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Lithium sorption to Yucca Mountain tuffs

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Abstract

The Li ion has been used as a reactive tracer in field tests performed in the saturated and unsaturated-zone in volcanic tuffs at Yucca Mountain, Nevada. Lithium sorbs weakly by cation exchange and permits field-scale testing of laboratory-based predictions of reactive-solute transport. A series of laboratory studies show that Li sorption is nonlinear and varies with lithology in the different horizons of the tuff. In particular, both Li sorption and Li-specific cation-exchange capacity vary as functions of tuff mineralogy, and can be predicted given quantitative X-ray diffraction data. These results indicate that Li sorption is dominated by clay and zeolite minerals, and that sorption coefficients can be predicted given mineralogic analysis results. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Field-scale tracer tests have been or will be conducted in the vicinity of the potential high-level nuclear waste repository at Yucca Mountain, both in the saturated zone (C-Wells and Alluvial Testing Complexes) and the unsaturated zone (Busted Butte Facility). Primary goals of the tests include confirmation of conceptual models of flow and transport, estimation of field-scale flow and transport parameters, and evaluation of the field-scale applicability of laboratory-based predictions of reactive-solute transport.

During Yucca Mountain site characterization activities, numerous laboratory studies of radionuclide transport behavior have been conducted (Triay et al., 1997). These batch sorption and column studies have yielded an extensive database of transport parameters that have been used by numerical modelers in predicting and analyzing the long-term performance of the potential repository. However, the applicability of laboratory-scale measurements to field-scale predictions remains an issue of concern. Environmental and regulatory concerns have precluded the use of actual radionuclides as tracers in field tests; surrogate reactive tracers have been turned to instead.

The Li ion has emerged as the most commonly used reactive tracer at Yucca Mountain for a number of reasons. There are minimal health and regulatory concerns associated with Li, it is relatively inexpensive and easy to analyze, has a low background level, and most important, it shows a significant but low degree of sorption. More highly sorbing tracers, such as the transition metals in use at the Busted Butte Facility, while closer in behavior to the actual radionuclides of concern, display slow transport and correspondingly long breakthrough times and test durations. In this regard, Li can be considered a generic reactive tracer that doesn't necessarily mimic the behavior of any radionuclides of concern but that has the desirable property of providing interpretable reactive-solute field responses in reasonable amounts of time.

In connection with the saturated-zone field-scale tracer tests at the C-Wells (Reimus et al., 1999), the authors conducted laboratory measurements of Li sorption and cation exchange capacity of a number of different tuffs that comprise the subsurface testing horizons at the C-Wells complex. These results provided the basis for Li transport predictions at the C-Wells. Comparison of these results to tuff mineralogy provides further insight into the detailed mineralogic basis of Li sorption behavior.

Previous studies of Li/rock interactions include Newman et al. (1991), who performed batch sorption experiments on a single sample of the Prow Pass tuff

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from Yucca Mountain, and a number of cation exchange experiments on mineral isolates, reviewed by Bruggenwert and Kamphorst (1982). Of particular interest is a set of cation exchange experiments conducted by Eckstein et al. (1970), discussed in Section 3.

2. Materials and methods

2.1. *Tuff samples*

Seven devitrified tuff samples, each representing different lithologic intervals below the water table at the C Wells, were selected from core samples collected during the drilling of the wells. These intervals were all within the Tram, Bullfrog, and Prow Pass members of the Crater Flat Group (Geldon, 1993). Following standard Yucca Mountain Project protocol, each sample was ground and wet-sieved to a particle size range of 75–500 μm. Previous studies have concluded that grinding and sieving have relatively minor effects on metal sorption, and that the 75–500 μm size range yields the most reproducible sorption results (Rogers and Meijer, 1993). The mineralogical composition of the samples was preserved as close as possible to the field conditions; therefore, no pretreatment was applied to remove carbonate or organic matter. Mineralogy of the samples was determined by quantitative X-ray diffraction (QXRD). Sample descriptions and QXRD results are presented in Table 1.

