Dynamics of reaction fronts in porous media

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Abstract

Typical examples of porous media are rocks and soils. They are composed of a solid skeleton and a network of void spaces, i.e. the pores. If the porosity is interconnected, then such a rock can be infiltrated by external fluids (groundwater). The chemical composition of such a fluid depends on its history. When it infiltrates a rock formation, it usually drives it out of chemical equilibrium. Chemical reactions occur: some minerals dissolve, and other precipitate. The chemical alteration does not proceed uniformly in the whole rock volume. Instead, there develop one or more reaction fronts: regions of increased chemical activity, which are boundaries between rock formations of different compositions. The reaction fronts propagate through the rock as it is infiltrated by the fluid.

The dynamics of reaction fronts is usually complicated due to positive feedbacks between the fluid flow, ion transport, and chemical reactions, which modify the properties of the rock (in principle, its permeability). In this thesis, selected aspects of their dynamics were studied, for certain classes of model hydrogeochemical systems. These are either dissolution systems, or dissolution-precipitation ones. We are interested in length scales which are significantly larger than typical pore sizes in the rock, and time scales which are connected with changes in the porous matrix, via dissolution or precipitation of minerals. Therefore continuum models are adapted in our analysis and Darcy's law is applied to account for the fluid flow.

As regards the dissolution systems, several approaches were applied to study the dissolution front dynamics at various stages of their evolution. Firstly, linear stability analysis of a dissolution front was performed. We have shown that such a dissolution front is always unstable with respect to long-wavelength perturbations of the front position. Short-wavelength perturbations can be stabilized by diffusion. The results are well known since 1980s, so their rederivation serves just as a starting point for our own results. Next, we analyzed the dissolution system in a weakly nonlinear regime. We applied a simplified approach and study only the coupling between the harmonic mode which dominates in the linear regime, and its first subharmonic. The analysis allowed us to observe the first nonlinear effects which emerge during a spontaneous front breakup: the competition between individual protrusions. The dynamics of the system was also studied using numerical simulations, which allowed us to observe two phenomena, which play the major role during the later stages of the evolution: merging and screening of individual dissolution fingers. Finally, we posed the problem of finding the geometry of two classes of dissolution forms, "tips" and "roots" of dissolution fingers. We assumed that during their evolution, both forms approach a stationary shape and analyze their geometry in such a steady state. In each case we were able to obtain a family of infinite parabolic (in two dimensions) or paraboloidal (in three dimensions) forms. We could find the flow field and the solvent concentration in the vicinity of such forms, as well as their propagation velocity.

The dissolution-precipitaton systems were analyzed in a similar manner. After considering one-dimensional profiles of mineral volume fractions and concentrations, the linear stability of such solutions was studied. We have shown that replacement fronts, whose characteristic feature is a porosity (and permeability) decrease in the replacement zone, can be unstable for a wide range of parameters. The most striking observation is a possible destabilization of the front in the case when permeability of the secondary rock upstream is lower than permeability of the primary rock downstream. Such a destabilization of the front is caused by the presence of a zone of lower permeability in the vicinity of the replacement zone. Next, we present numerical studies of the replacement system. If the secondary rock is more permeable than the primary one, a replacement system behaves similarly to a dissolution one. The initial instability causes the front breakup and the emergence of an array of protrusions. Due to nonlinear feedbacks, in course of the evolution some of the protrusions coarsen and grow into fingers, while others get screened and absorbed by their larger neighbours. However, there are some dissimilarities between the replacement and the dissolution systems. Firstly, in the replacement system the intermediate region between the primary and the secondary phases is characterized by a porosity decrease. Secondly, the secondary

mineral is not evenly distributed. Instead, its volume fraction distribution reflects the history of the system. Paths of increased porosity in the secondary phase coincide with the former positions of finger tips. Interestingly, similar effects can be observed in some natural replacement systems, in particular during calcite-to-dolomite replacement. If the secondary rock is less permeable than the primary one, a replacement front is also linearly unstable for a wide rage of other parameters. After the initial breakup, a wavy replacement front propagates through the porous rock. However, after a transient period, the amplitudes of the fingers cease to grow and large-scale fingers do not develop.

The models which are considered in the thesis are relatively simple, which makes them applicable to a variety of geological processes. On the other hand, they are complicated enough to exhibit a nontrivial and intriguing behaviour, which could hardly be predicted a priori.