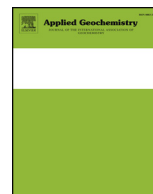




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^{137}Cs transport in crushed granitic rock: The effect of bentonite colloids

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ABSTRACT

The paper focuses on the study of caesium transport through crushed granite in the presence of bentonite colloids in a dynamic column arrangement with the continuous input of the liquid phase. The aim of the experiments was to investigate the effect of the presence of bentonite colloids on the behaviour of caesium in granitic rock. The behaviour of the tracer was studied under aerobic conditions applying a constant tracer concentration (activity) and constant flow rate. Defined volumes of the liquid phase were sampled periodically at the outlet of the column for the measurement of tracer concentrations (activity). Transport was described by means of breakthrough curves. The stepwise approach included the following steps: 1) the non sorbing tracer ^3H was used to evaluate the hydrodynamic properties of the column; 2) the conducting of a column experiment with bentonite colloids in deionised water; 3) the migration of ^{137}Cs in two liquid phases (deionised and synthetic granitic water); 4) the study of the transport of the radiocolloid suspension in deionised water. The results revealed the completely different behaviour of the bentonite colloids and the caesium in the granitic column and the effect of colloid particles on caesium sorption on granite. The bentonite colloids behaved as conservative non-sorbing tracers whereas, conversely, caesium sorbed strongly on the granitic material. It was determined that the behaviour of the caesium in the granitic rock was influenced by the strong sorption of caesium with respect to the bentonite colloids. A minor part of the caesium irreversibly sorbed on the bentonite colloids and passed through the granite immediately together with the bentonite colloids, and a major part of the caesium was desorbed from the bentonite colloids and was retained in the granite.

1. Introduction

The concept of the final storage of spent nuclear fuel and high-level radioactive waste in many countries, including the Czech Republic, is based on the deep geological multi-barrier system consisting of both engineered and natural barriers. The engineered barriers consist primarily of the waste package and bentonite which is used as the buffer, the function of which is to slow down the escape of radionuclides following the eventual degradation of the waste package in the deep geological repository (DGR). The natural barrier consists of the surrounding rock massif and makes up the final barrier to the release of radionuclides into the biosphere. The most important properties of the natural barrier in terms of the behaviour of radionuclides consist of the mineralogical composition including secondary minerals, porosity and the structure of the pores and the composition and electrochemical properties of the groundwater.

Caesium makes up one of the most critical radionuclides with respect to DGR disposal and constitutes one of the most abundant fission products present in spent nuclear fuel (SNF). The three principal

isotopes of Cs present in SNF have long half-lives (^{134}Cs , ^{135}Cs and ^{137}Cs isotopes) and ^{135}Cs makes up one of a number of dominating radionuclides in terms of far-field release calculations (Carbol and Engkvist, 1997; Crawford et al., 2006).

One of the most important parameters in terms of determining the degree of caesium sorption on the rock consists of the mineralogical composition of the crystalline material. A number of groups of minerals are present in the rock matrix: tectosilicates (e.g. quartz, feldspars), phyllosilicates (e.g. mica, chlorite, smectite, illite and kaolinite) and inosilicates (e.g. amphibole). The proportion of individual minerals in different rock matrices, which determines the sorption properties of the rock, varies considerably; thus, interactions between individual minerals and the liquid phase (Cornell, 1993) should be fully taken into account. The sorption of caesium on quartz is negligible due to the preference for ion exchange as the sorption mechanism as opposed to surface complexation. Moreover, quartz is characterised by weak surface complexation and, therefore, the degree of caesium sorption can be expected to be very low (Muuri et al., 2016). Caesium sorption on K-feldspars (e.g. orthoclase) is also low due to the low specific surface

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area which renders the occurrence of favourable sorption sites rare. The ionic radii of hexacoordinated K^+ and Cs^+ are similar and, consequently, ion exchange may occur within the structure of the mineral. Caesium sorption on Na/Ca-feldspars (plagioclases), however, is observed more frequently, most probably due to the larger specific surface area which offers a greater number of preferential sorption sites within the plagioclase structure (Muuri et al., 2016; Ebong and Evans, 2011; Stumpf et al., 2006). The dominant caesium sorbent group consists of phyllosilicates, with micas (e.g. biotite, muscovite) making up the most common sorbents in crystalline rock matrices. Caesium sorption on these layered minerals takes place via ionic exchange with the existence of several types of sorption sites, i.e. frayed edge sites (FES), layer sites and basal sites. With respect to low caesium concentrations ($< 10^{-8} \text{ mol l}^{-1}$), sorption is dominated by FES; however, with higher caesium concentrations, the FES become saturated and the greater part of the caesium is sorbed by means of the remaining two sorption sites. Caesium sorption via FES is strong, specific and irreversible due to the low hydration energy of Cs^+ ; moreover, FES sites are characterised by low sorption capacity and a high degree of affinity for caesium. Conversely, caesium sorption via interlayer and basal sites is non-specific and reversible and these sorption sites are characterised by low affinity and higher density values (Söderlund et al., 2011; Missana et al., 2004). Caesium sorption via these weaker sites is influenced by the composition of the liquid phase. In addition, such sites may be occupied by competitive ions, the most important of which with respect to caesium in groundwater are Na^+ , K^+ , Ca^{2+} and Mg^{2+} ; divalent ions compete with Cs^+ more strongly than do univalent ions (Cornell, 1993). A further significant caesium sorbent group is that made up of inosilicates which are characterised by high cation exchange capacity and which are presented as Ca-amphibole (e.g. hornblende) in the rock matrix. The sorption of caesium on hornblende takes place via ion exchange (Andersson et al., 1983). Generally, caesium sorption on individual minerals in the rock matrix decreases in the order: muscovite > biotite > hornblende > serpentine > orthoclase > magnetite > hematite > apatite > calcite = quartz > fluorite (Söderlund et al., 2011).

