Evaluation of Sorption Distribution Coefficient of Cs onto Granite using Sorption Data Collected in Sorption Database and Sorption Model

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Abstract

Based on the sorption distribution coefficients (K_d) of Cs onto granite collected from the JAERI Sorption Database (SDB), the parameters for a two-site model without the triple-layer structure were optimized. Comparing the experimentally measured K_d values of Cs onto Mizunami granite carried out by JAEA with the K_d values predicted by the model, the effect of the ionic strength on the K_d values of Cs onto granite was evaluated. It was found that K_d values could be determined using the content of biotite in granite at a sodium concentration ([Na]) of 1×10^{-2} to 5×10^{-1} mol/dm^3. It was suggested that in high ionic strength solutions, the sorption of Cs onto other minerals such as microcline should also be taken into account.

1. Introduction

It is well known that the sorption distribution coefficients (K_d) of fission products and actinides, which dominate long term annual radiation dose rate, support the safety assessment of high level radioactive waste and used nuclear fuel geological disposal. A database of K_d values or equilibrium constants for surface complexation reactions was compiled by JAERI (Japan Atomic Energy Research Institute; currently JAEA (Japan Atomic Energy Agency)), and an uncertainty analysis technique using the sorption database has been developed to improve the reliability of safety assessment [1]. However, it is unavoidable that variance of sorption data increases as the number of the collected data increases, leading to the increase in the uncertainty of sorption data and safety assessment.

In studies conducted by the author and coworkers [2, 3], the sorption data in the JAERI sorption database (JAERI SDB) was evaluated to determine the most probable K_d values and/or reliable K_d value range. We selected cesium (Cs) because: (1) a large number of sorption data are available in the JAERI SDB; and (2) the radioisotope ^{135}Cs (half-life = 2.3×10^6 years) is considered to be one of the key radionuclides which significantly contribute to the long term annual dose exposure in the safety assessments of geological disposal in both crystalline and sedimentary settings [4, 5]. Based on an evaluation of K_d values of Cs onto bentonite, the following conclusions were drawn:

1) K_d values were re-evaluated, considering their pH dependence. The combinations of elements and solids to which a surface complexation model could be applied were checked. As a result, only a few element/solid combinations in JAERI SDB were found to be applicable, with the K_d values of these combinations being measured in a sufficiently wide pH range.

2) The cause of the variation in K_d values of Cs on bentonite was investigated, and it was found that the differences of experimental conditions such as concentration of coexisting ions or presence/absence of sand mixture were the dominant factors causing the observed data variation. Hence, if we can adequately calibrate these differences of experimental conditions, the conventional errors and variation of K_d values might be able to be avoided.

3) In many literature publications, the information on the ion exchange coefficients of coexisting ions, cation exchange capacity and Cs concentration in liquid phase after solid/liquid separation, which is required to re-evaluate the K_d values, was not provided. A methodology to estimate the missing information was established using an ion exchange model.

4) A model analysis method was developed, in which surface complexation and ion exchange reactions were simultaneously taken into account. By applying this model analysis, experimental results of both batch and diffusion methods could be evaluated using the same parameter values.

5) Simple collection of K_d data only makes the variation of data larger. Hence, identification of the cause of variation and errors, whether it is just an artifact of the experiments or essentially unavoidable errors, becomes much more important. The evaluation with sorption models was shown to be effective.

JAEA performed sorption experiments of Cs onto Mizunami granite with Mizunami groundwater, and studied the effect of Na concentration on sorption [6]. In particular, JAEA discussed and evaluated the causes of variation in sorption data of Cs onto granite, granodiorite, tuff and mudstone in low ionic strength solutions. In this work, we focus only on K_d values of Cs onto granite. The sorption model for the evaluation of K_d values is applied to K_d data of Cs onto granite collected in the JAERI SDB [1]. The sorption model is also applied to the JAEA's sorption experimental results. The agreement between the model prediction and the experimental results is discussed.

2. K_d Data in JAERI Sorption Database

A total of 677 K_d values of Cs sorption onto granite were collected in the JAERI SDB. The K_d values are narrowed down by the following three criteria:

1) K_d values measured at $5 < \mathrm{pH} < 10$, which are the pH conditions expected in groundwaters at depth, were adopted.

