Competitive Sorption and Desorption Modeling of Sr Under the Binary Exchange System

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1. Introduction

The transport behavior of radioactive strontium (^{90}Sr, a pure β-emitter with $t_{1/2}$=28.1 y), which can be released into the subsurface environment during operation of NPPs and decommissioning/ decontamination of old NPPs, is greatly affected by the degree of Sr sorption and desorption at the solid-solution interface. The sorption reaction of Sr is commonly controlled by outer-sphere complexation of hydrated Sr ion onto the solid surface. However, if major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) coexist with Sr due to seawater intrusion to groundwater, the sorption behavior of Sr will be significantly affected by the cation-exchange reaction. Therefore, we investigated the competitive sorption and desorption of Sr as a function of Sr and other cations' concentrations with the ion-exchange model using the GWB software (v.12 with thermos.dat database) from batch binary exchange reactions.

2. Experiments

2.1 Materials

Core rock samples were collected at the Shin-Kori #3 and 4 nuclear reactor sites in South Korea. According to XRD data, quartz and feldspar are the dominant minerals with about 13% of mica and 4.5% chloride as clay mineral. The determined exchangeable values were 0.05, 1.13, 1.00, 8.66, and 17.0 meq/kg for Sr^{2+}, K^+, Na^+, Mg^{2+}, and Ca^{2+}, respectively, and the sum of these values was used as the total CEC value (28.00 meq/kg) of the solid material in all experiments.

2.2 Competitive sorption and desorption of Sr

The exchangeable batch sorption experiment was conducted in binary cation system at a constant pH (pH 7). Various solution concentrations of Sr^{2+} from 10^{-6} to 10^{-1} M were prepared with deionized water. The batch experiment was conducted in an individual 15 mL polypropylene centrifuge tube by mixing the sorbent and Sr-spiked solution. Sorbent (0.1 g) and 10 mL solution were reacted in the tubes on a slow moving platform shaker at 200 rpm for 12 hours. Then suspensions were centrifuged at 10,000 rpm for 30 minutes and supernatants were filtered through 0.45 μm PVDF syringe. Sorption of Sr^{2+} on the test tubes was reported to be negligible, and the final concentrations of Sr^{2+}, K^+, Na^+, Mg^{2+}, and Ca^{2+} in the filtered effluent solutions were determined using ICP-OES. For this experiments, nitrated form of Sr, $Sr(NO_3)_2$ solutions were prepared using analytical grade salts.

For the desorption experiments of Sr, the desorption solution concentration of the respective background cation ranged from 10^{-6} to 10^{-1}M in pH 7 for K^+, Na^+, Mg^{2+}, and Ca^{2+}, respectively. The sorptive and exchangeable Sr^{2+} on the solid surface would be replaced with simultaneous sorption of respective cation in solution. The experiment procedure was the same as exchangeable sorption of Sr experiment as binary cation exchange reaction. For the experiments, KNO_3, $NaNO_3$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$ were used to prepare for the respective desire concentrations in solution. The selectivity coefficients (K_{sel}) of binary ion exchange reaction were calculated by using Gaines-Thomas exchange convention over a large range of concentrations.

3. Results and discussion

When Sr^{2+} reacts on the surface of solid sample, the mineral precipitation, surface hydroxyl sorption as non-specific sorption, or ion exchange reaction with major cations controls Sr^{2+} surface reaction. The exchange affinity of major cations toward Sr^{2+} was in order of $Ca^{2+} > Mg^{2+} > K^+ > Na^+$ under both binary Sr^{2+} sorption and desorption reactions.

3.1 Competitive Sr sorption with modeling

The experimental and model fit results are shown in Fig. 1. The red dots are the exchangeable sorption amount of Sr^{2+} and dotted line is the best fi results. The K_{sel} value from exchange reaction between Sr^{2+} and CaX_2 (Ca^{2+} on the solid surface) was exceedingly valuable at relatively low ionic strength ($\sim 5x10^{-2}$ M), however, as increasing the equilibrium ionic strength the other exchange reactions must be applied to fit the data. Thus considering only ion exchange reaction is enough to observe the sorption behavior of Sr under low ionic strength condition. However, as the ionic strength increased, the additional sorption mechanism such as precipitation, non-specific surface sorption, or ion exchange reaction (even all major kind of cation exchange reaction) must be considered to describe Sr sorption behavior much more correctly.

3.2 Desorption of Sr with modeling

The exchangeable amounts of Sr^{2+} onto the solid surface after Sr^{2+} desorption reaction are shown in Fig. 2. As a result, the Sr^{2+} amount on the solid surface was decreased with increasing the equilibrium IS (Ionic Strength) for all the reactive cations. However, when SrX_2 (Sr^{2+} on the solid surface) reacted with Na^+ at 0.1 M of equilibrium IS condition, the exchange reaction between SrX_2 and Na^+ reached the equilibrium state. Therefore, approximately $4.5x10^{-2}$ µeq/kg of Sr^{2+} was considered as the maximum desorption amount of

exchangeable Sr^{2+} from the solid surface. The order of relative mean square is Ca^{2+} (0.0004) > Mg^{2+} (0.033) > K^+ (0.454) > Na^+ (1.000). Thus, we can make the best description and predict the desorption behavior of Sr^{2+} from the solid surface by using divalent data (Mg^{2+} and Ca^{2+}) with the modeling works.
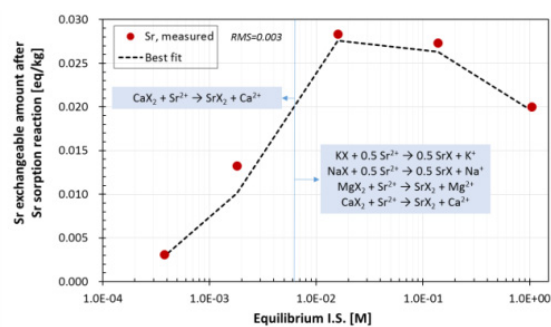

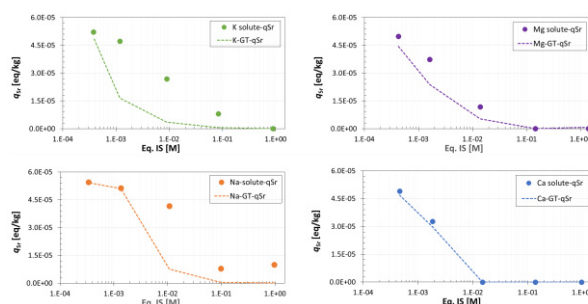Fig. 1. The measured exchangeable Sr^{2+} amount with the best model fit.

Fig. 2. The modeling fit results of exchangeable Sr^{2+} amount on the solid surface with respect to major cations.