Adsorption of Uranium(VI) on the MX-80 Bentonite

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Abstract

In present work, a coupled model of groundwater flow, thermal transport, and geochemical transport through saturated-unsaturated media, HYDROGEOCHEM, has been employing to simulate the uranium adsorption on the MX-80 bentonite. The numerical experiments were performed with different sodium and hydrogen concentrations. Uranium concentrations were kept below 10^{-7} mol/L to avoid precipitation of amorphous uranium-hydroxide. Adsorption of uranium on the bentonite shows significant dependency on sodium concentration, because of the competition between uranium and sodium ions. The numerical simulations of uranium transport in the MX-80 bentonite have also been proposed with deep groundwater condition. The simulation shows that the retention capacity of MX-80 bentonite and also demonstrate the capacity of HYDROIGEOCHEM model for simulation radionuclide migration in the near-field system.

1. Introduction

Radionuclide transport simulation is one of most import procedure for the safety assessment of spent nuclear fuel final disposal. How to calculate the release, transport and dose consequences of radionuclide for different scenarios and cases is a major topic for the procedure of safety assessment analysis.

The multi-barrier engineering system concept is one of the most popular design concepts for spent nuclear fuel disposal [3]. There are two major safety functions to prevent the release of radionuclide for multi-barrier engineering system. First is hydraulic function and chemical function is second safety function. Hydraulic function and chemical function are reducing the groundwater contact the canister and increasing the radionuclide retardation of the engineering barrier, respectively.

Bentonite is a material with high porosity and low hydraulic conductivity behavior and now in widespread use in spent fuel disposal for preventing the groundwater flow into the disposal. Furthermore, the bentonite also provides the capacity for retaining the nuclide [7, 12, 13]. Sorption is an important retention mechanism to control the concentration of contaminants in groundwater [12]. However, the capacity of sorption is close related with aqueous solution properties and characteristics of sorbing materials [13]. The surface complexation was an important mechanism for uranium sorption on the smectite.[7, 29]

In present work, a hydro-geo-chemical numerical model (HYDROGEOCHEM) has been adapted to study the adsorption of uranium(VI) on the MX-80 bentonite and a pseudo case is conducted to demonstrate the capacity of HYDROGEOCHEM model.

2. Bentonite material

Bentonite is a geological term for soil materials with a high content of a swelling mineral, which usually is montmorillonite [24]. In present work, the reference bentonite MX-80 was conducted to study.

2.1 Mineralogy

The chemical characterization of bentonite clay differs slightly, between different modeling studies, most due to the employed of different databases [3, 5, 8, 9, 25, 27]. These reports agree on primary prevalence minerals are quartz and calcite, apart from montmorillonite. The residual constituents, such as albite, analcime, chalcedony, cristobalite, gypsum, halite, illite, K-feldspar differs slightly but has less influence on the overall chemical stability.

In present work, the mineralogical composition of bentonite MX-80 [16] has been present in table 1. MX-80 is mainly composed of montmorillonite-Na

(90%), Quartz (7.63%) and Calcite (1.04%). Others have less influence on the overall chemical stability.

2.2 Transport parameters

The condition of bentonite is according to SKB-3V setup [21] which surrounds the canister. The dry densities and saturated density are 1,577 kg/m^3 and 2,000 kg/m^3, respectively. The porosity corresponding to the saturated density 2,000 kg/m^3 is 0.435 [23]. The diffusion coefficient is 1.4×10^{-10} m^2/s [23]. The hydrodynamic parameters are listed in table 2. In this work, we do not consider the permeability of bentonite and the migration is controlled by the diffusion mechanism.

