



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.

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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 N₂-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⁺, Mg²⁺, Cs⁺, Sr²⁺) and anions (F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) 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 solid/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

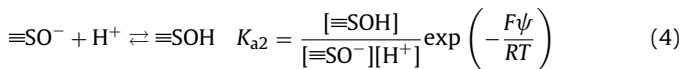
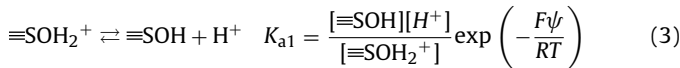
log K_S , respectively). The Cs sorption at structure sites was defined as:



where $\equiv X$ the number of structure sorption sites (mol/L), which is assume to be equal to $\equiv XNa$ (identical to its CEC value). $[Cs^+]$ and $[Na^+]$ are concentrations (mole/L) of Cs^+ and Na^+ , respectively. The equilibrium of ion exchange reactions are described namely:

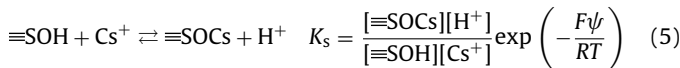
$$K_x = \frac{[\equiv XCs][Na^+]}{[\equiv XNa][Cs^+]} \quad (2)$$

The edge sorption sites are pH-dependent and the following protonation/deprotonation reaction is considered:



where $\equiv SOH_2^+$, $\equiv SOH$ and $\equiv SO^-$ refer to the positively charged, neutral and negatively charged edge sites, respectively, and K_{a1} and K_{a2} are the intrinsic equilibrium acidity constants, which are determined by potentiometric titrations. The exponential term accounts for the Coulombic correction factor accounting for the electrostatic effect, where F is Faraday's constant and ψ is electrical field [14].

Retention of cesium at edge sorption sites is considered as:



Treating argillite as iron oxide analogues (iron oxide model) has the advantage of reducing the number of variables. In this case, one assumes that the surface is homogeneous and the reactivity of sorption comes from available surface hydroxyl groups. Specifically, the term $-FeOH$ instead of the generalized term $-SOH$ is presented to emphasize the equilibrium constant $\log K_{Fe}$ was determined from iron oxide model. Numerical fittings were conducted according to Eq. (3) through (5).

Best fittings of the experimental results were reached by a trial-and-error procedure. To keep the modeling results to a tractable level, we discarded any reaction that did not improve the fitting.

3. Results and discussion

3.1. Characterization of argillite and in situ groundwater

A reliable safety assessment of radioactive waste repository depends strongly on the knowledge of interactions of nuclides with local geological substances. One important concern is the representativeness of the collected samples. At the beginning, two kinds of argillite were sampled, one from an exposed outcrop argillite and the other from an unexposed, embedded sample. Collected bulk argillite was first pulverized to facilitate the in-lab experiments. After washing out weathered products (such as fine clay particles), three groups of pulverized argillites were collected according to their particle size distributions (>0.85 mm, 0.85 – 0.231 mm, and <0.231 mm). All three groups from each type of argillites (18 samples with triplicate) were analyzed via EDS to quantify the surface chemical constituents (Table 1). From Table 1, it appears that the surface chemical compositions of outcropped and embedded argillite are very close to each other. This result implies the pulverized argillites are suitable argillite representations since they have very similar properties as those in situ potential host rocks. In addition to EDS analysis, all samples were subjected to XRD analysis to identify their mineral compositions. We did not compare the crystal domain size of the two types of argillite from the XRD peak

Table 1
The surface chemical composition of argillite.

Elements	Outcropped (wt%)	Std (wt%)	Embedded (wt%)	Std (wt%)
Na	2.40	1.81	3.40	0.50
Mg	2.88	1.38	2.51	0.80
Al	18.05	3.47	19.52	4.72
Si	33.60	5.61	35.78	3.33
K	2.56	1.21	3.52	1.69
Fe	1.72	0.64	1.89	0.88
Total	61.22		66.62	

widths since they are mixtures. However, it seemed that all samples possess very similar XRD patterns as shown in Fig. 1a. The mineral composition of argillites identified by comparing JCPDS database includes quartz (88-2487), chlorite (29-0381), muscovite (86-1386), kaolinite (87-2057), pyrophyllite (42-0569), contribute to surface potassium contents) and albite (84-0982), respectively.

Since all pulverized argillite have consistent properties in both the surface chemical composition and the mineral composition, we confidently mix the outcropped and embedded argillites together. Considering fine argillite particles may partially dissolve in SGW (we observed this during washing pulverized samples), the particle size distribution between 0.85 and 0.231 mm was selected

