Effect of Different Ions on Bentonite Minerals

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Abstract. Bentonite is widely used as backfill material for radioactive waste disposal as a natural mineral with high efficiency, stability and low cost. Since the safety evaluation time system of radioactive waste repositories lasts for ten thousand years, the mineral evolution of bentonite after ten thousand years and its effects on the adsorption and retardation properties of Pu are the key points of attention. In this paper, the mineral composition and porosity change of Ke Er Jian bentonite with five Na+/Ca2+/Al3+/K+/Mg2+ ion species in ten thousand year scale were simulated by PHREEQC(3.0) software, the changes of bentonite minerals and their effects on the adsorption properties of nuclide Pu were discussed from two aspects of groundwater transport distance and interaction time, which provided important reference for the safety evaluation of waste disposal.

1. Introduction
With the vigorous development of the world economy and society, the exhaustion of coal and petroleum energy has prompted human beings to develop and utilize nuclear energy to solve this problem. At the same time, people will produce a large number of spent fuels while developing nuclear energy. These spent fuels contain a large number of high-level radioactive wastes, which are highly toxic and have a long half-life. Therefore, the safe disposal of high-level radioactive waste has become a key issue affecting the human living environment and the sustainable development of nuclear energy.

For waste disposal schemes, the commonly used method both here and abroad is to bury radioactive wastes into deeper geological structures [1, 2], use multi-layer barrier system, store wastes in waste tanks, and wrap them with buffer backfilling materials. In the selection of buffer backfilling materials, it is generally believed that bentonite is the best material for nuclide retardation and adsorption. At present, a large number of studies [3-7] have reported the mineral stability and chemical properties [8] of Gao Miao Zi bentonite, while few studies have been done on the Ke Er Jian bentonite. In this study, geochemical software PHREEQC (3.0) was used to simulate the change of mineral composition and the effect on the adsorption retardation of nuclide Pu of Ke Er Jian bentonite under different ion species.

2. Simulated research method
Based on the thermodynamic equilibrium principle, the interaction between water and Ke Er Jian bentonite was studied. The dissolution/precipitation of minerals, ion exchange, surface complexation and dynamic dissolution rate of montmorillonite were considered in the reaction process. The whole simulation study adopts pore water “Flushing” model [9], and the database used in the simulation...
process is LLNL.dat. The length of Ke Er Jian bentonite mineral is set to 1m, which is consistent with the thickness of bentonite mineral used in previous works. Then the bentonite minerals are divided into ten small units with 0.1m. The initial infiltration water (table 3) flows from cell 1 and continuously replaces pore water in the next cell (figure 1). Various reactions of water-rock interaction occur during the process of continuous replacement (figure 2).

![Figure 1](image1.png)

**Figure 1.** Configuration chart of infiltration water passing through Ke Er Jian Bentonite.

![Figure 2](image2.png)

**Figure 2.** Simulation study on the reaction process of water-bentonite interaction.

3. **Input data**

Kinetic dissolution rate [10] of montmorillonite minerals:

\[
\text{Rate} = [10^{-12.30} (a_{\text{H}})^{0.40} + 10^{-14.37} (a_{\text{OH}})^{-0.27}] \text{mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}
\]  

(1)
Table 1. Mineral composition of Ke Er Jian bentonite.

| Minerals         | wt% |
|------------------|-----|
| Quartz           | 49.6|
| Calcite          | 9.2 |
| Kaolinite        | 4.9 |
| Hematite         | 6.1 |
| Gypsum           | 4.9 |
| K-feldspar       | 5.9 |
| Albite           | 5.5 |
| Mont-Na          | 10.3|
| Mont-Ca          | 3.7 |

Table 2. Thermodynamic constants of secondary minerals.