2) K_d values measured at extremely low ionic strength solutions such as distilled water condition were eliminated, because such low ionic strength cannot be expected under the actual geological conditions.

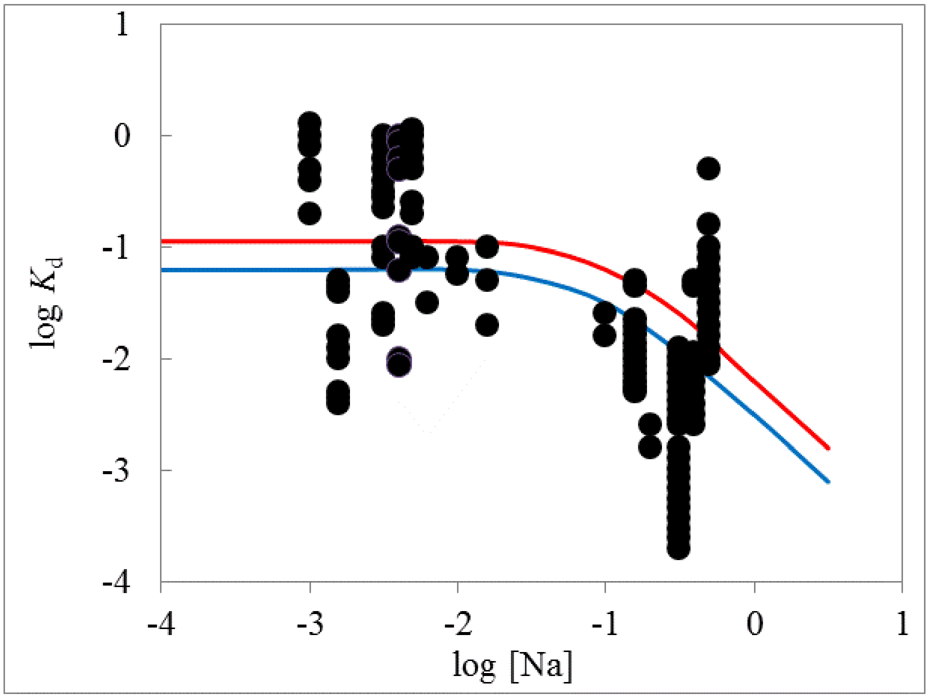

Figure 1 K_d data selected from the JAERI SDB and those predicted by the sorption model. Blue and red lines represent the sorption model prediction at biotite weight contents of 5 % and 10 %, respectively (see Section 3 for discussion).

3) K_d values measured at extremely high Cs concentrations ([Cs] > 1 mol/dm^3) were eliminated, because such high Cs concentration is not expected in the actual geological disposal system [4, 5].

Adopted K_d values are plotted in Figure 1. In Figure 1, Na concentration ([Na]) equivalent to the ionic strength at which each K_d value was measured is used. A discussion of the sorption model results presented in this figure is provided in the following section.

3. Sorption Model

JAEA re-evaluated the sorption experiments of Cs onto Inada granite and the mineral components which had been carried out by Kato et al. [7]. JAEA concluded that the contribution of biotite was significantly large to the sorption of Cs onto granite [6]. The same conclusion has also been reported by Huitti et al. [8] and Tsukamoto et al. [9]. On the other hand, Kitamura et al. [10] reported the sorption on microcline was a dominant mechanism of Cs sorption onto granite.

