Adsorptive Removal of Strontium by Binary Mineral Mixtures of Montmorillonite and Zeolite

Elvan Başçetin[†] and Gülten Atun*[,‡]

Çekmece Nuclear Research and Training Center, P.K.1 34149 Atatürk Airport, Istanbul, Turkey, and Chemistry Department, Engineering Faculty, Istanbul University, 34850 Avcilar, Istanbul, Turkey

The adsorption characteristics of montmorillonite and zeolite minerals and their mixtures for Sr removal have been studied by means of a radiotracer technique using the ^{90}Sr isotope. Experimentally measured distribution coefficients for both single and binary adsorbent systems are in agreement with mathematically calculated values. Adsorption capacities for Sr calculated from Dubinin−Radushkevich isotherm parameters increase with increasing zeolite fraction in binary mixtures, whereas they decrease in the presence of NaCl with respect to pure $SrCl_2$ solutions. Thermodynamic parameters have been estimated from the temperature dependency of the adsorption equilibrium constants evaluated from the selectivity coefficients in brines. Results show that Sr adsorption is an endothermic process, but the spontaneity of adsorption increases with increasing zeolite fraction and temperature. A site distribution function has been mathematically calculated by using the Freundlich isotherm parameters, which gives valuable information about the affinity of exchange sites on the adsorbents for binary exchange between Sr and Na.

Introduction

The radionuclides ^{90}Sr and ^{85}Sr are two important fission products because of their great yields. ^{90}Sr having a longer half-life is the more frequently encountered radionuclide in soil and groundwater at nuclear weapon test sites and nuclear waste repositories.[1] It can easily replace Ca in the bones of living organisms, being a source of long-term irradiation of bone marrow.[2−4] Adsorption of ^{90}Sr on surrounding minerals is one of the predominant processes controlling its mobility in an aquifer besides other interaction types including dissolution, precipitation, and redox reactions.[5,6] Natural zeolites and montmorillonite are effective clay minerals to improve the immobilizing ability of the matrix used for underground disposal of low and medium radioactive wastes.[7,8] Adsorption of Sr on montmorillonite,[9−19] clinoptilolite,[20−26] and natural clays consisting of these minerals[27−32] has been extensively studied by various researchers.

In sorption studies on pure clinoptilolite and zeolitized volcanic tuff from the Nevada nuclear weapon test site, it has been shown that sorption of Sr^{2+} is dependent on the ionic strength of the medium and independent of pH indicating that Sr^{2+} adsorption is controlled by ion exchange at permanent charge sites.[20] The fate and transport of Sr^{2+} ions in brines around the repositories in geological salt formations are controlled by their exchanging abilities on mineral surfaces with Na^+ ions. Since natural clays consist of mineral mixtures rather than pure minerals, the sorption behavior of Sr onto binary montmorillonite−zeolite systems will give valuable information about its ultimate disposal. In this study, experimental and mathematically calculated results of Sr adsorption on montmorillonite and clinoptilolite mixtures have been compared depending on the mineral ratio, initial Sr concentration, and temperature in the absence and presence of Na^+ ions.

* Corresponding author. E-mail: gultena@istanbul.edu.tr. Tel.: +90-212-4737031. Fax: +90-212-4737180.
[†] Çekmece Nuclear Research and Training Center.
[‡] Istanbul University.

Table 1. Chemical Analysis of the Clay Minerals (in % w/w)

	SiO_2	Al_2O_3	K_2O	CaO	Fe_2O_3	Na_2O	MgO	TiO_2
montmorillonite	56.77	9.32	1.25	9.39	2.10	0.53	3.57	0.33
zeolite	74.70	13.70	5.25	2.76	1.45	1.07	0.69	0.15

Experimental Section

Adsorbent Specifications. Montmorillonite and zeolite type clay minerals were supplied from the Enez region of Edirne and the Gördes region of Manisa in Turkey, respectively.