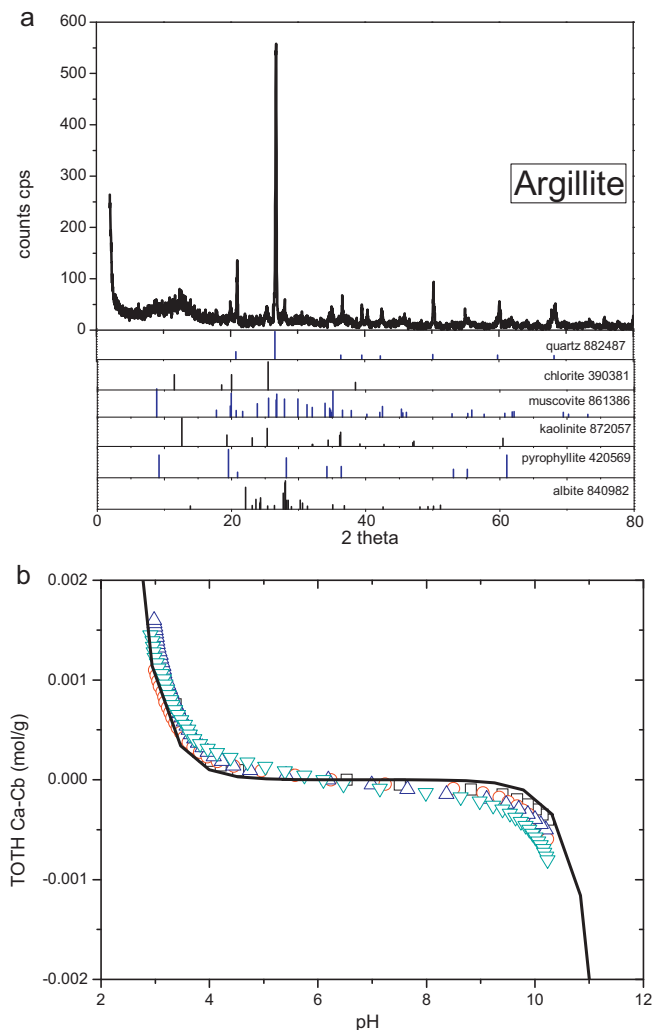


Fig. 1. (a) The mineral composition of argillite (b). The example of determining protonation/deprotonation constants by fitting experimental results with MINEQL code.

Table 2
The composition of in situ surface water.

Ions	Conc. (mg/L)	Std (mg/L)	Conc (M)	Equvi. (M)
Na ⁺	14.89	0.37	6.47E-4	6.47E-4
K ⁺	0.30	0.01	7.73E-6	7.73E-6
Ca ²⁺	15.36	0.14	3.84E-4	7.68E-4
Mg ²⁺	11.17	0.20	4.65E-4	9.31E-4
Sr ²⁺	0.12	0.01	1.36E-6	2.27E-6
Cs ⁺	<0.12		<9.02E-7	
Total cation				2.36E-3
F ⁻	0.37	0.01	1.92E-5	1.92E-5
Cl ⁻	22.53	0.71	6.35E-4	6.35E-4
Br ⁻	0.09	0.003	1.09E-6	1.09E-6
NO ₃ ⁻	0.12	0.004	1.98E-6	1.98E-6
SO ₄ ²⁻	14.18	0.496	1.48E-4	2.96E-4
Alkalinity	18.03	1.436	3.01E-4	6.01E-4
Total anion				1.55E-3
Cation-anion				+8.03E-4

for further surface chemistry characterization. In order to proceed with numerical fitting, it is necessary to define the surface property of argillites. The most important parameter in calculating the distribution of contaminants on solid surfaces and in solutions is the concentration of surface sorption sites (which also can be converted to site density). The determined BET surface area of argillite is $11.20 \pm 0.62 \text{ m}^2/\text{g}$ ($n=8$). Its concentration of ion exchangeable sites (CEC) is $6.33 \pm 0.17 \times 10^{-5} \text{ eq/g}$ ($n=12$). To determine the concentration of edge sites, several runs of titration ($n=12$) were conducted. The concentration of edge sites was estimated by considering the following equation [16]:

$$\text{SOH} = \frac{(\text{moles of H added (solid + system)} - \text{moles of H added (system)})}{2} \quad (6)$$

It is important to note that Eq. (6) works only when the titration starts with argillite being completely protonated and ends when all the involved SOH sites are deprotonated, and vice versa. Under these conditions, we derived edge site concentration as $4.29 \pm 0.82 \times 10^{-5} \text{ mol/g}$. After determining the concentration of edge sites, the protonation/deprotonation constant of SOH sites were assessed by considering Eqs. (3) and (4) with assistance of MINEQL (Fig. 1b). The protonation/deprotonation constant determined from fitting the potentiometric titration curves ($n=6$) is 6.52 and -7.99 , respectively. It is possible that a fraction of ion exchangeable sites may have participated in protonation/deprotonation reactions though, which led to an overestimation of the amount and the activity of edge sites. To reduce influence from this concern, it is suggested to use high ionic strength solution as we did in this study when assessing the properties of edge sites [17].

The composition of in situ surface water is shown in Table 2. It is a low ionic strength solution. As mentioned, using low ionic strength solution like this one during determination of the property of edge sites would result in an overestimation due to the participation of ion exchangeable sites. It is noted that the in situ surface water contains 0.12 mg/L ($1.36 \times 10^{-6} \text{ M}$) of Sr²⁺, which is another critical nuclide of LLW repository and deserves our attention as well. When conducting Sr sorption experiments in the future, the effect of Sr isotope exchange will be taken into account.