In this work, a two-site model without the triple-layer structure [11] was used to discuss the sorption of Cs onto granite. This sorption model consisted of two types of sorption sites: a site which has a stronger affinity to ions (strong site) and a site which has a weaker affinity to ions (weak site). In general, the total number of strong site is much less than that of weak site. At the experimental conditions that many K_d values in JAERI SDB were measured, and at which the JAEA sorption tests were conducted using Mizunami granite [6], the initial concentrations of Cs were high enough that all strong sites were occupied and sorption onto weak sites dominated the whole sorption phenomena. Therefore, only the sorption on weak sites in a two-site model without the triple-layer structure is considered in this work. The sorption model used in this work is described as follow:

$$K_\mathrm{d} = \frac{n_w K_7}{([\mathrm{H}^+]+K_5[\mathrm{H}^+]^2+K_6+K_8[\mathrm{Na}^+])+K_7\frac{V}{WK_\mathrm{d}+V}[\mathrm{M}^{n+}]_{ini}} \tag{1}$$

where

K_d: sorption distribution coefficient [$\mathrm{m^3/kg}$];
$[\mathrm{M}^{n+}]_{ini}$: initial concentration of Cs [$\mathrm{mol/dm^3}$];
$[\mathrm{H}^+]$ and $[\mathrm{Na}^+]$: concentration of H^+ and Na^+, respectively [$\mathrm{mol/dm^3}$];
V: volume of liquid phase [$\mathrm{m^3}$];
W: mass of solid phase [kg];
n_w: density of the number of sites on solid surface [mol/kg]; and
K_5, K_6, K_7 and K_8: equilibrium constants of surface reactions.

The values of n_w and K_i ($i = 5 – 8$) were determined as follows. Considering the composition of granite and the density of biotite and microcline, the weight contents of biotite and microcline in granite were calculated, and the K_d values for biotite and microcline were estimated by:

$$K_\mathrm{d}\text{ (biotite or microcline)} = K_\mathrm{d}\text{ (granite) / (weight content of biotite or microcline).} \tag{2}$$

In this work, the sorption model (1) was fitted to the pH dependence of K_d (biotite or microcline) by the least square method, and the optimized values of n_w and K_i ($i = 5 – 8$) were determined. The n_w and K_i ($i = 5 – 8$) values for biotite can be optimized by the fitting, but the fitting for microcline failed. Sasaki et al. [11] carried out the sorption experiments of Cs onto biotite, microcline, quartz and granite which were sampled at Andhra Pradesh in India at ionic strength solutions of 0.01 $\mathrm{mol/dm^3}$ and 0.1 $\mathrm{mol/dm^3}$, and applied the two-site model without the triple-layer structure to their sorption data of Cs. These authors reported the parameter values of strong site and weak site for quartz and granite, but only the parameter values of weak site for biotite and microcline. The parameters for biotite optimized in this work are summarized in Table 1, together with the optimized parameters for biotite and microcline by Sasaki et al. [11]. Because many literature publications [6, 8, 9, 12, 13] have reported that biotite contributes to the sorption of Cs onto granite and only Kitamura et al. [10] has reported the contribution of microcline, only the optimized values of n_w and K_i ($i = 5 – 8$) for biotite are used in the sorption model (1). The influence of microcline is neglected in this work.

The weight content of biotite in granite is 5 – 10 % in general. Calculated sorption results using the optimized parameters of n_w and K_i ($i = 5 – 8$) for biotite are illustrated in Figure 1, together with K_d values from the JAERI SDB.

Table 1 Optimized parameters of the sorption model

Parameters	Biotite in This Work	Biotite in Sasaki et al [8]	Microcline in Sasaki et al [8]
n_w	(3.70±0.10) x 10^{-5}	(6.63±0.78) x 10^{-6}	(3.03±1.09) x 10^{-6}
log K_5	2.00±0.01	2	2
log K_6	-8.00±0.01	-4.32±0.16	-3.05±0.30
log K_7	-2.02±0.02	-0.51±0.16	0.24±0.32
log K_8	-4.52±0.02	-4.53±0.24	-2.77±0.32

