

Reactive transport codes applied to gypsum dissolution in a laboratory column experiment focusing on the sensitivity of model concepts and data uncertainty

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Abstract Experimentally determined kinetic data for gypsum dissolution by pure water have been used to investigate different model concepts for mineral dissolution integrated into four different coupled codes. All concepts include a kinetic approach, but with different parameter dependency details. In the case of gypsum dissolution, only those concepts which included an explicit dependency on the actual gypsum mineral surface area gave good agreement with the measurements. Concepts which did not include such a dependency could not reproduce the measurements. More complex dissolution rate equations were necessary to describe the experiments. Nevertheless, the accessible mineral surface area, which decreased during the dissolution, was not directly measurable in the experiment and is a model parameter, albeit one which reproduced measured Ca^{2+} concentration in solution. Solution chemistry measurements required that the kinetic dissolution model included a temporally evolving accessible mineral surface area in order to correctly describe the gypsum dissolution experiment.

Keywords code comparison; column experiment; coupled codes; gypsum dissolution; mineral surface area; reaction rates

INTRODUCTION

The understanding of reactions between mineral surfaces and solutes in groundwater is important for the understanding of contaminant transport and related retardation processes. Mineral dissolution and precipitation reactions are directly involved in the solute transport processes since they modify the accessible mineral surface area. The number of accessible sorption sites and other transport parameters, e.g. porosity, change with time. The retardation processes of radionuclides and other heavy metals by sorption processes on mineral surfaces play an important role in predicting the evolution of contaminant plumes within the subsurface. Therefore, a sophisticated knowledge of the precipitation and dissolution kinetics of minerals is necessary because solution chemistry, as well as the sorption properties and porosity, will be affected by the mineral surface area.

In order to describe such complex geochemical processes in nature, two prerequisites are necessary: well defined experiments with comprehensive data sets, and reactive transport models able to describe correctly such experiments numerically and predict the behaviour of similar geochemical systems. Laboratory column

experiments provide complex data sets to investigate such coupled processes in detail, because well defined system parameters and boundary conditions limit parameter uncertainty at the laboratory scale. Reactive transport codes can then be used to identify the relevant geochemical processes and reproduce the laboratory measurements. Eventually, these reactive transport models will be applied to field-scale contaminant transport problems. Gypsum is a common constituent of sedimentary rocks causing the karstification of aquifers. Its solubility and dissolution kinetics are comparatively well known. Therefore, gypsum dissolution by pure water has been performed in a laboratory column experiment to provide data sets for reactive transport modelling (Kuechler & Noack, 2002). Four different reactive transport codes, POLLUTRANS (Kuechler *et al.*, 2002), HBGC (Yeh *et al.*, 1998), CRUNCH (Steefel, 2001), and MCOTAC (Pfingsten, 2002), with different model concepts for the kinetic dissolution of gypsum were applied to model the experimental results. This model comparison is presented.

RESULTS

Experiment

A column experiment had been performed to investigate the dissolution of gypsum. Milli-Q water was flowed through an unsaturated-saturated column, 1-m long with a diameter of 0.1 m, filled with a homogeneous mixture of dried fine sand and 0.2wt-% gypsum with a grain size between 0.2 and 0.3 mm. After an initial phase of about 20 days (Kuechler & Noack, 2002), a constant flow rate (Darcy velocity) of $8.3 \times 10^{-8} \text{ m s}^{-1}$ was reached. Electrolytic conductivity measurements were performed at 0.1, 0.3, 0.5, 0.7, and 0.9 m distances from the inlet over the corresponding cross sections of the column. Batch experiments at different Ca^{2+} and SO_4^{2-} concentrations and at different water saturations provided reference conductivity values for the column experiments.

Ca^{2+} measurements next to the inlet were not representative due to the initial unsteady flow phase. Later, steady-state flow and transport conditions applied for the column. This was indicated not only by flow measurements but also by electrolytic conductivity measurements for $x \geq 0.3 \text{ m}$, indicating constant Ca^{2+} concentrations and water saturation (Kuechler *et al.*, 2002). This also implied that the gypsum dissolution front had not reached locations at $x \geq 0.3 \text{ m}$ along the column during the initial experimental phase. However, the electrolytic conductivity measurements within the column may have errors of about 10%. This arises, not for technical reasons, but because the contacts between the electrodes and column infill material varies along the column and complicates the comparison with the reference batch measurements.