3.2. Cs sorption results

The results of kinetics under different temperatures and isotherm studies are shown in Fig. 2. There were several interesting features observed. First it is obvious that Cs sorption equilibrium was reached fairly rapidly (within 10 min) under all studied temperatures, solid/liquid ratios, and initial Cs concentrations. Fast sorption reactions usually happen to geological substances that

have little surface area with limited porous structure. Based on kinetic results, we are confident that one day is enough for reactions to equilibrate. Since the Cs sorption kinetics are so rapid that no significantly exponential features were found from the plots, we did not interpret them by any kinetic models (first order, or pseudo-second-order). In addition to reaction time, we found in general that Cs sorption decreased with increasing temperatures. This is because that at higher temperature, adsorbed Cs has higher thermal energy to desorb from solid surfaces and thus shift sorption equilibrium toward desorption [9]. In the case of trace amount of Cs, however, it seemed that Cs sorption was not affected by elevated temperatures (considering the relatively large standard deviations shown in Fig. 2b). The lower temperature dependency may be attributed to the majority of Cs being associated with “strong sites” [14]. Strong sites are sorption sites with higher surface energy, which tend to reduce their surface energy by association with foreign ions with larger equilibrium constants. From Fig. 2b, we observed almost 100% of sorption in all study environments. In this case, the number of sorption sites far exceeds that of Cs, whether they are strong sites or weak sites. We cannot distinguish the surface heterogeneity from Fig. 2b, although the fact that argillite is a mixture rather than a pure mineral.

Generally, the concentration of sorption sites is evaluated either from crystallography or from fitting experiment results [8]. If surface is homogeneous, for instance, one can determine the monolayer sorption site density by fitting experimental isotherm with Langmuir equation. On the other hand, the existence of surface heterogeneity, which is usually observed among most geological

substances, makes distinguish each type and number of sorption sites very difficult. Since argillite is a mixture consisting of many different minerals (micas and kaolinite), it is relatively difficult to determine the amount of sorption sites by summation of individual sites from each minerals. A practical alternative is the use of physical sorption models, such as Langmuir model, to fit isotherm results. Isotherm studies under different pH are shown in Fig. 2c. In this study, we found that Cs isotherms differ greatly from Langmuir isotherm. In contrast, Cs isotherms correlate with Freundlich equation very well as indicated by a high correlation coefficient ($R^2 > 0.90$, Fig. 2c). This indicates that Cs sorption did not follow monolayer sorption but rather adopted the multilayer sorption behavior. In addition, a higher a value obtained from Freundlich equation implies higher sorption affinity toward Cs. We found that argillite has higher affinity under neutral pH ($a \sim 0.31$), moderate affinity under low pH ($a \sim 0.28$) and lower affinity under high pH environments ($a \sim 0.17$, Fig. 2c). This is a very interesting result since we expected that argillite would have the highest affinity under alkaline environments since at high pH most of surface sorption sites are deprotonated and therefore greatly increase electrostatic interactions. The reason for this observation is not clear from the limited information we had in this study. In addition to the kinetic and the isotherm studies mentioned above, we also conducted Cs isotherm experiments under monoionic solutions ($[\text{Na}] = 2.36 \text{ mM}$, identical to the ionic strength of synthesized surface water). Results were very similar to those shown in Fig. 2c and thus we do not present them here. This implies that the competition between Sr and Cs toward argillite in this study is negligible.

Cs sorption under various pH, s/l ratios and different initial Cs concentrations and their best fitting are plotted in Fig. 3. Adjusting the initial Cs concentrations or s/l ratio can create an excess or a deficiency of sorption sites, which enables us to obtain further insight into the heterogeneity on argillite. Under high Cs concentration environments (100 mg/L), two features are observed. First, the Cs

