Bridging the gap between batch and column experiments: A case study of Cs adsorption on granite

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ARTICLE INFO

ABSTRACT

Both batch and column methods are conventionally utilized to determine some critical parameters for assessing the transport of contaminants of concern. The validity of using these parameters is somewhat confusing, however, since outputs such as distribution coefficient (K_d) from these two approaches are often discrepant. To bridge this gap, all possible factors that might contribute to this discrepancy were thoroughly investigated in this report by a case study of Cs sorption to crushed granite under various conditions. Our results confirm an important finding that solid/liquid (S/L) ratio is the dominant factor responsible for this discrepancy. As long as the S/L ratio exceeds 0.25, a consistent K_d value can be reached by the two methods. Under these conditions (S/L ratios > 0.25), the sorption capacity of the solid is about an order of magnitude less than that in low S/L ratios (<0.25). Although low sorption capacity is observed in the cases of high S/L ratios, the sorption usually takes place preferentially on the most favorable (thermodynamically stable) sorption sites to form a stronger binding. This is verified by our desorption experiments in which a linear isotherm feature is shown either in deionized water or in 1 M of ammonium acetate solutions. It may be concluded that batch experiment with an S/L ratio exceeding 0.25 is crucial to obtain convincing K_d values for safety assessment of radioactive waste repository.

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1. Introduction

A sound and reasonable prediction of the transport of contaminants of concern in groundwater or geological environments depends deeply on reliable and valid transport-related parameters. To reach this end, either batch or column methods are frequently conducted in the laboratory to estimate transport-related parameter such as distribution coefficient, K_d [1–4]. Batch experiments, also known as static systems, are carried out by adding certain amount of solid into solution containing specific concentration of contaminants with a specific solid/liquid (S/L) ratio. These mixtures are vigorously stirred or shaken during the entire reaction time. The concentration of contaminant in solution is monitored and its change is thus regarded as the amount of contaminant to be partitioned onto solid. The merit of the batch approach lies in that it does not require much space of experiment apparatus while all variables of interest could be obtained experimentally. However,

the batch approach is criticized because its S/L ratio is often different from that observed in the field. For this reason, the validity is doubted while applying the results from batch method in laboratory scale to estimate the transport of contaminants in field scale.

On the other hand, column experiments (or dynamic systems) involve packing the relevant geological material into columns where the transport of contaminants in the solution is monitored. Analysis of the obtained contaminant breakthrough curve leads to the determination of K_d from column method [5]. Since the contaminant travels in the interparticle pores of packed geological substances in the column approach, it offers a better simulation of the real environment. Accordingly, column method would be relatively suitable to determine the transport properties of relevant contaminants of concern in laboratory scale [6]. The drawback of time and space demanding, however, greatly reduces the informative benefit of column method. In addition, some derivative issues (such as the tourosity in microscale as well as the bulk density of packed substance, the length and diameter of columns, etc.) arise in column experiments from either experimental conditions or from experimental protocols. Therefore, using outputs of column experiments alone to assess the contaminant transport might be inappropriate.

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Although using both approaches could offer estimates of the transport-related parameters, the gap between the results of these two techniques is observed. This is an annoying phenomenon to evaluate the transport of contaminants, especially for the safety assessment of radioactive waste repository sites. In recent years, a huge amount of efforts were exerted to explore the cause of this disagreement. Several factors were proposed to explain this discrepancy [7]. The factors include: (i) differences in the batch experimental conditions such as solid/liquid (S/L) ratio [8,9], kinetics of adsorption [10,11], or the homogeneity of packed geological substance, particle spacing [12]; (ii) difference in column experimental protocols, such as loss of sorbent particles through the column end retainer, variations in contaminant flow [10], or the presence of immobile water zones [5].

