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Effect of layer charge density and charge location on the swelling of smectite: Implications for geological storage of CO_2 and high-level nuclear waste

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Abstract

Storage sites for CO_2 and high-level nuclear waste (HLNW) involve smectite due to its ability to increase in molar volume, known as swelling. However, the molar volume and dissolution of smectite can be affected by its layer charge density, charge location, and composition, as affected by variations in pressure (P), CO_2 pressure [$P(CO_2)$], temperature (T), and brine concentration. The molar volumes [$d(001)$] of Ca-exchanged high-charge montmorillonite (CaSAz1) and saponite (CaSapCa1) were examined by X-ray diffraction (XRD) under varying $P(CO_2)$-T in $CaCl_2$ brines. Additionally, geochemical modeling was used to analyze the extent of dissolution of these smectite phases. The results were compared to a Ca-exchanged low-charge montmorillonite (CaSWy2). Increasing the brine concentration (from 0.17 to 3.42 M) and T (from near 33 to 150 °C) results in a ≤16% and ≤14% decrease in $d(001)$ values for CaSAz1 and CaSapCa1, respectively, whereas no change was observed when $P(CO_2)$ was increased from ambient to 500 bars. The $d(001)$ values of CaSAz1 are ≤0.7 Å higher than CaSWy2 because of the higher charge density of CaSAz1, which increases the Ca^{2+} content in the interlayer. In contrast, the $d(001)$ values of CaSapCa1 are ≤0.8 Å lower than CaSWy2 because the deficit layer charge of CaSapCa1 occurs in the tetrahedral sheet. Geochemical modeling shows that the extent of smectite dissolution is affected by its composition. Under acidic conditions, CaSapCa1 is 35 times higher in % dissolution than CaSAz1 and CaSWy2 because CaSapCa1 has a higher Mg^{2+} content. The dissolution of CaSapCa1 results in a higher solution pH by the formation of bicarbonate and carbonate phases, which is an alternate way of storing CO_2. Thus, the smectite species must be considered when evaluating storage sites for CO_2 or HLNW.

Keywords: Smectite, XRD, montmorillonite, CO_2 storage, nuclear waste