| Mineral Phases       | Reactions                                                                 | logK  |
|----------------------|---------------------------------------------------------------------------|-------|
| Gypsum               | CaSO₄·2H₂O = Ca²⁺ + SO₄²⁻ + 2H₂O                                           | -4.4823|
| Calcite              | CaCO₃ + H⁺ = Ca²⁺ + HCO₃⁻                                                | 1.8487|
| Mont-Na              | Na₀.₃₅Mg₀.₃₃Al₀.₆₇Si₀.₆₇O₁₀(OH)₂ + 6H⁺ = 0.33Mg²⁺ + 0.33Na⁺ + 1.67Al³⁺ + 4H₂O + 4SiO₂ | 2.4844|
| Gismondite           | Ca₂Al₄Si₂O₁₀·9H₂O + 16 H⁺ = 2Ca²⁺ + 4Al³⁺ + 4SiO₂ + 17H₂O                  | 41.717|
| Dolomite-ord         | CaMg(CO₃)₂ + 2H⁺ = Ca²⁺ + Mg²⁺ + 2HCO₃⁻                                   | 2.5135|
| Hematite             | Fe₂O₃ + 6H⁺ = 2Fe³⁺ + 3H₂O                                               | 0.1080|
| Mesolite             | Na₀.₆₇Ca₀.₃₃Al₁₆Si₃₄O₁₀·2.₆₄7H₂O + 7.₉₆H⁺ = 0.₆₅7Ca²⁺ + 0.₆₇₆Na⁺ + 1.₉₉Al³⁺ + 3.₃₁O₂ + 6.₆₂H₂O | 13.6191|
| Gyrolite             | Ca₃SiO₇(OH)₂·1.₅H₂O + 4H⁺ = 2Ca²⁺ + 3SiO₂ + 4.₅H₂O                         | 22.9099|
| Diaspore             | Al₂O₃ + 3H⁺ = Al³⁺ + 2H₂O                                                | 7.1603|
| Beidellite-Ca        | Ca₁₆₂Si₁₆₃O₁₆(OH)₀·₁₆H₂O + 7.₃₂H⁺ = 0.₁₆₅Ca²⁺ + 2.₃₃Al³⁺ + 3.₆₇SiO₂ + 4.₆₆₆H₂O | 5.₉₅₀₀|
| Beidellite-Na        | Na₃₃Al₁₂₃Si₆₃O₁₀(OR)₀·₁₆H₂O + 7.₃₂H⁺ = 0.₃₃Na⁺ + 2.₃₃Al³⁺ + 3.₆₇SiO₂ + 4.₆₆₆H₂O | 5.₆₅₀₀|
| Saponite-Ca          | Ca₁₆₃Mg₁₆₂Si₁₆₃O₁₀(OR)₀·₁₆H₂O + 7.₃₂H⁺ = 0.₁₆₅Ca²⁺ + 0.₃₃Al³⁺ + 3.₆₇SiO₂ + 4.₆₆₆H₂O | 26.₂₉₀₀|
| Saponite-Mg          | Mg₃₃Al₁₆₂Si₁₆₃O₁₀(OR)₀·₁₆H₂O + 7.₃₂H⁺ = 0.₃₃Al³⁺ + 3.₆₇₆Mg²⁺ + 3.₆₇SiO₂ + 4.₆₆₆H₂O | 26.₂₅₂₃|
| Illite               | K₀.₆₈Mg₀.₂₅Al₀.₈₈Si₃₅O₁₀(OR)₀·₁₆H₂O + 8H⁺ = 0.₂₅₆Mg²⁺ + 0.₆₆K⁺ + 2.₃₃Al³⁺ + 3.₅₆SiO₂ + 5H₂O | 9.₀₂₆₅|
| Brucite              | Mg(OH)₂ + 2H⁺ = Mg²⁺ + 2H₂O                                              | 1₆.₂₉₈₀|
| Maximum microcline   | KAl₅Si₃O₁₀ + 4H⁺ = Al³⁺ + K⁺ + 2H₂O + 3SiO₂                               | -0.₂₇₅₃|
| Stilbite             | Ca₀.₁₅Na₁₃₅K₀.₆₆₈₂₁₈Si₆₈₂₈O₁₈·7.₃₃H₂O + 8.₇₂H⁺ = 0.₀₀₆K⁺ + 0.₁₃₆Na⁺ + 1.₀₁₉Ca²⁺ + 2.₁₈Al³⁺ + 6.₈₂SiO₂ + 1₁.₆₉₆H₂O | 1.₀₅₄₉|
| Talc                 | Mg₃SiO₁₀(OH)₂·6H⁺ = 3Mg²⁺ + 4H⁺ + 4SiO₂                                 | 2₁.₁₃₈₃|
| Muscovite            | KAl₅Si₃O₁₀(OH)₂·10H⁺ = K⁺ + 3Al³⁺ + 3SiO₂ + 6H₂O                          | 1₃.₅₈₅₈|

Table 3. Chemical parameters of five initial solutions (0.04mol/L).

