

Upscaling laboratory data towards in situ conditions

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ABSTRACT

Sorption and diffusion results of Cs from laboratory and in situ experiments were compared to assess the parameters for safety case analysis. The sorption process of Cs on biotite was also studied with molecular modelling. It was concluded that the sorption behaviour of Cs is overestimated in the laboratory experiments. However, upscaling of the laboratory data can be done with assistance of in situ experiments and modelling.

1 INTRODUCTION

The final disposal of high level nuclear waste in Finland and Sweden is based on the KBS-3V multiple barrier system in stable granitic-type rock formations [1]. The barriers in the system include the physical form of the fuel, the disposal canister and the surrounding bentonite buffer, the backfilling of the repository tunnels and, finally, the host rock. The radionuclide retaining properties of the rock are of interest as groundwater flow through rock formations is the main mechanism for radionuclide transport in case of a leakage [2, 3].

The batch sorption experiments are commonly used for obtaining distribution coefficients (K_d) for the radionuclide sorption onto solid mineral phases that are present in a KBS3 type repository [4]. However, there are difficulties relating to the upscaling of the data provided from the laboratory experiments into the in situ scale when all the factors of the actual migration environment are typically not known [5].

Both laboratory and in situ experiments are needed in the spent nuclear fuel repository safety evaluation in order to assess the parameters affecting the migration of radionuclides. The first in situ long-term diffusion was started in June 2007 and stopped in August 2009 in the underground rock laboratory in Grimsel test site. In the experiment 8 I

of tracer cocktail containing ^3H , ^{22}Na , ^{131}I ^{134}Cs , stable I and stable Na was circulated in the borehole section [6, 7]. The radionuclides were chosen as the safety relevant radionuclides in the high level nuclear waste.

In this study the sorption and diffusion of ^{134}Cs was studied in laboratory conditions. Molecular modelling was also incorporated to evaluate the sorption mechanism of Cs onto biotite. The results were compared to results obtained from the in situ experiment in the Grimsel test site.

2 MATERIALS AND METHODS

2.1 Grimsel site

The Grimsel test site is located in the central Swiss Alps at an altitude of 1730 m and at the depth of 450 m below the ground surface. The bedrock in the area is mainly composed of Aaregranite and Grimsel granodiorite [8]. The in situ long-term diffusion experiments have been conducted in the area consisted of granodiorite, which is homogeneous, medium grained and slightly preferentially-oriented. The main minerals of granodiorite are quartz (30-40 %) plagioclase (30-40 %), potassium feldspar (10-20 %) and biotite (5-10%).

The groundwater in the area is very alkaline and weakly saline. The chemical composition of the

used groundwater simulant is based on the fracture water data from Grimsel (Table 1) [6].

Table 1 The chemical composition of the Grimsel groundwater simulant used in the experiments [6].

Component	Molality
pH	9.7
Na ⁺	6.9·10 ⁻⁴
K ⁺	5.0·10 ⁻⁶
Ca ²⁺	1.4·10 ⁻⁴
Mg ²⁺	6.2·10 ⁻⁷
HCO ₃ ⁻	4.5·10 ⁻⁴
Cl ⁻	1.6·10 ⁻⁴
S	6.1·10 ⁻⁵
Br ⁻	3.8·10 ⁻⁷
F ⁻	3.6·10 ⁻⁴
[Si]tot	2.5·10 ⁻⁴
[Fe]tot	3.0·10 ⁻⁹
[Mn]tot	5.0·10 ⁻⁹

2.2 In situ experiment

In the first long-term in situ diffusion experiment starting in June 2007 ³H, ²²Na, ¹³⁴Cs, ¹³¹I, ¹²⁷I and ²³Na tracers in groundwater from the site (total volume 8 l) were circulated in the circulation interval (70 cm) between two pressure intervals at a depth of 8 m from the tunnel to ensure fully saturated conditions. The circulation was stopped in August 2009 after which the complete circulation interval was over cored and analysed.

2.3 Sorption experiments

The sorption of ¹³⁴Cs on granodiorite and its main minerals was studied with batch sorption experiments as a function of Cs concentration (1·10⁻⁸ to 1·10⁻³ M). Crushed rock having grain size below 0.3 mm were wetted in liquid scintillation bottles with Grimsel groundwater simulant made to resemble the groundwater in the fracture zones of the area (solid solution ratio 50 g/L). The bottles were agitated for two weeks after which the investigated Cs concentration was added. The bottles were again agitated for two weeks after which the samples were centrifuged and the supernatant was transferred into liquid scintillation bottles. The ¹³⁴Cs activity was measured with a Perkin Elmer automatic 1480 WIZARD 3" gamma counter with a 20 min counting period. The distribution coefficients of Cs on crushed

granodiorite were determined from the relative activities compared to the initial activities.

2.4 Diffusion experiments

For diffusion experiments the rock samples obtained from the Grimsel test site were first sawed to approximately 1 cm x 1 cm x 1 cm cubes to 1 cm x 1 cm x 1 cm cubes which were then equilibrated with 15 ml of the groundwater simulant for two weeks after which a radiotracer of ¹³⁴Cs (4600 Bq per 15 ml) was added. The decrease of tracer concentration in the solution was monitored as a function of time for four months. The results were modelled with Comsol Multiphysics program with the Transport of Diluted Species in Porous Media node.