2.2. *Lithium-specific cation exchange method*

A Li-specific cation-exchange capacity (CEC) method was developed to quantify the Li affinity for the selected tuffs. The method involved 2 steps: saturation of the exchange sites with Li, followed by displacement of the Li and other cations with Cs. The pH of all solutions was kept close to 8.2 to prevent calcite dissolution. The C-wells groundwater is a Na- and Ca–HCO_3-dominated water with an ionic strength of ~0.003 M and a pH of 7.5–8.

Five grams of crushed and sieved tuff (75–500 μm particle size) from each interval was briefly sonicated and then shaken for 30 min with 30 ml of Li-saturating solution (0.8N LiBr–0.2N LiOAc) in 50 ml Teflon centrifuge tubes. After centrifugation and decanting of the supernatant, the saturation step was repeated twice more, for a total of 3 stages. The supernatant from each step was combined and analyzed by ICP-AES for Na, K, Ca and Mg. Following Li saturation, the tuff samples were briefly sonicated and then shaken for 30 min with 30 ml of a Cs-saturating solution (1.0 N CsCl). The samples were centrifuged and decanted, and the process was repeated twice more. The supernatant from all 3 steps was combined and analyzed by ICP-AES for Na, K, Ca, Mg and Li. Residual Li saturating solution remaining in the centrifuge tubes was discounted by analyzing for Br and making the appropriate correction. Each tuff sample was tested in triplicate.

The method described yields two different CEC results: CEC-$\mathrm{Li_T}$, the total CEC available to Li, estimated from the total cations displaced by Li in the saturation step, and CEC-$\mathrm{Cs_T}$, the total CEC available to Cs, estimated from the total cations displaced by Cs in the displacement step. CEC-$\mathrm{Cs_T}$ can be further subdivided into CEC-$\mathrm{Cs_{Li}}$, based on the Li displaced by Cs, and CEC-$\mathrm{Cs_{Nat}}$, based on the native cations (Na, K, Ca, Mg) displaced by Cs. Each of these results is expressed in milliequivalents per 100g of dry tuff.

2.3. *Lithium sorption measurements*

Five grams of crushed and sieved tuff (75–500 μm particle size) from each of the 7 intervals was shaken for 24 h with 10 ml of a solution of Li Br solution in J-13 well water, taken from a saturated volcanic tuff horizon about 4 km from the C-wells (Harrar et al., 1990). Seven different Li concentrations ranging from 1–1000 mg/l were used for each type of tuff. Each combination of a given tuff and a given Li concentration was studied in duplicate. After sorption, samples were centrifuged and the equilibrium Li solution concentration in the supernatant was

Table 1
Sample descriptions and QXRD results*

Sample ID	Stratigraphic unit	Smectite	Clino-ptilolite	Mord-enite	Analcime	Quartz	Feldspar	Hematite	Calcite	Mica/ Illite	Kaol-inite
1	Upper Prow Pass	–	–	–	–	43±2	50±7	1±1	Trc.	1±1	4±1
2	Central Prow Pass	2±1	–	–	–	33±2	60±8	Trc.	2±1	Trc.	–
3	Lower Prow Pass	2±1	–	–	–	39±2	54±8	1±1	–	Trc.	–
4	Bedded Prow Pass	–	–	20±4	39±2	28±2	16±4	–	–	–	–
5	Central Bullfrog	2±1	–	–	–	34±2	60±8	Trc.	2±1	2±1	–
6	Lower Bullfrog	9±3	4±1	3±1	12±1	37±2	27±4	–.	4±1	4±1	–
7	Upper Tram	1±1	–	–	–	55±3	43±6	Trc.	–	–	–

QXRD results are % composition by weight. Trc. = trace abundance (<0.5%).

determined by ICP-AES. Sorbed concentration was calculated by difference. Sorption to centrifuge tube walls was checked by running blanks containing no tuff and was found to be negligible at all starting concentrations.