Bentonite colloids form in the DGR system due to the swelling of bentonite and the formation of a gel-like material which presents a potential source of colloid particles (Alonso et al., 2003). The generation of colloids may lead to the degradation of the engineered barrier, and the subsequent transport of radionuclides with colloids may result in a reduction in the efficiency of the natural rock barrier. The transport of radionuclides through the rock matrix in the presence of bentonite colloids has been studied extensively with experimentation tending to focus on the role of bentonite colloids and radionuclide transport in the natural barrier (Missana et al., 2008; Delos et al., 2008). It has been established that the presence of bentonite colloids may enhance the mobility of radionuclides; the radionuclides form radiocolloid complexes with the colloid particles which diffuse into the rock matrix and mediate the migration of formerly immobile contaminants (Alonso et al., 2007; Kretzschmar and Schäfer, 2005). Missana et al. (2008) observed that bentonite colloids significantly influence the retardation behaviour of multivalent actinides; the migration of radionuclides (^{152}Eu , ^{239}Pu) was found to be strongly mediated by bentonite colloids and, in the presence of colloids, the recovery of Eu and Pu was greater than that in systems without the presence of bentonite colloids. However, the question remains as to the reversibility of radionuclide sorption on bentonite colloids or, perhaps more significantly, the dissociation kinetics of radionuclides and colloid complexes. The literature suggests that the sorption of radionuclides is partly reversible and decreases over time (Huber et al., 2011; Missana et al., 2004; Albarran et al., 2011). Most probably, the reversibility of radionuclide sorption on bentonite colloids depends on the sorption mechanism. Bentonite consists of aluminium phyllosilicate clay which is made up principally of montmorillonite characterised (as are micas and illite) by FES and regular sorption sites (RES), i.e. planar and interlayer sites. The

sorption of radionuclides on FES takes place via surface complexation and the bond is strong and irreversible. However, FES are not accessible to large hydrated ions; therefore, for example, strontium cannot be sorbed via FES (Missana et al., 2004; Söderlund et al., 2011; Kolomá and Červinka, 2017). Conversely, the sorption of radionuclides on RES takes place via ion exchange and is weak and reversible (Söderlund et al., 2011; Missana et al., 2004). Both laboratory and in-situ experiments have revealed that a small proportion (a few percent) of radionuclides (^{85}Sr , ^{137}Cs) migrate rapidly (and with practically no retardation) through the rock matrix in the presence of bentonite colloids, one possible explanation for which is that the caesium migrates through the rock matrix sorbed on the FES of the bentonite colloids (Albarran et al., 2011; Bryan et al., 2014).

This paper concerned the study of caesium migration in the rock matrix in the presence of bentonite colloids. The experiments were conducted in a dynamic column arrangement with the continuous input of the liquid phase under aerobic conditions and applying a constant tracer concentration (activity) and constant flow rate. Caesium behaviour in the granitic rock was influenced by the strong sorption of caesium by the bentonite colloids. A minor part of the caesium irreversibly sorbed on the bentonite colloids and passed through the granite immediately together with the bentonite colloids, and a major part of the caesium was desorbed from the bentonite colloids and was retained in the granite. The presence of bentonite colloids affects caesium transport; colloid particles partially play the minor role of radionuclide carriers.

2. Materials and method

2.1. Solid and liquid phase

Granite and the mica mineral muscovite were used as the solid materials. The granite (fine-grained two-mica granite of the Lipnice type), which originated from the Rejčkov locality (Melechov Massif, Czech Republic), was extracted from a borehole core (depth of 97.5 m–98.7 m below the surface). The sample was crushed, sieved to defined fractions and washed in deionised water in an ultrasonic bath in order to remove the fine particles. A grain size fraction of 0.125–0.63 mm was chosen for the static and dynamic experiments. The X-ray diffraction analysis (XRD) of the crushed granite was performed using a Philips X'Pert System diffractometer using a graphite crystal monochromator and $\text{CuK}\alpha$ radiation at 40 kV and 40 mA over the range 2° – 85° 2θ , in steps of 0.05° . A summary of the mineralogical composition of the granite sample is provided in Table 1.

The muscovite was separated manually from the crushed granite; the remaining muscovite-depleted granite was not used in other experiments.

Deionised water (DW) and synthetic granitic water (SGW) were used in the preparation of the tracer solutions. The chemical composition of the SGW is shown in Table 2 (Havlová et al., 2010) and corresponds to granitic water from Czech granitic massifs at depths of 20 m–100 m. All the chemicals were of analytical grade and were dissolved in deionised water.

Table 1
Mineralogical composition of the granite sample (in wt%).

Mineral	Content (wt%)
Quartz	32
Orthoclase	31
Plagioclase	18
Mica	14
Chlorite	5

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