Table 1. Composition of bentonite MX-80

Mineral Phases	Volume (%)
Montmorillonite-Na	90.00
Quartz	7.63
Clacite	1.04
Phillipsite-Na	0.99
Illite	0.19
Saponite-Ca	0.12
Magnetite	0.02

Table 2. Various transport parameters

Parameter	Value
Dry Density (kg/m^3)	1577
Porosity (%)	43.5
Diffusion Coefficient (m^2/s)	1.4×10^{-10}
Tortuosity	1.0

2.3 Surface Complexation Reactions

For the modeling of uranium (VI) adsorb on the smectites, the surface complexation reactions are required. A multisite layer surface complexation model was developed by Zachara and Mckinley[29] to describe the uranium sorption by smectites. Their model is composed of pH independent exchange (X$^-$) sites and hydroxylated edge sites for SiOH and AlOH. Samer and Broder [7] propose that sorption of uranium on the selected smectites preferentially occur to the edge site of aluminol and silanol, even under acidic condition. This assumption is also based on the relatively high Na$^+$ concentration (0.01 and 0.025 mol/L) in comparison to very low uranium concentration (100 μg/L) in the solution.

In this study, surface complexation reactions on the smectites are based on the Samer and Broder [7] as shown in table 3. They used the non-linear least squares parameter estimation program PEST [2] in conjunction with PHAST [11] to determine the equilibrium constants of these sorption reactions. Sodium sorption was also incorporated in table 3

since the sodium was proven to sorb onto clay minerals [26].

The thermodynamic database thermoddem V1.10 [1] was employed as the reference thermodynamic database in the model calculations.

Table 3. Surface reactions and parameters used in the model calculations

Surface Reactions	Log K
$SiOH + H^+ \rightleftarrows SiOH_2^+$	-0.95
$SiOH \rightleftarrows SiO^- + H^+$	-6.95
$SiOH + UO_2^{2+} \rightleftarrows SiOUO_2^+ + H^+$	4.06
$SiOH + UO_2OH^+ \rightleftarrows SiOUO_2OH + H^+$	1.00
$SiOH + UO_2(OH)_3^- \rightleftarrows SiOH(UO_2)(OH)_3^-$	6.90
$SiOH + Na^+ \rightleftarrows SiONa + H^+$	-2.71
$SiOH + UO_2^{2+} + 3CO_3^{2-} \rightleftarrows SiO(UO_2)(CO_3)_3^{5-} + H^+$	6.65
$AlOH + H^+ \rightleftarrows AlOH_2^+$	12.30
$AlOH \rightleftarrows AlO^- + H^+$	-13.16
$AlOH + UO_2^{2+} \rightleftarrows AlOUO_2^+ + H^+$	7.51
$AlOH + Na^+ \rightleftarrows AlONa + H^+$	15.00
$AlOH + 2\,UO_2^{2+} + CO_3^{2-} + 3H_2O \rightleftarrows AlO(UO_2)_2(CO_3)(OH)_3^{2-} + 4H^+$	0.99

SiOH: silanol surface at edge sites, AlOH: aluminol surface at edge sites.

3. Numerical model

The computer program HYDROGEOCHEM was employed to model the radionuclide transport and hydrogeochemical reactions in this study. The HYDROGEOCHEM 4.1 and 5.1 [28] are two-dimensional and three-dimensional coupled model of water flow, thermal transport, solute transport, and geochemical kinetic/equilibrium reactions in saturated-unsaturated porous media, respectively.

HYDROGEOCHEM 4.1 and 5.1 iteratively solve two- and three-dimensional fluid flow, thermal transport, and reactive chemical transport equations. Richards' equation is solved for fluid flow, thermal transport equation is solved for temperature distribution, and advection-dispersion-reactive transport equations are solved for all mobile components and kinetic-variables in a two-step method or for all components and kinetic variables in a one-step method. The subsidence is calculated based on one-dimensional linear elasticity theory.

HYDROGEOCHEM 4.1 and 5.1 is designed for generic applications to reactive transport problems controlled by both kinetic and equilibrium reactions in subsurface media. The input to the program

includes the geometry of the system, the spatial distribution of finite elements and nodes, the properties of the media, reaction network, and the initial and boundary conditions. Output includes the spatial distribution of pressure head, total head, velocity fields, moisture contents, temperature, and chemical concentrations as a function of time as well as the distribution of all chemical species at user-specified nodes. Subsidence for the overall region is also calculated.