Chemical compositions of the minerals were determined by X-ray fluorescence (XRF) spectrometry and are given in Table 1.[33,34] Cation exchange capacities (CECs) of Enez (montmorillonite) and Gördes (zeolite) have been reported as 2.78 $meq \cdot g^{-1}$ and 2.46 $meq \cdot g^{-1}$, respectively.[34,35] All chemicals were analytical grade (Merck), while the radionuclide source ^{90}Sr was obtained from Amersham (U.K.).

Adsorbent Preparation. The mineral samples were crushed and dry-sieved to be below a size of 38 μm. They were converted to sodium form by four sequential treatments with 0.1 M NaCl at 298 K for an hour. The samples were dried to constant weight at 378 K following separation of the solid phase. The montmorillonite and zeolite were mixed to obtain a zeolite fraction of 0, 0.2, 0.4, 0.6, 0.8, and 1.0. These samples were abbreviated as M, MZ1, MZ2, MZ3, MZ4, and Z, respectively.

Adsorption Experiments. Initial concentrations of $SrCl_2$ solutions spiked with ^{90}Sr ranged from $(1 \cdot 10^{-6}$ to $1 \cdot 10^{-2})$ M. To investigate the effect of Na^+ ions on the transport of Sr^{2+} ions, the experiments were also carried out in the presence of $1 \cdot 10^{-2}$ M NaCl. Previous experiments show that a liquid−solid ratio of 250 $(cm^3 \cdot g^{-1})$ is suitable to study strontium adsorption.[9] Adsorbents were contacted with solutions for 7 days, being a time period sufficient to reach equilibrium.[12] Solid and liquid phases were separated by centrifuging at 4000 rpm for 15 min.

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Table 2. Experimentally and Theoretically Calculated Distribution Coefficients for Sr Adsorption on Montmorillonite and Zeolite Mixtures (in $L \cdot g^{-1}$)

C_0		298		313		333	
M	T/K	$K_{d(exp)}$	$K_{d(cal)}$	$K_{d(exp)}$	$K_{d(cal)}$	$K_{d(exp)}$	$K_{d(cal)}$
10^{-6}	M	0.745	0.690	0.818	0.770	0.946	0.946
	MZ1	1.876	1.930	2.997	3.656	4.467	5.252
	MZ2	3.156	3.170	7.103	6.542	13.639	9.558
	MZ3	3.822	4.411	10.620	9.428	16.417	13.865
	MZ4	5.702	5.651	13.639	12.314	22.477	18.171
	Z	8.312	6.891	14.456	15.200	22.477	22.477
		$\sigma = 0.099$		$\sigma = 0.123$		$\sigma = 0.174$	
10^{-5}	M	0.629	0.571	0.693	0.640	0.828	0.764
	MZ1	1.348	1.344	1.799	1.954	1.924	2.493
	MZ2	1.796	2.117	3.083	3.268	3.848	4.222
	MZ3	2.891	2.890	4.467	4.582	6.329	5.952
	MZ4	3.731	3.663	5.848	5.896	9.365	7.681
	Z	5.002	4.436	8.679	7.210	11.114	9.410
		$\sigma = 0.094$		$\sigma = 0.088$		$\sigma = 0.164$	
10^{-4}	M	0.568	0.535	0.640	0.590	0.730	0.730
	MZ1	0.947	0.936	1.373	1.214	1.630	1.570
	MZ2	1.452	1.337	1.799	1.838	2.002	2.410
	MZ3	1.571	1.739	2.044	2.462	2.691	3.250
	MZ4	1.949	2.140	3.083	3.086	4.467	4.090
	Z	2.939	2.541	4.380	3.710	6.000	4.930
		$\sigma = 0.090$		$\sigma = 0.119$		$\sigma = 0.144$	
10^{-3}	M	0.283	0.241	0.354	0.330	0.420	0.420
	MZ1	0.555	0.503	0.730	0.686	0.837	0.856
	MZ2	0.717	0.764	0.952	1.042	1.265	1.292
	MZ3	0.976	1.026	1.322	1.398	1.644	1.728
	MZ4	1.151	1.287	1.575	1.754	1.833	2.164
	Z	2.106	1.549	2.997	2.110	4.380	2.600
		$\sigma = 0.143$		$\sigma = 0.142$		$\sigma = 0.183$	
10^{-2}	M	0.223	0.218	0.314	0.300	0.373	0.339
	MZ1	0.264	0.265	0.358	0.372	0.401	0.436
	MZ2	0.301	0.311	0.399	0.444	0.448	0.534
	MZ3	0.356	0.358	0.572	0.515	0.615	0.631
	MZ4	0.398	0.404	0.659	0.587	0.861	0.729
	Z	0.467	0.451	0.659	0.659	0.861	0.826
		$\sigma = 0.022$		$\sigma = 0.079$		$\sigma = 0.114$	