The validity and confidence of using the results from either of the two methods depend on strongly identifying which factor(s) causes this gap [7]. To this end, a series of batch experiments under various conditions are carried out in this study. The derived K_d values were compared with those obtained from column methods. Batch experiments in this study were conducted as a function of solid/liquid ratios. Also, two solid/liquid ratios of 1 g/30 mL and 20 g/40 mL were selected for further study on pH as well as on desorption experiments. Results of dynamic transport were obtained by analyzing the breakthrough curves using a reactive transport model from advection–dispersion column experiments [13]. Cesium (Cs) was selected since Cs-137 is a critical nuclide of safety assessment of radioactive waste repository due to its being a high yield fission product along with a long half-life of 30 years. Granite was considered because it is a potential host rock for repository in Taiwan. Furthermore, excavated granite could be ground to be used as backfill materials for engineering barrier. The objective of this investigation is to bridge the gap of results from these two methods by considering factors which have been reported causing such disagreement. The impact of these factors on this discrepancy is thoroughly discussed and analyzed in this study.

2. Materials and methods

2.1. Solid and chemicals

The granite samples were taken from a deep geological environment with a depth of 177–178 m in an islet near Taiwan. These granite samples were first crushed and ground. The powdered samples were washed with deionized water (DW) to remove fine particles and then dried at 60 °C. The grain size of granite particles was in 60–80 mesh (0.25–0.18 mm). Analyzing by XRD (Philips PW1300), the major constituent minerals of crushed granite are quartz, biotite and feldspar. The oxides in the sample identified by an ICP-MS (Sciex Elan 5000, PerkinElmer) are SiO_2 (72.56%),

Al_2O_3 (12.9%), K_2O (8.84%), Na_2O (4.20%) and Fe_2O_3 (1.13%). The composition of synthetic groundwater (GW) is shown in Table 1. All chemical reagents used in this study were of analytical grade (Merck) and dissolved into DW (Milli-Q, 18.3 MΩ cm resistivity).

2.2. Adsorption/desorption batch experiments

To study the effect of solid/liquid ratio on cesium adsorption onto granite, 0.4–100 g of crushed granite was added into 40 mL of 0.1 mM CsCl DW or GW solutions spiked with appropriate amount of radioactive ^{137}Cs tracer. All batch adsorption experiments were performed using serum bottles (Schott, Germany) with neutral pH environments (pH ∼ 7.5). After shacking for 1 week, the upper suspension was collected by filtration and its radioactivity was recorded by a NaI(Tl) counter (Canberra 2000). The reduced radioactivity in filtrate is interpreted as the amount of Cs ions adsorbed on crushed granite. In addition, two distinct solid/liquid ratios (1/30 and 1/2) were selected for further isotherm studies along with adsorption in different pH values. The adjustment of pH was carefully made by adding negligible volume of HCl or NaOH solutions without altering the S/L ratios. All experimental processes were the same as those aforementioned. After completing these adsorption experiments, the granite solids were collected by filtration and then dried at a reduced pressure to make preparations for desorption experiments. In desorption experiments, one gram of dried crushed granite was immersed into 30 mL (S/L = 1 g/30 mL) of DW or of 1 M of neutral NH_4OAc (acetate ammonium) solutions to extract those adsorbed Cs ions. The neutral NH_4OAc solutions were prepared by diluting pure acetate acid solution (99.5%) with aliquot amount of concentrated ammonium hydroxide solutions.

2.3. Deduced K_d values from column experiments

Details of our deduced K_d values from column experiments will be reported in a companion paper [13]. In brief, advection–dispersion column experiments were carried out in crushed granite columns with a length of 8 cm. The Cs front in GW solution (0.1 mM) was continuously pumped through the column at a flow rate of 1 mL/min until the breakthrough was reached. The obtained breakthrough curves (BTCs) were then analyzed using a reactive transport model. The K_d value of column experiments is thus derived based on the following equation:

$$K_d(\text{column}) = k \times \frac{V}{m} = k \times \frac{70.65}{139} \, (\text{mL/g}) \tag{1}$$

where the value k, whose physical meaning is the sorption ratio of granite toward Cs ions, is estimated from model fitting; V and m are pore volume of the column and mass of the packed crushed granite, respectively.