HYDROGEOCHEM 4.1 and 5.1 are the comprehensive simulators of coupled fluid flow, hydrologic transport, thermal transfer, and biogeochemical transport under variably saturated conditions in two dimensions and three dimensions, respectively.
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4. Results and discussion

4.1 Effect of pH and Na+ concentration on Uranium Sorption

The purpose of this section is to understand the sorption behavior of the present MX-80 bentonite reaction model under different pH and Na^+ concentration condition. Here, the experiment procedure [7] was used for the comparison. The numerical experiments were carried out by reacting 1.67g of MX-80 bentonite and 1 liter of 10^{-7} mol/L uranium(VI) solution with 0, 10^{-3}, 10^{-2}, 10^{-1} mol/L NaCl and the pH value is range from 4 to 9. The uranium concentration 10^{-7} mol/L was chosen to avoid the precipitation of amorphous uranium-hydroxides. Here we define an equation to describe the capability of sorption on the MX-80 bentonite. The percentage of the sorbed uranium was calculated from the difference between the initial and final uranium concentration. The equation is as following,

$$Sorption(\%) = \left(\frac{c_i - c_f}{c_i}\right) \times 100\% \qquad (Eq. 1)$$

Where c_i and c_f are the uranium concentrations in the initial and final solutions, respectively.

The effect of pH and Na^+ concentration on the uranium sorption behavior onto the MX-80 bentonite is illustrated in Figure 1. The high sorption ability was observed at pH 4 even though the high Na^+ concentration that has competition with adsorption edge sites. In the pH range 6 to 9, a distinct reduced uranium sorption on MX-80 bentonite at higher pH. It shows that the uranium sorption decreases rapidly with increasing Na^+ concentration. When pH larger than 8, the uranium sorption gets close to 45% ~ 50% gradually. These results do agree with the research by

Samer and Broder [7]. They also found high sorption capability at pH 4 and reduced uranium sorption on smectites in the pH range 6 to 9. Higher pH is related to the low affinity of uranium carbonate complexes to the surface sites of clay minerals or to competition between carbonate ions and uranium species.
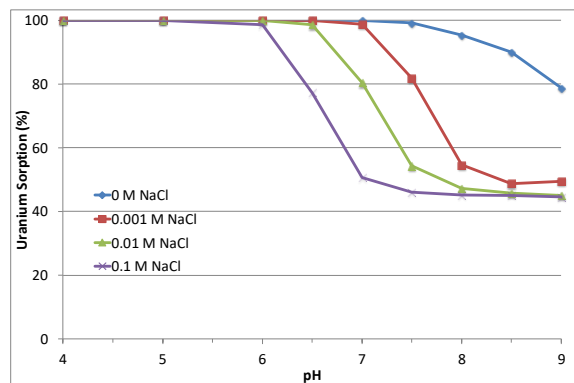

Figure 1. Comparison between different pH and Na^+ concentration data for uranium(VI) sorption onto the MX-80 bentonite.

4.2 Near-field transport simulation

In the framework of the spent fuel disposal safety assessment, a conceptual and numerical modeling of radionuclide reactive transport in the near-surface system [17, 18, 20] and the long-term performance of engineering barrier [14, 15, 16, 25] have been carrying out. These reports use the geochemical program PHREEQC [10] and PHAST [11] to solver reactive chemistry and reactive transport problems, respectively. In this section, a three-dimensional hydro-geo-thermo-chemical couple model, HYDROGEOCHEM, has used for solving the radionuclide transport in the near-field engineering barrier base on the SKB-3V concept [19] as shown in figure 2(a). In this concept, canister and buffer are two major components in this design. The canister is surrounding by the buffer material, here the buffer material is MX-80 bentonite. The detailed geometric parameters are presented in table 4.

The scenario is this single canister failure due to the shear force applies on the canister and makes damage. We assume an incline fracture across the system and conduct a 1.0 cm thickness crack on the canister and only diffusion process is considered in the present simulation according to the low permeability property of MX-80 bentonite. Because of the diffusion mechanism dominate the radionuclide migration, the computational domain is limited with 2.0 m of height for better computational efficiency. The three dimension computation domain is illustrated in figure 2(b).