Table 3. Experimentally and Theoretically Calculated Distribution Coefficients for Sr Adsorption on Montmorillonite and Zeolite Mixtures in the Presence of 0.01 M NaCl (in $L \cdot g^{-1}$)

C_0		298		313		333	
M	T/K	$K_{d(exp)}$	$K_{d(cal)}$	$K_{d(exp)}$	$K_{d(cal)}$	$K_{d(exp)}$	$K_{d(cal)}$
10^{-6}	M	0.301	0.301	0.366	0.360	0.448	0.410
	MZ1	0.672	0.685	0.832	0.871	0.946	1.227
	MZ2	1.091	1.069	1.384	1.383	1.799	2.044
	MZ3	1.310	1.452	1.602	1.894	3.848	2.860
	MZ4	1.937	1.836	2.467	2.406	4.380	3.677
	Z	2.333	2.220	3.426	2.917	4.852	4.494
		$\sigma = 0.054$		$\sigma = 0.099$		$\sigma = 0.187$	
10^{-5}	M	0.238	0.240	0.288	0.288	0.334	0.334
	MZ1	0.533	0.514	0.630	0.627	0.818	0.781
	MZ2	0.824	0.788	1.109	0.966	1.373	1.228
	MZ3	1.123	1.061	1.238	1.304	1.630	1.674
	MZ4	1.244	1.335	1.602	1.643	1.851	2.121
	Z	1.594	1.609	1.982	1.982	2.691	2.568
		$\sigma = 0.044$		$\sigma = 0.058$		$\sigma = 0.079$	
10^{-4}	M	0.193	0.190	0.239	0.234	0.288	0.278
	MZ1	0.358	0.370	0.398	0.441	0.462	0.525
	MZ2	0.540	0.550	0.676	0.648	0.832	0.771
	MZ3	0.761	0.730	0.929	0.856	1.080	1.018
	MZ4	0.938	0.910	1.073	1.063	1.332	1.264
	Z	1.084	1.090	1.274	1.270	1.511	1.511
		$\sigma = 0.027$		$\sigma = 0.058$		$\sigma = 0.071$	
10^{-3}	M	0.115	0.118	0.142	0.142	0.166	0.159
	MZ1	0.194	0.189	0.221	0.222	0.239	0.247
	MZ2	0.268	0.259	0.292	0.302	0.313	0.335
	MZ3	0.314	0.330	0.354	0.381	0.398	0.423
	MZ4	0.416	0.400	0.475	0.461	0.562	0.511
	Z	0.471	0.471	0.562	0.541	0.630	0.599
		$\sigma = 0.033$		$\sigma = 0.039$		$\sigma = 0.061$	
10^{-2}	M	0.093	0.093	0.159	0.162	0.134	0.134
	MZ1	0.127	0.121	0.178	0.185	0.172	0.170
	MZ2	0.144	0.149	0.223	0.208	0.192	0.206
	MZ3	0.175	0.178	0.251	0.232	0.268	0.243
	MZ4	0.204	0.206	0.277	0.255	0.270	0.279
	Z	0.236	0.234	0.277	0.278	0.318	0.315
		$\sigma = 0.026$		$\sigma = 0.056$		$\sigma = 0.051$	

