Temperature-Dependent Cation Exchange Behavior of Ca-type bentonite under High Ionic Strength Conditions

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1. Introduction

Bentonite, considered a primary buffer material for high-level radioactive waste repositories, is characterized by its high swelling, adsorption, and cation exchange capacities [1-3]. After disposal, it may be exposed to elevated temperatures from radioactive decay and groundwater with varying ionic strengths, conditions under which temperature-dependent interlayer cation exchange in smectite can significantly affect its properties and long-term stability [4-5].

This study investigates the effect of temperature on cation exchange behavior in Ca-type bentonite (Bentonil-WRK) under controlled high ionic strength conditions. Hydrothermal experiments were conducted using 1 M KCl solution at room temperature (RT), 100°C, and 150°C. Changes in interlayer cation behavior were analyzed along with mineralogical and chemical characterization to evaluate temperature-induced structural and property changes.

2. Methods and Results

2.1 Hydrothermal experiments

Ca-bentonite (50 g) was reacted with 100 mL of 1 M KCl solution at a solid-to-liquid (S/L) ratio of 1:2. To examine the temporal evolution of cation exchange behavior, reaction durations were set from 0.5 to 90 days at room temperature (RT), 100°C, and 150°C. After the reaction, the supernatant was separated by centrifugation and filtered through a 0.22 μm membrane. The run products were repeatedly washed with distilled water and centrifuged to remove excess salts. The samples were then freeze-dried, ground using a ball mill, and stored in a desiccator. Additional experiments were conducted under identical conditions using distilled water (DIW) to exclude the temperature-dependent influence of mineral dissolution. Mineralogical characteristics were analyzed by X-ray diffraction (XRD), and the chemical composition of the liquid samples was determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2 Reaction under high ionic strength conditions

XRD results for run products reacted in 1 M KCl showed that at both 100°C and 150°C, the S(001) peak intensity decreased and the full width at half maximum (FWHM) increased with longer reaction times (Fig. 1). These changes may be attribute to variations in basal spacing or hydration state associated with ion exchange. However, after ethylene glycol (EG) treatment, the S(001) peak was restored. This suggests that reversible interlayer ion exchange, rather than structural collapse, was the dominant process.

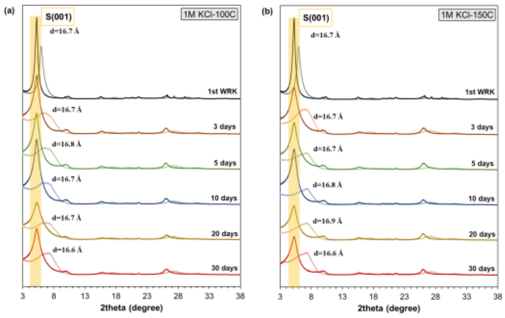

Fig. 1. XRD patterns of oriented clay mounts before (light color) and after (dark color) ethylene glycol treatment at (a) 100°C and (b) 150°C, showing the recovery of the S(001) peak (yellow shaded area).

Fig. 2 shows the amounts of interlayer cations (Ca^{2+}, Mg^{2+}, and Na^{+}) released by ion exchange during the reaction. The total cation exchange (TCE) was calculated from the sum of these values. At RT, the TCE gradually increased during the early stage (0.25-5 days), peaked at 10 days, and then decreased. In contrast, at high temperatures, it showed an initial increase, dropped to a minimum at 3 days, and then increased again. At the 90 day mark, TCE values reached 0.541 eq/kg at RT, 0.573 eq/kg at 100°C, and 0.648 eq/kg at 150°C. Notably, at 150°C, the exchange capacity increased continuously throughout the reaction period.

Even though the changes were small, the TCE showed different trends at each temperature (Fig 2d). After an initial drop (0.25–3 days), the RT samples showed a slight decreasing trend. In contrast, the 100°C samples remained relatively constant, while the 150°C samples showed a possible increase. Although comparison with the chemical composition of the residual solids is needed, these results suggest a temperature effect on cation exchange behavior.

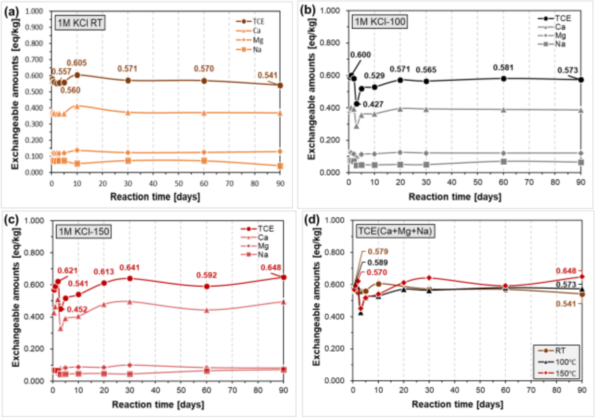

Fig. 2. Exchange amounts versus reaction time at (a) room temperature, (b) 100°C, and (c) 150°C. (d) Comparison of TCE trends at each temperatures.

3. Conclusions

This study compared ion exchange behavior across different temperatures and durations to evaluate thermal influences. At room temperature, the exchange capacity peaked at 10 days and then declined. At 100°C, the capacity remained relatively constant, reaching a final value similar to the room temperature results. In contrast, at 150°C, the exchange capacity showed an increasing trend and had the highest value among all temperatures, indicating that higher temperature promoted cation exchange behavior.

In future studies, additional analyses will be performed to investigate mineralogical and chemical composition changes in the residual solids. Further comparison with liquid sample analysis results will be needed for a more detailed understanding.

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