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Kinetic approach to sulphite chemical aggression in porous media

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ABSTRACT

A kinetic description is proposed of a fluid species moving in a porous medium and chemically interacting with it. The porosity is included in the model by a modification of the standard kinetic equations for two gaseous species diffusing in a background medium of two solid species. The validity of the proposed kinetic model is assessed by comparing the resulting macroscopic model, obtained by Chapman–Enskog expansion, with macroscopic models present in the literature.

1. Introduction

In this paper we propose a kinetic description of fluid species (gaseous or liquid) moving in a porous medium and chemically interacting with it. Specifically, we consider a binary irreversible reaction of the type

$$S+C\longrightarrow A+G, \tag{1}$$

where S, A are fluid species, while C, G are solid species. The porosity of the solid varies with time, as the solid species C is replaced by the solid species G. The name of the species comes from a specific application, the interaction of sulphite, SO_2, with calcium carbonate rocks, $CaCO_3$, which, in the presence of water, produces gypsum, $CaSO_4$. For this application, S stands for sulphite, A for unpolluted air, C for calcium carbonate, G for gypsum. In this case, the complete reaction follows a two-step mechanism, as explained in [1,2], but for practical purposes it is possible to assume the simplified one-step reaction (1), as already done in [3].

Extensive chemical literature is available on the deterioration mechanisms of natural building stones [2,4–7]. The main active components of these mechanisms are sulphur and nitrogen oxides, which are transformed, through complex reactions, into gaseous nitric and nitrous acids and into acid sulphates. In particular, SO_2 and NO_3 react with calcium carbonate stones to produce sulphates and nitrates which may form crusts, that eventually exfoliate [3,8]. One of the first quantitative descriptions of damage can be found in [9]. Other studies have tried to define the kinetics of the reaction of SO_2 with limestone materials [3,5–7].

More recently, starting from [10], a new class of mathematical models has been proposed for describing the diffusion and chemical action of sulphur dioxide or calcium carbonate stones by using basic physical relations, the balance laws of chemical reactions and Fick's law. The numerical approximation and qualitative analysis have been studied in [10]. A first comparison with experimental data has been performed in [11], obtaining a good agreement. Global existence of smooth solutions for the Cauchy problem in one space dimension has been established in [12]. A similar model has been considered in [13] for general gas–solid reactions, but assuming constant diffusivity.

A related model has been proposed in [14], taking into account the effect of the permeability of the porous medium. A qualitative discussion of the asymptotic behavior of the solutions to this model (for unbounded domain $x>0$), by using scaling arguments similar to the ones used in [15,10], can be found in [14], while a numerical investigation was performed in [16]. Several models with a similar mathematical structure have been proposed in the literature, with different geophysical and physical applications related to reactive flows in porous media [17–24]. In particular, in [17–20] the infiltration flow of a reactive fluid in a porous

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medium, in which porosity changes occur, is investigated and a mathematical model for this phenomenon is given in the form of a moving free boundary problem.

The models so far mentioned do not include a detailed mathematical description of the thermal effects which play a role in the considered reaction–diffusion phenomena. Sometimes a varying temperature is included in a standard way, by coupling with a heat equation [25]. A kinetic description is naturally capable of describing thermal effects, and in our opinion this might lead to a better understanding of the interplay between chemical reaction, diffusion process and temperature change, and possibly to the derivation of new macroscopic models.

In the description of a porous medium, several scales come naturally into play. At the microscopic scale – say, the typical dimension of a pore, d – we can distinguish between pores and regions occupied by solid material. The motion of the fluid particles can only take place through the pores. At the intermediate scale, the apparent randomness of the material disappears, and we can define the concept of porosity. To do so, we need to introduce the concept of Representative Volume Element (RVE), that is, the minimum material volume statistically representative of the neighborhood of a certain point $\mathbf{x}$ of our material system [26,27]. Thus, the material system is regarded as a continuum, and at each point $\mathbf{x}$ of this continuum is "attached" a corresponding RVE, which we denote by $\mathcal{V}(\mathbf{x})$, with typical dimension D. The porosity at the point $\mathbf{x}$ is defined as

$$\varphi(\mathbf{x}) = \frac{\text{volume of pores in } \mathcal{V}(\mathbf{x})}{\text{volume of } \mathcal{V}(\mathbf{x})}. \tag{2}$$

Finally, at macroscopic scale we see a continuum, with a continuous porous function $\varphi(\mathbf{x})$ which describes the porosity of a material sample of the porous medium, of length L. The main ideas of macroscopic modeling of filtration in porous media can be found in [28,29]. In this picture, what really matters is not the actual value of the scales d, D, L, but the relative ratios between them, that is,

$$\frac{d}{D} \ll 1, \quad \frac{D}{L} \ll 1. \tag{3}$$

A proper kinetic description should occur at the level of the microscopic scale, but this would be by far too difficult. In fact, we would need a discontinuous function describing the pores, with values zero on the void and one on the solid, which would also provide the contour of a boundary for the motion of the fluid particles. Moreover, this boundary is not fixed but it is affected by the chemical reaction.

