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Stability of reaction-fronts in porous media

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ABSTRACT

The stability of reaction-fronts in porous media is studied with analytical and numerical methods. A stability criterion has been derived using linear stability analysis assuming a sharp font. The sharp front assumption is an approximation of the mathematical model in the limit of an infinite rapid reaction. The criterion shows that the stability of a sharp reaction front is dependent on the permeability that develops behind it. The sharp front is unstable for perturbations of any wave-length if the permeability increases behind the front. The criterion shows that short wave-length perturbations are more unstable than long wave-length perturbations. The sharp front is labile when the permeabilities are the same at both sides of the front. This means that the perturbed front moves unchanged forward. Finally, perturbations will die out in case the permeability decreases behind the sharp front. The stability of non-sharp fronts are simulated numerically when dissolution is by first order kinetics, the transport is by convection and diffusion and when the permeability and specific reactive surface depends on the porosity. The numerical experiments behave according to the stability criterion.

1. Introduction

The injection of a reactive fluid into a porous medium leads to alteration of the reactive part of the solid rock matrix and to changes of the porosity and permeability. Familiar examples are the dissolution of the matrix and increasing porosity in carbonate rocks by CO_2 rich brine [1,2]. The entire rock matrix may also be dissolved with the results that “wormholes” develop Golfier et al. [3]. Under certain conditions of flow and reaction the alteration pattern becomes a reaction front. The front is a transition from fully reacted to unreacted rock over a “short” distance. The reactive part of the matrix has fully reacted behind the front and it is unreacted ahead of the front.

Laboratory experiments and simulation studies have shown numerous examples of reaction fronts that develop in an unstable manner Golfier et al. [3]. Small perturbation on a linear front develops into fingers Ortoleva et al. [4]. The stability of such reaction fronts has been studied by Chadam et al. [5,6], Ortoleva et al. [4] and [7] and more recently by Zhao et al. [8]. Through a linear stability analysis these authors obtained a critical pressure gradient as a condition for stability, where the critical gradient is a function of the ratio of permeabilities ahead of and behind the front. The linear stability analysis was based on a sharp front in the porosity and permeability, but not the concentration. Hirch and Bhatt [9] obtained analytical results for the linear stability of reaction fronts in the cases of small and large wave numbers, and small variations in the permeability. They are building on the work of Sherwood [10] and they take into account that the front has finite width.

Here we suggest a simpler linear stability analysis than the one developed by Chadam et al. [5], Sherwood [10], Ortoleva et al. [4], Chadam et al. [6], Hirch and Bhatt [9] and Xin et al. [7]. It is derived for the limit of a sharp front (zero width), where the porosity, permeability and concentration are step-functions. The derivation follows the same line of reasoning as applied

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to the stability of the interface between two immiscible fluids during vertical displacement in a Hele-Shaw cell, as for instance shown by Marle [11]. This analysis gives a simple condition for the stability of sharp fronts in terms of the permeabilities at the two sides of the front. The stability criterion shows that the stability of a sharp front depends on the permeability that develops behind the front. It does not involve a critical pressure gradient that in turn depends on the ratio of the permeabilities of the two sides of the front, as shown by Chadam et al. [5], Ortoleva et al. [4], Chadam et al. [6] and Xin et al. [7]. Furthermore, the analysis presented here shows in a simple way how the stability depends on the wave length of the front perturbation.

The stability of non-sharp fronts are studied numerically when dissolution is by first order kinetics, the transport of dissolved matter is by convection and diffusion and when the permeability and specific reactive surface depend on the porosity. The sharp front assumption is an approximation of the mathematical model in the limit of an infinite rapid reaction. Numerical solutions of the mathematical model demonstrate the different cases of stability when the reaction is restricted to a narrow zone.

The paper is organized as follows: The numerical model is first explained and the assumptions about permeability and the specific surface area of the rock are then discussed. The stability criterion of sharp reaction fronts is presented, the derivation of the stability condition is given, before numerical examples of stable, labile and unstable fronts are shown.

