



## Sorption and diffusion of selenium oxyanions in granitic rock



Jussi Ikonen<sup>a,\*</sup>, Mikko Voutilainen<sup>a</sup>, Mervi Söderlund<sup>a</sup>, Lalli Jokelainen<sup>a</sup>,  
Marja Siitari-Kauppi<sup>a</sup>, Andrew Martin<sup>b</sup>

<sup>a</sup> University of Helsinki, Laboratory of Radiochemistry, Department of Chemistry, P.O. Box 55, FIN-00014 Helsinki, Finland

<sup>b</sup> Nagra (National Cooperative for the Disposal of Radioactive Waste), Wetztingen, Switzerland

### ARTICLE INFO

#### Article history:

Received 22 March 2016

Received in revised form 16 July 2016

Accepted 4 August 2016

Available online 5 August 2016

#### Keywords:

Selenium

Selenite

Selenate

Diffusion

Sorption

TDD-modelling

### ABSTRACT

The processes controlling diffusion and sorption of radionuclides have been studied extensively in the laboratory, whereas, only a few in-situ experiments have been carried out in order to study in-situ diffusion over the long-term (several years). This is largely due to the fact that in-situ experiments are typically time consuming and cost intensive, and it is commonly accepted that laboratory scale tests are well-established approaches to characterizing the properties of geological media. In order to assess the relevance of laboratory experiments, the Swiss National Cooperative for Disposal of Radioactive Waste (Nagra) have been conducting extensive experiments in the Underground Rock Laboratory (URL) at the Grimsel Test Site (GTS) in order to study radionuclide transport and retention in-situ. One of the elements used in these experiments is non-radioactive selenium, as an analog for the radiotoxic isotope Se-79, which is present in radioactive waste.

In this work, two laboratory through-diffusion experiments using selenium as a tracer were carried out in block (decimeter) scale rock specimens to support one of the ongoing radionuclide transport and retention in-situ experiment at the GTS mentioned above. The through-diffusion tests of selenium were performed under atmospheric conditions in both Kuru grey granite (KGG) and Grimsel granodiorite (GG). The decrease of selenium concentration in an inlet hole drilled into each of the rock samples and the breakthrough of selenium into sampling holes drilled around the inlet were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The effective diffusion ( $D_e$ ) and distribution coefficients ( $K_d$ ) of selenium were then determined from the changes of selenium concentration in the inlet and sampling holes using a Time-Domain Diffusion (TDD) simulations. In addition,  $K_d$  of selenium was measured by batch sorption experiments as a function of pH and Se concentration in atmospheric conditions and nitrogen atmosphere. The speciation of selenium was studied by HPLC-ICP-MS in simulated ground waters of each of the rock types.

The  $K_d$  of selenium was found to be in the range of  $(6.2\text{--}7.0 \pm 2.0) \times 10^{-3} \text{ m}^3/\text{kg}$  in crushed rock whereas the  $K_d$  obtained from block scale through diffusion experiment varied between  $(1.5 \pm 0.3) \times 10^{-3} \text{ m}^3/\text{kg}$  and  $(1.0 \pm 0.6) \times 10^{-4} \text{ m}^3/\text{kg}$ . The  $D_e$  of selenium was significantly higher for GG;  $D_e = (2.5 \pm 1.5) \times 10^{-12} \text{ m}^2/\text{s}$  than for KGG;  $D_e = (7 \pm 2) \times 10^{-13} \text{ m}^2/\text{s}$  due to the higher permeability of GG compared with KGG.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

The geological disposal of high-level radioactive waste and spent nuclear fuel has been studied in many countries, e.g. in Finland, Sweden, Switzerland, France etc. Host rocks considered viable have included deep-lying crystalline rock, clay formation sand salt (Witherspoon, 1996, Posiva 2013-01). The main mechanism responsible for radionuclide transport in crystalline rock is groundwater (GW) flow through water conducting fractures. The most significant processes that delay radionuclides flowing through fractures are diffusion into the rock matrix (i.e. matrix diffusion) and sorption onto the mineral surfaces (e.g.,

Dai et al. 2007, Grisak and Pickens, 1980, Neretnieks, 1980, Séby et al. 1998).

