

Understanding Uranium Migration in Hard Rocks

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Abstract. Uranium is a major radioactive constituent of spent nuclear fuel and high-level radioactive waste. However, its migration behaviour in crystalline rocks is still inadequately understood. This paper describes the results of controlled laboratory migration experiments and attempts made to simulate them using numerical models. Initial models employing generic information in “blind predictions” are progressively enhanced by data-supported interpretation. Such an approach is intended to mimic the stages of a site assessment, where conceptual and numerical models are progressively refined.

Introduction

Geological disposal is the preferred management end-point for high-level waste (HLW) and, in some countries, spent fuel (SF). Safety assessment (SA) procedures are intended to demonstrate that any releases of radionuclides that will almost certainly occur at some time in the future have negligible impact. SA is made up of various components that are designed to represent the behaviour of the repository itself and the surrounding geological environment, and to predict its long-term behaviour. Although a large body of information on alternative rock matrices for disposal and on pertinent processes and events has been accumulated over the past 30 years, several potentially important processes have not yet been adequately characterised. In particular, the micro-scale behaviour of uranium in crystalline rocks remains poorly understood.

In the course of a site assessment, increasingly detailed information is collected in order to construct and refine numerical models. The process of developing numerical models, such as those for the transport and retention of radionuclides, helps to better understand the repository system as a whole and to identify those

processes that need to be known with greater precision. Iterative model development is a powerful tool and helps to target resources for further investigations and research. The current paper illustrates this point using a laboratory microcosm of uranium migration through crystalline rock cores.

At the early stages of an investigation very little may be known about water compositions and the reactions taking place. Blind predictions using sparse data sets challenge the modeller to carefully document the assumptions employed in scenario construction (Read, 1991). Assumptions regarding newly formed secondary phases incorporating the radionuclide of interest will have to be made on the basis of earlier experimental evidence, ‘analogues’, or literature data. The major adjustable variables, in addition to those governing the hydraulic properties, are the nature of solubility-controlling solid phases. The model is refined step-by-step with experimental data, thus arriving at a more realistic input-output estimate. The latter may include estimates of reaction kinetics and assumptions regarding ‘active’ and ‘inert’ phases. After termination of the actual experiments and analysis of the solids, these results can be compared with the predictions from the model.

Experimental set-up

Two core sections of Syry granodiorite from Sievi, Finland (49.5 mm diameter and 47.34 mm length) were placed in a triaxial cell (Figure 1). A disc cut from a depleted uranium (DU) penetrator (armour piercing ammunition) was inserted between the two rock slices. The DU is in the form of 25 mm diameter discs, 0.5 mm in thickness (Trueman et al., 2004). The total surface area is 1021 mm² and the uranium mass is 4.688 g.

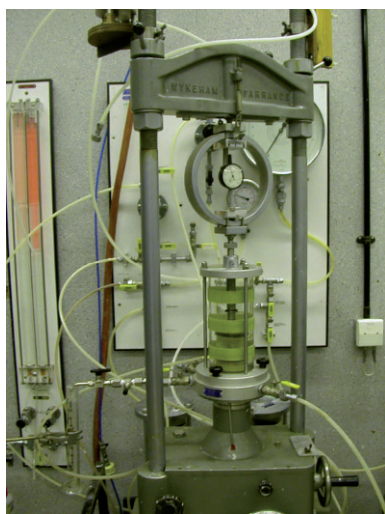


Fig. 1. Experimental set-up.

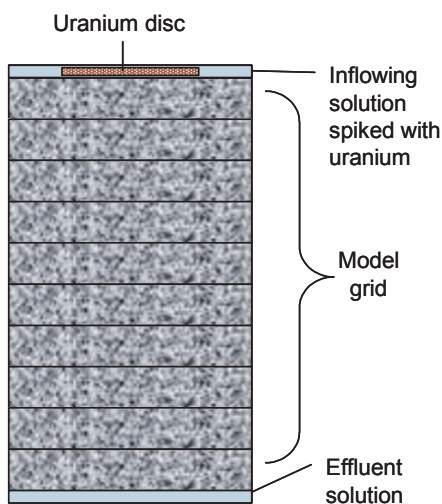


Fig. 2. Conceptual layout of model.

