Interaction of Radionuclides and Colloids Released from Materials Related to the Disposal of SNF – 14273

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ABSTRACT

Colloid-facilitated transport of radionuclides may significantly contribute to the long-term performance of a spent nuclear fuel repository in crystalline bedrock. Colloids can be formed in the repository from degraded engineered barriers like bentonite and grouting materials. The potential relevance of colloids for radionuclide transport is highly dependent on the stability of colloids in different chemical environments and their interaction with radionuclides. The objective of this work was to study the stability of bentonite colloids and radionuclide and colloid interaction by means of the batch sorption and column experiments. The stability of colloids was followed by analyzing the particle size distribution, concentration and zeta potential applying the dynamic light scattering method. The transport of Sr-85 and Eu-152 in a fracture column and crushed rock columns was studied without and with colloids. The stability of bentonite colloids depended on the ionic strength of the medium and the valence of the cations in the solution. The obtained results confirmed the influence of ionic strength also on the sorption of Sr-85 and Eu-152. The distribution coefficient (K_d) decreased when the ionic strength increased. Particularly Eu-152 but Sr-85 were strongly retarded in the fracture column and altered crushed rock column without colloids. In the presence of bentonite colloid suspension, the elution of radionuclides was obtained. The results showed the effect of the water flow rate and thus the residence time on the colloid recovery indicating colloid filtration in a fracture or crushed rock surfaces. At current saline groundwater conditions in Olkiluoto, colloids released from the bentonite barrier are aggregated and unstable do not have an influence on the migration of radionuclides.

INTRODUCTION

In Finland, the repository for spent nuclear fuel will be excavated at a depth of about 500 meters in the fractured crystalline bedrock in Olkiluoto at Eurajoki, the site proposed by Posiva Oy. Colloid-facilitated transport of radionuclides may significantly contribute to the long-term performance of a spent nuclear fuel repository. Several studies have indicated radionuclide (especially actinide) sorption on colloids and the mobility of radiocolloids. Field-scale studies at hazardous waste sites have evidenced that colloid transport can enhance actinide migration [1, 2]. Laboratory experiments confirmed that colloids can accelerate the transport of cationic and anionic metals through porous and fractured media [3-5]. Colloids are very small particles between 1nm and 1µm in diameter. Inorganic and organic colloids are present in natural groundwater [6]. Colloids can also be produced from degraded Engineered Barrier System (EBS) materials such as the bentonite clav barrier, copper or steel container, and grouting materials as well as from uranium fuel itself. In Olkiluoto, the determined natural inorganic and organic colloid contents in groundwater are low - less than 1 ppm - but the bentonite buffer used in the EBS system is assumed to be a potential source of colloids [7, 8]. For colloid-facilitated transport it is essential that colloids must be generated, contaminants must associate with the colloids and colloids must be transported through the groundwater. The potential relevance of colloids for radionuclide transport is highly dependent on the stability of colloids in different chemical

environments and their interaction with radionuclides [9]. Objective of this work is to study the stability of bentonite colloids and radionuclide and colloid interaction with a rock in different groundwater conditions. The overview of ongoing experimental work and examples of preliminary results are given.

EXPERIMENTAL

Materials and Methods

The bentonite used was MX-80 Volclay type bentonite powder which consists mainly of montmorillonite. Cation exchange capacity determined using Cu(II)-triethylenetetramine-method is 0.89 eq kg⁻¹ [10]. Colloid dispersion solution was made from MX-80 bentonite clay powder which was mixed with Milli-Q water at a solid/solution ratio of 1:20. The suspension was shaken for one week and the colloidal fraction was then separated by centrifugation and the concentration of the bentonite colloids was determined by a gravimetric method after drying the suspension in an oven at 105 °C for 3 days. Allard, low salinity granitic (I = 4.2 10⁻³ M) and diluted OLSO (I = 0.517 M) reference groundwater were used as solutions. OLSO simulates the current saline groundwater in Olkiluoto in oxic conditions. Electrolyte solutions, NaCl (I = 1 M – 1 10⁻⁷ M) and CaCl₂ (I = 3 M – 3 10⁻⁷ M) were used to study the effect of salinity.

