# Changes in Sorption Properties of Copper Exchanged Bentonite

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## 1. Introduction

Bentonite considered a buffer material to hold the release of radionuclides from canisters containing radioactive waste owing to its high swelling pressure and high sorption capacity for cationic radionuclides. It is generally known that the sorption of radionuclides onto mineral surfaces is a main retardation mechanism of radionuclide migration in a deep geological environment[1]. The sorption of radionuclides is highly affected by various geochemical conditions such as pH, redox potential, dissolved carbonate, ionic strength, dissolved organic matter, and the concentration of radionuclides. In a deep geological environment, $Cu^{2+}$ can corroded and dissolved from a canister into a bentonite-groundwater interface, which can exchange with cations such as $Na^+$ and $Ca^{2+}$ located between the interlayers of bentonite.

Uranium is one of the important actinides in the nuclear fuel cycle because it exists as a source material for nuclear fuels, and finally results in radioactive wastes. The migration of U(VI) in a deep geological disposal environment is highly influenced by sorption by a clay or engineered barrier system (EBS). Hence the understanding of the sorption behavior of U(VI) onto bentonite is an important aspect to understand the migration behavior of U(VI) in a deep geological disposal system. An exchange of $Cu^{2+}$ with cations within the bentonite interlayers can induce changes in the physicochemical properties of bentonite. Consequently, $Cu^{2+}$-exchanged bentonite can show quite different sorption behaviors from the raw bentonite.

In this work, we prepared Cu2+-exchanged bentonite and batch type sorption experiments were also conducted to compare the sorption behaviors of U(VI) onto the raw and $Cu^{2+}$ treated bentonite.

## 2. Methods and Results

### 2.1 Materials and Method

$CuCl_2$, $NaClO_4 \cdot H_2O$, $HClO_4$, $NaOH$, and $UO_2(NO_3)_2 \cdot 6H_2O$ were used for preparing $Cu^{2+}$-exchanged bentonite and sorption experiments. Kyungju bentonite used for this study is Ca-type obtained from Bolclay Korea Ltd. (Korea). The chemical composition of Kyungju bentonite was as follows (wt. %); $SiO_2$-63.25, $Al_2O_3$-17.08, $Fe_2O_3$-3.60, CaO-3.00, MgO-2.96, $K_2O$-0.89, $Na_2O$-2.27, $TiO_2$-0.36, ignition loss-6.38. The cation exchange capacity (CEC) of Kyungju

bentonite is 57.6 meq/100 g. $CuCl_2$ was dissolved in distilled water to achieve $Cu^{2+}$ concentrations equivalent to 0.5, 1.0, and 2.0 CEC. Bentonite was added to $Cu^{2+}$ solution with a solid-to-solution ratio of 1 g/100 mL and then vigorously shaken for 6 days at room temperature. Bentonite solutions were settled overnight to separate solid from solution, and the supernatant was discarded. $Cu^{2+}$, $Ca^{2+}$, and $Na^+$ in a supernatant was analyzed using an ICP-MS. XRD patterns were taken using Cu-Kα radiation and a Rigaku D/MAX 2200 Ultima X-ray diffractometer.

### 2.2 Copper-Exchanged Bentonite

Changes in XRD patterns as a function of $Cu^{2+}$ concentration are shown in Fig. 1. The $d_{001}$ diffractions of bentonite are shown at 5.89, 5.91, 5.97, and 6.22 ($2\theta$) with $d_{001}$ spacings of 15.0, 14.9, 14.8, and 14.2 Å as the $Cu^{2+}$ concentration increased from 0.0, 0.5, 1.0, and 2.0 CEC, respectively. This means that the distance of the interlayers of bentonite can reduced when $Cu^{2+}$ exchanged with $Ca^{2+}$ and $Na^+$ within the interlayer of the raw bentonite owing to the differences of the hydration energy among $Cu^{2+}$, $Na^+$, and $Ca^{2+}$. When $Cu^{2+}$ added at a concentration of 0.5 CEC, the $Na^+$ dissolved into the solution quickly. However as the $Cu^{2+}$ concentration was increased to >1.0 CEC, the $Cu^{2+}$ was exchanged with $Ca^{2+}$ rather than $Na^+$.
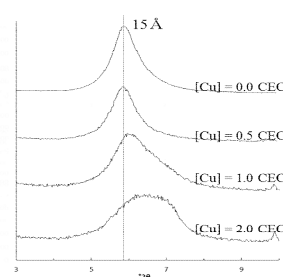


Fig. 1. Changes in XRD patterns of bentonite as a function of $Cu^{2+}$ concentration.

