.

#### 7. Fingering induced by precipitation reactions

A hydrodynamic deformation of an interface can occur when a high-mobility fluid displaces a less mobile one as in VF. Fingering can also result from a change in permeability because of dissolution of a porous matrix induced by chemical reactions. In this case, the injection into soils of fluids containing chemicals that dissolve the solid matrix leads to an increase in porosity behind the reaction front. As a result, the resistance to flow decreases in the higher-mobility reactive zones, which favours further dissolution, giving, thus, a positive feedback leading to a fingering instability [87–91]. The reverse case of precipitation is not expected to destabilize a front, as the related decrease in mobility behind the front can block the flow rather than destabilize it.

We have nevertheless demonstrated both experimentally and theoretically that a precipitation reaction can trigger fingering patterns in a Hele-Shaw cell provided it is *localized* at the interface between two reactive solutions [11,12,92]. Our demonstration has first been obtained with a simple  $A + B \rightarrow C$  type of precipitation reaction, where A and B are reactants in solution and C is a solid precipitate [11]. We have further shown in a Hele-Shaw cell using the injection of cobalt chloride into silicate that a large variety of precipitation patterns can be obtained [92–95]. This reaction belongs to the rich family of chemical 'gardens', known to produce amazing plant-like mineral forms existing in nature at various scales [96]. Chemical gardens share properties with self-assembled structures such as nanoscale tubes, corrosion filaments, brinicles or chimneys at hydrothermal vents.

For environmental applications, the analysis of such patterns is also of importance in the context of CO<sub>2</sub> sequestration techniques. Mineralization, by which CO<sub>2</sub> injected into soils could undergo precipitation reactions, is indeed promising in view of the permanent safe storage of CO<sub>2</sub> in geological strata [97–102]. Understanding the conditions in which precipitation can affect the stability of the spreading CO<sub>2</sub> plume is thus particularly important. In contact with water, this carbon dioxide produces carbonates that can react with minerals such as Ca<sup>2+</sup> or Mg<sup>2+</sup> ions, for instance, to produce solid precipitates. This reaction is of interest as it transforms this greenhouse gas into a solid product, which ensures safer sequestration. To understand how the amount of precipitate varies with the injection speed and concentrations, we have performed laboratory-scale experiments in a horizontal Hele-Shaw cell in which an aqueous solution of carbonate is injected into an aqueous solution of Ca<sup>2+</sup> [102]. A wealth of different precipitation patterns is observed (figure 7). Interestingly, such experiments show that the amount of solid phase produced drops strikingly at large concentrations and flow rates. This points to the need



**Figure 7.** Variety of CaCO<sub>3</sub> precipitation patterns as a function of the reactant concentrations, obtained when an aqueous solution of carbonate is injected at an injection speed of 1 ml per minute into an aqueous solution of calcium ions contained in a horizontal Hele-Shaw cell. Time = 3 min and field of view = 122 mm  $\times$  98 mm. Courtesy of G Schuszter [102].

for further laboratory studies to understand the optimal transport and injection conditions for optimal trapping.

#### 8. Conclusion

Reactive flows are ubiquitously encountered in geological applications, ranging from oil recovery and pollution site remediation to CO<sub>2</sub> sequestration and mineralization, to name but a few. We have reviewed here some of these applications, explaining how chemical reactions can modify flows due to hydrodynamic instabilities, such as viscous fingering, Rayleigh–Taylor, convective dissolution or double diffusive instabilities, by changing the viscosity or density of the reactive solutions at hand. In particular, reactions can profoundly modify the symmetries of a fingered pattern by favouring development of the fingers in one direction. They can, as well, decrease the amplitude of an instability or on the contrary enhance it. More strikingly, reactions are also able to destabilize interfaces that would be hydrodynamically stable in non-reactive conditions. This is typically the case when a non-monotonic density, viscosity or permeability profile builds up in time due to the reaction.