The measured water saturation along the column was used to calculate the flow velocity in the unsaturated zone of the column under constant flow conditions. The total porosity of the sand/gypsum mixture was measured to be 0.38. Due to the small amount of gypsum (0.2wt-%) the porosity changes caused by gypsum dissolution were negligible. Unfortunately, a non-reactive tracer has not been used to deduce other transport parameters, e.g. dispersivity, for the column experiment. Additional error estimates on the experimental parameters yield about 3% for the Darcy velocity and porosity; the error for water saturation is lower than 1%.

Reactive transport simulations by different codes

The four reactive transport codes used to describe the column experiments include different concepts or details for the description of the mineral dissolution rate. A general equation for the mineral reaction rate is given by:

$$R_m = A_m k_m \prod_s a_s^n f_m(\Delta G) \quad (1)$$

where A_m is reactive surface area of mineral m per volume of rock; k_m is the reaction rate constant (in units of moles per unit surface area per unit time); a_s is the activity of an inhibiting or catalysing species, raised to an empirically determined power n ; and $f_m(\Delta G)$ is a function describing the dependence of the rate on solution saturation state.

In MCOTAC, the mineral surface area is given as $A_m = 4\pi r_m^2 N_G$ for spherical grains with the grain radius r_m of solid m grains, or as $A_m = 130 d^2 N_G$ for cuboidal grains with edge lengths of d , $5d$ and $10d$. N_G is the number of grains per m^3 . For $f_m(\Delta G)$ different, quite complex and diverse functions are implemented within the different codes. Here a common representation has been used within all codes, i.e. $f_m(\Delta G) = (1 - q_m / K_m)$, where q_m is the ion activity product and K_m is the solubility product for mineral m .

In principle, equation (1) is taken into account by all four reactive transport codes but with different degrees of complexity. To distinguish between these different levels of complexity the parameterization of equation (1) yields:

$$R_m = \eta A_m k_m \left(1 - \frac{q_m}{K_m} \right) \quad (2)$$

where $\eta(x,t)$ accounts for the decrease in gypsum mass, and hence in reactive surface, due to mineral dissolution. The four terms on the right hand side of equation (2) are differently accounted for in the rate equations used by the different codes as shown in Table 1. For all model concepts and calculations a rate coefficient $k_m = (1.1 \pm 0.16) \times 10^{-4} \text{ mmol cm}^{-2} \text{ s}^{-1}$ is assumed (error $\pm 50\%$, Jeschke *et al.*, 2001). For all code calculations similar values for the transport parameters such as dispersion length (0.01 m), flow velocity, spatial discretization $\Delta x = 0.01 \text{ m}$, etc. have been used.

Figure 1 shows the modelling results—“best fits” achieved with all codes—compared to the measured free calcium concentration at 0.3 and 0.5 m within the column. For comparison, the breakthrough of a non-reacting tracer has been calculated to show the calcium retardation effect. For the different gypsum dissolution models, the shape of the calculated breakthrough curves varies in a characteristic manner.

Only HDBG uses a constant mineral surface area and a constant η ; the other codes adopted concepts taking into account mineral dissolution rates which decrease with the amount of gypsum. A comparison of the calculated breakthrough curves shows that only the latter approach is successful in simulating the measured calcium breakthrough with acceptable accuracy. The HBGC calculations yield an equilibrium-sorption-like breakthrough curve, as the comparison with the calculated non-reactive tracer breakthrough reveals (Fig. 1). CRUNCH calculations yield calcium concentrations that decrease too fast compared to the measurements. Only after the introduction of an additional “geometry” factor, $\eta(x,t)$, and a grain size dependency of the dissolution rate

Table 1 Reactive transport codes and their model concepts for mineral reactions and related parameters.