The fracture column from Olkiluoto tonalite drill core was artificially fractured along the natural fracture containing an altered zone and filling minerals witch where mainly chlorite. The porosity of unaltered tonalite is 0.1 - 0.3 %. The porosities of altered areas were not determined. The fracture width in the column was about 3.5 cm, the column length 6.8 cm and the fracture aperture 100 µm. The crushed rock columns were made of Kuru Grey granite and strongly altered tonalite from the Syyry area in Sievi. The rock matrix of Kuru gray granite is intact, fine-grained, non-foliated and equigranular. The total porosity is 0.2 % and the density is 2660 kg m⁻³. The rock matrix of Syyry column was strongly and homogeneously altered containing visible mm scale pores. The total porosity is 2 - 8 % and the density is 2400 kg m⁻³. The crushed rock column diameter was 1.5 cm and length 15 cm or 30 cm. The grain size of crushed rock was 1.95 - 5 mm.

Colloidal particle size distribution was determined applying the dynamic light scattering method and zeta potential applying the dynamic electrophoretic mobility (Malvern Zetasizer Nano ZS). Dynamic light scattering (DLS) called also Photon correlation spectroscopy (PCS) is a method based on the analysis of the temporal fluctuation of the scattered laser light intensity originating from the Brownian movement of dispersed particles [11, 12]. The intensity of the scattered light strongly depends on the hydrodynamic particle diameter (Z-Ave d) which is an equivalent sphere diameter derived from a measurement technique involving hydrodynamic interaction between the particle and fluid. DLS is very insensitive to small particles in the presence of larger sized particles, which produce the major part of the scattering light intensity. Zeta potential (ζ) is a measure of the magnitude of the repulsion or attraction between particles. An electric field is applied across the dispersed particles, which will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. The frequency shift of an incident laser beam caused by moving particles is measured as the particle mobility which is converted to the zeta potential by the application of mathematical theories. Colloid concentration was determined using a standard series made from MX-80 bentonite and a derived count rate obtained DLS measurements. The count rate is roughly proportional to the concentration of particles and can be used to estimate colloid concentrations. The calibration curve was

constructed by measuring the known concentrations of particles with the same size and shape as the colloids in the samples. Colloid concentration determination was verified by analyzing the aluminum content of montmorillonite using ICP-MS.

Experiments

In the colloid stability experiments, 1 g of MX-80 bentonite powder was weighed in a sample tube and 45 mL of solution was added. The samples were then mixed and left to equilibrate and stored in order to study colloid stability as a function of time. All of the experiments were made in ambient conditions and in triplicate. Samples have been taken from the top of the liquid phase so far for three years. The formation and stability of bentonite colloids was followed by analyzing pH, particle size distribution, particle concentration and zeta potential.

Radionuclide sorption onto bentonite colloids was studied using colloid dispersion solution made from MX-80 bentonite clay powder. Colloid solution was added to the solution spiked with Sr-85 or Eu-152 tracer, 4.7 mL aliquot were taken after 2 h, 1, 2 and 7 days and solid colloid fraction was separated by ultracentrifugation (90000 rpm/60 min). The gamma activity of Sr-85 or Eu-152 was detected from the separated liquid phase using a Wizard gamma counter. Particle size distribution and concentration in the separated liquid phase were determined in order to check the number and size of remaining particles. Sorption was quantified by the determination of the distribution ratio of radionuclide activity between solid and liquid phase.

The flow experiments were performed using a set-up shown in Figure 1. Water was pumped through the fracture of crushed rock column at different flow rates of $5-25 \ \mu L \ min^{-1}$ using a peristaltic pump to control water flow rate. A short tracer pulse ($20 \ \mu L$) was injected into the water flow using an injection loop and the out flowing tracer was collected using a fraction collector.



Fig. 1. The experimental set-up for the fracture and crushed rock column experiments.

The hydraulic properties in the columns were determined using conservative tracer I-125 without colloids. The column experiments were performed in the low salinity Allard reference groundwater, in which the colloids are assumed to be stable and mobile. The transport of Sr-85 or

Eu-152 in the columns was studied without and with bentonite colloids. In the experiments, the injected activity was 3 - 6 kBq. When the potential effect of colloids on the migration of Sr-85 or Eu-152 was studied, the tracer pulse was injected in the bentonite colloid suspension flow.