Then, 2 cm^3 of the supernatant was evaporated in Al capsules, and the distribution coefficient (K_d) and amount of adsorbed Sr at equilibrium (q_e) were determined by measuring the β-radioactivity with an ERD Mullard G-M tube type MX 123 system as follows

$$K_d = \frac{(A_i - A_e)}{A_e} \cdot \frac{V}{m} \tag{1}$$

$$q_e = C_i \frac{A_i - A_e}{A_i} \cdot \frac{V}{m} \tag{2}$$

where A_i and A_e are initial and equilibrium activities of the solutions, respectively; C_i is the initial Sr concentration (in $mol \cdot L^{-1}$); and V/m is the solution/adsorbent ratio (in $L \cdot g^{-1}$).

Results and Discussion

Distribution Coefficients. Accurate and reliable knowledge of the distribution coefficients of the nuclides between the solutions and minerals is needed in adsorption studies to estimate their transport rates.

Experimentally determined distribution coefficients ($K_{d,exp}$) according to eq 1 are shown in Table 2 for montmorillonite, zeolite, and their mixtures depending on the initial Sr^{2+} concentration and temperature. The effects of Na^+ ions on distribution coefficients are also presented in Table 3.

The distribution of radionuclides between mineral mixtures and the solution phase is characterized by the quantity, $K_{d(mix)}$. Assuming ion exchange to be responsible for Sr adsorption and no interaction between montmorillonite and zeolite, the $K_{d(mix)}$ values can be calculated using the individual distribution coefficients of the minerals as follows[9,32,34]

$$K_{d(mix)} = \frac{m_M}{m_M + m_Z} K_M + \frac{m_Z}{m_M + m_Z} K_Z \tag{3}$$

where m_M and m_Z are the masses of montmorillonite and zeolite in the mixture (on a dry mass basis), respectively, and K_M and K_Z are their individual distribution coefficients. The distribution coefficients ($K_{d,cal}$) for pure minerals and their mixtures were mathematically calculated according to eq 3 by starting from their individual experimental distribution coefficients to obtain a minimum standard deviation using eq 4.

$$\sigma = \left[\frac{1}{n_e} \sum_{i=1}^{n} \left(\frac{K_{d,exp} - K_{d,cal}}{K_{d,exp}} \right)^2 \right]^{1/2} \tag{4}$$

where n_e is the number of experimental observations.

The calculated distribution coefficients ($K_{d,cal}$) for pure and mixed minerals are compared with their experimental values ($K_{d,exp}$) in Table 2 and Table 3 for single Sr and Sr/Na binary systems, respectively. As can be seen from the tables, the values of $K_{d,cal}$ are quite consistent with the $K_{d,exp}$ values. Both experimental and calculated values of distribution coefficients for the mixtures fall into those of pure minerals, and they increase with increasing zeolite fraction at a given Sr concentration. On the other hand, Sr adsorption decreases as the kaolinite content increases in montmorillonite mixtures collected from the same region.[9] Since adsorption of Sr^{2+} ions on mineral

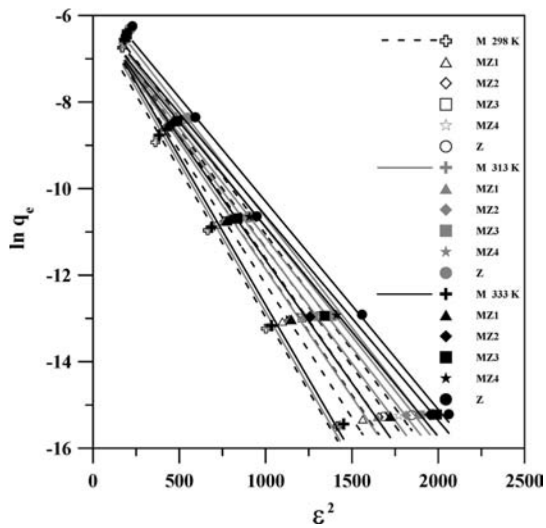

Figure 1. Dubinin−Radushkevich (D−R) adsorption isotherms for Sr adsorption onto montmorillonite, zeolite, and their mixtures at different temperatures.