	POLLUTRANS	CRUNCH	HBGC	MCOTAC
$\eta(x,t)$	$\left(\frac{m(x,t)}{m_0}\right)^\beta$ β , geometry fit coefficient	$\left(\frac{m(x,t)}{m_0}\right)^\beta$ $\beta = 2/3$ (constant)	1	$\left(\frac{r_m(x,t)}{r_{m0}}\right)^\beta$ β , geometry fit coefficient
A_m	constant	fit parameter	constant	$4\pi r_m(x,t)^2 N_G$ (sphere geometry, grain radius r_m , multiple spheres (radii) are possible) $130 d(x,t)^2 N_G$ (cuboidal geometry with edge lengths of d , $5d$ and $10d$)
k_m	constant	constant	constant	constant
$f_m(\Delta G)$	$\left(1 - \frac{q_m}{K_m}\right)$	$\left(1 - \frac{q_m}{K_m}\right)$	$\left(1 - \frac{q_m}{K_m}\right)$	$\left(1 - \frac{q_m}{K_m}\right)$

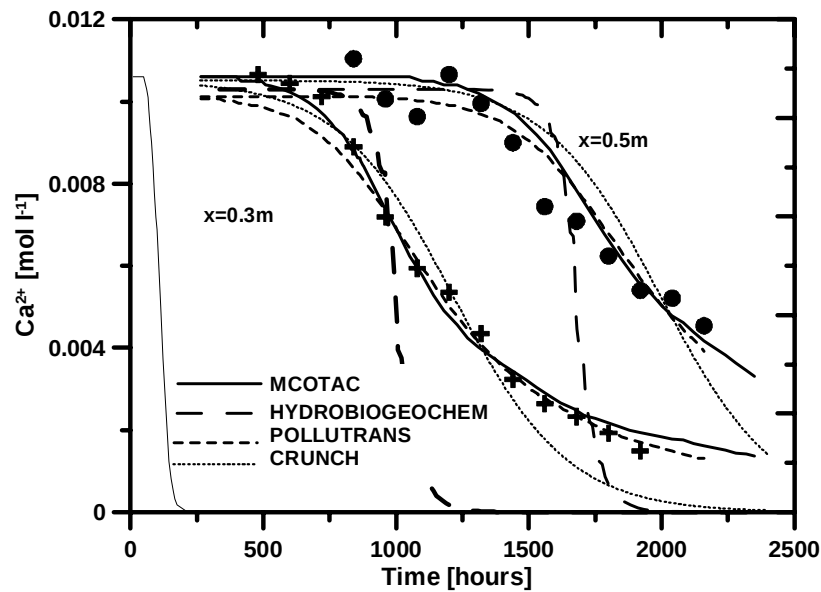


Fig. 1 Ca^{2+} concentrations measured (error about 10%) and calculated by different reactive transport codes at 0.3 m (+) and 0.5 m (●) along the column. In order to illustrate the retarded Ca^{2+} leaching out of the column caused by gypsum dissolution, the calculated leaching of a non-reactive “tracer” at $x = 0.3$ m is shown for comparison (thin line decreasing to zero at roughly 200 hours).

in POLLUTRANS and MCOTAC, could the tailing in the calcium breakthrough curves be reproduced simultaneously with sufficient accuracy. The meaning of the factor $\eta(x,t)$ defined as the ratio of mass (grain diameter) of gypsum at time t divided by mass (grain diameter) of gypsum at time $t = 0$ to the power of β (Table 1), is based on the fact that there are unsaturated conditions in the upper part of the column and there, the contact between gypsum the water flowing through the partly saturated pores is less.