RESULTS AND DISCUSSION

Colloid Stability

The characteristics of the bentonite colloids were strongly affected by the ionic strength and the valences of the cations in the solution. Formation of bentonite colloids in diluted OLSO reference groundwater as a function of ionic strength (I = 0.001-0.03 M) is shown in Figure 2. A noticeable colloid concentration can be seen only in the most diluted (1 and 5 mM) solutions. A thin layer between bentonite suspension and colloidal fraction is a result of bentonite erosion via gel formation. The size of the bentonite colloids increased strongly as the ionic strength of the solution was increased. In dilute solutions (0.001-0.01 M), the mean particle diameter was less than 500 nm and the colloid size distribution has been rather constant during the following time. In saline solutions, the mean particle size indicated that reversible flocculation or irreversible coagulation had taken place. In the presence of divalent calcium cations, the bentonite colloids were larger and less stable than when there were only monovalent cations present.



Fig. 2. The formation of bentonite colloids in diluted OLSO reference groundwater. Ionic strength from the left 0.001-0.03 M .

Mean zeta potential of released bentonite colloids in OLSO reference groundwater is presented as a function of time in Figure 3. In stable dispersion, all suspended particles have a large negative or positive zeta potential and they will tend to repel each other. The colloidal system is least stable near the isoelectric point where zeta potential is near zero and there is no force to prevent the particles from aggregating. In high salt concentrations, initial aggregation (flocculation) can be reversible and weak flocs may dissociate under an externally applied force such as vigorous agitation. The particles in colloidal dispersion may adhere to one another and form aggregates of successively increasing size that separates out by sedimentation.



Fig. 3. The mean zeta potential of bentonite colloids in diluted OLSO reference groundwater.

High negative zeta potential values indicated the existence of rather stable bentonite colloids. After three years, in dilute solutions, mean zeta potential values were lower than -30 mV, indicating stable colloid dispersion. In more saline solutions, zeta potential values were near zero indicating particle aggregation and instable colloids. There has been no notable change in the stability of colloids during three years.

Radionuclide and Colloid Interaction

Radionuclide sorption onto bentonite colloids was quantified by batch experiments that give a distribution ratio of radionuclide between solid and a liquid phase. A distribution coefficient, K_d (m³ kg⁻¹) was calculated from the equation:

$$\frac{(A_0 - A_L)}{m} \cdot \frac{V}{A_L}$$
(1)

where A_0 is tracer activity, A_L is a measured activity in solution after separation, m is a solid phase mass (g) and V is liquid phase volume (mL). The determined distribution coefficient, K_d (m³ kg⁻¹) values of Sr-85 for bentonite colloids in OLSO reference groundwater are shown as a function of ionic strength in Figure 4. The corresponding K_d values of Eu-152 are shown in Figure 5. Nearly all of Sr-85 and Eu-152 was rapidly sorbed onto bentonite colloids in 0.001 M solutions. Sorption was nearly 100 % and measured radioactivity in a liquid phase was at the background level resulting in inaccurate K_d determination. The distribution coefficient (K_d) decreased when the ionic strength increased. When the ionic strength was low, there was no difference in sorption between sodium chloride and calcium chloride solutions. The obtained results confirmed the influence of ionic strength and Ca²⁺ concentration on the sorption of Sr-85 and Eu-152 onto bentonite colloids. In the case of small colloid concentrations, obtained K_d -values are not based on the equilibrium and are not accurate.



Fig. 4. The distribution coefficient, K_d -values of Sr-85 for bentonite colloids in OLSO reference water.



Fig. 5. The distribution coefficient, K_d -values of Eu-152 for bentonite colloids in OLSO reference water.

In the column experiments, different sorption processes taking place on fracture surfaces can be considered the main factor causing radionuclide retardation. The retardation factor can be estimated from the breakthrough curves of the conservative tracer and the radionuclide when the same experimental conditions have been used. The retardation factor is an approximation, because in the course of column experiment equilibrium between sorbed and dissolved species may not have been attained.