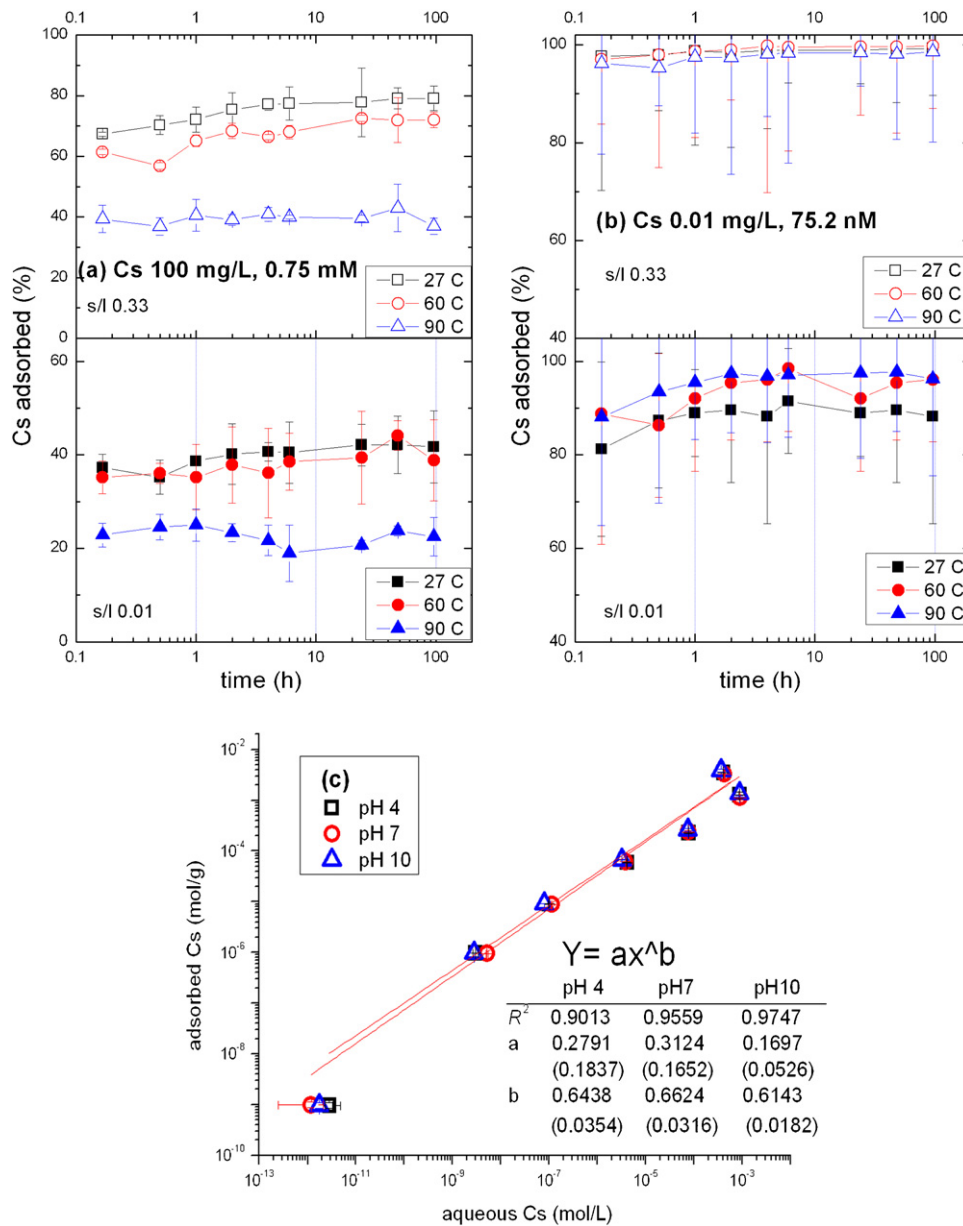


Fig. 2. Cs kinetic sorption under (a) high Cs (100 mg/L), (b) low (0.01 mg/L) concentration; (c) Cs isotherms under different pH environments, numbers shown in the figure are fitting results from Freundlich equation, values in parentheses are the standard deviation.

sorption ratio rises as the *s/l* ratio increases. This expected result is in good agreement with the literature, showing that the more sorption sites that are available, the higher Cs sorption one can reach [9]. Second, the Cs sorption edges appear around pH 6–8 in all investigated cases. The presence of sorption edges is usually regarded as the consequence of surface complexation. This indicates that in addition to ion exchange, surface complexation also contributes to Cs uptake. Besides, Cs sorption edges are more significant in the case of the highest (1/2) *s/l* environments. This is probably because the amount of sorption sites started to exceed the number of Cs cations and thus most of Cs cations are homogeneously adsorbed. This will be discussed later.

Appropriate interpretation strongly relies on the quality of experimental results. In the case of trace Cs concentration, as shown in Fig. 2b, the high error bars were the inevitable consequence of the analysis in trace level, depending on the precision of the instrument used. Regarding the radioactivity measurement, the deviation ranges from less than 3% up to near 20%, which closely relates to

signal/noise (*S/N*) ratio. The deviation of stock solution was lower than 3%, however, in the end of sorption experiment with 90%+ sorption ratio, the deviation greatly rose up to near 20%. Undoubtedly, higher initial radioactivity of stock solution can help to keep a reasonable *S/N* even after 90%+ of sorption reaction. But it exposes operators to significantly higher radiation levels. More importantly, it produces more radioactive wastes, which conflicts with the concept of radioactive waste repository about reducing amount of wastes in the first place. Recently, inductively coupled plasma mass spectrometer (ICPMS) has demonstrated its sensitivity with Cs detection limit down to $\mu\text{g/L}$ level [25], which is competitive with tracer method and produces no radioactive wastes. Since that ICPMS is not that accessible, one might alternatively use crown ethers or some inorganic crystals to concentrate/extract Cs before introducing into a flame atomic absorption spectrometer or a fluorescence spectrometer [26,27]. In addition to difficulty in trace level analyses, heterogeneity of geological substances propagates error bars. Spread among triplicate samples could be significant