The dissolution rate and solubility limit of uranium in spent fuel are 10^{-7} 1/yr and 9.5×10^{-10} mol/L [22],

respectively. Besides, the inventory of uranium in mole per canister is 7,200 mol/canister. The selected groundwater [20] in present work was deep groundwater (underground 300 m) which is the Na-Cl type with moderate salinity. The groundwater composition is reported in table 5.

The spatial discretization of the computational domain was shown in figure 3(a). There are total 73,359 tetrahedron elements and 16,622 nodes to describe the computational domain. In order to get a good approximation, the crack of the canister has been used fine grids to describe the geometry (see figure 3(b)).
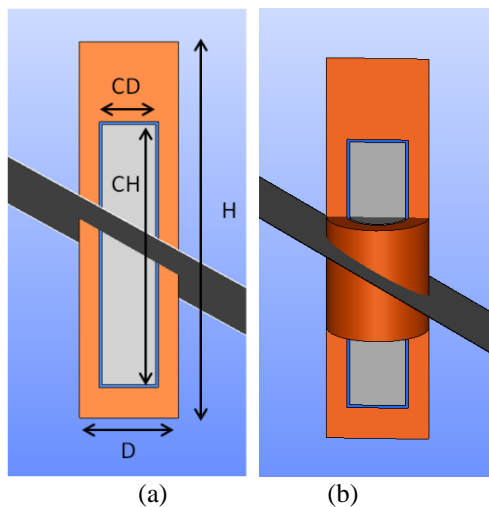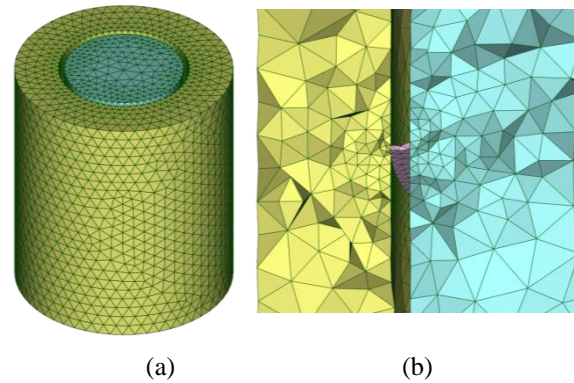

(a)   (b)
Figure 3. The computational grid for radionuclide migration simulation. (a) the full domain, (b) zoom in view at the crack position of canister.

(a)   (b)
Figure 2. Sketch of simulation case.

Table 4. The geometric parameters.

Parameter	Value
Height of the canister (CH)	4.835 m
Diameter of the canister (CD)	1.05 m
Height of disposition hole (H)	6.835 m
Diameter of disposition hole (D)	1.75 m
Void inside canister	1.0 m^3
Thickness of canister wall	0.05 m

Table 5. Chemistry of the selected groundwater.

Species	Value (mol/L)
Na$^+$	6.13x10^{-2}
K$^+$	7.98x10^{-4}
Ca^{++}	1.82x10^{-2}
Mg^{++}	4.73x10^{-3}
HCO3$^-$	4.72x10^{-3}
Cl$^-$	1.04x10^{-1}
SO4^{--}	2.21x10^{-3}
H4SiO4	5.63x10^{-4}
Fe	5.78x10^{-5}
pH	7.6

The figure 4 and figure 5 show the uranium(VI) concentration in the solution and on the sorption site at the simulation time 500 year, respectively. The high uranium(VI) concentration is observed near the crack position of the canister, then the concentration decreases rapidly due to the sorption reaction. This phenomenon also observed in figure 5. Higher uranium(VI) concentration in solution will result in high uranium(VI) concentration sorbed on the solid surface. Because of the migration is dominated by the diffusion mechanism, therefore the uranium(VI) migrate uniformly in space.

