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The diffusion of SO_4^{2-} in Opalinus Clay: Measurements of effective diffusion coefficients and evaluation of their importance in view of microbial mediated reactions in the near field of radioactive waste repositories

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ABSTRACT

Through-diffusion experiments with $^{36}Cl^-$, $^{35}SO_4^{2-}$ and HTO in Opalinus Clay (OPA) samples from a deep borehole in North-East Switzerland (Benken; BE) have been performed. The effect of burial depth on the experimental results has been investigated.

It could be shown that the effective diffusion coefficients decrease with sample depth for all three tracers. Moreover, there was a good correlation with the texture of the samples. The diffusion coefficients for HTO are the largest ($D_e = 5.4–8.8 \times 10^{-12}\ m^2\ s^{-1}$), followed by those for $^{36}Cl^-$ ($D_e = 0.7–1.9 \times 10^{-12}\ m^2\ s^{-1}$), and finally $^{35}SO_4^{2-}$ ($D_e = 0.2–0.6 \times 10^{-12}\ m^2\ s^{-1}$). $^{36}Cl^-$ was partially excluded from the total porosity resulting in an accessible porosity smaller than the total porosity ($\varepsilon_{Cl} = 0.041–0.064$). $^{35}SO_4^{2-}$, on the other hand, showed interaction with OPA resulting in a capacity factor (α) larger than the total porosity ($\varepsilon_{tot} = 0.13–0.16$). Using extended Archie's law the accessible porosity for $^{35}SO_4^{2-}$ was estimated between 0.013 and 0.030. This enabled to evaluate the sorption coefficient of $^{35}SO_4^{2-}$ from the measured capacity factor, resulting in values of K_d between 6×10^{-5} and $9 \times 10^{-5}\ m^3\ kg^{-1}$.

1. Introduction

A basic design principle for safe long-term deep geological storage of radioactive waste is to rely on multiple barriers to attenuate the release of radionuclides into the biosphere. The Swiss design foresees three main barriers in a repository for high-level radioactive waste: the canister, the tunnel backfill and the host rock. The evolution of the barrier properties evolves accordingly to the repository evolution and the geochemical boundary conditions.

The basic concept of this design has been described elsewhere (Nagra, 2014): the designated host rock is a low permeability indurated clay rock from the Mesozoic called Opalinus Clay (Nagra, 2002), the buffer material consists of densely packed bentonite (Nagra, 2014) and the canister material is carbon steel or copper-coated steel. The choice of canister material for high level waste in a deep geological repository affects its long-term integrity, but equally important are the conditions that prevail in a deep geological repository, which eventually define the lifetime of a canister. For disposal canisters made of metal, corrosion plays an important role in the definition of their lifetime. Of particular interest is the use of copper as a canister material - either as a coating or as a shell - as it can lead to very long canister lifetimes that will delay radionuclide release (Nagra, 2016). The main process that can reduce copper's longevity under disposal conditions is sulfide-enhanced corrosion. The rate and extent of corrosion depends on the availability of sulfide at the surface of the canister. As a result, the flux of sulfide towards the canister is a critical parameter, which depends on a number of near-field properties and biogeochemical processes occurring in the near field (Cloet et al., 2017).

Studies on sulfide availability and transport have been reported by other waste management organizations that consider the use of copper-bearing canisters. The Swedish Nuclear Fuel and Waste Management organization (SKB, 2010) has calculated by mass balance that a maximum corrosion depth of 0.1 mm is possible, assuming MX-80 bentonite (including 0.07 wt.-% pyrite) as backfill material (SKB, 2010). A more advanced sulfide transport model including the geochemistry of the near field was made by Posiva (Wersin et al., 2014). More recently, Canada's Nuclear Waste Management Organization (NWMO) has also developed and published a sulfide diffusion model (Briggs et al., 2016,

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In Opalinus Clay sulfide might originate from different sources:

- Sulfide is naturally present in Opalinus Clay in the form of pyrite (FeS_2) and its concentration is 0.3–3.7 wt.-% (Mazurek, 2011). Under anoxic and reducing conditions pyrite is very insoluble, which results in very low sulfide concentration in the porewater, i.e. $< 10^{-8}$ M (Wersin et al., 2014). Pyrite is therefore usually assumed not to contribute to the sulfide concentration in the porewater.
- The sulfate inventory in Opalinus Clay may indirectly contribute to sulfide-enhanced Cu-corrosion when sulfate-reducing bacteria are present in e.g. the Excavation Damaged Zone (EdZ). The main sulfate-containing mineral in Opalinus Clay is Celestine ($SrSO_4$), which can be found in very low concentrations of 0.02–0.06 wt.-% (Wersin et al., 2013).