### 2.3 U(VI) Sorption by Raw and Cu2+ Treated Bentonite

The sorption of U(VI) onto raw bentonite was found to be highly dependent on the pH and ionic strength compared to that of the $Cu^{2+}$-exchanged bentonite as shown in Fig. 2. When the ionic strength was 0.01 M of $NaClO_4$, the maximum sorption of U(VI) by the raw bentonite was shown at a neutral pH region. However the sorption of U(VI) slightly decreased at the acidic and alkali pH region (Fig. 2a). Trends in the sorption of

U(VI) by the raw bentonite at I = 0.1 M system were similar to those of I = 0.01 M system (Fig. 2b). This means that U(VI) competitively sorbed onto the raw bentonite in the presence of competing cations such as $Na^+$. However, the effects of pH and ionic strength on the U(VI) sorption by $Cu^{2+}$-exchanged bentonite were not observed. More than 99% of U(VI) was sorbed by $Cu^{2+}$-exchanged bentonite irrelevant to the pH and ionic strength. A chemical analysis of the filtrate showed that a large amount of $Ca^{2+}$ ($>2.5\times10^{-5}$ M) were released into the solution when U(VI) sorbed onto the raw bentonite, while there was no significant dissolution of cations from the $Cu^{2+}$ treated bentonite. This implies that $Na^+$ can compete with U(VI) for the sorption sites and the $Ca^{2+}$ dissolved from the raw bentonite forms a new U(VI) aqueous species.
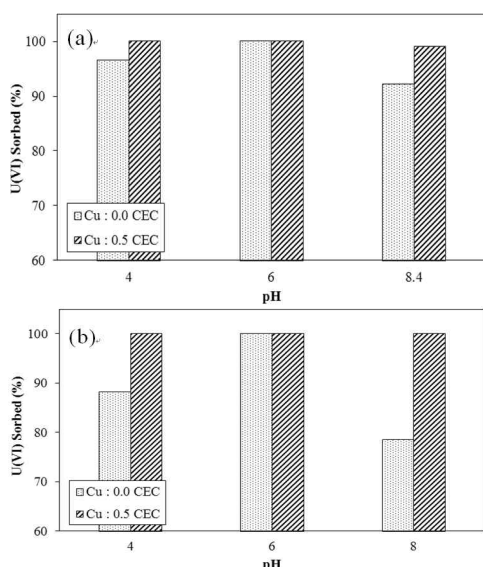


Fig. 1. U(VI) sorption by raw and $Cu^{2+}$-exchanged bentonite as a function of pH.

*2.4 U(VI) Speciation*

$Ca^{2+}$ was released at the alkali pH region when U(VI) sorbed on the raw bentonite. Hence, $Ca^{2+}$ can influence the sorption of U(VI) by forming calcium uranyl carbonate complexes at >pH 8.0[2]. Aqueous U(VI) speciation as a function of pH was calculated to understand the U(VI) sorption with the geochemical code MINTEQA2 using the OECD/NEA thermodynamic data for U(VI). The distribution of the major aqueous species for $10^{-6}$ M of U(VI) at an atmospheric condition ($p$CO$_2$ = $3.16\times10^{-4}$ atm) is given in Fig. 3a. The distribution of aqueous U(VI) species not considered $Ca^{2+}$ is similar to $2.5\times10^{-5}$ M $Ca^{2+}$ system. Free uranyl ion ($UO_2^{2+}$) is predominant in an acidic pH of up to pH 5. $UO_2OH$ and $(UO_2)_2(CO_3)(OH)_3^-$ are the dominant species in a pH range of pH 5 to 8. However, U(VI) speciation shows that $UO_2(CO_3)_3^{4-}$ is dominant in the pH range of pH 8 to 9 when not considered $Ca^{2+}$ while $CaUO_2(CO_3)_3^{2-}$ is the dominant species for

$2.5\times10^{-5}$ M $Ca^{2+}$ system, as shown in Fig. 3b. Consequently, $CaUO_2(CO_3)_3^{2-}$ species is not likely sorbed by a bentonite surface since it is negatively charged and unlikely to bond with the sorption sites via Ca atoms which are already bonded to oxygen atoms of the carbonate anions[3].
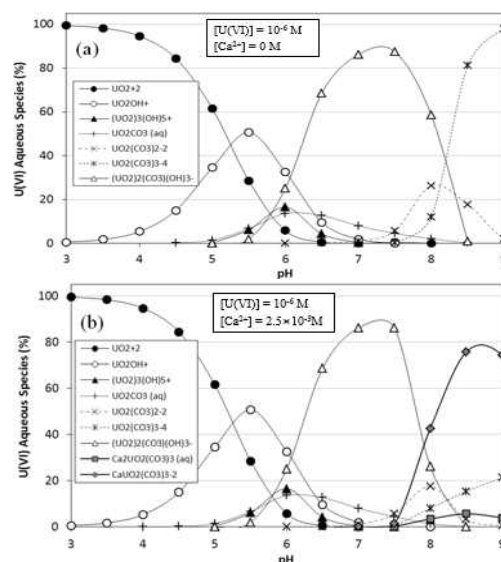


Fig. 3. Distribution of aqueous U(VI) species at atmospheric condition($p$CO$_2$ = $3.16\times10^{-4}$ atm).

**3. Conclusions**

$Cu^{2+}$ can be easily exchanged with cations such as $Na^+$ and $Ca^{2+}$ within the interlayer of Kyungju bentonite. XRD patterns show that the distance between the interlayer of $Cu^{2+}$-exchanged bentonite reduced from 15.0 to 14.2 Å as the $Cu^{2+}$ concentration increased equivalently from 0.0 to 2.0 CEC. The results of batch sorption experiments show that the UV(I) sorption capacity of $Cu^{2+}$-exchanged bentonite is higher than that of the raw bentonite for these experimental conditions; $Cu^{2+}$ concentration exchanged, pH and ionic strength. The calculation results for aqueous U(VI) speciation insinuate that the formation of calcium uranyl carbonato complexes such as $CaUO_2(CO_3)_3^{2-}$ can hinder the sorption of U(VI) onto raw bentonite.

**REFERENCES**

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