In the previous section, the Eq. 1 has been used for calculating the percentage of sorption. Here, the solid/liquid partition coefficient (KD) is proposed to define the concentration of uranium(VI) in the solid phase over its concentration in pore water. Since the concentration of uranium(VI) in figure 4 and figure 5 are reported as mole per liter water, but the concentration of uranium(VI) on the sorption site need to be converted to mole per kilogram of rock in order to determine the KD value. For this calculation, we need the porosity and the density of bulk rock. According to table 2, the porosity of MX-80 bentonite is 0.435 and the density is 1577 kg/m^3. The calculation of KD is shown as following,

$$KD = \frac{[Sorbed]mol/L}{[Solute]mol/L} \times \frac{0.435}{1.557kg/L} \qquad \text{(Eq. 2)}$$

The distribution of KD at the simulation time 500 year is illustrated in figure 6. The result shows well retention capability of MX-80 bentonite for uranium(VI). We can observe that the KD value near the crack position is lower than the average. Because of the uranium is continued release from the canister and the free edge site in the bentonite will decrease gradually. Therefore, in the beginning, the KD value can be approached 1.2x10^5 L/kg and reducing to 10^4 L/kg at the simulation time 500 year.

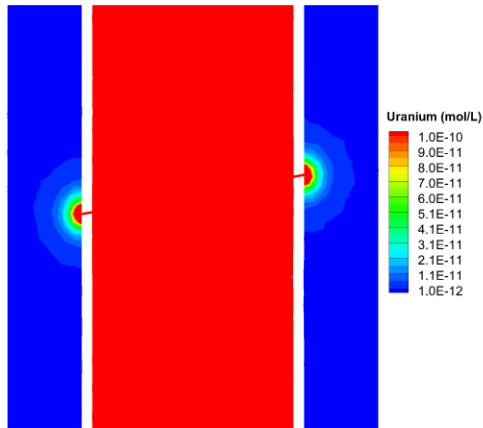Figure 4. The distribution concentration contour of uranium in solution at x=0 plane.

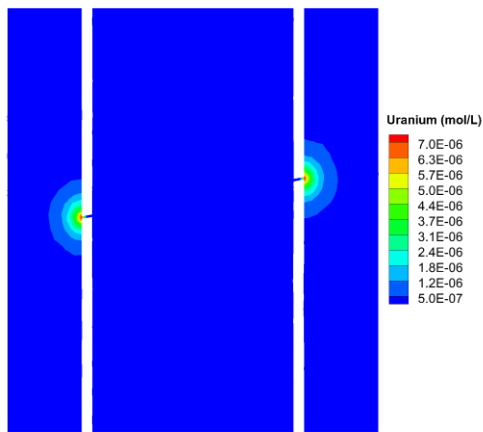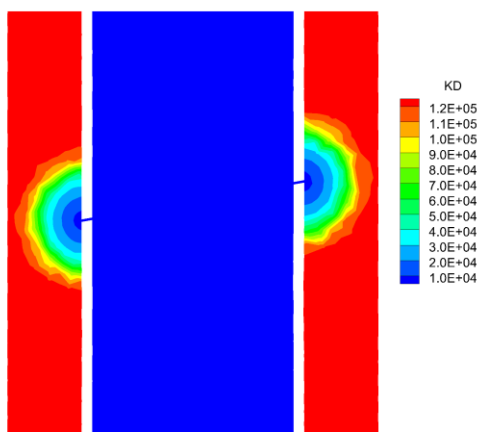Figure 5. The distribution concentration contour of uranium on sorption site at x=0 plane

Figure 6. The distribution contour of KD value for uranium at x=0 plane.

5. Conclusion

A geochemical numerical model of MX-80 bentonite with uranium surface complexation reaction has been proposed in present work. Furthermore, batch numerical experiments with different NaCl concentration and a simplify KBS-3V type repository case implement in the present numerical model.

Batch experiments clearly showed that the much higher uranium sorption capability in the pH range 4 to 6 and rapidly reduce in the pH range 6 to 9. Higher Na^+ concentration will result in lower sorption capability.

The established reactive model also implement to a KBS-3V type case. In this case, a shear force causes the failure of the canister, and only diffusion mechanism is assumed to control the migration of uranium(VI). The results demonstrated that the HGC model has the capacity to modeling the uranium reactive transport in the near-field and calculate the retention capacity of the buffer system.

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