The DU serves only as a well-characterised source of uranium ions and is not meant to mimic exactly the dissolution of SF. Previous studies (Trueman *et al.*, 2003; Baumann *et al.*, 2006) demonstrated the rapid degradation of DU under a range of experimental conditions when exposed to excess solution. In the present experiments, rock matrix/aqueous solution ratios are more representative of those found in the field and, in addition, the fate of the radionuclides released is assessed.

In addition to a confining pressure, a slight upward directed flow is imposed on the triaxial cell. The initial volumetric flow rate was $0.017 \text{ cm}^3/\text{s}$.

Three basic sets of data will be generated from the experiments : (1) the chemical composition of the effluent as a function of time, (2) evolving alteration products on the disc surface and (3) spatially resolved data from analyses of the rock samples upon termination of the experiment. Together these data will allow a time-resolved (uranium) mass balance for the experiment to be constructed.

Conceptual Model

A one-dimensional ten-cell model (Figure 2) was set up in PHREEQC (Parkhurst & Appelo, 1999). The chemical calculations were performed using the Lawrence Livermore Laboratory thermodynamic database (Version 85 from 02/02/05) that was delivered together with the code (Version 2.12.05).

Initial water compositions

It was assumed that little more ‘real data’ were available other than that the material in the experiment is a granodiorite from Central Finland. Thus, the first step consisted of modelling the initial water composition (Table 1) based on literature data for comparable material, viz. groundwater from Äspö (quoted in Bruno *et al.*, 1999).

Initial calculations showed that the water is close to equilibrium with respect to albite, quartz and several clay minerals, reflecting the main constituents of granitic rock and its weathering products. Subsequent calculations maintained equilibrium with H-saponite, which provides for silicate and pH-buffering in the system. The infiltrating solution was brought into equilibrium with O_2 and CO_2 at their respective atmospheric partial pressures. The resulting water composition was slightly supersaturated with respect to ferric hydroxide and, hence, precipitation of it was allowed, which provides for additional pH-buffering.

Table 1. Calculated (data for Äspö from Bruno et al (1999)) and measured water compositions [mol/dm³].

Component	Äspö	measured	Component	Äspö	measured
Na ⁺	$9.13 \cdot 10^{-2}$	$9.27 \cdot 10^{-4}$	HCO ₃ ⁻	$1.64 \cdot 10^{-4}$	n.d.
K ⁺	$2.05 \cdot 10^{-4}$	$5.81 \cdot 10^{-5}$	PO ₄ ³⁻		$3.13 \cdot 10^{-6}$
Ca ²⁺	$4.73 \cdot 10^{-2}$	$8.85 \cdot 10^{-4}$	Cl ⁻	$1.81 \cdot 10^{-4}$	n.d.
Mg ²⁺	$1.73 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$	SO ₄ ²⁻	$5.83 \cdot 10^{-3}$	$9.12 \cdot 10^{-5}$
Fe ²⁺	$4.30 \cdot 10^{-6}$	$1.33 \cdot 10^{-3}$	pH	7.7	6.64
Mn ²⁺	$5.28 \cdot 10^{-6}$	$8.45 \cdot 10^{-5}$	Eh [mV]	-300	n.d.
H ₄ SiO ₄	$1.46 \cdot 10^{-4}$	$2.75 \cdot 10^{-5}$			

The hydraulic properties of the experimental system

The porosity of the two samples used was 9.1% and 13.6% respectively, by the helium method. An average value of 10% for the total porosity was assumed for the modelling runs and the effect of different effective porosities explored numerically. The mixing cell model in PHREEQC does not allow the effective porosity to be entered explicitly, only implicitly via the average porewater flow velocity.