3. Results and discussion

3.1. CEC Measurements

Results of the 4 CEC measurements on the 7 tuff samples are presented in Fig. 1 and Table 2. In all cases, we see that the total CEC available to Cs (CEC-Cs_T) exceeds that available to Li (CEC-Li_T). This result is not surprising; Cs's hydrated ionic radius (0.33 nm) is smaller than that of Li (0.38 nm-Israelachvili, 1992), which permits Cs access to internal exchange sites in zeolites that are not available to Li. More surprising is the consistent observation that Cs displaces more Li during the displacement step than Li displaced other cations during initial saturation (i.e. CEC-Cs_{Li} > CEC-Li_T). This phenomenon, a "lithium excess" during the displacement step, was also reported by Eckstein et al. (1970). They attributed this Li excess to a separate process that occurs in addition to normal cation exchange: selective and specific adsorption of Li, particularly to amorphous silicates and to edges and broken bonds of non-expanding clay minerals. They state that "it [is] difficult or even doubtful that a "true" value for the exchange capacity can be given for any specific clay." They further conclude that "the sum of cations replaced by Li will usually give a better value for the exchange capacity than the amount of Li retained and replaced by $Ca(OAc)_2$.

Inspection of the mineralogy of the samples, presented in Table 1, indicates that the primary minerals likely to participate in cation exchange include smectite and the zeolite minerals clinoptilolite and mordenite. [Although analcime has a high theoretical CEC (Ming

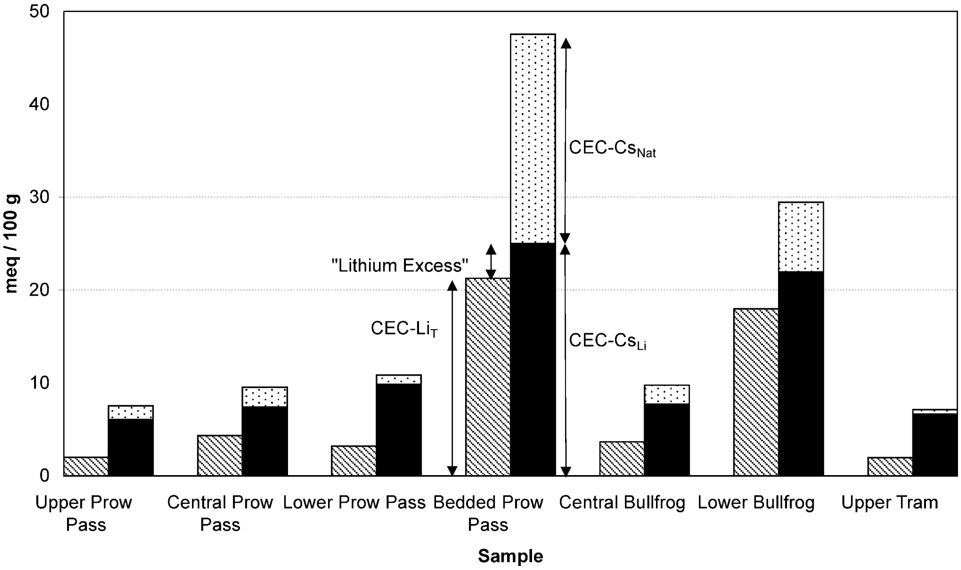

Fig. 1. CEC results for the 7 different C-Wells tuff intervals (attached).