3. Results and discussion

3.1. Adsorption batch experiments under various solid/liquid ratios

The effect of solid/liquid ratio factor on K_d value obtained from our experiments is shown in Fig. 1. Derived K_d values from dynamic column experiments are also presented in Fig. 1. The results from batch experiments display a distinct feature: a rapid decease of K_d value as S/L ratio increases in the low solid/liquid ratio region (S/L < 0.25). Then, K_d value reaches a steady state as the S/L value exceeds 0.25, which is the recommended S/L ratio of ASTM [14]. In our work, the derived K_d values are about 3.8 and 0.8 mL/g in DW and GW, respectively. Since K_d value stands for the sorption capacity per gram solid to sorb Cs ions (mole), the curve demonstrates

Table 1
The composition of synthetic groundwater employed in this study; pH ∼ 7.5; ionic strength ∼ 0.35

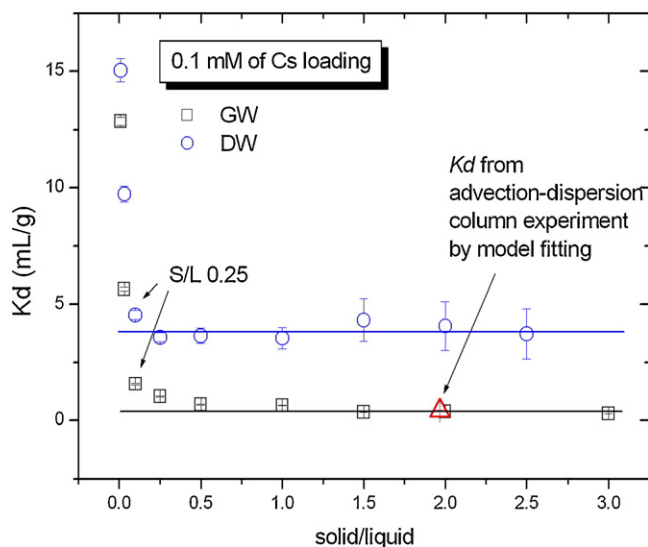| Ions	GW (M)
Cl^-	1.78E-01
Br^-	5.01E-04
F^-	8.00E-05
HCO_3^-	1.64E-04
SO_4^{2-}	5.83E-03
Na^+	9.13E-02
K^+	2.07E-04
Li^+	1.44E-04
Ca^{2+}	4.72E-02
Mg^{2+}	1.73E-03
Sr^{2+}	4.00E-04

Fig. 1. Cs sorption on powdered granite as a function of S/L ratios.

the fact that the amount of adsorbed Cs ions to per gram of crushed granite deceases as S/L ratio increases. This phenomenon is related to the thermodynamic stability of sorption sites on solid [5,8,9]. In the case of low S/L ratio, the Cs loading overwhelms the sorption capacity of granite particle. Consequently, Cs ions are sorbed on all available sites, resulting in a high sorption density. However, under the conditions of high S/L ratio, favorable sorption sites are abundant. Since the most favorable sorption sites are filled preferentially by Cs ions from solution, a low sorption density is observed [5]. Accordingly, the steady K_d values appeared in the high S/L ratio region indicate that the adsorbed Cs ions are partitioned on the most favorable sorption sites.

In addition, the K_d value determined from dynamic column experiment also falls in this steady K_d region. This finding agrees with reports by other investigators that the discrepancy in K_d values determined from these two methods could be attributed to the factor of S/L ratio. Nevertheless, this conclusion may be drawn too soon. In fact, the dynamic column experiments were conducted with a continuous Cs front flow. In other words, the amount of Cs ions in solution exceeds the available sorption sites of solids. It is possible that the factor of S/L ratio, which is mainly related to the abundance of sorption sites rather than Cs ions concentration in solution, may not be the only factor causing the gap between the sorption parameters determined by the two techniques.