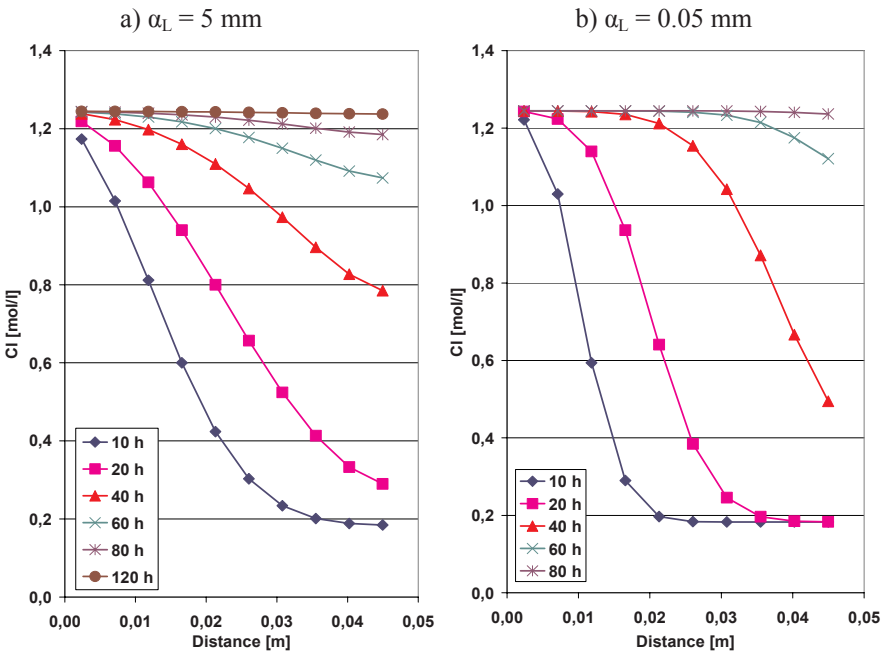


Fig. 3. Sample tracer profiles as a function of dispersion length α_L .

The tortuosity, or length of the stream-tubes within the rock, is defined through the average flow velocities. The cells are modelled as a continuum and as stream tubes so that their length distribution is represented by the dispersivity. A typical choice for the dispersion length is 1/10 of the cell length, here approximately 0.5 mm. In sensitivity calculations this value was varied over several orders of magnitude. Figure 3 exemplifies the effect on the shape of tracer break-through profiles.

For further calculations, a value of 5% for the effective porosity and of 0.5 mm for the dispersion length were chosen, based on the preliminary hydraulic assessment; these correspond to a time step in the PHREEQC model of $18000\text{ s} = 5\text{ h}$.

Safety cases for disposal of HLW and SF in fractured hard rocks rely heavily on the concept of dual porosity and the related concept of matrix diffusion (e.g. SKB, 2006). These assume that, although only the effective porosity takes part in advective-dispersive transport, there will be diffusive exchange between this fraction and the remaining porosity. This exchange lowers peak concentrations and is also responsible for longer tails in concentration distributions. The PHREEQC code allows dual-porosity cases to be formulated for various geometries, which are introduced via a 'shape factor'. Here, a stream-tube geometry embedded in a one-layer deep tube of stagnant cells was considered the most appropriate.

Solubility Controlling Phases for Uranium

Secondary uranium phases that may control solubility were identified by simulating batch experiments with incremental amounts of uranium added. The thermodynamically most stable phases are predicted to be $\text{UO}_2(\text{OH})_2$ and $\text{UO}_3 \cdot n\text{H}_2\text{O}$. The latter may actually be polymorphous and have the formula $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}](\text{H}_2\text{O})_{12}]$ (Finch *et al.*, 1996). The LLNL database contains solubility products for $\text{UO}_3 \cdot n\text{H}_2\text{O}$ with $n = 2, 1, 0.9, 0.85, 0.648$ and 0.393 . $\text{UO}_3 \cdot n\text{H}_2\text{O}$ has been identified as the major corrosion product from the dissolution of DU in soils (Trueman *et al.* 2003). Considering the persisting uncertainty regarding relevant thermodynamic constants (e.g. Jang *et al.*, 2006), schoepite was used as a proxy here.

