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Effects of velocity and concentration on diffusive transport in low permeability geological systems

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ABSTRACT

A new micro-fluidic method, which is known as the Micro-Reactor Simulated-Channel (MRSC) method, has been employed to rapidly determine the effective diffusion coefficients of lithium in three important representative low permeability lithologies including: Melechov granite (Czech Republic), Borrowdale tuff, and Land's End Cornish granite (both UK). The concept of MRSC is similar to the micro chemical reactor which enables fast measurements to be done on a small intact sample. The effective diffusion coefficients were measured and comparisons between the MRSC results and conventional column methods showed excellent agreement. Our measured effective diffusion coefficient for Melechov granite is 1.7×10^{-12} m^2/s, directly comparable to previous conventional measurements. However the measurement time of the MRSC method is at least one order of magnitude faster than the conventional method and only requires small reaction volumes (as small as 10 ml). In addition, by exploiting the advantages of the MRSC method, the effects of velocity and concentration on diffusive transport for the two different UK rock types have also been investigated. Depending on flow rate and inlet tracer concentration, the effective diffusion coefficient for lithium in the Cornish granite ranges between 0.9 and 1.5×10^{-11} m^2/s while that measured for the Borrowdale tuff varies between 1.2 and 1.6×10^{-11} m^2/s.

1. Introduction

The engineered and surrounding geological barriers in a Geological Disposal Facility (GDF) are intended to preclude the development of meso-scale fracture pathways, therefore diffusive flux should be considered as an alternative risk for the loss of containment, especially for the extended period of time over which sequestration is required. Diffusion and sorption are the critical parameters for estimating the interaction between the rock, groundwater and the radionuclide. The effect of diffusion into the rock matrix has been ignored in early transport models because it has been conservative for estimating the transport of the radionuclide, but over the last three decades many studies have shown that diffusion delays the migration of the solute and attenuates peak concentration. However peak concentration values are crucial for assessing the risks of contamination. “Crystalline rock” (low permeability) with quartz and feldspar as prominent minerals is a typical choice for a repository host and is a favoured medium in Sweden, Finland, Britain, and Japan. In this context the term has become a common expression for granite and similar igneous and metamorphic rocks. The big advantages of crystalline rock are: 1) small disturbances by temperature rise, 2) alkaline, weakly reducing groundwater, and 3) low permeability which ensures a slow rate of canister mass transfer and slow release of many radionuclides. However, the joints and shear zones universally present in a low permeability system provide possible paths for groundwater movement leading to diffusive flux of the concerned radionuclides into the surrounding bedrock.

Travel time in a fracture system is significantly enhanced with matrix diffusion included as compared to when only advective transport is taken into account (Sudicky and Frind, 1982). In crystalline rocks with very low porosity, the role of diffusion remains significant: a matrix porosity of 1% may delay concentration peaks by a factor of 5 in time as well as lower the maximum concentration by one order of magnitude over 100 m of travel. Many factors related to matrix porosity influence diffusion such as: connected pore volumes, tortuosity, and constrictivity, which all contribute to make efforts to study diffusion difficult. Therefore, a novel method

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has been developed, referred to as the Micro-Reactor Simulated-Channel (MRSC) method, which is able to determine the effective diffusion coefficients of a range of tracers in non-friable solid specimens rapidly at realistic contaminant concentrations (Okuyama et al., 2007, 2008).

Here, the experiments were performed with rocks of critical relevance to GDF strategies. The Melechov granite represents one type of potential crystalline host rock and diffusion measurements have been performed on this lithology using traditional through diffusion methods (Havlova et al., 2012). This gives us a critical and pertinent benchmark for our method. Our experiments have also been completed with Borrowdale tuff, a lithology which represents another potential type of host rock. Finally, we have included a Cornish granite for comparison to the Melechov samples. Also, the relationship between important parameters such as channel velocity, initial concentration and diffusion was investigated. Based on the experimental results, numerical modelling was carried out to further understand the dynamic behaviour of the system.

2. Methods

A conceptual diagram of the MRSC set-up employed in our experiments is shown in Fig. 1. This is comparable to the micro-chemical reactor. Here, a narrow fluid channel in the middle of the solid system increases the rate of surface reactions between the solid rock system and tracer fluid due to a high surface area to liquid volume ratio. Unlike the conventional column method, an intact hard rock sample can be used for determining both diffusion and retardation. In addition, installing the small reactor directly into an excavated deep borehole in the actual geologic environment can provide the possibility for in situ measurements. More details of the apparatus and reaction unit are available in Okuyama et al. (2007) and Ohe et al. (2012).