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In the Olkiluoto fracture column and Svvrv altered tonalite crushed rock column, particularly Eu-152 but also Sr-85 was strongly retarded without colloids. In the presence of bentonite colloid suspension, the slow elution of Eu-152 and Sr-85 was obtained. The breakthrough curves of Sr-85 in Olkiluoto tonalite fracture column without and with bentonite colloids are shown in Figure 6. Retardation factor, R_f of 56 was estimated without the presence of colloids at water flow rate of 0.6 mL h⁻¹. In the presence of colloids, R_f of 7.1 was estimated. In the Kuru grey unaltered granite crushed rock column, slight effect of bentonite colloids was found in the breakthrough curves of Sr-85. No breakthrough of Eu-152 activity was detected during two week experiment without the addition of bentonite colloids. Bentonite colloid filtration in a fracture or crushed rock surfaces was observed and the migration of colloids was affected primarily by colloid size but also by the type of column and/or rock alteration. The distribution of radionuclides between mobile colloidal and immobile rock phases determines radionuclide mobility. The main uncertainties remain in the quantification of colloids under realistic repository conditions and how mobile colloids are. If colloids are sufficiently stable and thus mobile, irreversible sorption on silica colloids may increase radionuclide transport. The reversibility or irreversibility of radionuclide-colloid association must be further investigated in a simple system and in repository relevant conditions.



Fig. 6. The breakthrough curves of Sr-85 in Olkiluoto tonalite fracture column without (red) and with (blue) bentonite colloids.

CONCLUSIONS

Stability bentonite colloids released from EBS material bentonite and interaction between radionuclides and colloids have been studied. The release and stability of bentonite colloids depend strongly on the ionic strength of the medium and the valence of the cations. The stability bentonite colloids in dilute solutions did not change substantially during three years. The obtained results confirmed the influence of ionic strength and Ca²⁺ concentration on the sorption of Sr-85 and Eu-152 onto bentonite colloids. Bentonite colloids were observed to have a significant influence on the migration of Sr-85 and Eu-152 in the fracture and crushed rock column experiments. Migration of bentonite colloids in columns was affected primarily by colloid size but

also by water flow rate and column type. The main uncertainties remain in the quantification of colloids under realistic repository conditions and how mobile colloids are. If colloids are sufficiently stable and thus mobile, irreversible sorption on colloids may increase radionuclide transport. The reversibility or irreversibility of radionuclide-colloid association must be further investigated in a simple system and in repository relevant conditions. At current conditions in Olkiluoto, the ionic strength of the groundwater is around 0.5 M and the colloids released from the bentonite barrier are aggregated and unstable do not have an influence on the migration of radionuclides. However, this knowledge and understanding about bentonite erosion in colloidal form can be utilized in the estimation performance of the bentonite barrier. The possibility of a future glacial period and subsequent post-glacial phase when the infiltration of fresh, glacial melt water dilutes groundwater, implies that dilute groundwater conditions cannot be excluded and the influence of bentonite and other colloids has to take into consideration.

REFERENCES

- 1. A. B. Kersting, D. W. Efurd, D. L. Finnegan, D. J. Rokop, D. K. Smith and J. L. Thompson, *Nature* **397**, 56 (1999).
- 2. A. P. Novikov, S. N. Kalmykov, S. Utsunomiya, R. C. Ewing, F. Horreard, A. Merkulov, S. B. Clark, V. V. Tkachev and B. F. Myasoedov, *Science* **314**, 638 (2006).
- 3. R. W. Puls and R. M. Powell, Environ. Sci. Technol. 26, 614 (1992).
- 4. P. Vilks and M. Baik, J. Contam. Hydrol. 47, 197 (2001).
- 5. T. Yamaguchi, S. Nakayama, T. T. Vandergraaf, D. J. Drew and P. Vilks, *J. Power and Energy Systems* **2**, 186 (2008).
- 6. J.N. Ryan and M. Elimelech, M., Colloids Surf A Physicochem Eng Asp. 107, 1-56 (1996).
- 7. U. Vuorinen and H. Hirvonen, Posiva WR–2005–03 (2005).
- 8. M. Takala and P. Manninen, Posiva WR–2006–98 (2006).
- 9. T. Schäfer, F. Huber, H. Seher H, T. Missana, U. Alonso, M. Kumke, S. Eidner, F. Claret and F. Enzmann, *Appl.Geochem.*, **27**(2), 390-403 (2012).
- 10. S. Kumpulainen and L. Kiviranta, Posiva Oy, Working Report 2010-52 (2010).
- 11. Malvern Instruments Ltd., Zetasizer nano series user manual, Issue 1.0, Malvern Instruments Ltd. (United Kingdom,

2003). http://www.malvern.co.uk/LabEng/industry/colloids/colloids_home.htm.

12. M. Filella, J. Zhang, M. E. Newman and J. Buffle, Colloids Surf. A 120, 27 (1997).

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