Study of radionuclides migration through crushed granite in presence of bentonite colloids

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Introduction

- Multibarrier system of deep geological repository (DGR)
  - Engineered and natural barriers

- Bentonite colloids
  - Formation in engineered barrier system of DGR
  - Generation in contact of bentonite barrier with groundwater
  - Direct impact on repository safety
    - Generation of colloids may degrade the engineered barrier
    - Colloidal transport of radionuclides may reduce the efficiency of the natural barrier

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The goals of experiment

- Macroscale investigations on colloid mobility in near-natural systems
  - Study of radionuclide transport in granitic rock
  - Influence of bentonite colloids on radionuclides migration in granite
  - Study of radionuclide, colloid and rock interactions
Experimental background

- Crushed granitic rock $\rightarrow$ simulation of disturbed granite with fissures network

- Bentonite colloids (BC): pure bentonite B75Na$^+$, 400 nm

- Radionuclides
  - $^3$H
  - $^{85}$Sr
  - $^{137}$Cs

- Radiocolloids (RC): $^{85}$Sr-BC, $^{137}$Cs-BC

- Synthetic granitic water (SGW)

- Deionised water (DW)

- Dynamic column experiments
  - Breakthrough curves: transport parameters $K_d$, $R$

- The simplified system of:
  - Cationic radionuclides
  - Crushed granite $\rightarrow$ simulation of disturbed granite (fissure network)
$^{85}\text{Sr}$-bentonite colloids-granite

$^{3}\text{H}$: Conservative tracer, non-sorbing behavior

BC: Conservative tracer, non-sorbing behavior

$^{85}\text{Sr}$ (SGW): Sorption in granite, $K_d = 6.5 \text{ ml/g}$

$^{85}\text{Sr}$ (RC): Influence of colloids presence, $K_d = 56.2 \text{ ml/g}$

$^{85}\text{Sr}$ (DW): Significant sorption, slow transport, $K_d = 210.9 \text{ ml/g}$

B75 (RC): Slight delay in granite
Transport of colloids was fast and comparable with $^3$H transport.

Sr transport in SGW was significantly faster than Sr transport in DW.

After injection of radiocolloids, bentonite colloids without Sr appeared first followed by Sr much more later.

Sr transport through granite in presence of bentonite colloids in DW was faster than Sr transport in DW.

Colloids migration in presence of Sr was slightly slower than transport without Sr presence.
$^{137}$Cs-bentonite colloids-granite

- **$^{3}$H**: Conservative tracer, non-sorbing behavior
- **BC**: Conservative tracer, non-sorbing behavior
- **$^{137}$Cs (SGW)**: Sorption in granite, $K_d = 24.2$ ml/g
- **$^{137}$Cs (DW)**: Significant sorption, slow transport, $K_d = 66$ ml/g
- **$^{137}$Cs (RC)**: Influence of colloids presence, $K_d = 81.2$ ml/g

$n_{PV}$ vs. $c_{rel}/A_{rel}$
137Cs-bentonite colloids-granite

- Transport of colloids was fast and comparable with ³H transport.

- Cs transport in SGW was significantly faster than Cs transport in DW.

- After injection of radiocolloids, bentonite colloids with small part of Cs appeared first followed by Cs much more later.

- Part of Cs passed through granite with bentonite colloids, the most of is sorbed.

- Cs transport through granite in presence of bentonite colloids in DW was not same as Cs transport in DW.
**$^{137}$Cs-bentonite colloids-granite**  

**$^{85}$Sr-bentonite colloids-granite**

- Different behavior of Cs and Sr, even though they are cationic, sorbing RN.

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![Graphs showing different behavior of $^{137}$Cs and $^{85}$Sr](image)
Sorption of cesium
Bentonite structure:
  • **Layer sites** – permanent negative charge \(\rightarrow\) cation sorption, weak bond of cesium \(\rightarrow\) desorption of cesium from bentonite and follow sorption on granite.
  • **Freyed edge sites (FES)** – surface complexation, less available but highly selective sites \(\rightarrow\) strong bond of cesium.

Sorption of strontium
  • Sorption by ion-exchange
  • Divalent ion \(\rightarrow\) large hydration energy \(\rightarrow\) the freyed edge sites are not accessible for \(\text{Sr}^{2+}\).

\[ ^{85}\text{Sr} \text{ is reversible sorbed on bentonite colloids by ion-exchange.} \]

The minor part of \(^{137}\text{Cs} \text{ is strongly sorbed on freyed edge site and passed through granite with colloids.} \]

Most cesium was desorbed from **layer sites** of montmorillonite on granite.
Different mechanism of Cs and Sr sorption on colloid particles

**Sorption of cesium**

**Bentonite structure:**

- **Layer sites** – permanent negative charge → cation sorption, weak bond of cesium → desorption of cesium from bentonite and follow sorption on granite.

- **Freyed edge sites** – surface complexation, less available but highly selective sites → strong bond of cesium.

<table>
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<th>Days</th>
<th>Activity at column outlet</th>
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<td></td>
<td>A (CPM)</td>
<td>A (%) (liquid phase)</td>
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<td>8</td>
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<td>30</td>
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</table>

![Graph showing sorption of cesium and strontium over time]
Conclusions
Colloid mobility controlling processes
Clay colloids as radionuclide (RN) carriers?
Is there an upper bound for colloids-mediated transport?

- RN transport through granite in presence of bentonite colloids was faster than RN transport in distilled water without presence of bentonite colloids.
  - Colloids carried RN further in column with earlier breakthrough.

- Influence of liquid phase composition
  - RN transport in SGW is significantly faster than RN transport in distilled water.
  - Competition of other ions with RN at sorption sites.

[Graphical representation of data]
Retention processes
Can retardation of colloids in the far field cause the delay of RN arrival in biosphere?

- The colloids migration in presence of RN was slightly slower than transport without presence of RN.
- The delay of RN caused by retardation of colloids in granite was not observed.
- On the contrary, the colloid particles speed up the RN transport in granite.
Radionuclide sorption
Equilibrium sorption of radionuclides (RN) onto mobile colloids.
Reversible sorption of radionuclides on colloids?

• The sorption of RN onto mobile colloids was confirmed.
  • Time of equilibration: 7 days
  • V (colloids) : V (RN) = 1:1
  • Separation of phases: centrifugation

• Sr-colloids: 80% of $^{85}\text{Sr}$ was sorbed on bentonite colloids
• Cs-colloids: 75% of $^{137}\text{Cs}$ was sorbed on bentonite colloids

• Reversible sorption: The RN affinity towards the granite was higher than toward the bentonite colloids.
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References