2.5 Molecular level studies

Density functional theory calculations were utilized to verify the sorption of Cs onto mineral surfaces. The calculations were done with the CASTEP code [9] implemented into Materials Studio version 8.0 [10]. The exchange-correlation was described with generalized gradient approximation GGA-PBE, and the ultrasoft pseudopotentials were used for each element: Al_00PBE.usp for aluminum, Cs_00PBE.usp for cesium, H_00PBE.usp for hydrogen, K_00PBE.usp for potassium, Mg_00.usp for magnesium, O_soft00.usp for oxygen, and Si_soft00.usp for silicon. The kinetic cut-off energy for a plane wave expansion of the wave function was 310 eV.

3 RESULTS AND DISCUSSION

It was discovered in the batch sorption experiments (Figure 1) that the distribution coefficient values of Cs on granodiorite were 0.107 ± 0.003 m³/kg at concentrations of 10⁻⁸ M [11]. Distribution coefficients values of 7.6·10⁻³ m³/kg have been obtained for Cs from the in situ – experiments [12]. The difference can be explained by the difference in the specific surface areas between the crushed and intact rock [11].

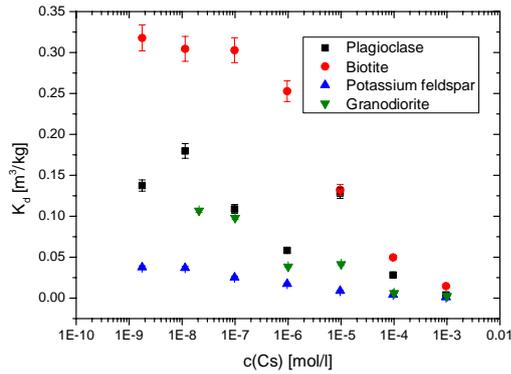


Figure 1: Concentration dependent Cs sorption on crushed granodiorite in the weakly saline Grimsel groundwater simulant.

The distribution coefficients of Cs were largest on biotite with values of $0.304 \pm 0.005 \text{ m}^3/\text{kg}$ at concentrations of 10^{-8} M . Molecular modelling was done to confirm that the Cs is mainly sorbed on the interlayer sites of the magnesium-rich biotite, phlogopite. The Cs ions replace the K ions in the structure (Figure 2) due to their similar ionic radius and charge.

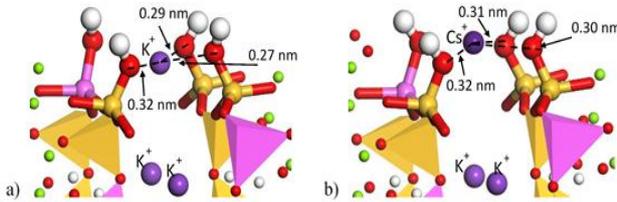


Figure 2: The hydroxylated (110) surface of phlogopite. a) Phlogopite with the interlayer distance 0.35 nm, b) the uppermost K^+ ions replaced with Cs^+ ions: the interlayer distance 0.32 – 0.35 nm.

It was discovered in the diffusion experiments that the tracer concentration decrease was fastest and largest in the first 500 hours of the experiment (Figure 3). This is most probably due to disturbed surface caused by sawing, which offers plenty of specific surface area for the sorption to occur. The results were modelled with Comsol Multiphysics and distribution coefficient of $2 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and diffusion coefficient of $2 \cdot 10^{-12} \text{ m}^2/\text{s}$ were obtained. These are in line with results obtained from in situ experiments ($7.6 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and $3 \cdot 10^{-12} \text{ m}^2/\text{s}$) [12].

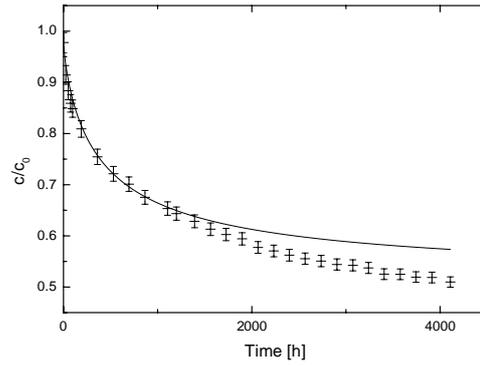


Figure 3: The relative tracer depletion of Cs in solution and the diffusion model acquired by Comsol Multiphysics (curve) on granodiorite.

CONCLUSIONS

Cs sorption behavior on crushed granodiorite followed the trend of its main minerals with distribution coefficient values of $0.107 \pm 0.003 \text{ m}^3/\text{kg}$ in 10^{-8} M . The sorption results obtained from the laboratory experiments were systematically larger than the sorption results obtained from the in situ experiments conducted in the Grimsel test site, which can be explained with the effect of the specific surface area. The diffusion parameters obtained from the diffusion experiments were in good accordance with the results obtained from the in situ experiments. The mineral and structural heterogeneity of the rock is needed to take into account in order to fully understand the sorption and diffusion of radionuclides in rock.

ACKNOWLEDGEMENTS

This work was supported by Finnish Research Program on Nuclear Waste Management KYT2014.

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