Uncertainties in modelling and parameterization of fluid–rock consumption–production interaction in porous media

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Abstract Modelling and parameterization of the fluid-rock interaction with consumption or production of mineral or organic rock compartments is discussed here in relation to quantification and macroscopic formulation of transport and reaction processes. One major uncertainty is quantifying the relationship between the internal specific reactive surface and the concentration of the reactive minerals. Proper understanding and quantification of microscopic phenomena like fluid-surface reaction is one precondition for prognostic extrapolations to macroscopic spatial and temporal scales. Thus, appropriate formulations are needed that describe microscopic heterogeneous reaction phenomena on macroscopic scales. The authors propose therefore to formulate potential functionality of the reaction rate on mineral concentration as being appropriate to describe reaction-induced changes in reaction rates caused by variations in the inner reactive surface. Sample calculations, including the reaction of acid mining water with calcium carbonate and the oxidation of coal demonstrate this proposition. To find functional correlations between the inner reactive surface and the reaction rates, the authors suggest paying more attention to the experimental investigation and quantification of the inner reactive surface of solid minerals. However, keeping in mind that reaction kinetics such as combustion modelling at high temperatures may have little control over an overall process, we should estimate the relevance of parameter sensitivity to reduce effort.

Keywords aquifer; Arrhenius; coal fire; fluid–rock interaction; numerical simulation; petrophysics; rock properties; stochastic

INTRODUCTION AND MATHEMATICAL FORMULATION

Fluid–rock interaction with consumption or production of mineral or organic rock compartments is an important process in the Earth's crust. Erosion and cementation of calcium carbonate and other minerals are ongoing in the natural environment. In mining and civil engineering projects, chemical reactions with mineral consumption have to be included in the project planning. Examples are acid mining water and its neutralization with calcium carbonate, and the oxidation of pyrite to acid water in mining heaps. Salt erosion at salt domes is important for saltwater production in groundwater and for the safety of waste disposal in salt formations. In geothermal energy development, hydraulic stimulation with acid water to enlarge the pore and fracture systems is regarded as an important technical process for improving the productivity of boreholes. In the production phase of a geothermal power plant, mineral dilution and the mineral content of the circulating water is of great technical

importance. Oxygen-coal interaction is a basic process of coal-fire propagation in coal mining areas and coal heaps.

The above-mentioned examples have in common their heterogeneous chemical reactions between fluid and solid mineral or maceral components, which are frequently formulated in terms of a second-order source (Lichtner, 1996):

$$Q \sim Kc_f c_s \tag{1}$$

proportional to the product of fluid concentration c_f and mineral concentration c_s . However, the influence of the inner reactive surface on the chemical reaction has gained little attention. A different mathematical formulation (equation 4) considers a linear relationship to the inner reactive surface, with the authors suggesting the consideration of micro-scale observables such as the inner reactive surface, to be a necessary precondition for prognostic extrapolations of reactive transport phenomena to macroscopic spatial and temporal scales.

The simplest case for the mathematical process description of the fluid–mineral reaction is given by two mass conservation equations, one reactive transport equation for the fluid component and one for the formulation of solid mineral consumption or production. The reactive transport equation for the reactive fluid component c_R is given by:

$$\nabla ((D_R + \alpha_R \mathbf{u}) \nabla c_R) - \nabla (\mathbf{u} c_R) - \frac{\partial c_R}{\partial t} = -Q_{R-M}$$
⁽²⁾

where Q_{R-M} is a source term describing mass exchange between the fluid and matrix (kg m⁻³ s⁻¹), c_r is the concentration of the reactive fluid component (kg m⁻³), D_r is the diffusion coefficient of the reactive fluid component (m² s⁻¹), α_R is the dispersion length of the reactive fluid component (m), **u** is fluid velocity (m s⁻¹), and *t* is time (s).

Equation (2) has frequently been used for describing reactive transport processes (Stumm & Morgan 1981; Kinzelbach, 1992; Diersch, 1994; Zysset *et al.*, 1994; Yeh, 2000). Consumption or production of immovable reactive minerals in the matrix is expressed by a similar equation, in which the transport term does not appear:

$$\frac{\partial c_M}{\partial t} = \beta Q_{R-M} \tag{3}$$

where c_M is the concentration of the reactive mineral component (kg m⁻³), and β is the conversion coefficient between solid mineral and fluid component (–).

Based on a molecular kinetic reaction model, the probability of a molecular reaction is proportional to reacting components, which are the fluid with concentration, c_R , and the internal reactive surface of the solid mineral for the heterogeneous system considered. Assuming only one-way reactions (for the sake of simplicity), this proportionality can thus be formulated as:

$$Q_{R-M} = K\tau c_R \tag{4}$$

where τ the internal reactive surface area (m² m⁻³) and K is a factor (m s⁻¹).

