Competitive Binding Reaction of Strontium as A Function of Ionic Strength

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1. Introduction

Accurate predictions of transport behavior of reactive radionuclides can be often achieved based on the knowledge of the sorption or exchange process for the chemicals of interest. Cation exchange is a special case of either competitive sorption or extraction. The classical way to treat the competitive sorption and/or transport of cations is to define cation exchange reaction with constant exchange stoichiometry based on charge equivalents. Strontium, Sr, was selected as the target radioactive cation because of its sensitive sorption behavior via weakly bound outer-sphere surface complexes at the solid water interface [9, 11].

In this study, we investigate the competitive extraction for Sr and other major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) from chemically heterogeneous rock material collected at Korea NPP site by studying each major cation individually over a wide range of solution composition.

2. Methods and Results

In this section, some of the experimental methods used to model the binding of Sr are described. The binding fate of Sr was defined by not only cation-exchange convention, but also sorption affinity distribution on surface of sorbent.

2.1 Sorbent characterization

The Core rock material was sampled from Shin-Kori 4 nuclear reactor site in depth of 6.6-7.4 m (shattered zone). For cation-exchange experiments, an aggregate size fraction between 75 and 150 µm was separated by dry sieving following crushing process. The solid material used in the experiments has 93.45 mg/kg total carbon, 3.21 g/cm^3 dry density, and 1.42 % porosity. The cation-exchange capacity (CEC) determined by 1 M of $NaNO_3$ and KNO_3 mixed solution at pH 7 is 24.21 µeq/g. X-ray diffraction analysis showed that the material contained quartz, albite, orthoclase, and smaller amount of muscovite, biotitie, chlorite, and actinolite. The determined specific surface area is 1.22 m^2/g using N_2-BET method. Activities of all ions were corrected by Geochemist's Workbench (ver. 9) with Debye-hückel model.

2.2 Sr Binary ion-exchange experiments

Either competitive sorption of major cations to the solid material or extraction of Sr from the same material was investigated by measuring sorption or exchange isotherms for several constant cations in solution. Solutions of $NaNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ were used for making the concentrations of target element from 10^{-6} to 10^{-1} eq/L at constant pH 7. About 0.5 g of the solid material was mixed with 10 mL of each solution for 12 hr. After reaction, supernatants were centrifuged (3,000 rpm for 10 min), and filtered using 0.45 µm syringe filter, and measured for the concentration of Sr, Ca, Mg, Na, and K by ICP-MS (Perkin Elmer, NexIon300).

2.3 Models for reactive cations with cation-exchange conventions

The binding of Sr and major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) to solid materials is commonly described by cation-exchange reaction [4, 7]. The basic assumption of this mechanism is that the biding sites in solid are always occupied with one of the cations and that the existence of vacant binding sites can be neglected [12]. The rationale behind this premise is that the negative surface charge of the exchanger phase is always balanced by a charge-equivalent amount of adsorbed cations [3, 6].

To derive sorption or an exchange isotherm, the appropriate mass action law must be formulated. The heterovalent exchange reaction between Sr and monovalent cation, A^+, is commonly written as [3, 6]

$$SrX_2 + 2Na^+ \leftrightarrow 2NaX + Sr^{2+}$$
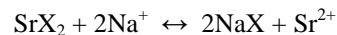
where X is a surface site with -1 charge. The total concentration of sites, X is given by

$$S = 2q_{Sr} + q_A$$

where S is the total site concentration in moles per unit mass of the solid. In this case, the quantity S is related to the cation exchange capacity, Q (in moles of charge equivalents per unit mass of sorbent) by $Q = S$.