4. Comparison with Sorption Data for Mizunami Granite

The weight content of biotite in Mizunami granite is 10 % and pH of Mizunami groundwater is approximately 8. The predicted results by the sorption model (1) and K_d values measured by JAEA are shown in Figure 2. The predicted results are consistent with the experimental results at [Na] = 1 x 10^{-2} – 5 x 10^{-1} mol/dm^3. On the other hand, the sorption model underestimated the K_d values at [Na] = 9.6 x 10^{-4} and 5 mol/dm^3. At the present, the reason for the underestimation at [Na] = 9.6 x 10^{-4} mol/dm^3 is not known. Neglect of the contribution of microcline is considered to be one of the reasons for the underestimation at [Na] = 5 mol/dm^3. Kitamura et al. [10] studied the sorption of Cs onto granite at [Na] = 1 mol/dm^3 and concluded that microcline dominates the sorption of Cs at the experimental conditions considered. Experimental results of Kitamura et al. [10] suggest that microcline has affinity sites for Cs which are not as strong as those of biotite at low Na concentration ([Na] < 1 mol/dm^3), but

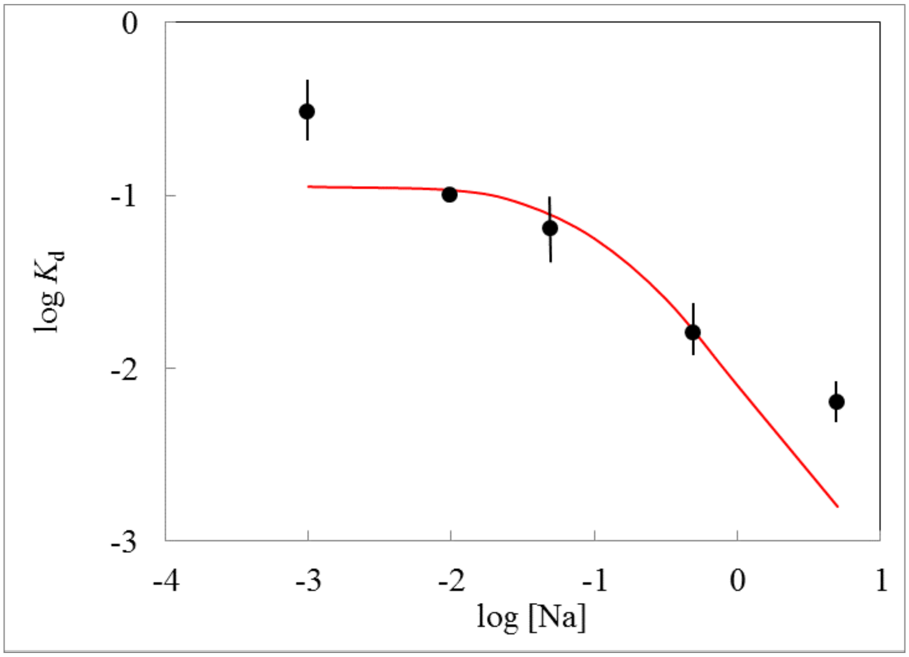

Figure 2 K_d values experimentally measured using Mizunami granite by JAEA [6]. Solid line represenrs K_d values predicted by sorption model.

become comparable at high Na concentration (e.g. [Na] > 1 mol/dm^3). This suggests that the K_d values at [Na] > 1 mol/dm^3 or at high ionic strength equivalents to [Na] > 1 mol/dm^3, for example, in brines could be evaluated by sorption models that consider the contribution of both biotite and microcline.

5. Summary

This work suggests that K_d values of Cs onto granite collected in the JAERI sorption database can be evaluated by the sorption model with the sorption on biotite at the Na concentration between 1 x 10^{-2} mol/dm^3 and 5 x 10^{-1} mol/dm^3. On the other hand, K_d values of Cs measured in higher ionic strength solutions may have to be evaluated with the sorption model including the sorption on both biotite and microcline.

In this work, a simple relationship, K_d (granite) = K_d (biotite) x (weight content of biotite) was supposed. However, in general, the value of K_d (rock) is not identical to the sum of K_d value of each mineral components (K_d (rock) $\neq \sum K_d$ (mineral component)). Furthermore, the migration behavior of Cs in actual environments should be expressed using K_d values obtained by diffusion method, but not by K_d values measured by batch method. Unfortunately, many K_d values in sorption databases were measured by batch method. In addition, Cs concentration in the geological repository system is expected to be much lower than the Cs concentrations being used in the laboratory measurements in the literature. This means that the actual K_d value of Cs under repository conditions would be larger than the K_d values in the sorption database.

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