Table 2
Cation exchange capacity measurements. Range shown is ±1 standard deviation[a]

Sample	CEC-Li_T	CEC-Cs_{Nat}	CEC-Cs_{Li}	CEC-Cs_T	Li excess
			(meq/100 g)		
1: Upper Prow Pass	2.0±0.5	1.5±0.1	6.1±0.8	7.5	4.1
2: Central Prow Pass	4.3±0.1	2.1±0.0	7.4±0.4	9.5	3.1
3: Lower Prow Pass	3.2±0.4	1.0±0.9	9.8±1.9	10.8	6.6
4: Bedded Prow Pass	21.3±0.1	22.5±0.4	25.0±1.4	47.5	3.8
5: Central Bullfrog	3.7±0.1	2.0±0.5	7.7±0.6	9.7	4.1
6: Lower Bullfrog	18.0±0.2	7.5±0.4	21.9±0.2	29.5	4.0
7: Upper Tram	1.9±0.1	0.5±0.2	6.6±0.5	7.1	4.7

[a] Refer to text for definitions.

and Mumpton, 1989), kinetic factors prevent significant cation exchange at normal environmental temperatures, (Vaughan, 1978).] To test whether a simple two-mineral model could explain the observed measurements, multivariable linear regression were conducted on the CEC results, using measured smectite and (clinoptilolite + mordenite) fractions (f_{smec}, $f_{\text{clin/mord}}$) as independent variables, and 3 CEC estimates as the dependent variables. In all cases, the model yielded excellent results:

$$\text{CEC-Li}_{\text{T}} = 106 \pm 8\text{meq}/100\ \text{g}\cdot f_{\text{smec}} + 99 \pm 3\ \text{meq}/100\ \text{g}\cdot f_{\text{clin/mord}} + 1.5 \pm 0.3\ \text{meq}/100\ \text{g},\ r^2 = 0.997$$

$$\text{CEC-Cs}_{\text{Li}} = 103 \pm 13\ \text{meq}/100\ \text{g}\cdot f_{\text{smec}} + 99 \pm 5\ \text{meq}/100\ \text{g}\cdot f_{\text{clin/mord}} + 6.1 \pm 0.5\ \text{meq}/100\ \text{g},\ r^2 = 0.990$$

$$\text{CEC-Cs}_{\text{T}} = 90 \pm 13\ \text{meq}/100\ \text{g}\cdot f_{\text{smec}} + 199 \pm 5\ \text{meq}/100\ \text{g}\cdot f_{\text{clin/mord}} + 7.7 \pm 0.5\ \text{meq}/100\ \text{g},\ r^2 = 0.997$$

The exchange factors for the individual minerals can be compared to literature values of 110±23 meq/100 g for smectite (Borchardt, 1989) and 220 meq/100 g for both clinoptilolite and mordenite (Ming and Mumpton, 1989). Starting with the model for CEC-Li$_{\text{T}}$, it can be seen that the specific exchange capacity for smectite matches previously reported values, while the modeled capacity for the zeolite minerals is less than half that reported elsewhere. This discrepancy is consistent with the inaccessibility of some of the internal zeolite exhange sites to the relatively large Li ion. The CEC-Li$_{\text{T}}$ model includes a relatively small constant term, indicating that almost all of the observed behavior can be explained by smectite and clinoptilolite/mordenite cation exchange. Comparing this model to the CEC-Cs$_{\text{Li}}$ model, it is seen that the major difference lies in the constant term; the larger constant term in the second model reflects the observed Li excess. The similarity of the other two terms demonstrates that the Li excess effect is not a result of exchange onto either smectite or clinoptilolite/mordenite; additional correlation analysis shows that the Li excess is not proportional to any of the mineral phases identified by QXRD. These observations, combined with the overall uniformity of the Li excess among these widely varying tuff samples, leads the authors to agree with Eckstein et al. (1970) and attribute the Li excess to a non-cation exchange sorption process.

The final model, for CEC-Cs$_{\text{T}}$, reveals a similar specific CEC for smectite as the literature and the previous models, but shows a much higher specific CEC for the zeolite minerals, more in line with published values. This demonstrates the accessibility to the smaller Cs ion of internal exchange sites that were unavailable to Li.