Lithium, a non-sorbing tracer (from dissolved Li_2SO_4 kept at neutral pH), was spiked at different concentrations into the influent and pumped into the bottom channel at a constant rate. The effluent was collected and analysed in order to determine the breakthrough curve. The breakthrough curve was constructed by time resolved analysis of the effluent solution until pseudo-steady-state was observed. Because the outlet concentration was not equal to inlet concentration, non-sorbing Li could only be lost through diffusion from channel into matrix, thus accounting for the inlet-outlet difference. Changing the pumping rate as well as the depth of the channel leads to different velocities in the channel, therefore diffusion experiments may be carried out with both different velocities and different influent concentrations in the channel. This flexibility makes the investigation of how velocity and concentration may influence diffusion rates relatively simple. Product fluids were acidified by adding 2 ml of 2% nitric acid in preparation for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Lithium standards were prepared in a solution identical to the experimental solutions to ensure that they were analysed in the same chemical matrix as the test samples. Samples, standards and blanks were sealed and prepared for ICP spectroscopy analysis on a Fison Instruments 4700 ICP-AES spectrometer.

Three low permeability rocks, two granites and one tuff, were studied in this work. One of the granites is from Land's End, West Cornwall, UK. The other granite is from Melechov Massif, part of the Central Bohemian Massif, Czech Republic. The tuff is part of the Borrowdale Volcanic Group (BVG), originating from the Old Man of Coniston area, Cumbria, UK. The three rock types were characterized by standard petrographic optical microscope and X-ray diffraction (XRD). XRD scans were completed on a Bruker D8 diffractometer; scans ran from 5 to 70° 2θ with a step size of 0.02° and analysis time of 1 s per step. Data analysis was completed using the Bruker EVA software.

For comparison to other diffusion studies, the porosity of the Melechov granite was determined by utilizing a Digital Helium Porosimeter (DHP-100), a precision instrument which accurately determines the grain volume and pore volume of porous materials

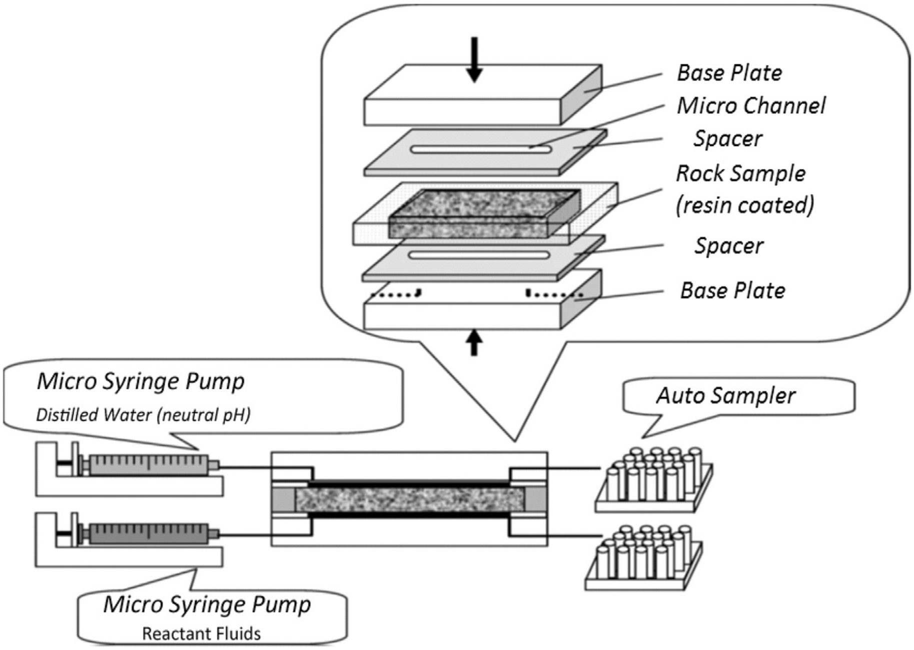

Fig. 1. Experimental set up for the MRSC device (top) (modified from Okuyama et al., 2007). The new apparatus consists of two injection syringe pumps, a reaction unit, and two auto-samplers. The reaction unit contains two base plates, two spacers with a micro channel at the centre and a rock sample polished and non-reacting surfaces coated with epoxy resin placed in the middle of the whole unit. The reason to have the coated epoxy at the side edge surfaces is to avoid the evaporation of the test solution during the experiment. In this method, all the plates are made from stainless steel and spacers are created by using Teflon.