Although column experiments are informative of the transport of contaminants under high S/L conditions, it is rather difficult to deduce the behaviors and mechanisms of interaction. Some investigations have pointed out that the presence of immobile water regions, which might result from aggregated solids in columns, or operation under unsaturated conditions (varying moisture contents) will produce a lower K_d value [7,8]. For examples, at low moisture content, transport of these aqueous Cs ions to granite surface by diffusion becomes much slower as some granite particles are "dry". For heterogeneous interface like aqueous Cs ions sorption to solid granite surface, sorption could take place only when the aqueous Cs ions "collide" with granite surface. As a result, the portion of available sorption sites is reduced at low moisture contents which further restrict the type of sorption sites available [5]. Moreover, incomplete separation of aggregated soil might cause the nonsettling colloid-size particles presented in the liquid fraction [8]. These nonsettling particles will directly alter the tourosity in microscale by clogging or creating some micro-ducts. As a con-

sequence, this might cause the inaccessibility of Cs ions to those sorption sites that might otherwise be accessible in a batch system. Also, this might moderate the sorption rate till all sorption sites are ultimately accessible if given enough reaction time [5]. However, the effect of immobile water region in the column seems trivial in this study since only 5–8% of the column is occupied by immobile water region at the most [5]. Most importantly, these immobile water regions might also be observed under the unsaturated condition in batch experiments with high S/L ratios. Therefore, this factor is not likely to lead to such discrepancy since it should appear in both column and batch experiments.

In addition to the aforementioned factors, the velocity-dependent retardation factor (R), which could be readily converted to K_d value by considering the porosity and bulk density of columns, has also been proposed to depict such deviation [7,10,11]. In these cases, the factor of nonequilibrium sorption during transport results in lower R values, and consequently lower K_d values, compared with those estimated from a batch method. The nonequilibrium may involve transport- and/or sorption-related behaviors. Transport-related nonequilibrium is caused by slow solute diffusion into and out of immobile water regions. Sorption-related nonequilibrium originates from slow chemical reaction or slow diffusive transport within the sorbent or within the interparticle spacing [7]. It is noted that most of these nonequilibria are strongly involved in phase transferring. For example, the sorption of hydrophilic solid such as micas toward hydrophobic organic contaminants is relatively slow because of heterogeneous sorption [15–18]. By contrast, sorption of these solids toward aqueous Cs ions is much faster due to relatively homogeneous sorption behavior [19,20]. Consequently, although the nonequilibrium might occur during dynamic column experiments, it would have only a minor influence on K_d value determination because the sorption reaction is almost instantaneous in this case.

3.2. Adsorption under high and low solid/liquid ratios

Since either the immobile water region or nonequilibrium sorption in columns has only minor contribution to this disagreement of K_d value determination, one may come to the conclusion that the discrepancy of batch- and column-determined K_d value mainly depends on the factor of S/L ratio. Therefore, a series of batch experiments were carried out with S/L ratios of 1/30 and 20/40 to further study the difference of effects from low and high S/L ratios. Results of isotherm sorption experiments under high (20 g/40 mL) and low (1 g/30 mL) S/L ratio in DW and GW solutions are shown in Fig. 2. In addition, these results are fitted by a derivative Langmuir model, a built-in program of Origin 6.0 Profession software (OriginLab Corp., USA) and expressed as follows:

$$[Cs]_s = \frac{B_{max}[Cs]_l}{(k_1 + [Cs]_l)} \tag{2}$$

where B_{max} represents the maximum sorption sites and k_1 is the Langmuir constant.