3.2. Lithium sorption

Lithium sorption data were log-transformed to ensure homogeneity of variance (Bowman et al., 1984) and fit to the Freundlich isotherm (Sposito, 1980); resulting isotherms are presented in Fig. 2. and fitted parameters are listed in Table 3. (Three data points for sample No. 5 were clear outliers and have been excluded from the analysis.) In general, the Freundlich isotherm is a good fit to the data ($r^2 < 0.87$); as expected, data scatter is more apparent in the less sorbing rocks, where the sorbed concentration is calculated as a small difference between two large numbers. In all cases, the fitted isotherm is markedly nonlinear, with Freundlich exponent n ranging from 0.64 to 0.92. The batch sorption data is also fitted using a Langmuir isotherm model (Fetter, 1993), but the Langmuir fits were poorer than the Freundlich fits for 5 of the 7 tuffs, and they were only marginally better for the 2 remaining tuffs (Lower Prow Pass and Bedded Prow Pass). Also, the fitted Freundlich isotherms were much better predictors of the measured CEC-Li$_{\text{T}}$ values

Table 3
Lithium sorption isotherm parameters[a]

Sample	K_{F} (mg/kg) (mg/l)$^{-n}$	n	r^2	K_{Lin} (l/kg)
1: Upper Prow Pass	0.054 (0.035–0.082)	0.92±0.10	0.871	0.032
2: Central Prow Pass	0.51 (0.39–0.66)	0.73±0.06	0.916	0.093
3: Lower Prow Pass	0.56 (0.50–0.63)	0.64±0.03	0.976	0.058
4: Bedded Prow Pass	3.28 (2.87–3.75)	0.68±0.03	0.970	0.441
5: Central Bullfrog	0.65 (0.57–0.75)	0.81±0.04	0.979	0.191
6: Lower Bullfrog	2.03 (1.81–2.27)	0.72±0.03	0.981	0.338
7: Upper Tram	0.33 (0.28–0.38)	0.76±0.04	0.971	0.070

[a] K_F and n are Freundlich isotherm parameters, K_{Lin} is a linearized distribution coefficient, calculated with $C_{\max} = 1000$ mg/l (see text for details). Range shown is ±1 standard error.

