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Cs sorption to potential host rock of low-level radioactive waste repository in Taiwan: Experiments and numerical fitting study

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ABSTRACT

A reliable performance assessment of radioactive waste repository depends on better knowledge of interactions between nuclides and geological substances. Numerical fitting of acquired experimental results by the surface complexation model enables us to interpret sorption behavior at molecular scale and thus to build a solid basis for simulation study. A lack of consensus on a standard set of assessment criteria (such as determination of sorption site concentration, reaction formula) during numerical fitting, on the other hand, makes lower case comparison between various studies difficult. In this study we explored the sorption of cesium to argillite by conducting experiments under different pH and solid/liquid ratio (s/l) with two specific initial Cs concentrations (100 mg/L, 7.5×10^{-4} mol/L and 0.01 mg/L, 7.5×10^{-8} mol/L). After this, numerical fitting was performed, focusing on assessment criteria and their consequences. It was found that both ion exchange and electrostatic interactions governed Cs sorption on argillite. At higher initial Cs concentration the Cs sorption showed an increasing dependence on pH as the solid/liquid ratio was lowered. In contrast at trace Cs levels, the Cs sorption was neither s/l dependent nor pH sensitive. It is therefore proposed that ion exchange mechanism dominates Cs sorption when the concentration of surface sorption site exceeds that of Cs, whereas surface complexation is attributed to Cs uptake under alkaline environments. Numerical fitting was conducted using two different strategies to determine concentration of surface sorption sites: the clay model (based on the cation exchange capacity plus surface titration results) and the iron oxide model (where the concentration of sorption sites is proportional to the surface area of argillite). It was found that the clay model led to better fitting than the iron oxide model, which is attributed to more amenable sorption sites (two specific sorption sites along with larger site density) when using clay model. Moreover, increasing s/l ratio would produce more sorption sites, which helps to suppress the impact of heterogeneous surface on Cs sorption behavior under high pH environments.

1. Introduction

Nuclear energy plays an important role in energy generation of the modern society, but the disposal of radioactive wastes is an issue of great concern. To isolate radioactive wastes from our environment effectively, a repository facility based on the multibarrier concept is applied. The multibarrier concept involves placing the radioactive wastes into canisters, which are further surrounded by barrier layers including buffer materials (clay), cement/concrete (engineering barriers), and isolating geological substances. Should nuclides leach out, they are expected to be retarded by these sorbents, and as a result the possibility of radioactive contamination of our environment can be greatly reduced.

To improve containment of radioactive nuclides, much effort has been made to improve the understanding of the interaction between nuclides and sorbent materials, including the study of Cs sorption to zeolite [1] and Se sorption to metal oxides [2]. In addition, mobility studies such as Cs and Co diffusion [3,4] and reactive transport phenomenon [5] are interesting topics in this field. On the other hand, improvements on the theoretical side, mostly focused on numerical methods, provide a better model for the explanation of experimental results while maintaining an acceptable calculation speed [6–8]. Although considerable progress has been made, certain areas may yet be improved. For example, Cs, the critical nuclide in the low-level radioactive waste repository, is believed to adsorb to solid surfaces via ion exchange, which is characterized by insensitivity to pH [9]. However, experimental results revealed that solution pH had certain influence on Cs sorption to geological substances such as clay, illite, and mica unless they were pre-conditioned (i.e., replacing all surface exchangeable

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cations by sodium ions) prior to Cs sorption experiments [10]. As a result, a more in-depth study to collect representative data is necessary. Model development and verification are important issues of concern too since they are closely related to the quality of model simulation. Model verification can be achieved by numerical fitting of experimental results. Discrepancy usually appears during numerical fitting, but it can help us to rule out improper data. On the other hand if acquired data are highly reproducible, discrepancy can indicate how one would need to adjust his hypothesis. These efforts would in turn give us ability to predict with confidence nuclide transport in a large time frame and in the field scale.

Here, we report both experimental and numerical fitting results of Cs sorption to argillite. Argillite attracts our attention since it is the potential host rock for the low-level radioactive waste (LLW) repository in Taiwan. In this article the sample collection, sample processing, surface characterization of obtained samples, and Cs sorption experiments are described step-by-step. The method of selecting a sorption model and verification of selected model is also discussed.

2. Experimental

2.1. Sampling

The argillite used here was sampled at NanTain village, south-eastern part of Taiwan (N 22°15.691′ E 120°53.516′). It was washed with deionized water to remove surface contaminants and then air dried. The cleaned argillite was mechanically crushed, sieved, washed with deionized water and air dried. The surface water near sampling site was collected using a 1 L glass jar. The chemical composition of in situ surface water was determined, and synthetic groundwater (SGW, Table 2) based on the determined chemical constituents was prepared accordingly for the use of Cs sorption experiments.