One could make the most of Langmuir model to obtain the changes of sorption capacity (B_{max}) under various experimental conditions as shown in Fig. 2. It is exhibited that under low S/L ratios, only nearly half of the sorption sites remain in GW, compared with that in DW solution. This indicates plenty of cations such as Na, K, Ca and Mg in GW occupy about nearly half of sorption sites that were available for Cs ions in DW solutions. Under high S/L ratios, less than 20% of sorption sites remain in GW. In addition, available sites under high S/L ratios show a sharp reduction of about 67% and 89% in DW and GW, respectively, in contrast with those under low S/L ratios. Based on these findings, it could be deduced that about 33% of sorption sites on granite surface are of high affinity toward
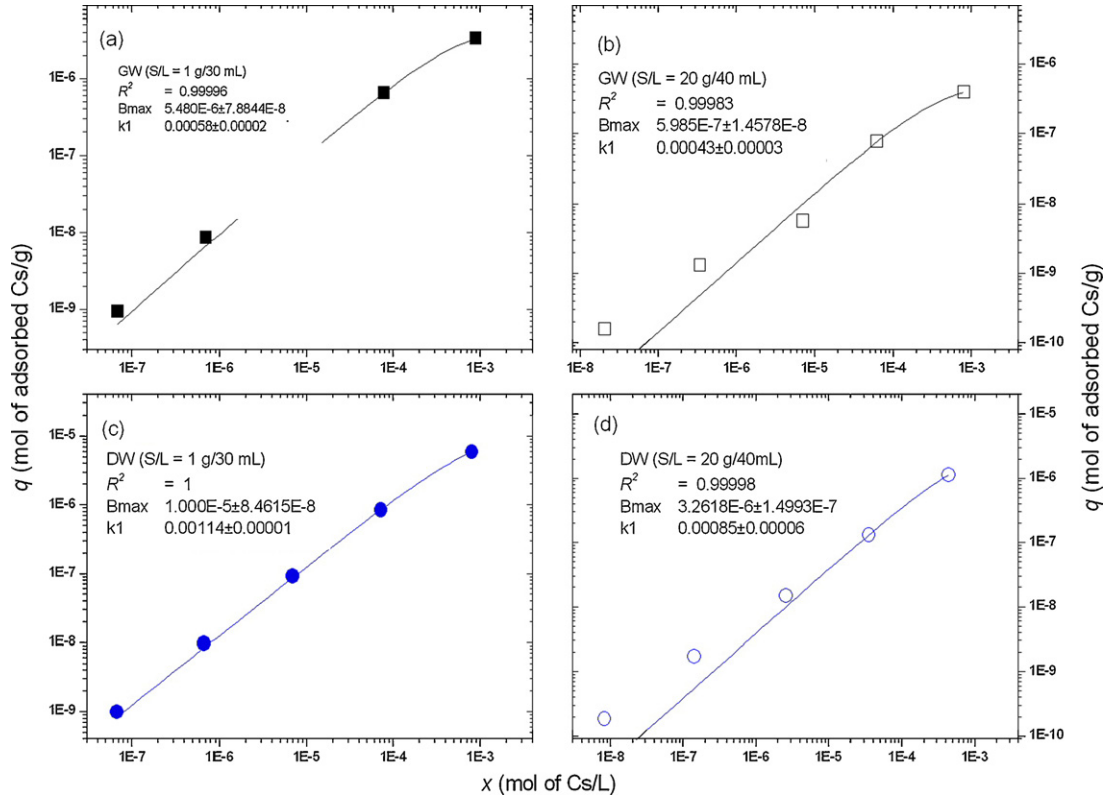
Fig. 2. Isotherm of Cs sorption on crushed granite under high and low S/L ratios.
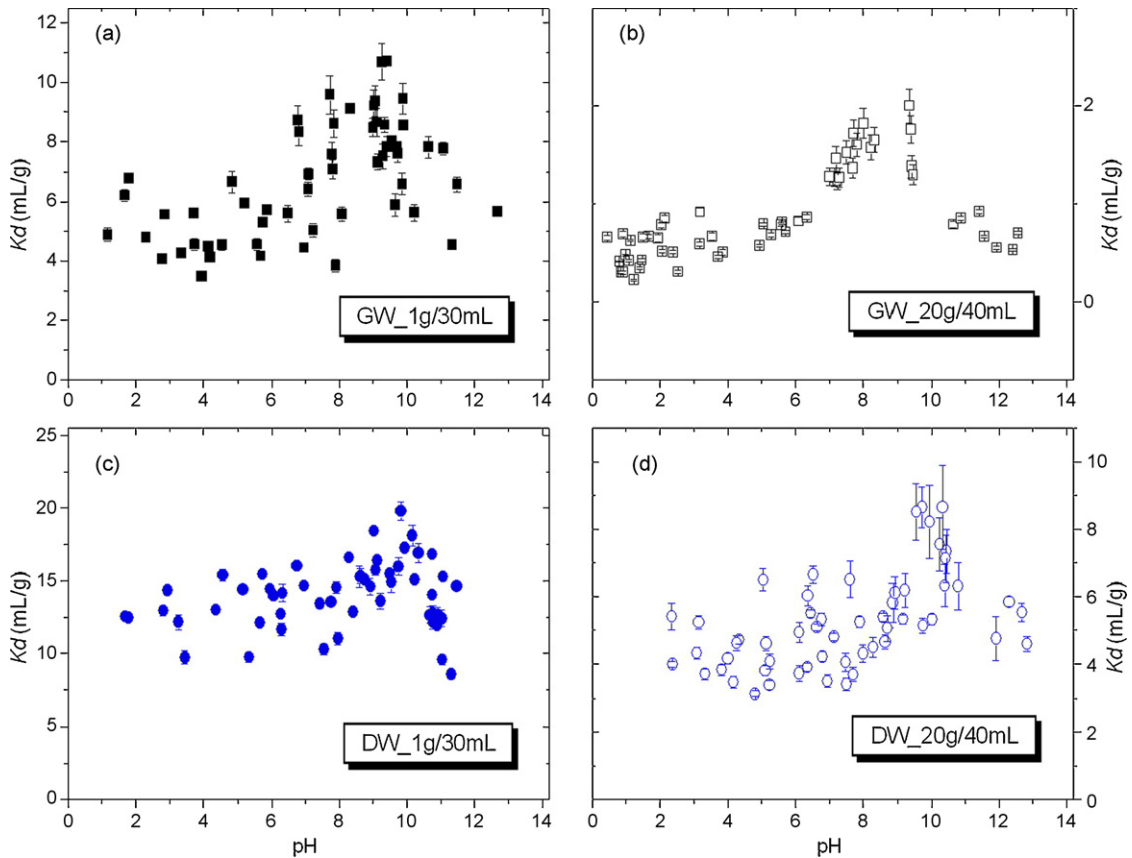

