

## 4.62.46

### The hydrogeochemical dynamics of fractured porous media in the unsaturated zone

E. PILI, S. BUREAU, F. PERRIER AND P. RICHON

CEA, Département Analyse Surveillance Environnement, BP12, 91680 Bruyères-le-Châtel, France (Eric.Pili@cea.fr)

Contaminant transport in unsaturated fractured porous media presents a large variability in space and time due to variation in water contents, in flow pathways and regime, and chemical reactions. The dynamics of these systems in response to external forcing such as meteorology, deformation, chemical or hydrogeological disturbances remains poorly known. To build reliable predictive models, there is a strong need to obtain data from complex but well characterized natural observatories at the 10 m to 1 km scales.

For this purpose, we set up a monitoring experiment in a ~150 m long tunnel where drippings give access to ground water flowing from over 50 m of unsaturated fractured gneiss. This tunnel is located close to and above the artificial Lake Roselend (France) where large seasonal variations in level induce in reproducible deformation and hydrogeological disturbances. This mountainous area is also characterized by contrasted infiltration regimes with alternating snow, rain, and dry periods. In addition, we performed a multi-tracer test with the surface injection of dyes and salts. In order to get water samples representative of different contributions of matrix porosity and fractures, we compared several zones with different settings (structures and flow rates) in the tunnel and looked for changes in flow rates and ion concentrations in ground water over several years. In addition, we monitored the activity of radon gas in the atmosphere of the tunnel.

Water composition reflects a yearly steady-state dynamic equilibrium, with low salinity, cold, rain and/or melted snow water input with kinetically limited reactivity along fractures (high flow rates), and limited input of more saline water stored in the matrix porosity (low flow rates). We observed transient increases of sulfate and magnesium concentrations associated with radon bursts into the tunnel air and that are not related to meteorology. This indicates that transient enhancement of conductance, with discharges of saline water and radon from the matrix porosity to the fractures, is a mechanism able to produce both ground-water and gas anomalies in response to hydrogeological or mechanical processes such as increases in pore pressure or changes in crack geometry. After the surface injection of tracers, we observed in the tunnel variously delayed breakthrough curves depending on the sampling zones. Some tracers initially present in very low concentrations in the natural system show enrichment factors of several orders of magnitude and are associated with ions that were not injected. This indicates mobilization of ions either from colloids, surface exchange reactions or low accessibility reservoirs.

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### The CO<sub>2</sub> enhanced removal of fluoride using a calcite permeable reactive barrier

B.D. TURNER<sup>1</sup>, P. BINNING<sup>2</sup> AND S. SLOAN<sup>1</sup>

<sup>1</sup> School of Engineering, University of Newcastle, University Drive, Callaghan, NSW, 2308, Australia (Brett.Turner@Newcastle.edu.au; scott.sloan@newcastle.edu.au)

<sup>2</sup> Environment and Resources, Technical University of Denmark, Lyngby 2800, Denmark (pjb@er.dtu.dk)

A calcite (CaCO<sub>3</sub>) permeable reactive barrier (PRB) is proposed for removing fluoride from contaminated groundwater. As the pH increases during the removal reaction, pH control is also necessary. Here the pH is regulated by bubbling air through the barrier thereby providing a CO<sub>2</sub> source that contributes to the carbonate equilibrium. The efficiency of a calcite permeable barrier for removal of fluoride from groundwater is demonstrated in column experiments.

Experiments were conducted at room temperature (~25±2 °C) in a polycarbonate column 41.0cm in length and 4.75cm in diameter (id) using groundwater samples containing fluoride concentrations of up to 2,300 mg/L. Such high concentrations are found at some industrial sites. Approximately 1.2 kg of pre-washed (with 18 MΩcm<sup>-1</sup> deionised water) and dried 1.18 mm diameter calcite was packed into the column. Approximately four pore volumes of 18 MΩcm<sup>-1</sup> deionised water was pumped through the column to ensure any loose calcite powder was washed out. Various fluoride solutions were then introduced into the column via a peristaltic pump at a constant flow rate. The flow rate was such that a residence time of between two and six hours was achieved. The effluent pH and fluoride concentration were logged via multi-channel datalogger connected to Orion ion selective electrodes (ISEs) located in a flow-through cell.

Our observations show that fluoride removal is pH dependant with removal increasing with decreasing pH. Barrier performance can be increased via CO<sub>2</sub> addition with the point of injection critical for optimising column performance. Experimental and model results show that approximately 99% of 2,300 mg/L fluoride can be removed when CO<sub>2</sub> is injected directly into the column. This can be compared to approximately 30-50% removal when the influent solution is equilibrated with atmospheric CO<sub>2</sub> before contact with calcite. Results also show that influent water composition affects barrier performance.