One radionuclide found in radioactive waste and spent fuel that is of particular concern for the long-term safety of radioactive waste repositories is Se-79 due to its long half-life ( $3.7 \times 10^5$  years) and its high mobility in the geological environment, especially in crystalline rocks (Atwood 2010; Lehto and Huo 2011). Other isotopes of selenium found in radioactive waste as a result of neutron activation of selenium includes Se-75, however, because Se-79 is produced from selenium bearing materials found in nuclear fuel and reactor construction materials, it is by far the most ubiquitous radioisotope of selenium found in radioactive waste.

The mobility of Se-79 depends largely on the oxidation state of selenium; there are five possible oxidation states. Under oxic conditions, oxidation state VI dominates and selenium exists in the form of selenate

\* Corresponding author.

E-mail address: [jussi.ikonen@helsinki.fi](mailto:jussi.ikonen@helsinki.fi) (J. Ikonen).

( $\text{SeO}_4^{2-}$ ). At lower redox potentials, oxidation state IV is found and selenium exists in the forms of selenite ( $\text{SeO}_3^{2-}$ ) and biselenite ( $\text{HSeO}_3^-$ ) (Lehto and Huo 2011). The reduction of selenate to selenite occurs slowly when redox potential is lower than +400 mV under neutral pH. Under intermediate redox potentials (approximately +200 mV, pH ) selenium is reduced to elemental selenium. Under low redox potentials selenium forms selenide ions  $\text{Se}^{2-}$  at oxidation state -II (Lehto and Huo 2011). Selenate and selenite are the most common forms found in natural waters. In the soil, selenate, selenite and elemental selenium are the most prevalent forms (Atwood 2010).

After being released to the host rock from a geological repository, selenium is assumed to be at oxidation states IV and VI. However thermodynamic calculations show that selenium exists also at lower oxidation states 0 and -II due to contact with the iron canisters that the waste is contained in (Altmann 2008). Selenium reduction is slow and kinetically hindered because it involves the transfer of multiple electrons along with multiple oxygen atoms between its various oxidation states (VI, IV, 0, -I, -II) (De Cannière et al. 2010, Grambow 2008, Savoye et al. 2012, Séby et al. 1998).

Sorption of anionic species typically decreases as a function of pH because the mineral surfaces become negatively charged which leads to the higher mobility of selenium oxyanions in neutral and basic pH (De Cannière et al. 2010). Sorption of selenium oxyanions is known to be strong only on aluminium and iron minerals, such as goethite, hematite and pyrite, through surface complexation (Boult et al. 1998, Duc et al. 2003, Parida et al. 1997, Rovira et al. 2008). Selenate forms weakly bound outer sphere complexes while selenite forms stronger inner sphere complexes with hydrous aluminium oxides and iron oxides (De Cannière et al. 2010). Adsorption capacity of selenium on aluminium oxides is higher than on iron oxides (Chan et al. 2009, Peak 2006) and retention of selenium is controlled by reduction of selenium to lower oxidation states or by surface complexation. However, selenate ions were not reduced along their migration path in Boom Clay even though IV and -II were thermodynamically stable oxidation states. Indications of selenite reduction to 0 and -II was observed in diffusion experiments in Callovo-Oxfordian clay-stones (Beauwens et al. 2005, Descostes et al. 2008, Savoye et al. 2012). Contrary to clays the content of aluminium and iron bearing minerals is low in crystalline rock leading to slight sorption. Presence of the iron bearing minerals increase the retention significantly because they act as selective sorbent for selenium species (Videnská et al. 2013; 2015, Yllera de Llano et al. 1996). The effective diffusion coefficient ( $D_e$ ) of highly mobile selenium oxyanions decrease with decreasing salinity due to anion exclusion that is caused by the negative surface charge of minerals (Iida et al. 2011).

Distribution coefficients ( $K_d$ ) of radionuclides can be determined by batch sorption and diffusion experiments. Most of them have been determined using simple crushed rock batch sorption method (Posiva 2012–41). These values are typically slightly higher than the ones from diffusion experiments (Bradbury and Stephen 1985, Tachi et al. 1998). To be able to compare results obtained from the batch and in-situ diffusion experiments reliably, block scale diffusion experiments are a useful step for upscaling  $K_d$  derived from batch sorption experiments. In the block scale diffusion experiments a measurement geometry similar to in-situ experiments is used and the samples contain less disturbances than crushed rock.