Understanding the related chemo-hydrodynamic patterns paves the way to a chemical control of the hydrodynamic instabilities important in geological challenges such as optimizing oil recovery or trapping greenhouse gases in the most efficient and secure way. However, several difficulties remain on this path. The very first difficulty is to recognize that chemical reactions can really have a huge influence on a flow. Too often modelling of the dynamics of reactive systems simply neglects the feedback that changes in concentrations can have on flows and treats the chemicals as mere passive scalars. Of course, taking the active role of chemicals into account makes the models more complex, but this fortunately opens the path to new dynamics and new ways of control that makes the price worth paying.

Next, in chemo-hydrodynamic systems, another major problem is that the hydrodynamic instabilities typically develop around time-dependent reaction-diffusion base states. This makes the prediction of onset time and wavelength of the convective patterns difficult. Indeed, most of the time the linear stability analysis of such time-dependent problems predicts the onset time as the time at which growth rates of the perturbations become positive. This time is typically not the time at which patterns first become visible in experiments, as perturbations must have already grown to become detectable. The question is then: at which time should theoretical growth rates

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and wavelengths be computed to be compared to experiments? The frontier between the linear regime in which perturbations grow exponentially and the nonlinear regime where perturbations interact is also difficult to delineate. Moreover, in simulations, instabilities start at a time that is influenced by the amplitude of the noise seeding the development of convection. It is of course quite impossible to know what noise is present in experiments such that quantitative comparisons are again difficult. Efforts should therefore be developed to find a consensus on the optimum way to quantitatively compare linear stability predictions, nonlinear simulations and experimental data. In that respect, simplified Hele-Shaw experiments are good candidates to achieve this goal, because the dynamics is easy to track and some effects can be isolated. Obtaining quantitative agreement between Hele-Shaw data and theoretical predictions can thus be an important first step to benchmark the theoretical models and be able to trust their predictions on larger field scales.

A third difficulty is the large variety of temporal and spatial scales involved in the field in environmental applications. There are of course differences between the results of a quasi-twodimensional Hele-Shaw experiment, a real three-dimensional laboratory-scale porous matrix (like a shale sample for instance) or on-site localized monitoring. Efforts should be made to be able to study the same problem at all three levels to understand how lessons learned from laboratory-scale reactors can then be extrapolated to the field. As an example, precipitation experiments as discussed in the previous section (figure 7) could be done in both Hele-Shaw cells and small-scale three-dimensional porous matrices using chemical compositions close to that of the CarbFix CO<sub>2</sub> sequestration site in Iceland [98] for which detailed field data are available. Changes in concentrations and flow rate in the laboratory systems could shed light on the more complex real site problem.

We see thus that a lot of work still has to be done to unravel the complexity of chemohydrodynamic patterns in porous media. However, the rewards of studying such RDC systems are numerous. Understanding how reactions can control flows, or vice versa how a flow can control the spatio-temporal distribution of chemicals in soils, is at the heart of possible progress in petroleum, soil remediation or CO<sub>2</sub> sequestration engineering. From a more fundamental point of view, pattern selection theories are already well developed in hydrodynamics, on the one hand, and in reaction–diffusion systems, on the other. Studies of RDC pattern selection promise a wealth of new dynamics and instabilities still to be deciphered.

In that respect, developing experimental and theoretical studies on chemo-hydrodynamic geological systems calls for multidisciplinary collaborative efforts of chemists, physicists, engineers and geologists. Benchmarking and testing of numerical models of geological applications can benefit from experiments and modelling developed in pattern formation and nonlinear sciences. This multidisciplinary and synergetic approach to environmental issues opens thus new horizons in which important societal or economical challenges will be addressed.

Competing interests. The author declares no competing interests.

Funding. Funding from Prodex, the ITN Multiflow network and the FRS-FNRS Forecast programme are gratefully acknowledged.

Acknowledgements. The results presented in this review have been obtained with numerous co-workers. I thank them warmly for fruitful collaborations throughout the years. I thank in particular those who have provided me with the figures used here.

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