Fig. 3. Cs sorption on crushed granite under high and low S/L ratios with various pH.
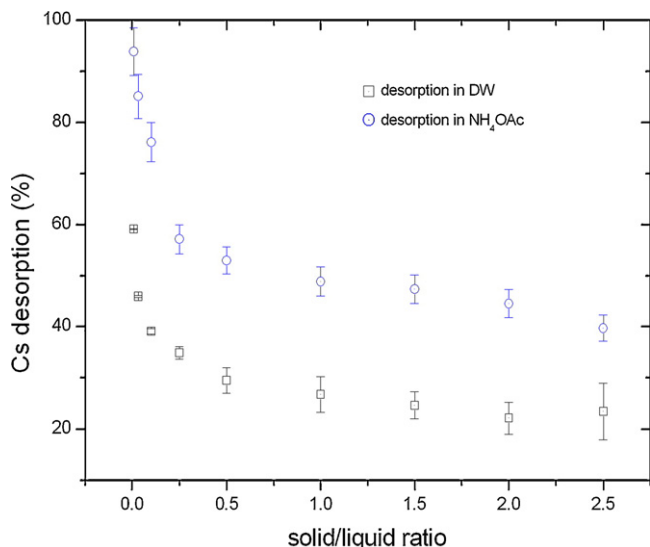
Fig. 4. Cs desorption from granite samples collected from previous sorption experiments under different S/L ratios.

Cs sorption. About 20% among these high affinity sorption sites, which accounts to approximately 6% of the total, are the most favorable sorption sites toward Cs ions. To interpret this phenomenon in detail, models with two or three groups of distinct sorption sites were proposed [21–23]. In these investigations, the sorption capacities and affinities of these sites are estimated by fitting the cesium adsorption isotherms in the presence of given electrolyte solutions with a three-site ion-exchange model. Briefly, the most abundant

group designated as Site III, or planer site is the site with low affinity. Site II, the intermediate group, has intermediate affinity and intermediate sorption capacity whereas Site I, the group of frayed edge site (FSE) has the highest affinity and the closest connection to the "irreversible sorption". The exact volume of FES of rock minerals may be affected by many factors including the particle size of the grain, the weathered condition the grain and the nature of rock minerals. However, a relatively similar modeling result has been shown that these high affinity FES may only account for 0.25% of sorption capacity of pure illite and micaceous minerals [21–23]. Detailed EXAFS study reveals that these different affinity sorption sites provide distinct coordination environments toward Cs ions, leading to the formation of outer-sphere complexes or inner-sphere complexes of adsorbed Cs ions on solid surface [24]. Hence the occurrence of different sorption behaviors under high and low S/L ratio is strongly related to the coordination environments where Cs ions situate in. Sorption mechanisms involving these coordination environments will be addressed in later sections.

