

Geochemical reaction modeling of CaCO_3 polymorphs formation at hyperalkaline springs in Oman.

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In Japanese transuranic (TRU) waste disposal facilities, ¹²⁹I is the most important key nuclide for the long-term safety assessment. Thus, the K_d values of I to natural minerals are important factor in the safety assessment. However, the degradation of cement materials in the repositories can produce high pH pore fluid which can affect to anion transport behavior. Therefore, it should be necessary to understand behavior of anions such as I⁻ under the hyperalkaline conditions.

Natural hyperalkaline spring water (pH>11) has known to generate from the partly serpentinized peridotite in the Oman ophiolite. The spring water is characteristically hyperalkaline, reducing, low-Mg, Si and HCO_3^- , and high Ca, while the river water is moderately alkaline, oxidizing, high-Mg and HCO_3^- . The mixing of these spring and river water caused the formation of secondary minerals. Naturally-occurring hyperalkaline conditions near the springs in Oman were used as natural analogue for the interaction between cement pore fluid and natural Mg- HCO_3^- groundwater.

Anraku *et al.* (2009) said that calcite (CaCO_3), aragonite (CaCO_3), hydrotalcite [$\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}$] were observed in the precipitates, and their mineral compositions were varied depending on the difference of sampling points. Moreover, Anraku *et al.* (2009) also said that Iodine can be remarkably fixed in aragonite. If aragonite can also form in disposal condition, safety ratio in the long-term safety assessment will be increased by generation of aragonite.

The main goal of this work is to incorporate the effect of fixing iodine by aragonite into safety assessment. With this aim, we carried out the in-situ synthesis experiment in order to simplify the condition of secondary minerals formation in Oman. Moreover, we tried to model which can express the reaction of the in-situ synthesis experiment.

The in-situ synthesis experiment was conducted by mixing different ratios between spring and river water. The precipitates were synthesized by letting mixing solutions stand for 2 days. The mineralogy of the precipitates was determined by X-ray diffractometer (XRD), scanning electron microscope (SEM). In addition, mass of minerals in the precipitates were obtained by Rietveld method. In the result of this experiment, aragonite formed in all precipitates, and increasing the percentage of river water caused decreasing the percentage of calcite in the precipitates.

The geochemical reaction modeling was performed by using Geochemist's workbench R8.0 based on the result of the in-situ synthesis experiment. Aragonite is well-known as more unstable phase than calcite in earth's surface condition. In equilibrium state, aragonite will not form. Berner (1975) said that Magnesium ion is a inhibitor of calcite growth kinetics. And there is no inhibition of aragonite growth by magnesium ion. Our result showed the same tendency with Berner (1975). Thus, We incorporated Mg inhibition model calculated by Lin and Singer (2009) into our models. the percentage of calcite/aragonite in modeling results corresponded approximately to experimental results. Since generation of aragonite can be possible to calculate, safety ratio in the long-term safety assessment can be increased by generation of aragonite.

Keywords: Calcium carbonate mineral, Polymorphs, Geochemical reaction modeling, Kinetics, Radioactive waste disposal, Natural analogue