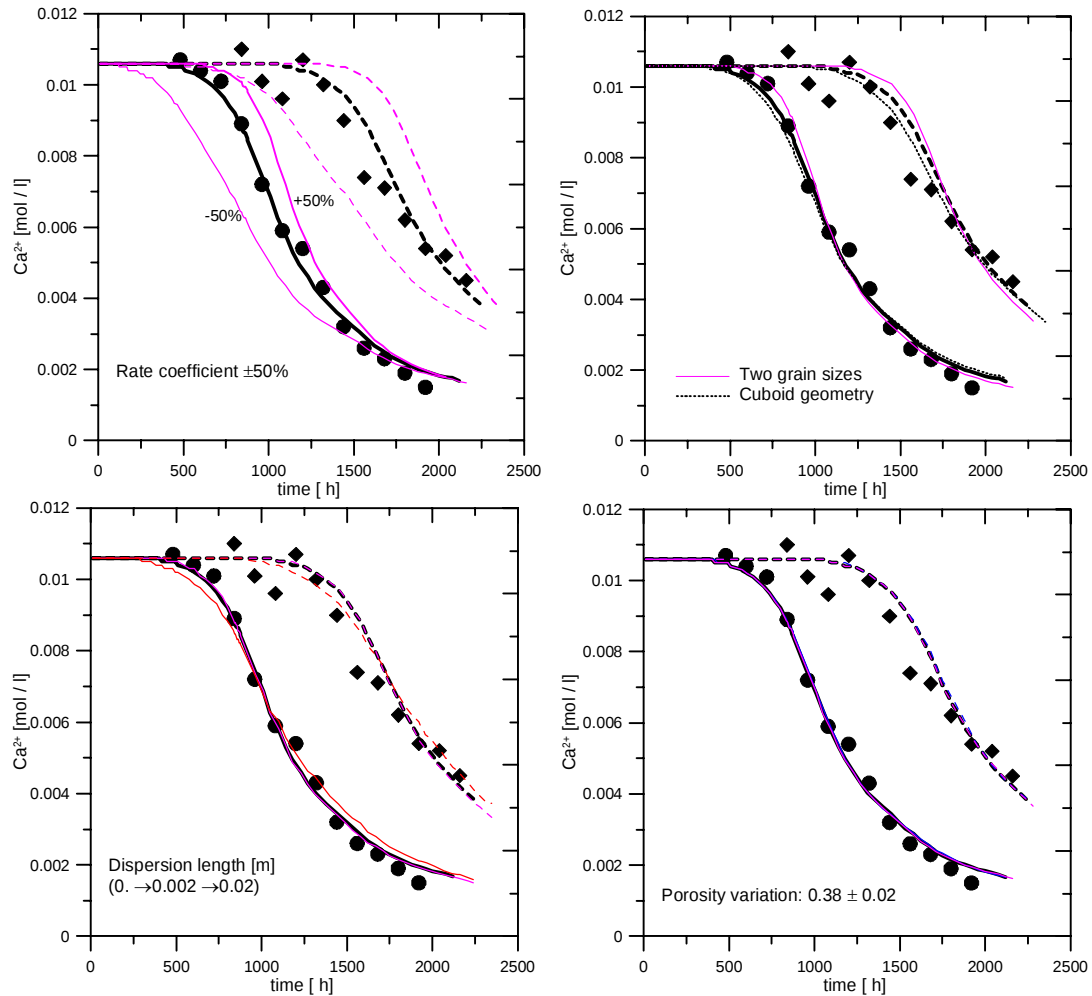


Fig. 2 Ca^{2+} concentrations measured at 0.3 m (●) and 0.5 m (◆) and calculated by MCOTAC to illustrate the sensitivity of the (fit) parameters: rate coefficient, number of differently sized spherical gypsum grains, gypsum grains of cuboidal geometry, dispersion length and porosity. Bold lines represent calculations for the “best fit” parameters; thin lines represent calculations with parameter variations from these “best fit” parameters as indicated in the lower left corner of each figure.

Model uncertainties may apply to the modelling of the unsaturated part of the column. There, it is very likely that the gypsum grains are similarly in contact with the water as in the saturated part. However, air-filled pores may hinder the access of water to some of the gypsum grains causing a less efficient dissolution within the unsaturated part of the column. After producing the “best fit” parameter sets for each model, we investigated the sensitivity of predicted Ca^{2+} breakthrough curves to the transport parameters. The aim here was to show which experimental parameters have to be measured in detail and which are not so important with respect to modelling the measured gypsum dissolution. MCOTAC was used to calculate calcium breakthrough curves assuming the maximum parameter uncertainty for the reaction rate coefficient, porosity, dispersion length and grain size distribution. From these calculations, it is clear that the flow parameters appeared to be the least dominant parameters influencing the fit. Variations in the dispersion length, porosity, changes in the water flow velocity and the water to mineral ratio, yielded only minor changes in the