To overcome the difficulty of the microscopic kinetic description, we propose a mesoscopic kinetic description. At this level of description, a fluid particle has not to be identified with a constituent particle of the fluid species but rather with an average of the constituent particles present in an RVE. Then, for a kinetic description of the process in such "homogenized" environment, one could imagine and build up, also at this different level, a model in which the molecular velocity is in turn correspondingly scaled. In other words one should consider that, if an "average molecule" at the point $\mathbf{x}$ has velocity $\boldsymbol{\xi}$, then this velocity results from the average of the molecular velocities in the RVE centered in $\mathbf{x}$. Of course, in the latter picture, one must forget about the meaning of individual binary collisions and of balance in the molecular phase space, usually attached to the Boltzmann kinetic equations, but rather one should look at their scaled versions as a working tool in order to restore the effects of porosity, which otherwise could not be taken into account by a reasonably simple kinetic approach.

Actually, we do not try to work out in this paper a rigorous derivation of a mesoscopic kinetic model for the chemical aggression of a porous medium. We confine ourselves to the problem of introducing the porosity into the picture, and, for that purpose, we propose a modification of the standard kinetic model for two gaseous species and two solid species, and discuss its continuum limit, showing how, according to different options, it may recover the main features of the macroscopic models, and/or introduce some significant difference. Of course, the quantitative validity will be assessed a posteriori, by a quantitative comparison with numerical results predicted by the existing fluid-dynamic models and with experimental data, all of which is planned as future work.

In the next section, we review the main models used for a fluid-dynamic description of chemical aggression in porous media. Then, in Section 3 we introduce a kinetic description for the chemical interaction of two gaseous species in a host medium made of two solid species. In the subsequent Section 4 we perform a Chapman–Enskog expansion, obtaining macroscopic models in the form provided by the kinetic theory. Finally, in Section 5 we compare the resulting macroscopic equations with the fluid-dynamic equations presented in Section 2, and in Section 6 we draw some conclusions.

2. Macroscopic models for chemical aggression in porous media

In this section we outline the main models present in the literature for the description of the chemical aggression in porous media. The level of the presentation will be pretty general, but we always keep in mind the main application, to calcium carbonate rocks chemically attacked by sulphite.

We consider the binary irreversible chemical reaction (1), where the species S, A are gases, while C, G are solid materials. The solid material is a porous medium, so it is possible to define a porosity function which measures the density of pores in it. We denote by n_C, n_G the number densities of the solid species C, G. The number densities are functions of $\mathbf{x} \in \Omega \subset \mathbb{R}^d$ and $t \in \mathbb{R}^+$. The porosity depends on the concentration of the solid species, so we have

$$\varphi = \varphi(n_C, n_G).$$

The starting equations are the chemical reaction equations [30]

$$\frac{\partial n_S}{\partial t} + \nabla \cdot (n_S \boldsymbol{v}_S) = -\mathcal{K} n_S n_C, \tag{4}$$

$$\frac{\partial n_A}{\partial t} + \nabla \cdot (n_A \boldsymbol{v}_A) = \mathcal{K} n_S n_C, \tag{5}$$

$$\frac{\partial n_C}{\partial t} = -\mathcal{K} n_S n_C, \tag{6}$$

$$\frac{\partial n_G}{\partial t} = \mathcal{K} n_S n_C, \tag{7}$$

written with additional flux terms for the gaseous species n_S, n_A. Here, $\mathcal{K}$ is the reaction rate, while $\boldsymbol{v}_S$ and $\boldsymbol{v}_A$ are the fluid velocities, defined at macroscopic scale. Eqs. (4)–(7) are usually written for the mass densities,

$$\rho_i = m_i n_i, \quad i \in \{S,A,C,G\}. \tag{8}$$

Here the number densities are used for a better comparison with the model derived in this paper.

Eqs. (6) and (7) can be used to derive

$$\frac{\partial}{\partial t}(n_C + n_G) = 0, \tag{9}$$