surfaces is mainly dominated by cation exchange mechanisms,[31] these results may be correlated to the CECs of the minerals of which increase in the order kaolinite < montmorillonite < zeolite.[33−35] An increase in the initial concentration of Sr causes a decrease in distribution coefficients, while they increase with temperature. Experimental distribution coefficients for pure montmorillonite and zeolite are found to be (0.745 and 8.312) $L \cdot g^{-1}$ at the lowest Sr^{2+} concentration of 10^{-6} M at 298 K, but they decrease to (0.223 and 0.467) $L \cdot g^{-1}$ in 10^{-2} M Sr^{2+} solutions, respectively. These values increase in the range of (0.946 to 22.477) $L \cdot g^{-1}$ and (0.373 to 0.861) $L \cdot g^{-1}$ for the lowest and the highest concentrations at 318 K. The distribution coefficients for pure montmorillonite can be compared with Jih-Sing bentonite (in the range of (0.510 to 0.846) $L \cdot g^{-1}$),[17,18] whereas the data for zeolite are comparable with the reported values for natural clinoptilolites from Bulgaria and the USSR (in the range of (1.300 to 3.800) $L \cdot g^{-1}$).[26]

The experimental distribution coefficients for montmorillonite and zeolite decrease up to (0.093 and 0.236) $L \cdot g^{-1}$ in the presence of 10^{-2} M NaCl. The decrease in distribution coefficients shows that Sr^{2+} ions can migrate in brines.

Adsorption Isotherms. The adsorption data were fitted to the Dubinin−Radushkevich (D−R) and the Freundlich isotherm equations, and their parameters were used for determination of adsorption characteristics such as adsorption capacity, adsorption energy, and surface heterogeneity.

a. Dubinin−Radushkevich (D−R) Isotherm. The D−R isotherm equation can be written in the following linear form[36]

$$\ln q_e = \ln q_m - K\varepsilon^2 \qquad (5)$$

where q_e is the equilibrium amount of solute adsorbed per unit weight of solid (in $mol \cdot g^{-1}$); q_m is the adsorption capacity of adsorbent per unit weight (in $mol \cdot g^{-1}$); K is the constant related to the mean adsorption energy (E). ε is the Polanyi potential calculated from

$$\varepsilon = RT \ln(1 + 1/C_e) \qquad (6)$$

in which R is the gas constant ($kJ \cdot mol^{-1} \cdot K^{-1}$) and T is the absolute temperature (K).

As shown in Figure 1, a plot of $\ln q_e$ vs ε^2 allows the estimation of q_m from the intercept and K from the slope. The mean adsorption energy is given by

$$E = (-2K)^{-1/2} \qquad (7)$$

The D−R isotherm constants found from fitting the adsorption data to these isotherms for three temperatures are presented in Table 4 together with the correlation coefficients, r. The adsorption capacity of the adsorbents and the mean adsorption energy decreased from zeolite to montmorillonite and increased with increasing temperature. Similar trends were also observed in the presence of the supporting electrolyte, but the values of the adsorption capacity and energy were slightly lower. The mean adsorption energy values fall into the energy range of ion exchange reactions, (8 to 16) $kJ \cdot mol^{-1}$.[37]

b. Freundlich Isotherm. The Freundlich equation describes well the adsorption characteristics of heterogeneous natural adsorbents, and the model parameters can be used for calculation of a site distribution function for the adsorbent surface in binary solutions. The Freundlich isotherm equation can be represented in the following linear form[38]

$$\ln q_e = \ln k + n \ln C_e \qquad (8)$$

where k and n are the Freundlich parameters. They were calculated from the slopes and intercepts of the straight lines of $\ln q_e$ vs $\ln C_e$ plots in Figure 2 and presented in Table 4. Both montmorillonite and zeolite gave smaller values of n than unity, which may be correlated with their surface heterogeneity.[39]