The uranium source term

Previous experiments (Trueman *et al.* 2003) have shown that *in extremis* one year is sufficient to completely dissolve a DU disc. Given a total mass of 0.1674 moles of U, an approximate mass loss of $5.4 \cdot 10^{-9}\text{ mol/s}$ can be calculated. This value has been used as a linear reaction rate. Previous experiments have also shown that not all uranium would move away, but that alteration products accumulate on the surface of the discs (Baumann *et al.*, 2006). The instantaneous (equilibrium) precipitation of schoepite as modelled in PHREEQC would constrain aqueous uranium concentration to about $3 \cdot 10^{-5}\text{ mol/dm}^3$.

At 5% effective porosity the rock sample contains $4.55 \cdot 10^{-3} \text{ dm}^3$ mobile solution. Hence, $2.134 \cdot 10^{-2} \text{ mol U/time step}$ must be added. With the initial volumetric flow rate of $0.017 \text{ cm}^3/\text{s}$, this translates into a concentration of $3.176 \cdot 10^{-4} \text{ mol/dm}^3$ in the inflowing solution.

Results of Blind Modelling

Figure 4 shows that the zone where schoepite saturation is reached moves along the column. Steady state effluent uranium concentrations would be attained quickly for an equilibrium model that assumes instantaneous precipitation once saturation is reached. Such a model would cause all precipitation to occur in the first cell, resulting in rapid clogging of the pore space.

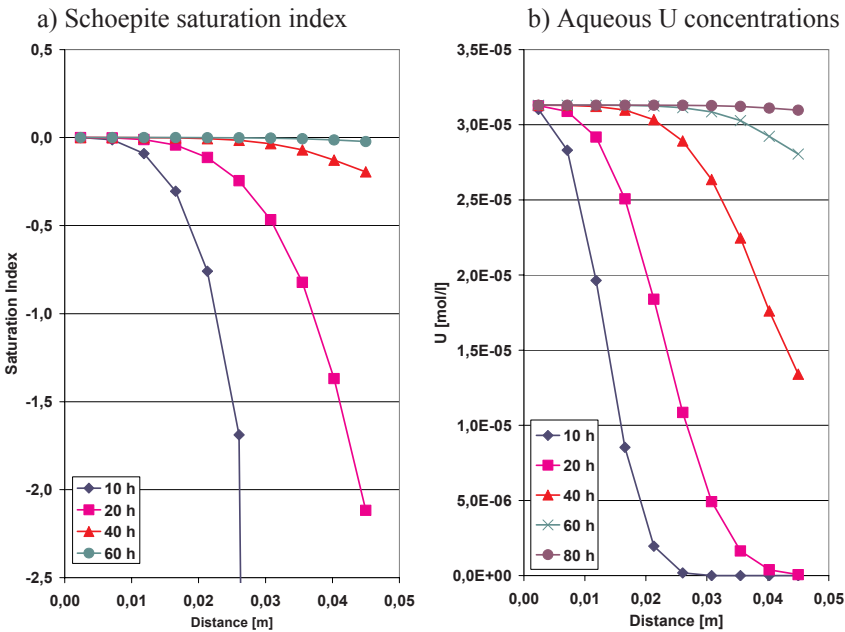


Fig. 4. Flooding the core with a uranium solution of $3.176 \cdot 10^{-4} \text{ mol/dm}^3$ while allowing schoepite to precipitate.

Based on a molar volume of $66.61 \text{ cm}^3/\text{mol}$, one can calculate a precipitation rate of $0.031 \text{ cm}^3/\text{day}$, leading to the total pore volume of 9.6 cm^3 being completely filled within just under 300 days. Of course, with increasing clogging of the pore volume the flow rate and hence the supply of uranium would decline.