Fig. 3 shows the effects of pH on Cs adsorption under low and high S/L ratios. Although these plots scatter, sorption edges are observed in the pH range of 8–10 in DW or GW solutions regardless of the S/L ratios. The presence of these sorption edges implies that surface complexation reactions played a key role among the Cs adsorption mechanisms. It is noted from observation of these sorption edges that Cs adsorption behavior is relatively insensitive to variations in pH, which is the principal characteristic of ion-exchange reactions [25]. Accordingly, it could be concluded that Cs sorption behaviors are only slightly affected by pH regardless of the S/L ratios. In other words, the change in sorption mechanism is barely related to the discrepancy of K_d values between batch and column experiments.
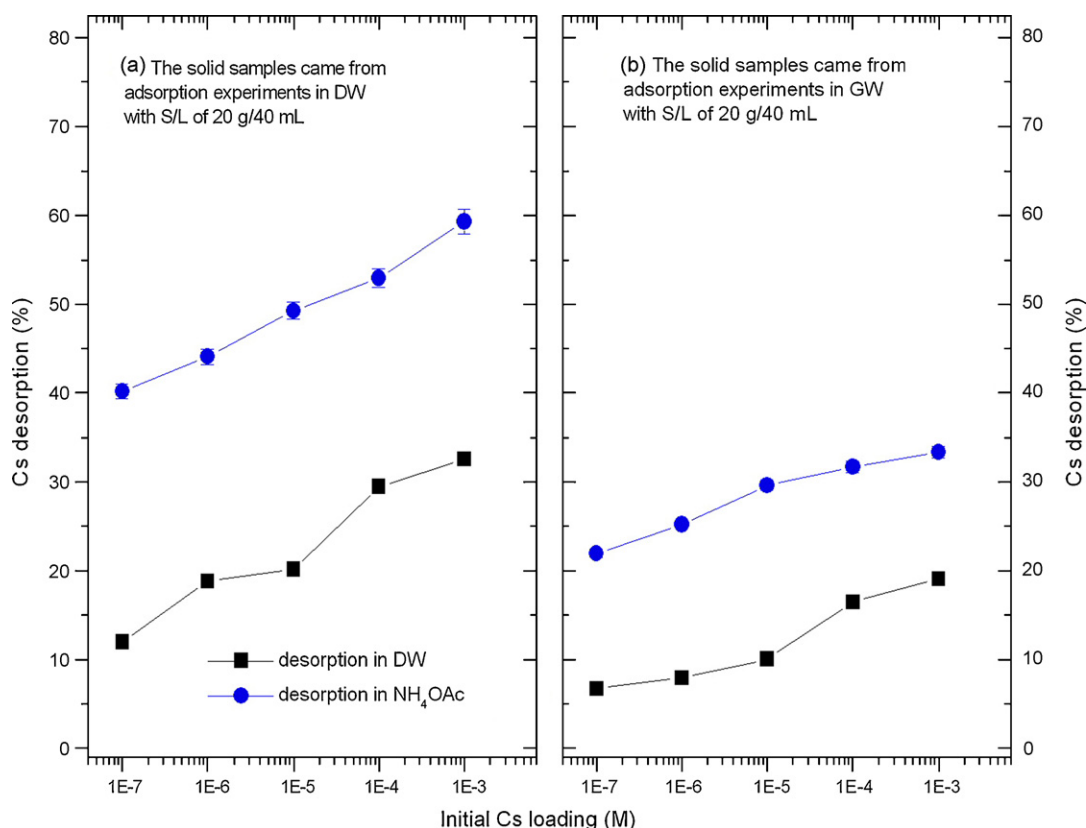

Fig. 5. Cs desorption percentage from granite samples collected from (a) DW and (b) GW solutions under high S/L (S/L = 20 g/40 mL) conditions.

