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Comparison of the solution behaviour of a pyrite–calcite mixture in batch and unsaturated sand column

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Abstract

A successful application of reaction transport algorithms to calculate the chemical evolution of natural systems requires accurate methods to compute the rates of mineral/fluid surface reactions. Regarding the transport of radio-nuclides in mining dumps the dissolution of minerals is of special importance. Using a kinetic rate law of the mineral dissolution verified for unsaturated conditions will allow a realistic modelling of the mineral weathering in the environment. Dissolution rates of minerals in an aqueous solution are determined by several characteristics. These are surface reaction rates, morphology of the mineral's surface and, in case it is the unsaturated zone, the degree of the water saturation. For this process, the quantity of the particle surfaces which are in contact with percolating water is most decisive. In order to study the differences of mineral dissolution under saturated and unsaturated conditions batch and column experiments were carried out with a pyrite–calcite mixture. The experimental results were verified by calculations. Comparing the dissolution in batch with those in the column experiment, which was performed with a water flow velocity of 0.64 cm/day and was analyzed in the region of a water saturation of 0.11, one can conclude that only a small portion of about 5% of the grain surface is chemically reactive in this unsaturated flow.

Keywords: Pollutant transport; Unsaturated soil; Pyrite–calcite dissolution; Transport modelling

1. Introduction

The unsaturated transport of water and pollutants in a dump is a significant topic of environmental research. Rainwater penetrating into a dump on its flow path dissolves various

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minerals and can transport reacting species through the dump down to the ground water. Although not representing the full complexity of a natural system, modelled batch and column experiments play an important role. Not only with regards to according research, but especially, with respect to code verification. Moreover, with the help of suitably designed experiments which are combined with appropriate numerical modelling the investigations may be focussed on certain single phenomena among a complex system of interacting effects. With our experiments and calculations we generally follow this line and are presently studying the mineral dissolution under unsaturated conditions. There is an undisputed need for research in this field (Oelkers, 1996; Drever, 1997). In recent years we developed a system of numerical codes called POLLUTRANS which calculates water and pollutant transports through the unsaturated zone (Kuechler and Noack, 2002). It is based on diverse appropriate models describing the complex physical and chemical phenomena, being involved in the transports. The dissolution of minerals, however, is one of the most important processes. It decisively affects the amount of pollutants emitted to the ground water. Goals of our investigations in mineral dissolution on unsaturated conditions are:

– The partial verification of dissolution rate laws of several minerals as they are written in literature, e.g., of calcite, uraninite, gypsum and pyrite (Plummer et al., 1978; Bruno et al., 1991; Gerda et al., 1993; Münze and Ullrich, 1997; Jeschke et al., 2001), as these minerals are of relevance for the transport of radio-nuclides in mining dumps on water saturated conditions.
– The examination of the applicability of these rate laws as source terms of pollutant transport through the unsaturated zone.

The focus of this research is directed on dissolution of a mineral mixture of pyrite and calcite grains. This was done for the following two reasons: firstly, on natural conditions calcite is virtually always available and secondly, the presence of calcite will give the possibility of studying pyrite dissolution within an alkaline milieu at high pH values.

This contribution reports on batch and column experiments, which were performed with a pyrite–calcite mixture, present the most important experimental results, explain the adapted numerical models and compare experimental results with numerical ones. Finally, conclusions are drawn concerning the distinction between dissolutions of pyrite grains under saturated and unsaturated water flows.

2. Batch and column experiments with pyrite–calcite mixture

The pyrite–calcite mixture used in batch and column experiments, was compounds of the natural minerals calcite from Mexico Creel and pyrite from Elba. The purity of the minerals powders of both has been investigated by means of the Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) and of the X-ray Powder Diffraction (XRD). In addition, pyrite and calcite solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP/MS). Table 1 shows the substantial impurities in weight percent relating to Fe for pyrite and to Ca for calcite. The amounts of other elements remained below the detection limit.

For both experiment types the minerals had to be prepared as follows. After crushing and dry sieving the grains came up to the desired size of about 200–300 μm, which is adequate to the mean grain size of the sand matrix. The powder has been washed with MilliQ-water and has been dried at a temperature of 50 °C in order to remove small particles from the grain surface.