In formulating the mass action laws for cation exchange, one usually assumes ideal exchange behavior and approximates the activity of adsorbed species either with mole fractions or equivalent fractions of bound cations [3-5,8]. The mole fractions are given by

$$x_A = q_A / (q_A + q_{Sr})$$

$$x_{Sr} = q_{Sr} / (q_A + q_{Sr})$$

with the condition $x_A + x_{Sr} = 1$. Correspondingly, the equivalent (charge) fractions are written as

$$y_A = q_A / (q_A + 2q_{Sr})$$
$$y_{Sr} = 2q_{Sr} / (q_A + 2q_{Sr})$$

with $y_A + y_{Sr} = 1$. The mass action law due to Vanselow's law [1] is based on heterovalent exchange reaction, assuming that the activities of adsorbed species are given by their mole fractions, leading to

$$K = a^2_A x_{Sr} / a_{Sr} x^2_A$$

where K is the exchange selectivity coefficient. Combination of the mass action law and the mass conservation law leads to the isotherms given in Table 1. The convention due to Gaines and Thomas' law [4] is also based on heterovalent exchange reaction but employs equivalent fractions instead of mole fractions:

$$K = a^2_A y_{Sr} / a_{Sr} y^2_A$$

The corresponding expression for the isotherm based on the Gains-Thomas convention is in Table 1.

Alternatively, one can also consider the reaction

$$SrY + 2A^+ \leftrightarrow A_2Y + Sr^{2+}$$
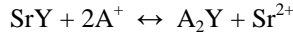
where Y now denotes the site with -2 charge [7, 10]. In this case, the total site concentration of Y is given by

$$S = q_{Sr} + q_A/2$$

and S is related to the conventional cation-exchange capacity Q by $S = Q/2$. Cernik et al. [7] have considered that the site charge is -2 (Y) and formulated a mass action law in terms of the equivalent fraction:

$$K = a^2_A y_{Sr} / a_{Sr} y_A$$

For all equations, the bound amounts, q_{Sr} and q_A (moles per unit mass of sorbent) is a function of the corresponding activities a_{Sr} and a_A (moles per liter).

Table I: Binding isotherms for binary exchange reaction according to different conventions [12]

Convention	Binding isotherms
Vanselow ($Q = S$)	$q_{Sr} = S/2[1- (a^2_A/(a^2_A + 4Ka_{Sr}))^n]$ $q_A = S(a^2_A /(a^2_A + 4Ka_{Sr}))^n$
Gaines-Thomas ($Q = S$)	$q_{Sr} = S/2\{1 + (a^2_A/2Ka_{Sr}) - [(1 + (a^2_A/2Ka_{Sr}))^2 -1]^n\}$ $q_A = S\{[(1 + (a^2_A/2Ka_{Sr}))^2 - 1]^n$
	$- (a^2_A/2Ka_{Sr})$
Cernik ($Q = 2S$)	$q_{Sr} = S(Ka_{Sr}/(a^2_A + Ka_{Sr}))$ $q_A = 2I(a^2_A/(a^2_A + Ka_{Sr}))$

2.4 Performance of one-site cation binding models

Figure 1 shows a comparison of the experimental data with calculated cation binding isotherms based on the different exchange conventions, assuming a single type of binding site.

