Coupled flow and reaction: a modelling and experimental study of zeolite diagenesis

K. Bateman   *British Geological Survey, Keyworth, Notts NG12 5GG, UK.*
D.J. Noy
J.M. Pearce
D. Savage   *Intera Information Technologies Ltd, 47 Burton Street, Melton*
Mowbray, Leics LE13 1AF, UK.

Introduction

Modelling fluid flow and reaction is key to understanding many natural water-rock systems and also to predicting the behaviour of those systems perturbed by man's intervention, e.g. the disposal of toxic and radioactive wastes. An especially challenging problem is that of modelling coupled flow and reaction in systems of changing porosity. Here we present results of a study to investigate aspects of this problem. As an example, we have chosen the replacement of feldspar by zeolites during sediment diagenesis which involves a large solid volume increase (of the order of tens of percent).

Experiments

Experiments were conducted in a tube reactor (80 × 7 mm) at 150°C, 30 MPa to accelerate reactions for purposes of scale. Reactants consisted of a mixture of anorthite, quartz and laumontite. The reactant fluid was 0.05 M NaCl/0.006 M NaOH (pH = 9.2 @ 150°C). A flow rate of ~19 ml/day was maintained throughout the experiment duration (60 days). Rate constants of dissolution of each of the reactant minerals were determined in separate experiments. Fluids were analysed for pH, Al, Ca, Si and Na. Solids retrieved at the end of the experiment were investigated by scanning electron microscopy and X-ray diffraction.

Modelling

The code 'PRECIP' was used to model the system. PRECIP is a finite difference code, allowing mineral dissolution and precipitation reactions to occur along a porous medium flow path. Chemical reactions are described by kinetic rate laws, with aqueous components transported by advection and dispersion. Porosity changes may be linked to changes in permeability and thus affect the flow field. The transport and reaction equations are fully coupled and solved simultaneously. The experimental system was modelled in a 'blind' fashion (initially) employing rate constants determined in separate experiments and thermodynamic data for mineral hydrolysis and aqueous species from the EQ3/6 database.

Results

Output concentrations of Si versus time for experiment and model simulations are shown in Figure 1. It may be seen that the modelled system comes to steady-state within one day of reaction commencement. Superficially, the experimental system shows similar behaviour, but in detail, there are slight decreases in concentrations throughout the experiment duration. Measured and modelled output Si concentrations are in good agreement ($\sim 1.5 \times 10^{-3}$ M), but modelled output Al concentrations are an order of magnitude lower than those measured. Modelled profiles of Al along the column with time show a maximum at ~2 cms from the inlet. The position of this peak remains invariant after 3 hours of the computer simulation. Modelled concentrations of other components show increases along the reactor tube (Si, Ca), or slight decreases (Na).
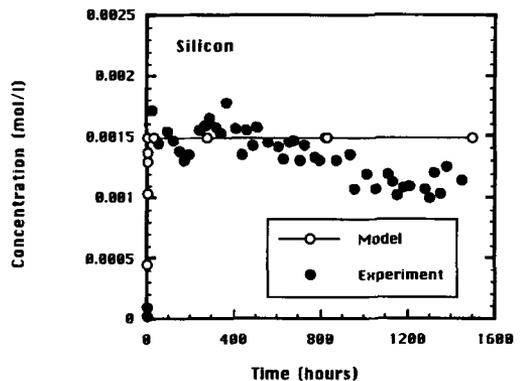

FIG. 1. Modelled and experimentally-determined concentrations of Si in output fluids.

PRECIP predicted progressive decreases of quartz and anorthite with time, with the removal of the latter enhanced at the inlet. This concurs with SEM observations which show greater etching of anorthite, both at the inlet, and in comparison with quartz. A prominent feature of the SEM observations was the 'zonal' distribution of product solids. The zeolite offretite (similar to erionite) was particularly pronounced near the column inlet, whereas analcime was most abundant 2–4 cms from the inlet. Additional solids identified included secondary laumontite and an unidentified cubic aluminosilicate mineral. Initial runs with PRECIP indicated secondary solids dominated by mesolite (a substitute for offretite in the model database) which suppressed the precipitation of all other minerals. Reducing the growth rate of mesolite from 5×10^{-7} mol/ m^2/s to 5×10^{-14} mol/m^2/s enabled precipitation of both analcime and laumontite in the downstream half of the column. The matching of the location of the onset of analcime precipitation in the PRECIP simulations was achieved by increasing the rate of anorthite dissolution by an order of magnitude over the initial value.

Conclusions

PRECIP is a powerful interpretive and predictive tool. It was not possible to completely predict output fluid chemical and mineralogical profiles *a priori*, but modelling with PRECIP enabled key variables to be evaluated. The nature and spatial distribution of the zeolites synthesised depended strongly on the mobility of Al and the Al/Si ratio of the fluid.