In order to model the behaviour of uranium more realistically, precipitation kinetics were assumed in subsequent calculations.

Precipitation Kinetics

PHREEQC allows the definition of different kinetic models and reaction rates for each cell. The data would normally be derived from experiments by curve-fitting. In a blind prediction case no such data are available and modelling of precipitation kinetics is purely conjectural. In order to set up the model for later curve-fitting exercises and to demonstrate the effect of precipitation kinetics, a simple case with arbitrary kinetics was developed. It was assumed that the kinetics of precipitating schoepite would depend on the activity concentration of the uranyl ions in solution with different scaling factors. Figure 5 exemplifies such calculations and the resulting concentration profiles for different (arbitrary) rate constants.

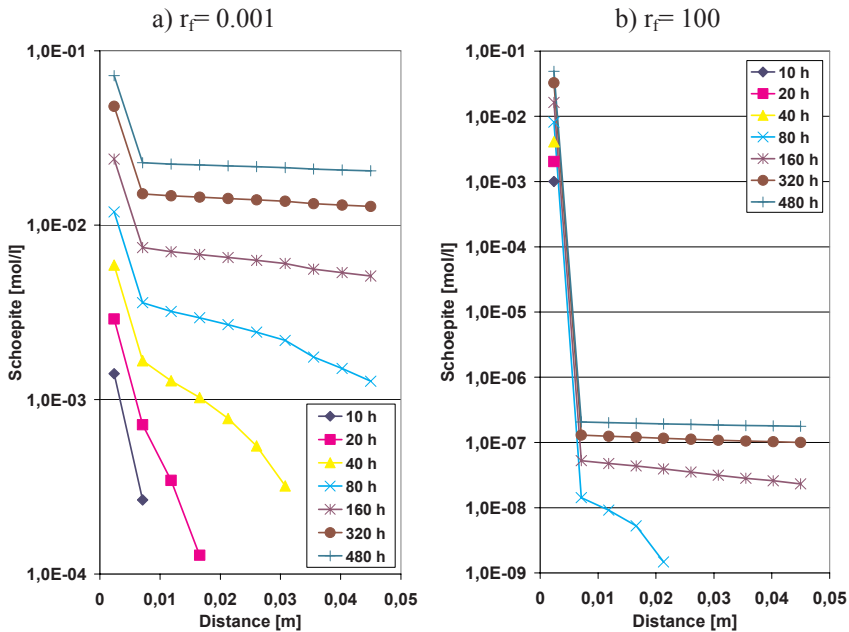


Fig. 5. The effect of different arbitrary precipitation kinetics rate factors r_f on the distribution of total precipitated schoepite along the sample.

Discussion and Conclusions

The first model was constructed solely from the average volumetric flow rate and the total porosity. In the next phase, the actual flow rates will be imposed onto the hydraulic model, as a drop in volumetric flow rates was actually observed. This automatically constrains the degree of freedom for any precipitation kinetics. The

measured bulk chemistry of the effluent will then be compared with that predicted by the model, which helps to identify the various processes that may control pH and redox potential. In addition, those elements that are involved in heterogeneous reactions can be identified on the basis of mass balances. With this information a refined model of the bulk chemical processes will be developed. In turn, better knowledge of the development of the bulk chemistry will help to constrain heterogeneous processes involving uranium. Given the assumed inertness of much of the rock matrix, at least on the time scale of the experiment, and considering the large mass of uranium available, it is quite likely that heterogeneous reactions involving uranium do have a noticeable influence on the bulk pore water chemistry. The modelling study will help to show this.

Blind predictive modelling and subsequent parameterisation of the model with actual experimental data is a valuable process that helps to better understand system behaviour. The blind predictions indicate which system variables are likely to be critical and thus helps to direct priorities for the analytical programme.

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