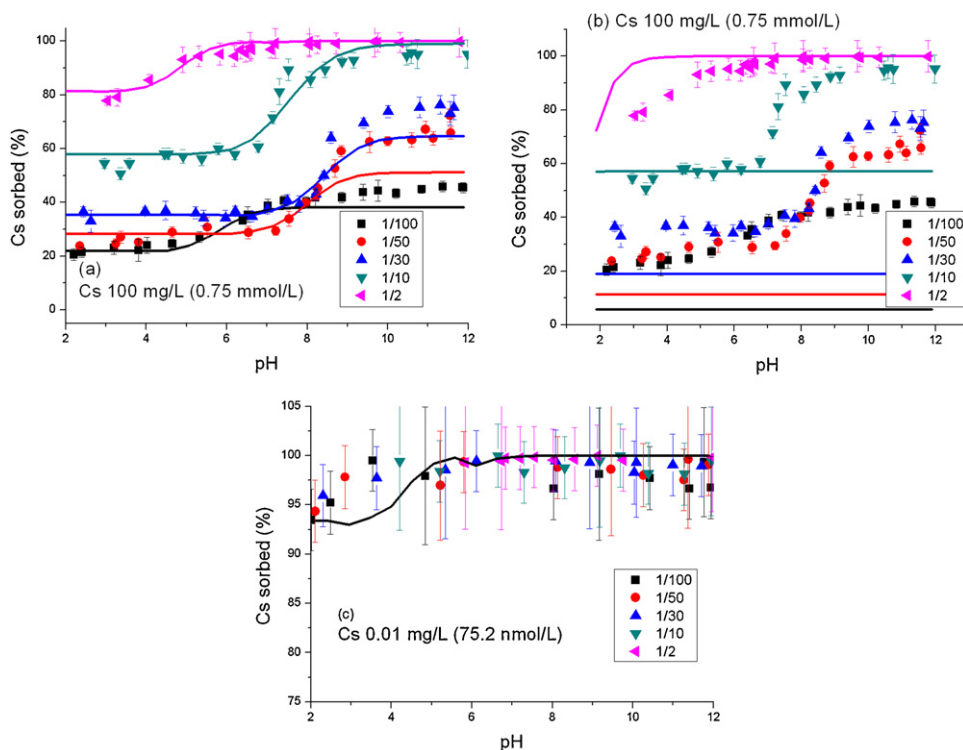


Fig. 3. Cs sorption to argillite with high Cs loadings (100 mg/L) (a) fitting by clay model, (b) fitting by iron oxide model, and (c) Cs sorption to argillite with low Cs loadings (0.01 mg/L) and fitting by both model since both models gave the same resulting fit.

and determination of outlet value becomes an issue of concern. We reported the average from triplicate samples without screening out any one of them because we would like to emphasize the influence of heterogeneous geological samples. The last factor accounting for large error bars came from converting values into percentage. Above three reasons holds for the large error bars shown in Figs. 3 and 4.

Since we knew the reasons for the large error bars, we were confident on the results from trace Cs level. Unlike relatively smaller sorption ratios observed under high Cs concentration environments, nearly complete sorption of cesium occurs when one lowers

the initial Cs concentration by four orders of magnitude compared to the previous case. The reason for this near complete sorption is that the concentration of sorption sites overwhelms that of Cs cation. Under these circumstances, the Cs sorption edges disappear and Cs sorption becomes independent of *s/l*. This is a desirable result in the prospect of radioactive waste management. The Cs sorption characteristics are, on the other hand, difficult to observe nearly complete sorption of cesium occurs. This would suggest that it might not be necessary to use radioactive tracer to explore interaction in this case.

3.3. Numerical fitting results

Numerical simulation is an essential technique in exploring interactions between radionuclides and geological substances. By applying an appropriate and reasonable physical sorption model, one can assess the detailed interactions that are difficult to observe directly through experiments as well as make a confident prediction of nuclides transport, which is impossible to acquire at the laboratory/field scale [18]. It is pertinent to mention here that while the inclusion of more parameters could in theory lead to a better simulation, in practice this can lead to computational difficulties. Often it is better to simplify the simulation by selecting fewer more relevant parameters, so as to accelerate processing and to promote compatibility with other simulations such as performance assessment of LLW. For example, the majority of codes for performance assessment use K_d values rather than thermodynamic reaction constants. This means that derived reaction constants from thermodynamic model require further conversion to comply with performance assessment codes. Despite these concerns, using thermodynamic reaction constants is always considered more advantageous since they allow insight into sorption reaction mechanisms.

Surface complexation models (SCMs) have been demonstrated to be capable of describing ion sorption behavior onto mineral sur-

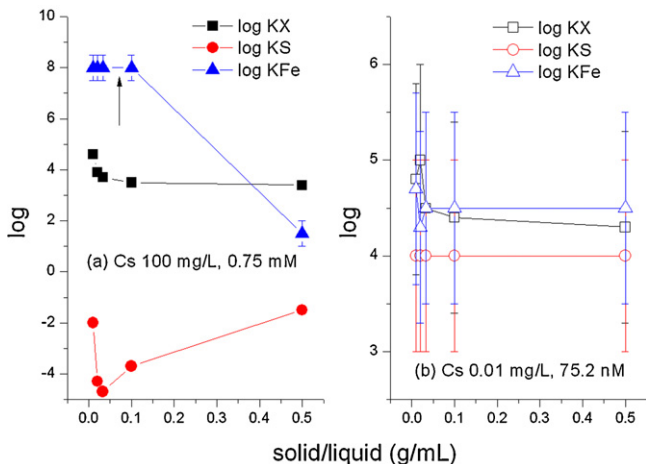


Fig. 4. The influence of solid/liquid ratios on determined reaction constants from two fitting strategies. Here, $\log K_X$ and $\log K_S$ stands for equilibrium constant of ion exchange sites and edge sites in clay model, defined by Eq. (2) and by Eq. (5), respectively; while $\log K_{Fe}$ refers to general sorption sites on solid surface defined by Eq. (5) with *S* replaced by *Fe* as follows: $\equiv\text{FeOH} + \text{Cs}^+ \rightleftharpoons \equiv\text{FeOCs} + \text{H}^+$ $K_s = \frac{[\equiv\text{FeOCs}][\text{H}^+]}{[\equiv\text{FeOH}][\text{Cs}^+]}$ $\exp\left(-\frac{F\psi}{RT}\right)$.

Table 3
The determined log *K* values by two different fitting strategies.