While the inventory for naturally occurring sulfide is rather low, the sulfate in the porewater may contribute to the formation of sulfide through microbial reduction of sulfate in the nearfield of the repository. In a recent study Cloet et al. (2017) showed that, when taking into account sulfate reduction in the EdZ, the diffusion coefficient of sulfate in the host rock (Opalinus Clay) plays an important role in limiting the sulfide flux towards the canister. The same conclusions were drawn in Leupin et al. (2016) for the oxidation processes of hydrogen in a repository for low- and intermediate level waste. In both reports generic diffusion coefficients that were based on $^{36}Cl^-$ diffusion data ($D_e = 2 \times 10^{-12}\ m^2\ s^{-1}$) in Opalinus Clay (Van Loon et al., 2003b; Van Loon, 2014) were derived for the diffusion of sulfate. Experimental values of the effective diffusion coefficient of SO_4^{2-} in Opalinus Clay are not available. Given the importance of sulfate diffusion through Opalinus Clay, a better understanding of the diffusion behavior of sulfate is thus required. Bazer-Bachi et al. (2007) studied the sorption, transport and diffusion behavior of SO_4^{2-} in Callovo-Oxfordian argillites and concluded that SO_4^{2-} was sorbed and that sorption depended mainly on the mineralogical composition of the solid phase and on the sulfate concentration in the pore water. Sulphate was also partially excluded from the total pore space. Although SO_4^{2-} is a bivalent anion, its exclusion was similar to that of a monovalent anion such as Cl^-. A similar observation was made in Febex bentonite (García-Gutiérrez et al., 2008).

This papers reports on the diffusion of tritiated water (HTO) and anions in Opalinus Clay. Through-diffusion experiments with HTO, $^{36}Cl^-$ and $^{35}SO_4^{2-}$ on Opalinus Clay samples have been performed using the classical through-diffusion technique (Van Loon et al., 2003a). HTO is used because it will enable to define the total transport porosity of the samples. The chloride anion was studied because $^{36}Cl^-$ does not sorb on OPA and shows pure anion exclusion. $^{35}SO_4^{2-}$ is the anion of interest and is a bivalent anion, and probably adsorbs on the solid phase. The parameters obtained from the study are the diffusion accessible porosity (ε) or the rock capacity factor (α), and the effective diffusion coefficient (D_e, $m^2\ s^{-1}$). The study will thus provide more reliable values for the diffusive behavior of sulfate in Opalinus Clay. Moreover, by using samples originating from different depths, the effect of sample depth and the resulting effect of sample texture on diffusion properties can be evaluated.

2. Materials and methods

2.1. Samples

The samples (BE-1–BE-4) used were Opalinus Clay samples from the deep borehole in Benken. The Benken borehole (coordinates: 690′988.80/277′842.90, 404.30 m a.s.l.) is located in the community of Benken in Canton Zürich, approximately 0.7 km SSW of the village boundary and to the west of the main road between Winterthur and Schaffhausen. Drilling commenced in September 1998 and continued until May 1999. The samples used in this study originate from the following depths: BE-1: −564 m; BE-2: −589 m; BE-3: −636 m; BE-4: −651 m. The average mineral composition of Opalinus Clay is given in Table 1. More detailed information on the main composing minerals (clay, calcite and quartz) can be found in Wenk et al. (2008). The samples were stored under anoxic conditions to avoid oxidation. The preparation of the samples has been described in detail in Van Loon et al. (2003a).

Table 1
Average mineral composition of Benken Opalinus Clay (Nagra, 2001).

Mineral	Wt %
Calcite	16 ± 10
Dolomite/Ankerite	1.0 ± 0.4
Siderite	4.0 ± 2.4
Quartz	20.0 ± 0.5
K-Feldspar	2 ± 1
Albite	1.0 ± 0.3
Pyrite	1.1 ± 1
Clay minerals	
Illite	18 ± 6
Illite/smectite mixed layers	14 ± 4
Chlorite	5 ± 2
Kaolinite	17 ± 6

2.2. Porewater

The porewater in equilibrium with Opalinus Clay is a NaCl solution with minor amounts of K, Mg, Sr and Ca salts. The composition of the porewater used is summarized in Table 2. The water was prepared by dissolving Cl-salts of Na, Ca, Mg and Sr and Na_2SO_4. The pH was adjusted to the desired one by adding HCl or NaOH.

The speciation of SO_4^{2-} as calculated with Phreeqc is given in Table 3. As can be seen, ca. 70% is present as free SO_4^{2-}, ca. 15% as a monovalent $(Na,K)SO_4^{2-}$ complex and 15% as a neutral (Ca,Mg,Sr) SO_4^0 complex.

2.3. Through-diffusion experiments

Diffusion experiments on the samples were performed in 2002, shortly after the drilling campaign. Cylindrical samples (diameter = 0.0254 m, thickness = 0.011m) were mounted in a diffusion cell (Fig. 1) sandwiched between two stainless steel filter plates (Stainless steel: 316L; pore diameter: 10 µm; diameter = 0.0254 m; thickness = 0.0016 m; MOTT industrial division, Farmington, USA). The geometrical setup of the experiment was such that the direction of diffusion was perpendicular to the bedding of the clay. A confining

Table 2
Composition of the synthetic OPA porewater used in the diffusion experiments (Van Loon et al., 2003b).

Element	$mol{\cdot}m^{-3}$
Na	$1.50{\cdot}10^2$
K	$4.31{\cdot}10^0$
Mg	$5.21{\cdot}10^0$
Ca	$7.24{\cdot}10^0$
Sr	$3.97{\cdot}10^{-1}$
Cl	$1.60{\cdot}10^2$
SO_4	$1.00{\cdot}10^1$
CO_3/HCO_3	$3.11{\cdot}10^{-1}$
pH	7.9
Σcations	$1.80{\cdot}10^2\ eq{\cdot}m^{-3}$
Σanions	$1.80{\cdot}10^2\ eq{\cdot}m^{-3}$
ionic strength	0.20