Sr$_{Solid}$ - Na$^+$

Sr$_{Solid}$ - K$^+$
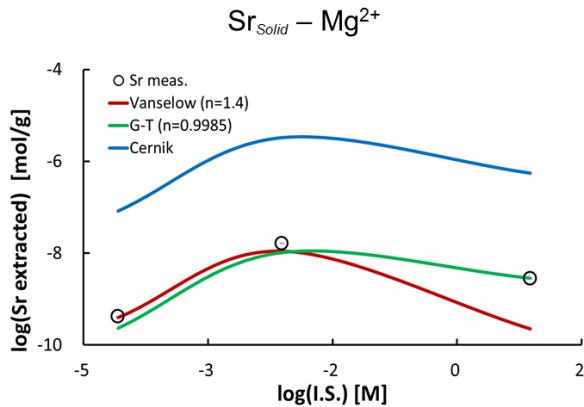

Sr$_{Solid}$ – Ca^{2+}
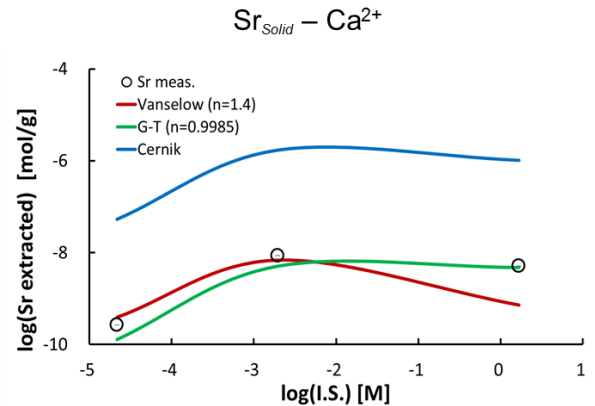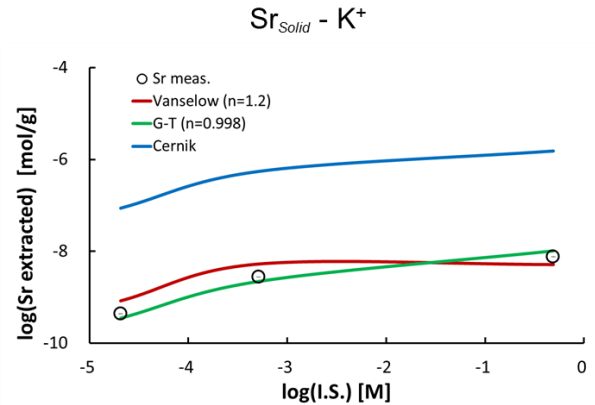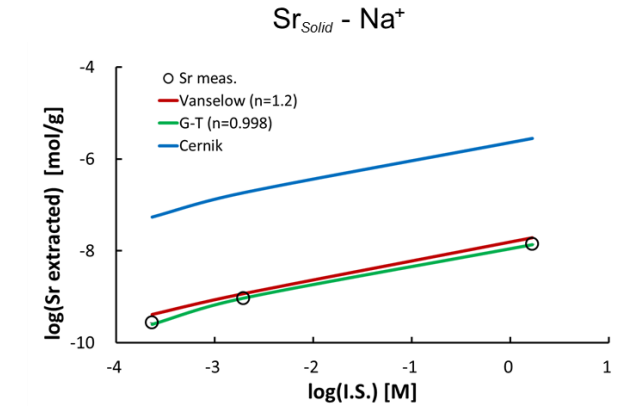
Fig. 1. Experimental (symbols) and calculated (lines) binding isotherms based on different cation-exchange conventions with different types of binary system.

The comparison of different binding models with the data can be straightforward because of the wide range of ionic strength and availability of the isotherms for Sr and major cations. The extraction amount of Sr from the solid material as exchangeable phase increased with increasing the ionic strength under Sr_{solid}-Na^+ system. However, in case of the other system, the extracted amount of Sr which used to increase was reduced by more increasing the ionic strength. And as evident from Fig. 1, Vanselow's and Gaines-Thomas' conventions do provide a rather reasonable description for the data, while the Cernik convention fails. Detailed analysis of the model performance also shows that Vanselow's convention for one-site model does notprovide a perfect fit for the data in the hetero exchange system ($Sr_{solid} - Ca^{2+}$, and $Sr_{solid} - Mg^{2+}$) under high ionic strength. The reason for this behavior is that the Sr extraction data depend more strongly on the divalent cation concentration than predicted by the model. Therefore, introduction of additional type of binding site is needed to describe better quantitative description of the experimental data.

3. Conclusions

Accurate model of Sr cation exchange is prerequisite to predict the transport of Sr in underground environment condition. In this study we investigated the competitive extraction of Sr depending on different concentration (or different ionic strength) of major cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. The Vanselow's and Gains-Thomas' conventions show good prediction when only one-binding site exists. However, Vanselow's convention was not useful to match the experimental data in high concentration of divalent cations (Ca^{2+} and Mg^{2+}). It indicates that satisfactory description of all data is not possible using any of these models. Therefore, additional model (or site) is needed to resolve this problem.

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