Solid/liquid ratio	Strategy 1 ^a							
	100 mg/L				0.01 mg/L ^c			
	log <i>K_s</i>	log <i>K_x</i>	<i>r</i> *	<i>p</i> **	log <i>K_s</i>	log <i>K_x</i>	<i>r</i> *	<i>p</i> **
1/100	−2.0	4.6	0.9824	1.42E−14	4.0	4.8	0.6531	2.93E−02
2/100	−4.3	3.9	0.9719	9.43E−13	4.5	5.0	0.7965	5.83E−03
3.33/100	−4.7	3.7	0.9821	1.69E−14	4.0	4.5	0.9148	2.08E−04
10/100	−3.7	3.5	0.9915	1.77E−14	4.0	4.4	0.2381	5.08E−01
50/100	−1.5	3.4	0.8287	6.38E−06	4.0	4.3	0.6367	4.78E−02
	Strategy 2 ^b							
	100 mg/L			0.01 mg/L ^c				
	log <i>K_{Fe}</i>	<i>r</i> *	<i>p</i> **	log <i>K_{Fe}</i>	<i>r</i> *	<i>p</i> **		
1/100	8.0	Poor	Poor	4.7	0.7419	1.40E−02		
2/100	8.0	Poor	Poor	4.3	0.8521	1.74E−03		
3.33/100	8.0	Poor	Poor	4.5	0.8964	4.44E−04		
10/100	8.0	Poor	Poor	4.5	0.1676	6.44E−01		
50/100	1.5	0.0536	8.37E−01	4.5	0.7183	1.93E−02		

*: The *r*-value is Pearson correlation coefficient and **: the significance. Both values are obtained by comparing the best fitting curve and the experimental data with the built-in program of OriginPro 8 (OriginLab, USA).

^a Strategy 1: the argillite is treated as clay mineral, consisting of both structure and edge sorption sites (6.33E−05/4.29E−05 mol/g) and their concentration is individually determined from CEC and surface titration.

^b Strategy 2: the argillite is treated as iron oxides, consisting of only one kind of surface sorption sites and its concentration is determined from the amount of surface area (4.30E−05 mol/g).

^c There are a range of values that are capable of fitting experimental data very well and thus the values shown here are with the highest *r*-value and with lowest *p*-value, please see text for more details.

faces [18]. However, when applying SCMs, it is necessary to process a self-consistent approach toward defining parameter values. Here, we used two strategies to proceed to the fittings and summarize them in Table 3. Strategy 1 considers argillite as a clay analog (clay model), which possesses both ion exchange sites and edge sorption sites on surfaces. Strategy 2 regards argillite as iron oxide analog (iron oxide model) since iron oxides are the most active species in most of the geological substances [14,19]. In the latter case, one assumes the surface sites of argillite are generic surface sites and their density could be directly converted from BET surface area measurements by a recommended value of 3.84 μmol/m² [20].

Comparing the fitting results under high Cs concentration (lines in Fig. 3a and b), it is clear that a better fitting is obtained using the clay model. The poor fit of the iron oxide model can be observed in Fig. 3b. The poor fit of the iron oxide model can be inferred to be due to too few sorption sites being present. It is indicated that not until the *s/l* (solid/liquid) rises to 1/2 does the fit approach the experimental results. A good fitting result in this case can never be achieved unless more sorption sites were given for Cs uptake. It is inappropriate to increase the surface area since this value is quantified by BET measurements. A reasonable alternative is to increase greatly the surface site density. A window of given surface site density among an order of magnitude is reported in literature when fitting uranium sorption to ferrihydrite [8]. When using this assumption, it is very likely to achieve a good fit, i.e., using the available sorption site in the case of *s/l* = 1/10 to fit experimental result in the case of *s/l* = 1/100). One should always keep in mind that a good model does not mean a fit curve, which exactly matches all of the experimental data (of course it is still the goal to achieve for every researcher). Rather, it is acceptable if a fit curve is able to describe the sorption features by catching the onset of steeply rising (sorption edge) and the onset of saturation (sorption capacity). Every adjustable variable used during fitting should correspond to a precisely defined physical characteristic. Fit curves produce this way can reveal information, which is not easily assessed from macroscale experiment. As a result, it would be helpful to conduct parameter calibration in advance if one tries to increase the sorption site density in the model [8], e.g. using Langmuir isotherm to

determine sorption site density. However, another issue emerges at the same time since the calibrated value is expected valid only for a particular nuclide. We might therefore produce an array of calibration values for most elements in the periodic table in order to take into account of all possible nuclides. In light of connect fundamental study and practical application, it would be good to reduce the number of variables to the lowest reasonable extent. This is why we did not calibrate the sorption site density in advance, of course it is not an easy task considering our isotherm results (Fig. 2c). Instead, we used an established value from the literature since we would like to pursue a general sorption site density rather than a specific one (for Cs only).