calculated breakthrough curves (Fig. 2). The most sensitive parameters seemed to be the rate coefficient and, implicitly, the temporal evolution of the gypsum mass or mineral surface area during the dissolution experiment. As a consequence, the gypsum mineral surface area had to be taken into account as a time-dependent heterogeneous distribution along the column. This is the reason that the “constant mineral surface area approach” failed. On the other hand, codes which included a temporal dependency of the dissolution rate on porosity (mineral volume fraction), gypsum mass or gypsum grain geometry, yielded acceptable agreement with measured calcium concentrations. An even better fit could be achieved assuming two different grain sizes (distribution of two grain types with different values for N_G and r_m) or cuboidal grain geometry (edge lengths d , $5d$, $10d$) for the gypsum grains within the column (Fig. 2). The latter might represent the geometry of the gypsum grains more realistically. However, some parameter values used for the fitting procedures, e.g. β and A_m , are either only valid for this experiment, i.e. not extrapolatable to other conditions, or are not deducible accurately enough from the experiment.

CONCLUSION

The application of four different reactive transport codes to model the measured gypsum dissolution by pure water in a laboratory column experiment has shown that all codes are able to reproduce the measured gypsum dissolution. However, the comparison of the different model concepts yielded fits to the measured calcium concentrations of different quality. It became clear that the dissolution rate of gypsum, and how it is incorporated within the different codes, is of major importance. Depending on the model complexity of the dissolution rate, more or less accurate agreement with the measurements could be attained. To achieve sufficient agreement, however, the rate equation for gypsum dissolution had to be dependent on the actual gypsum mineral surface area accessible by the leaching water. Rate equations without such a dependency failed to model the gypsum dissolution correctly. Additional assumptions on grain geometry also yielded improved agreement of measured and calculated calcium breakthrough curves. The fits were less sensitive to other transport parameters, e.g. dispersion length, or porosity or flow velocity. However, with increasing model complexity the number of parameters, which are either not known or only poorly known, increases.

It was not possible to achieve a unique parameter fit which allowed discrimination between the different model concepts. Parameter uncertainty exists for the data available from the column experiment, especially concerning the dominating influence of the rate dependency on the temporal heterogeneous mineral surface area, or grain size distribution along the column. Such data would be necessary to improve the understanding of the gypsum dissolution process, and more generally, to improve the understanding of mineral surface reactions and their impact on sorption processes of radionuclides and other heavy metals within the groundwater regime.

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REFERENCES

- Jeschke, A. A., Vosbeck, K. & Dreybrodt, W. (2001) Surface controlled dissolution rates of gypsum in aqueous solutions exhibit nonlinear dissolution kinetics. *Geochimica et Cosmochimica Acta* **65**(1), 27–34.
- Kuechler, R. & Noack, K. (2002) Transport of reacting solutes through the unsaturated zone. *Transport in Porous Media* **49**, 361–375.
- Kuechler, R., Noack, K. & Zorn, T. (2002) Results of column and batch investigation of gypsum weathering. *Report no. FZR-342, Forschungszentrum Rossendorf*, Rossendorf, 63–70.
- Pfingsten, W. (2002) Experimental and modeling indications for self-sealing of a cementitious L&ILW repository by calcite precipitation. *Nuclear Technology* **140**(1), 63–82.
- Steefel, C. I. (2001) CRUNCH Version 1.2. Lawrence Livermore National Laboratory, Livermore, USA.
- Yeh, G.-T., Salvage, K. M., Gwo, J. P., Zachara J. M. & Szecsody, J. E. (1998) HYDROBIOGEOCHEM: A Coupled Model of HYDROlogic Transport and Mixed BIOGEOCHEMical Kinetic/Equilibrium Reactions in Saturated-Unsaturated Media. Report no. ORNL/TM-13668, Oak Ridge National Laboratory, Center for Computational Sciences, Oak Ridge, TN 37831, USA.