However, results of block scale diffusion experiments are difficult to analyze using analytical or traditional tools since either the initial or boundary conditions are challenging to handle due to the geometry of the experiment or complex sampling procedure. Such challenges could be solved using, e.g., commercial numerical solvers of partial differential equations or continuous time random walkers (Noetinger and Estebenet, 2000, Noetinger et al. 2001, Glaus et al. 2015). One possibility to handle the challenges is to apply the Time Domain Diffusion (TDD) method which has been developed for simulating diffusion in heterogeneous media (McCarthy 1993, Delay et al. 2002, Delay and

Porel 2003). TDD is a rapid particle-tracking method that makes it possible to simulate diffusion in heterogeneous media when the local porosities and diffusion coefficients are known. In this method a particle is forced to jump to a neighboring point during a certain random transition time, which makes it faster than the traditional particle-tracking methods (Sardini et al. 2003). The TDD method has been used to study the effect of structural heterogeneities on diffusion in various cases (Sardini et al. 2007, Robinet et al. 2008, Robinet et al. 2012, Voutilainen et al. 2013). Dentz et al. (2012) have also modified the method by including the sorption of migrating element in heterogeneous media. They included a trapping frequency parameter which may be used to mimic chemical sorption and desorption processes. The idea from Dentz et al. (2012) can be applied so that the distribution and diffusion coefficients, which are typically used for geological materials, can be utilized. The method has also been found to be a powerful tool for analyzing results of both in-situ and laboratory experiments especially when initial or boundary conditions are complicated (Voutilainen et al. 2013, Soler et al. 2014, Ikonen et al. 2016). Recently the method has been developed further by including flow in fractured media (Gjetvåg et al. 2015, Noetinger et al. n.d.).

The Swiss National Cooperative for Disposal of Radioactive Waste (Nagra) has been conducting extensive in-situ experiments at the Grimsel test site (GTS) in the field of radionuclide migration and retention in the rock matrix. The second Long Term Diffusion (LTD) experiment was started in spring 2014 using radionuclides H-3, Na-22, Cs-134, Cl-36 and Ba-133 as well as nonradioactive selenium. The aim of this work was to study the sorption and diffusion of selenium in granitic rock at laboratory to provide data for modelling and to compare the results with the ones from the in-situ experiment. Furthermore, sorption of selenium was studied with batch sorption experiments on crushed rock in atmospheric conditions and in nitrogen atmosphere. The  $K_d$  values were measured as a function of pH and selenium concentration. Speciation of selenium was followed using HPLC-ICP-MS. The data from the block scale diffusion experiment was analyzed using TDD method that utilizes the  $K_d$  and  $D_e$  of selenium and the results were compared to the ones from batch sorption experiments.

## 2. Experimental

### 2.1. Materials

KGG is a homogeneous, non-oriented fine grained granitic rock quarried from Kuru in the central part of Finland. The main minerals present are plagioclase (21%), quartz (35%), potassium feldspar (36%) and hornblende + biotite (8%). Minor assemblages are muscovite, chlorite, sericite, zircon, apatite and opaque minerals. The porosity of KGG is 0.47% (Jokelainen et al. 2009) and permeability  $(3 \pm 1) \times 10^{-18} \text{ m}^2$  (Kuva 2016). GG is a homogeneous, medium grained and slightly foliated granodiorite. The main minerals are plagioclase (37%), quartz (33%), potassium feldspar (17%) and biotite (6%). The remaining minerals, which do not exceed 5% in volume, are green amphibole (hornblende), muscovite, epidote, titanite and opaque minerals; most probably iron sulphides like pyrite (Jokelainen et al. 2013). The porosity of GG is 0.65% (Kelokaski et al., 2006) and permeability  $(1.3 \pm 0.3) \times 10^{-17} \text{ m}^2$  (Kuva 2016).

The selenium used as a tracer in all experiments was stable Se (Romil) in oxidation state +IV with a concentration of 1000 mg/L in 0.5 M nitric acid. This solution was added into the two different GW simulants so that the concentrations in the inlet hole in the blocks were the same as the initial concentration of selenium in the in-situ experiment at 50 mg/L. This high concentration was chosen to make sure that detectable levels of the tracer reached the sampling holes. Selenium concentration in the GW from the Grimsel LTD experiment site was measured to be below 15  $\mu\text{g/L}$  (Giroud 2016).

Table 1 presents the elemental composition of the two GW simulants that were used in the experiments. In the case of GG

Download English Version:

<https://daneshyari.com/en/article/6386362>

Download Persian Version:

<https://daneshyari.com/article/6386362>

[Daneshyari.com](https://daneshyari.com)