The internal reactive surface τ depends on the chemical history of the mineral: in other words, changes in c_M result in changes in τ during the reaction. Hence:

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$$\tau = \tau(c_M) \tag{5}$$

An additional requirement for the expression in equation (5) is that τ vanishes when c_M approaches zero. Since this is valid for power law functions (Kessels & Gäbler, 1997), we used the potential functionality between inner reactive surface and mineral concentration of the form:

$$\tau = \tau \left(c_M \right) = \alpha \left| \frac{c_M}{c_M^0} \right|^{n-1} c_M \tag{6}$$

where α is a constant. Finally, the source term Q_{R-M} for the chemical reaction between fluid concentration and mineral concentration becomes:

$$Q_{R-M} = \hat{K} \left| \frac{c_M}{c_M^0} \right|^{n-1} c_M c_R = k e^{-\frac{E}{RT}} \left| \frac{c_M}{c_M^0} \right|^{n-1} c_M c_R$$
(7)

n is an exponential factor (–), *k* is a factor (m³ kg⁻¹ s⁻¹), $\hat{K} = K^* \alpha = \text{factor} (\text{m}^3 \text{ kg}^{-1} \text{ s}^{-1})$, *T* is temperature (K), and *E*/*R* is the exponential Arrhenius factor (K).

The temperature dependency of the chemical reaction in equation (7) applies to the Arrhenius function, where an energy conservation equation also has to be solved. Three reactive examples will now be discussed. The first conceptual model shows the variation in the internal surface during the reaction process, with special attention paid to the influence of the exponential factor n in equation (7) for a one-dimensional contaminant transport scenario. The second example gives experimental results for the exponential factor n on CaCO₃ dissolution with acid water and the third example discusses the problem of self-ignition of coal deposits. Instead of presenting a complex sensitivity analysis such as the one in Kessels & Lengnick (1996), we will focus on the relationship between the inner reactive surface and mineral concentration, as well as the difference in the sensitivity between fast and slow kinetic reactions.

SOLIDS WITH CUBIC REACTIVE GRAINS

The relationship between inner reactive surface and mineral concentration depends on the shape and size of pores and sediment grains. This dependency will form the main topic below; however, the time scale of the inner pore diffusion is assumed to be short compared to the time scale of the macroscopic processes. Figure 1 shows the relationship between inner reactive surface and mineral concentration for three different mineral shapes, as discussed by Kessels *et al.* (1996).

The grain size distribution of the reactive minerals is the most important petrophysical condition for the inner reactive surface. The relation between the internal reactive surface and mineral concentration is demonstrated with a cubic grain model. Here, a reaction process is determined by the small grain component of the reactive mineral at the beginning of the reaction process. The large grains dominate the process at a later stage with low reactivity. The grain size distribution, as shown in Fig. 2, indicates the relation shown in Fig. 3. The power law equation $\tau = kc^n$ as introduced



Fig. 1 Relationship between inner reactive surface and mineral concentration using different mineral shapes.



Fig. 2 Calculated grain size distribution for cubic reactive minerals before (left) and after (right) a fluid reaction process (Kessels & Gäbler, 1997).



Fig. 3 Calculated relationship between partial reactive volume and reactive internal surface for cubic minerals and power law relationships (Kessels & Gäbler, 1997).

in equation (6) makes the reactive transport system of equations (2) and (3) solvable. A more inhomogeneous mixture of the reactive grains can lead to exponents, n, of up to 10 (Kessels & Gäbler, 1997).

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Figure 4 presents the consequences of a high power-law exponent, where calculations for a salt disposal suddenly acted on by freshwater flow have been made with the finite-difference program, NTRANS-EX (Kessels, 2004). The salt was removed from the deposit and dissolved in the water, causing the build-up of a saltwater halo downstream. A relatively sharp front in the mineral concentration of a linear fluid-mineral reaction is shown on the left-hand side of Fig. 4. A highly nonlinear exponent (n = 4) describes a more realistic process in which the fine grained mineral reacts very fast, while the coarse grain minerals are very stable (see right-hand side of Fig. 4). One of most important uncertainties in modelling and parameterization of fluid-rock chemical reaction for these systems is a lack of experimental results related to the power law exponent.



Fig. 4 Comparison of two reactive transport calculations with linear (n = 1) and nonlinear (n = 4) power law mineral reactions (calculated with the NTRANS-EX code). The concentrations are shown in time steps of two years. The fluid flow is directed from left to right. Higher power law exponents lead to a low solvable ground mineral concentration.

The experiments presented in the next section demonstrate how power law exponents are investigated through calcium carbonate dissolution.