While the clay model can give a relatively good fit, it is obvious that the simulations are still unable to describe Cs sorption at pH > 8, which is particularly significant in the cases where solid/liquid = 1/100, 1/50, and 1/30, respectively (Fig. 3a). This reveals the fact that there are not sufficient sorption sites to accommodate adsorbed Cs ions under alkaline environments in the above sorption model. The two most likely causes for this failure are the surface heterogeneity and the alkaline effect. Surface heterogeneity accounts for some surface sorption sites that are particularly active and thus are able to adsorb more than one cation (multinuclear sorption) [21]. Surface heterogeneity is easily detected by means of EDS where the adsorbed ions are particularly concentrated in certain regions, resulting "hot" zones on the mapping images [12]. Increasing solid/liquid ratio creates an environment with more high affinity site available. This explains the disappearance of sorption edge in the case of *s/l* = 1/2 since more sorption sites are available to accommodate adsorbed Cs ions. To interpret surface heterogeneity, modelers tend to add more distinct sorption sites according to either crystallography studies (sorption occurs on −SiOH and −AlOH sites) [17] or experiment results (assuming strong and weak sorption sites) [14]. In addition, reactions such as multinuclear sorption and surface precipitation are suggested to be taken into consideration [21].

One the other hand, the alkaline effect describes the interaction between OH anions and solid surfaces under alkaline environments [22]. The alkaline environment is the result of interaction between

groundwater with cement. Subjected to alkaline plumes for six months, kaolinite, smectite and illite are reported to be partially dissolved, which is accompanied by a decrease in their layer charge and in their cation exchange capacity [23]. A dramatic rise in macropore void of argillite also results [24]. While argillite dissolution is not significant over the timeframe of this study, it is likely that the sorption affinity of argillite for cesium will be affected by interaction with alkaline water.

When the initial Cs concentration is lowered by four orders of magnitude (0.01 mg/L), good fitting results can be easily achieved with either strategy. A serious concern emerges when considering the deviation (~one log unit) of experimental data. Taking into consideration of one log unit of deviation, neither the feature of sorption affinity nor the sorption capacity under these different *s/l* conditions can be precisely determined. This can be attributed to low surface coverage, where the number of sorption sites far exceeds the number of cesium cations. This introduces great uncertainty into fitting results since a wide range of values can produce a good fit. Our fitting results clearly point out this difficulty when estimating or modeling sorption behaviors under low nuclide concentration, which is exactly the presumable scenario where nuclides might leach out from the repository facilities.

In general, the clay model can give a good fit since the greater number of sorption sites more easily allows one to explain features regarding sorption edges and capacities. Under high Cs concentrations (Fig. 4a), determined $\log KS$ (edge sites) varies with *s/l* ratios due to the heterogeneous sorption as well as the alkaline effect; while the $\log KX$ seems constant regardless of *s/l* ratios (solid/liquid ratios). This means the structure sorption sites govern Cs uptake on argillite. The $\log K_{Fe}$ values pointed by the arrow in Fig. 4a are the results of failure in fitting and hence we only report a minimum value that produces a maximum sorption site number (any larger value is meaningless since it produces no more sites). It is the consequence of the number of Cs cations far exceeding the number of available sorption sites. In contrast (Fig. 4b), determined $\log KS$ is constant regardless of *s/l* but the $\log KX$ slightly decreases with the increase in *s/l*. The latter indicates less contribution from structure sites as the *s/l* increases even though they are in relatively large population. Despite contribution from the edge sorption sites being the same (constant $\log KS$), structure sorption sites still govern Cs uptake under low Cs concentrations due to their relatively large population. On the other hand, since the concentration of sorption sites overwhelms that of Cs cations, obtained $\log \log K_{Fe}$ is also independent of *s/l*. Under this circumstance, we are unable to define precisely the interactions between Cs nuclides and argillite. This means that tracer experiments might not necessitate conducting in the light of reducing the amount of radioactive wastes produced.

4. Conclusion

In this study, Cs sorption to argillite under high and low initial Cs concentrations and under various solid/liquid ratios was explored. Further numerical fittings were conducted to investigate the mechanisms behind these conditions. We found that the concentration of sorption sites is the critical factor affecting fitting results. In the case of high Cs concentration (100 mg/L) using clay model leads to a better fitting due to the fact that the more sorption sites are available. In contrast for the iron oxide model the fitting results are not accurate since the Cs concentration is far higher than the concentration of sorption sites. Under low surface coverage such as the case of low initial Cs concentration (0.01 mg/L), concentration of sorption sites overwhelms that of Cs cations. Using either model one can obtain good fitting results in this case but the uncertainty

introduced is large for both cases. We also found that heterogeneous sorption as well as alkaline effect plays an important role in Cs sorption under high pH environments.