2. The mathematical model

The mathematical model consists of three coupled macroscopic equations as shown by Ortoleva et al. [4], Chadam et al. [6] and Xin et al. [7]. They are solved on a rectangular domain of length l_0, where the side at $x = 0$ is the inlet and the opposite side at $x = l_0$ is the outlet. The other sides are closed for fluid flow.

The first equation is the pressure equation that follows from conservation of fluid mass and Darcy's law (see Appendix A)

$$\nabla \cdot \left(\frac{\varrho_f \, k(\phi)}{\mu} \nabla p \right) = -(\varrho_s - \varrho_f) \frac{\partial \phi}{\partial t}, \tag{1}$$

where ϕ is the porosity, ϱ_f is the fluid density, ϱ_s is the solid density, $k(\phi)$ is the permeability, μ is the viscosity and p is the fluid pressure. The fluid density is taken to be constant, independent of the concentration of the dissolved solid, since it is assumed that the concentration is low. The solid density is also taken to be constant. The pore space is assumed incompressible and the porosity is changing only because of chemical reactions. A constant fluid density also implies that the fluid pressure can be taken to be a fluid flow potential [12]. The pore space has an isotropic permeability $k(\phi)$, which changes with the porosity. The right-hand-side of Eq. (1) is a source term that expresses that the solid matrix being dissolved enters the fluid phase. It is shown in Appendix A that this source term has a negligible impact on the Darcy flow, and that it can be approximated by zero. Boundary conditions for pressure Eq. (1) are a constant volume flux at the inlet and zero pressure at the outlet. The initial fluid pressure is zero.

The dissolution of the porous matrix is modeled with a one-component reaction-transport equation

$$\frac{\partial (\phi c)}{\partial t} + \nabla \cdot (c\mathbf{w} - \phi D \nabla c) = k_d S(\phi) \left(1 - \frac{c}{c_{\mathrm{eq}}} \right), \tag{2}$$

where c is the concentration of the reactive species in the pore fluid (in units mol m^{-3}) and $\mathbf{w} = -(k/\mu)\nabla p$ is the Darcy flux. The term in parentheses, after the divergence-operator, accounts for transport of the dissolved species by Darcy flow and by Fickian diffusion. The diffusivity in the fluid filling the pore space is denoted D (in units m^2 s^{-1}). The right-hand-side is a reaction term, where dissolution is by first order kinetics. The reaction constant for dissolution is k_d (in units mol s^{-1} m^{-2}), the specific (reactive) surface of the pore space is $S(\phi)$ (in units m^2 m^{-3}), and the specific reactive surface area changes with the porosity. The equilibrium concentration is c_{eq}. We notice that the right-hand-side is positive as long as $c < c_{\mathrm{eq}}$, and that it acts as a source term. The boundary conditions are $c = 0$ at the inlet and $c = c_{\mathrm{eq}}$ at the outlet and the pore fluid has initially $c = c_{\mathrm{eq}}$.

The third equation gives the rate of the change of porosity caused by the dissolution process as

$$\frac{\partial \phi}{\partial t} = \mathcal{V}_s k_d S(\phi) \left(1 - \frac{c}{c_{\mathrm{eq}}} \right), \tag{3}$$

where the $\mathcal{V}_s$ is the molar volume of the reactive solid (in units m^3 mol^{-1}). The three Eqs. (1)–(3) are the basis of the reaction-transport model.

It should be mentioned that the reaction-transport Eq. (2) can be approximated as

$$\phi \frac{\partial c}{\partial t} + \mathbf{w} \cdot \nabla c - \nabla \cdot (\phi D \nabla c) = \frac{1}{\mathcal{V}_s} \left(1 - c \mathcal{V}_s \frac{\varrho_s}{\varrho_f} \right) \frac{\partial \phi}{\partial t} \approx \frac{1}{\mathcal{V}_s} \frac{\partial \phi}{\partial t} \tag{4}$$

by use of the expression (1) for fluid conservation. See also Eq. (53) for conservation of fluid mass in Appendix A. The approximation on the right-hand-side follows from the assumption $c_{\mathrm{eq}} \mathcal{V}_s \ll 1$ since $0 \leqslant c \leqslant c_{\mathrm{eq}}$.