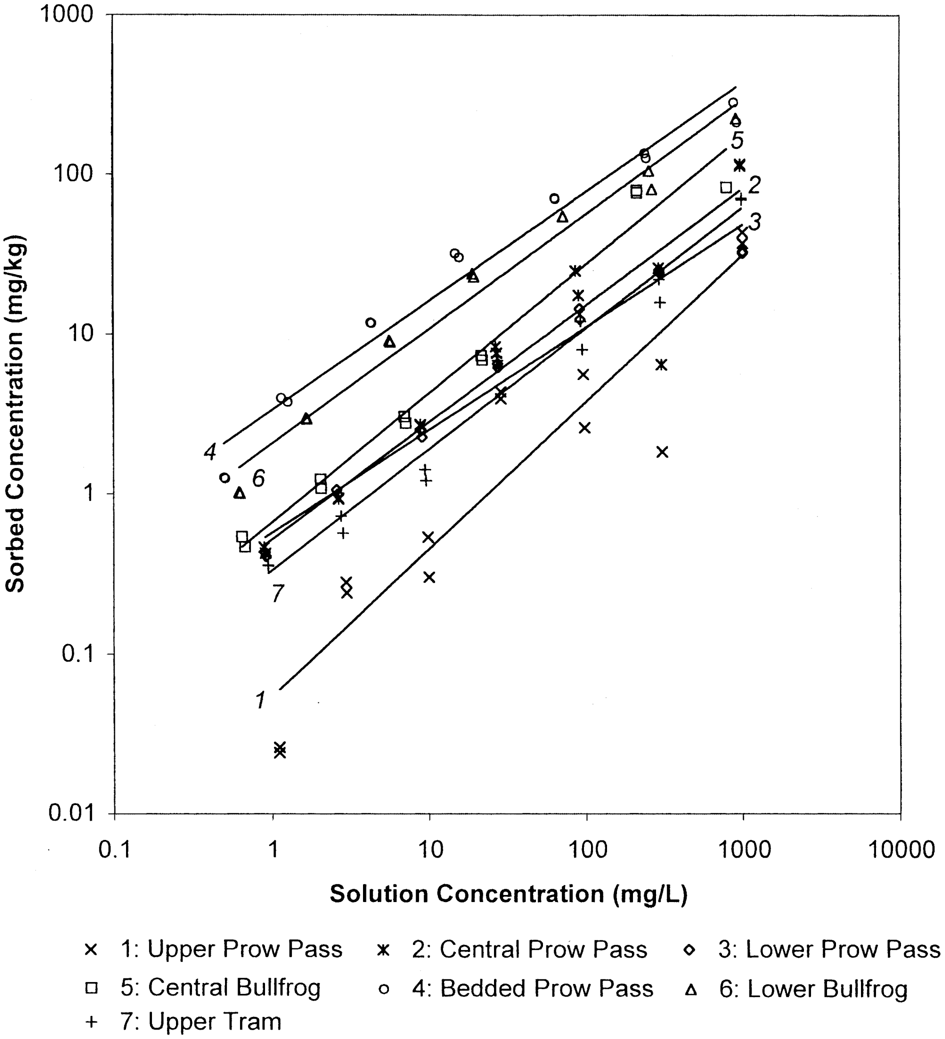

Fig. 2. Lithium sorption isotherms for the 7 different C-Wells tuff intervals (attached).

than the Langmuir isotherms (predictions obtained by substituting a 1N Li concentration into the iostherm expressions). It is concluded that the Freundlich isotherm best describes the Li sorption behavior over the range of concentrations studied.

Because the units of K_F vary with the value of n, it is not strictly possible to directly compare the different K_F values in Table 3. However, to a first approximation, it can be seen that the two samples that sorb Li most strongly have the highest isotherms in Fig. 2 and the largest K_F values in Table 3. These two rocks also showed the highest CEC values. To quantify the sorption relationships more rigorously, we must first linearize the nonlinear isotherm and calculate K_{Lin}, an effective distribution coefficient with uniform units, identical to those of K_D. For this purpose, the equal-area linearization of van Genuchten et al. (1977) is used:

$$K_{\mathrm{Lin}} = \frac{2K_F C_{\max}^{n-1}}{n+1}$$

where $C_{\max}$ is the maximum concentration of interest; in this case, 1000 mg/l. The resulting K_{Lin} values are presented in Table 3. Using the same multivariate linear regression methods described above, K_{Lin} can be modeled as a function of smectite and clinoptilolite/mordenite content:

$$K_{\mathrm{Lin}} = 1.70 \pm 0.71\ \mathrm{l/kg} \cdot f_{\mathrm{smec}} + 1.87 \pm 0.29\ \mathrm{l/kg}$$

$$f_{\mathrm{clin/mord}} + 0.06 \pm 0.03\ \mathrm{l/kg},\ r^2 = 0.924$$

This model does not fit the data as well as the CEC models described above, but nevertheless demonstrates that Li sorption can be estimated fairly accurately for these tuffs, given smectite, clinoptilolite, and mordenite concentrations. The small constant term in the model indicates that other minerals' contribution to Li sorption is quite low.

4. Conclusions

Lithium ion sorption onto devitrified tuffs from the saturated zone near Yucca Mountain follows Freundlich isotherm behavior. Both the Li sorption parameters and the Li-specific cation exchange capacities of the tuffs are highly correlated with the clay (smectite) content and the zeolite (clinoptilolite plus mordenite) content of the tuffs. Multiple linear regression analyses show that these two classes of minerals account for the majority of the observed Li exchange. Regression of Cs cation exchange data yields results that are consistent with the accessibility of the smaller Cs ion to internal zeolite exchange sites that Li cannot access. The Cs CEC data also suggest that some of the Li sorption to the tuffs can be attributed to a non-cation exchange process. The results of this study support the development and use of mineralogy-based models for predicting cation sorption in the environment.

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