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References

- [1] E.H. Borai, R. Harjula, L. Malinen, A. Paajanen, Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals, *J. Hazard. Mater.* 172 (2009) 416–422.
- [2] R.R. Sheha, E.A. El-Shazly, Kinetics and equilibrium modeling of Se(IV) removal from aqueous solutions using metal oxides, *Chem. Eng. J.* 160 (2010) 63–71.
- [3] D. Aldaba, A. Rigol, M. Vidal, Diffusion experiments for estimating radiocesium and radiostrotrium sorption in unsaturated soils from Spain: comparison with batch sorption data, *J. Hazard. Mater.* 181 (2010) 1072–1079.
- [4] T. Itakura, D.W. Airey, C.J. Leo, T.E. Payne, G.D. McOrist, Laboratory studies of the diffusive transport of Cs-137 and Co-60 through potential waste repository soils, *J. Environ. Radioact.* 101 (2010) 723–729.
- [5] J. Gimenez, J. de Pablo, M. Martinez, M. Rovira, C. Valderrama, Reactive transport of arsenic(III) and arsenic(V) on natural hematite: experimental and modeling, *J. Colloid Interface Sci.* 348 (2010) 293–297.
- [6] F. Kulahci, Z. Sen, Potential utilization of the absolute point cumulative semi-variogram technique for the evaluation of distribution coefficient, *J. Hazard. Mater.* 168 (2009) 1387–1396.
- [7] A. Florido, C. Valderrama, J.A. Arevalo, I. Casas, M. Martinez, N. Miralles, Application of two sites non-equilibrium sorption model for the removal of Cu(II) onto grape stalk wastes in a fixed-bed column, *Chem. Eng. J.* 156 (2010) 298–304.
- [8] T.E. Payne, J.A. Davis, O. Michael, O. Markus, C.J. Tweed, Uranium adsorption on weathered schist—intercomparison of modeling approaches, *Radiochim. Acta* 92 (2004) 651–661.
- [9] R.M. Cornell, Adsorption of cesium on minerals: a review, *J. Radioanal. Nucl. Chem.* 171 (1993) 483–500.
- [10] J.M. Zachara, S.C. Smith, C.X. Liu, J.P. Mckinley, R.J. Serne, P.L. Gassman, Sorption of Cs+ to micaceous subsurface sediments from the Hanford site, USA, *Geochim. Cosmochim. Acta* 66 (2002) 193–211.
- [11] D. Karamanis, P.A. Assimakopoulos, Efficiency of aluminum-pillared montmorillonite on the removal of cesium and copper from aqueous solutions, *Water Res.* 41 (2007) 1897–1906.
- [12] S.C. Tsai, T.H. Wang, M.H. Li, Y.Y. Wei, S.P. Teng, Cesium adsorption and distribution onto crushed granite under different physicochemical conditions, *J. Hazard. Mater.* 161 (2009) 854–861.
- [13] W.D. Schecher, D.C. McAvoy, MINEQL+: a chemical equilibrium modeling system, version 4.5 for Windows, in: User's Manual, v2.00, Environmental Research Software, Hallowell, Maine, 2003.
- [14] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley-Interscience, New York, 1990.
- [15] T.H. Wang, M.H. Li, W.C. Yeh, Y.Y. Wei, S.P. Teng, Removal of cesium ions from aqueous solution by adsorption onto local Taiwan laterite, *J. Hazard. Mater.* 160 (2008) 638–642.
- [16] J. Tang, K.H. Johansson, Adsorption of rare earth elements onto Carrizo sand: experimental investigations and modeling with surface complexation, *Geochim. Cosmochim. Acta* 69 (2009) 5247–5261.
- [17] I.C. Bourg, G. Sposito, A.C.M. Bourg, Modeling the acid–base surface chemistry of montmorillonite, *J. Colloid Interface Sci.* 312 (2007) 297–310.
- [18] J.A. Davis, J.A. Coston, D.B. Kent, C.C. Fuller, Application of the surface complexation concept to complex mineral assemblages, *Environ. Sci. Technol.* 32 (1998) 2820–2828.
- [19] L.J. Criscenti, D.A. Sverjensky, A Single-site model for divalent transition and heavy metal adsorption over a range of metal concentrations, *J. Colloid Interface Sci.* 253 (2002) 329–352.
- [20] J.A. Davis, D.B. Kent, M.F. Hochella, A.F. White (Eds.), Mineral–Water Interface Geochemistry, Reviews in Mineralogy, vol. 23, Mineralogical Society of America, Washington, 1999, pp. 177–248.
- [21] L.E. Katz, K.F. Hayes, Surface complexation modeling 1, strategy for modeling monomer complex-formation at moderate surface coverage, *J. Colloid Interface Sci.* 170 (1995) 477–490.
- [22] A.S. Kinsela, A. Tjitrajaja, R.N. Collins, T.D. Waite, T.E. Payne, B.C.T. Macdonald, I. White, Influence of calcium and silica on hydraulic properties of sodium montmorillonite assemblages under alkaline conditions, *J. Colloid Interface Sci.* 343 (2010) 366–373.
- [23] M. Honty, M. De Craen, L. Wang, J. Madejová, A. Czimerová, M. Pentrák, I. Stríček, M. Van Geet, The effect of high pH alkaline solutions on the mineral stability of the Boom Clay—Batch experiments at 60 °C, *Appl. Geochem.* 25 (2010) 825–840.

- [24] O. Cuisinier, F. Masrouri, M. Pelletier, F. Villieras, R. Mosser-Ruck, Microstructure of a compacted soil submitted to an alkaline plume, *Appl. Clay Sci.* 40 (2008) 159–170.
- [25] W.-J. Li, F.-Y. Wang, W.-H. Zhang, D. Evans, Measurement of stable and radioactive cesium in natural waters by the diffusive gradients in thin films technique with new selective binding phases, *Anal. Chem.* 81 (2009) 5889–5895.
- [26] E.D. Roper, V.S. Talanov, M.G. Gorbunova, R.A. Bartsch, G.G. Talanova, Optical determination of thallium (I) and cesium (I) with a fluorogenic calyx[4]arenebis(crown-6 ether) containing one pendent dansyl group, *Anal. Chem.* 79 (2007) 1983–1989.
- [27] A. Clearfield, Ion-exchange materials seizing the cesium, *Nat. Chem.* 2 (2010) 161–162.