3.3. Desorption experiments of granite obtained from high solid/liquid ratios

Based on information shown in Figs. 1–3, it is quite clear that the S/L ratio is the dominant factor causing the gap of K_d values obtained from column and batch experiments. It is also evident that Cs ions are preferentially distributed onto high affinity sorption sites, resulting in a low sorption density (amounts of adsorbed Cs ions per unit mass of solid) in the cases of high S/L ratio. To investigate this phenomenon further, we conducted desorption experiments by using those granite samples collected from the aforementioned sorption experiments. In this series of experiments, we used DW solution to quantify sites of weakly adsorbed surface whereas we adopted 1 M of NH_4OAc (acetate ammonium) solution to estimate amounts of high affinity ion-exchangeable sites. It is noted in Fig. 4 that desorption percentage drops rapidly for samples with low S/L ratios, while a gradual decrease of desorption percentage is observed for samples with high S/L ratios (S/L > 0.25), regardless solutions that we used. This indicates that under the low S/L conditions, more cesium would have to be released from unit mass of granite to reach a thermodynamic equilibrium concentration. By contrast, under high S/L conditions, cesium is strongly bound (formation of inner-sphere complexation) in solids resulting in less release of Cs ions. Therefore, it is reasonable to infer that for a radioactive waste repository surrounded by granite host rock, the distance that the released cesium can migrate would be limited.

A more substantial evidence is presented in Fig. 5, where the linear desorption percentage shown is an indicator of the unsaturated sorption of granite toward Cs ions [9]. The absence of sorption plateaus is due to the fact that the available sorption sites exceed the amount of Cs ions in solution. Accordingly, Cs ions have easy access to sorption sites with high affinity. The high affinity sites are found on the sheet structure of micaceous minerals (biotite, the dominant sorbent in granite). These laminar solids consist of cations, mainly aluminum and silicon, bound with oxygen in octahedral or tetrahedral coordination [23]. Charge neutrality between sheets is compensated by ion-exchangeable cations presented in interlaminar sites. These sorption sites are perceived as being surface hydroxyl groups (−SOH) situated along the edges of the sheet ("edge" or "broken bond" sites) which can undergo protonation (−SOH^{2+}) and deprotonation (−SO−) reaction. Faces with either different crystalline or imperfections (edges and corners, etc.) will form sorption sites with different energies, resulting in different affinity sites [25]. Weakly bound Cs ions come from outer-sphere complexes, which is the consequence of electrostatic associations of hydrate Cs with anionic surfaces within the basal plane or interlayer and dissociated edge hydroxyl groups. In contrast, the strongly sorbed Cs ions, which are the majority under high S/L ratios, are generated by inner-sphere complexes, involving formation of strong electronic bonding of Cs ions to the frayed edge sites, external basal plane or within the interlayer [24]. These high affinity sites govern the transport of cesium at low concentration under high S/L ratio environments (in field). Consequently, it is reasonable to expect that much of the released Cs ions from radioactive waste repository site would be firmly adsorbed by the geological substances. The threat of contaminating the biosphere with radioactive nuclides will be greatly reduced.

4. Conclusions

The sound performance assessment of radioactive waste repository sites is built upon the foundation of using valid and reliable transport parameters such as distribution coefficient, K_d, of radionuclides. In this work, results (K_d) determined from column experiments were analyzed and compared with those from batch experiments under various conditions. Discrepancy of results obtained from these two methods is studied by examining all relevant factors one by one. Based on our experiments, derived K_d values from batch experiments would be consistent with those from column experiments only when the S/L ratio exceeds 0.25. The low sorption density calculated from high S/L ratio conditions is characterized by high sorption affinity, which is confirmed by the linear feature of desorption isotherm. Consequently, it is concluded that the S/L ratio contributes substantially to the gap between these two methods. To make a convincing safety assessment, batch experiment with S/L ratio greater than 0.25 is essential to obtain a reliable transport parameter.

Acknowledgements

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