CALCIUM CARBONATE GRAINS IN ACID WATER

Calcium carbonate is an important sedimentary mineral for neutralizing acid water produced by pyrite oxidation in lignite mine areas or in waste deposits. Kessels & Gäbler (1997) investigated the CaCO₃ dissolution with pH-stationary experiments. The kinetics of CaCO₃ sand dissolution were measured under constant pH conditions by the amount of acid water injection. The results are given in Table 1 according to:

$$\frac{\partial \frac{c_M}{c_{M,0}}}{\partial t} = -K \left(\frac{c_M}{c_{M,0}}\right)^{n_{\text{CaCO}_3}}$$
(8)

with $c_{M,0}$ being the initial mineral concentration. The mean value for the exponent determined, $n_{CaCO_3} = 1.54 \pm 0.14$, shows the nonlinear reactivity for this fine-grained

pН	Experiment no.	$n_{CaCO3}(-)$	$K(s^{-1})$
6.0	B4159	1.815	1.536×10^{-4}
5.5	B4167	1.662	$1.912 imes 10^{-4}$
5.0	B4070	1.552	$2.190 imes 10^{-4}$
4.5	B4157	1.469	3.166×10^{-4}
4.0	B4060	1.458	$9.034 imes 10^{-4}$
3.5	B4156	1.489	$2.540 imes 10^{-3}$
3.0	B4055	1.412	1.006×10^{-2}

Table 1 Kinetic parameters from pH-state experiments using CaCO₃ grains (Kessels & Gäbler, 1997).

 $CaCO_3$ sand. The main uncertainty in quantifying the natural reactive transport by prognostic calculations is the unknown chemical history of the sediment (sand). The present chemical dissolution depends on the processes in the past.

COAL FIRE OBSERVATIONS AND THE REACTIVE COMBUSTION PROCESS

Gas-maceral chemical reactions illustrate the importance of understanding chemical reactions in heterogeneous systems. Worldwide there is the continuing problem of spontaneous combustion of coal seams, coal waste heaps and coal storage heaps. Several million tons of coal are annually destroyed by coal fires in the north of China (Zhang *et al.*, 2004). Companies permanently fight against spontaneous combustion of the many coal heaps using water cooling and mechanical destruction of fire nests.

The combustion process is difficult because temperature-dependent reaction rates cannot be ignored. The high reactivity at higher temperatures leads to the burning of coal whenever enough oxygen is available for the reaction. Underlying the still poorly known relationship between coal reactivity and the inner reactive surface (Arenillas *et al.*, 2003) is the additional uncertainty of the transport of oxygen to the combustion centre. Convection dominated exhaust gas outflow, with gas velocities of more than 1 m s⁻¹ is measured in fractured zones (Wessling & Kessels, 2004). Pure diffusion cannot transport enough oxygen through the several metres of overlying sediments to the combustion centre, as calculations with realistic diffusion coefficients show. Additionally, oxygen and temperature measurements at a coal heap near Hanover, Germany, document the convection process with a chimney effect (Fig. 5).

For calculations at room temperature the reaction process is very sensitive to the kinetic parameters from equation (7). At higher temperatures the reaction rate increases rapidly (Hobbs *et al.*, 1993) due to the exponential increase. At 300°C, total oxygen vanishes at time smaller than 10^{-3} s. At high temperatures, the limiting mechanism controlling the chemical reaction between coal and oxygen is gas flow, so that reaction kinetics become irrelevant.

The fundamental processes assumed for coal combustion are demonstrated by considering a mining gallery and an overlying coal seam as a sample scenario (Fig. 6). Stoichiometric reaction formalism and kinetic parameters were used as in Schmidt *et al.* (2003). A major outcome of these scenario calculations was that self-ignition of the overlying seam was seen to be possible without mining activity, even in this overlying

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Fig. 5 Oxygen and temperature measurements at a depth of 1.5 m below the surface of a coal heap and the flow interpretation (measurements from 16 May 2005).



Fig. 6 Reactive transport calculations where the air flow over a year is strong for 20 equidistant time steps (using the finite-difference program, NTRANS-EX).

seam. The combustion development strongly depends on the air velocity penetrating the overlying coal seam. Calculations show a maximum sensitivity for the combustion progress that depends on the air velocity of 0.72 (m h^{-1}). Figure 6 shows this air velocity, calculated temperature, and oxygen and coal concentration trends.

The oxygen passes the coal seam at low temperatures during the first weeks. During this time modelling of the microscopic reaction process is recommended. At high temperatures coal concentration shows a sharp combustion front. The front velocity is proportional to the air velocity.

CONCLUSION AND FUTURE PROSPECTS

The experimental and numerical representations here represent common examples in which the chemical reaction takes place between fluid and solid reactive components.

The major uncertainty in modelling and parameterization is the lack of experimental observations on the relationship between the internal reactive surface and mineral concentrations. This relationship is an essential observable, which has to be sufficiently understood for prognostic calculations. This means that more attention will have to be paid to the experimental and theoretical investigation of dependencies between the inner reactive surface, which is a microscopic observable, and the mineral concentration at macroscopic scales. Also, it should be kept in mind that different physico-chemical processes may vary in importance in controlling overall effects. Thus, processes with minor controlling effects will require less attention in the sensitivity analysis. For surface–fluid reactions, we must accept that all sediments, rocks or coal deposits have a history determining the reactive mineral quality.

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