| T(°C) | pH   | Na⁺(mg/L) | K⁺(mg/L) | Mg²⁺(mg/L) | Ca²⁺(mg/L) | Al³⁺(mg/L) |
|-------|------|-----------|----------|------------|------------|------------|
| 11.8  | 12.6 | 920       | 1560     | 960        | 1600       | 1080       |
4. Results and Discussion

In the process of interaction between groundwater and Ke Er Jian bentonite, the dissolution/precipitation of minerals is the main reaction to be considered. Figure 3 shows the changes of mineral composition of the whole bentonite mineral with the continuous inflow of infiltration water. The flow direction of infiltration water is from left to right (figure 1). From the five figures above, it can be seen that quartz in leftmost cell 1 and 2 dissolves seriously, and a large number of silicate ions will be produced, the initial infiltration water entering from cell 1 will carry a large amount of Na⁺/Ca²⁺/Al³⁺/K⁺/Mg²⁺, and form new minerals with dissolved silicate ions. After that, the dissolution of quartz minerals in cell 3-10 becomes slower. Figure 3b shows that a large number of calcium ions influx into cell 1, which results in the formation of gyrolite at the front of bentonite, with infiltration water continuously entering the depth of bentonite, calcium ions and silicate ions are not excessive compared with cell 1, thus producing beidellite-Ca. Similarly, in the presence of large amounts of Al³⁺, the minerals originally formed are those with a large proportion of aluminium, such as stilbite, mesolite, gismondine, diaspore and so on. For the initial infiltration water carrying a large amount of Mg²⁺ ions, saponite-Mg will be formed at the front of bentonite, when the concentration of Mg²⁺ in bentonite decreases slowly, beidellite-Ca, dolomite-ord and illite will be formed.

Figure 3. Change of minerals in Ke Er Jian bentonite by initial infiltration water of 0.04M (a) NaOH, (b) Ca(OH)₂, (c) Al(OH)₃, (d) KOH, (e) Mg(OH)₂.
Figure 4 shows the change of mineral composition of Ke Er Jian bentonite with the increase of reaction time. It can be seen that the change of composition of montmorillonite minerals (Mont-Na and Mont-Ca) are not obvious, which also proves the stability of montmorillonite minerals. Comparing the changes of mineral composition by five different ions, it is found that the change of mineral composition by Al$^{3+}$ is obvious, in figure 4c, quartz (SiO$_2$) was consumed completely around 2000 year, Al$^{3+}$ ions combine with silicate ions that were generated from quartz to form new minerals, such as stilbite, gismondine, mesolite and beidellite, with the prolongation of reaction time, a large amount of precipitation of stilbite leads to the consumption of Na$^+$, which leads to the formation of a series of minerals (mesolite, gismondine, diaspor, etc.). In figure 4b, when Ca$^{2+}$ ions enter bentonite continuously with infiltration water, it is easier to form gyrolite and stilbite, and with the dissolution of quartz minerals, the consumption of Na$^+$ ions eventually leads to the increasing content of gyrolite. Similarly, in figure 4d, when K$^+$ ions are abundant, maximum_microcline is the main mineral. In figure 4e, in the presence of Mg$^{2+}$ ions, it is easier to form saponite-Ca and saponite-Mg, while in the first thousand years, some illite was formed. Compared with the influence of five different ions on minerals, illite is obviously formed in the presence of Mg$^{2+}$ because the contents of K$^+$ and Mg$^{2+}$ are abundant and illite (K$_{0.6}$Mg$_{0.25}$Al$_{1.8}$Si$_{3.5}$O$_{10}$(OH)$_2$) is easy to form. After that, with the reaction time prolonged and infiltration water continuously supplemented, the concentration of Mg$^{2+}$ ions increased. According to the thermodynamic equilibrium equation, it is very beneficial to the formation of saponite. Therefore, saponite-Ca and saponite-Mg dominate for thousands of years.

![Figure 4. Changes of mineral composition of bentonite with time increasing. (a) NaOH, (b) Ca(OH)$_2$, (c) Al(OH)$_3$, (d) KOH, (e) Mg(OH)$_2$.](image-url)
5. Conclusion
From the above discussion, bentonite minerals will produce zeolite, illite, saponite and other minerals with similar structure under the influence of different ions, these minerals have little effect on the adsorption and retardation of nuclide Pu. Therefore, in general, bentonite minerals will produce different secondary minerals with different ions in 10,000 years reaction time, while montmorillonite in bentonite still maintains good stability and adsorption retardation of Pu.

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