2.2. Characterization

The surface area of argillite was determined by N_2-BET method. The cation exchange capacity (CEC) was estimated by a standardized method (sodium acetate, US EPA 9081 A). Potentiometric titration was applied to determine the protonation/deprotonation constant of argillite. The concentration of active surface hydroxyl groups (–SOH) of argillite was evaluated by mixing 1.0 g argillite with 0.1 M sodium chloride solution (100 mL) under vigorously stirring. The pH of the mixture was first raised to 11 by adding 0.1 M NaOH dropwise. Titration was conducted by adding 0.1 mL of HCl (0.01 M) into the mixture each time until acid environment (pH ~3) was reached. Inert nitrogen gas was bubbled throughout the titration to reduce the influence from the dissolved carbon dioxide. The amount of consumed HCl was recorded. A reference titration was executed by the identical protocol to evaluate HCl consumed by the system. By comparing the amount of HCl consumed in the system with/without argillite between pH 11 and pH 3, the concentration of active surface hydroxyl sites was determined. All the characterizations mentioned above were repeated in triplicate (unless otherwise indicate) to reduce interference from matrix.

X-ray diffraction (XRD) analysis of argillite were recorded by Shimadzu 6000 X-ray diffractometer with scan range between 2° and 80° (2θ) and the scan rate of 4°/min, using Cu Kα radiation (λ = 0.15406 nm) at 30 kV and 20 mA. The surface chemical composition was determined by energy dispersion spectrum (EDS) and the mineral composition was estimated by comparing obtained XRD patterns with reference patterns in JCPDS database.

The chemical composition of in situ surface water was determined by the ICP-OES (OPTIMA 2000 DV, PerkinElmer, for cation) and by ion chromatography (Dionex DX-120 IC-Conductometry, for anion). The concentration of cations (Na^+, K^+, Ca^+, Mg^{2+}, Cs^+, Sr^{2+}) and anions (F^-, Cl^-, Br^-, $NO_3{}^-$, $SO_4{}^{2-}$, $PO_4{}^{3-}$) were determined. The alkalinity of in situ surface water was estimated by titration as mentioned above.

2.3. Sorption batch experiments

The Cs sorption experiments were carried out in polypropylene centrifuge tubes at room temperature in triplicates. In these experiments, 0.1 g of powdered argillite was mixed with SGW to achieve desired sold/liquid ratio (*s*/*l*; 1/100, 1/50, 1/30, 1/10, 1/2) where the initial Cs concentration was either 100 mg/L (7.5×10^{-4} M, stable isotopes) or 0.01 mg/L (7.5×10^{-8} M, radioactive isotope Cs-137). High Cs concentration is selected to assess Cs sorption features while low Cs concentration is to mimic the possible leaching in the repository site (which is expected to be within μg/L levels) [11]. Negligible amount of 0.01 M HCl/NaOH solutions were added to adjust the pH of sorption experiments. Mixtures were continuously shaken in a reciprocal shaker for 24 h. Our preliminary test showed that 24 h is sufficient for sorption reactions to equilibrate (Fig. 2) and in good agreement with our previous study [12]. At the end of reaction, solutions were separated and collected by centrifuge under 12,000 rpm for 10 min. In cases of high *s*/*l* such as 1/2 at which centrifuge is unable to efficiently separate solutions from argillite, solution samples were obtained by filtration through a 0.45 μm Millipore filter cell.

The aqueous Cs concentrations were determined either by measuring their concentration with acetylene-air flame atomic absorption spectroscopy (100 mg/L of initial Cs loadings) or by counting their radioactivity (0.01 mg/L of initial Cs loadings) with a NaI(Tl) detector (Wallac 1470 Wizard). Since no significant Cs sorption on polypropylene tubes was found, the difference in Cs concentration/radioactivity was interpreted as the amount of Cs being adsorbed by argillite. In addition to the above experiments regarding effect of solid/liquid ratio, further Cs sorption experiments, including isotherm studies, effects of temperature and ionic strength were conducted in the similar manner to clarify interactions between Cs and argillite.

2.4. Numerical fitting

In order to evaluate Cs sorption to argillite quantitatively as well as to verify the model, experimental results were fitted using MINEQL+ 4.6 code [13] with the two-layer model. MINEQL+ is a chemical equilibrium modeling code developed to solve mass balance expressions using equilibrium constants. It combines WATEQ3 database and MINEQL numerical structure. The two-layer model was selected to reduce uncertain variables because it does not require any fixed parameter, i.e., capacitance. The physical assumption of the two-layer model consists of one charged surface layer and one layer of diffusion ions. The surface potential is calculated from the net surface charge density through Gouy–Chapman theory. Here, two strategies were selected to fit Cs sorption results; one treated argillite as a clay mineral (clay model) and the other regarded argillite as analogues of iron oxides (iron oxide model). The use of the clay model was based on assumptions that the active mineral constituents of argillite are clay related minerals (kaolin and micas) and hence we expected argillite to possess sorption features similar to those of clay minerals. Alternatively, the iron oxide model is the generalized composite concept, which assumes iron oxides are the most active minerals regulate cation and anion distribution between solid surfaces and solutions [14,15].

In the clay model regime, Cs uptake occurs either at structure sites via ion exchange or at edge sites by surface complexation (two equilibrium constants are thus determined, namely log *KX* and