Site Distribution Functions. A site distribution function is very similar to a Gaussian curve centered on q_{max}, and it can be

Table 4. Isotherm Parameters for Sr Adsorption onto Montmorillonite, Zeolite, and Their Mixtures

		Freundlich				D−R		
		$k \cdot 10^2$				$q_m \cdot 10^3$	E	
		$mol \cdot g^{-1}$	n	q_{max}	r	$mol \cdot g^{-1}$	$kJ \cdot mol^{-1}$	r
				T/K = 298				
−	M	11.75	0.871		0.999	2.18	8.55	0.993
	MZ1	11.63	0.818		0.999	2.38	9.00	0.994
	MZ2	11.77	0.794		0.999	2.48	9.25	0.993
	MZ3	13.57	0.789		0.999	2.79	9.35	0.995
	MZ4	10.01	0.771		0.999	2.78	9.55	0.994
	Z	17.08	0.767		0.997	3.36	9.67	0.995
NaCl	M	4.96	0.873	−0.37	1.000	1.08	8.36	0.991
	MZ1	5.65	0.830	0.01	1.000	1.36	8.71	0.992
	MZ2	5.88	0.802	0.22	0.999	1.51	8.94	0.994
	MZ3	6.97	0.799	0.45	0.998	1.78	8.99	0.995
	MZ4	7.88	0.792	0.65	0.999	1.91	9.13	0.994
	Z	8.61	0.787	0.79	0.999	2.05	9.21	0.994
				T/K = 308				
−	M	15.63	0.885		0.999	2.58	8.52	0.993
	MZ1	12.56	0.801		0.999	2.55	9.21	0.993
	MZ2	10.33	0.753		1.000	2.27	9.71	0.990
	MZ3	10.65	0.738		0.999	2.34	9.93	0.989
	MZ4	14.37	0.743		1.000	2.79	9.98	0.990
	Z	20.39	0.753		0.998	3.74	9.92	0.995
NaCl	M	5.90	0.872	−0.17	1.000	1.26	8.40	0.991
	MZ1	5.95	0.816	0.15	1.000	2.11	8.40	0.99
	MZ2	6.57	0.795	0.40	0.999	1.67	8.27	0.993
	MZ3	8.56	0.804	0.67	0.999	2.01	9.02	0.994
	MZ4	8.89	0.788	0.83	0.999	2.06	9.22	0.993
	Z	9.03	0.774	0.95	1.000	2.1	9.38	0.992
				T/K = 318				
−	M	18.96	0.885		0.999	2.91	8.54	0.993
	MZ1	13.08	0.801		0.999	2.53	9.39	0.990
	MZ2	9.51	0.753		0.999	2.08	10.08	0.985
	MZ3	10.66	0.738		0.999	2.39	10.16	0.989
	MZ4	12.95	0.743		1.000	2.75	10.28	0.991
	Z	22.11	0.753		0.997	4.11	10.21	0.995
NaCl	M	7.06	0.872	0.04	1.000	1.43	8.45	0.991
	MZ1	6.79	0.816	0.31	0.999	1.59	8.84	0.992
	MZ2	6.41	0.795	0.37	0.999	1.68	9.18	0.993
	MZ3	6.97	0.804	0.42	0.999	1.69	9.52	0.987
	MZ4	8.01	0.761	0.88	0.999	1.96	9.51	0.989
	Z	9.02	0.774	0.94	1.000	2.12	9.58	0.992

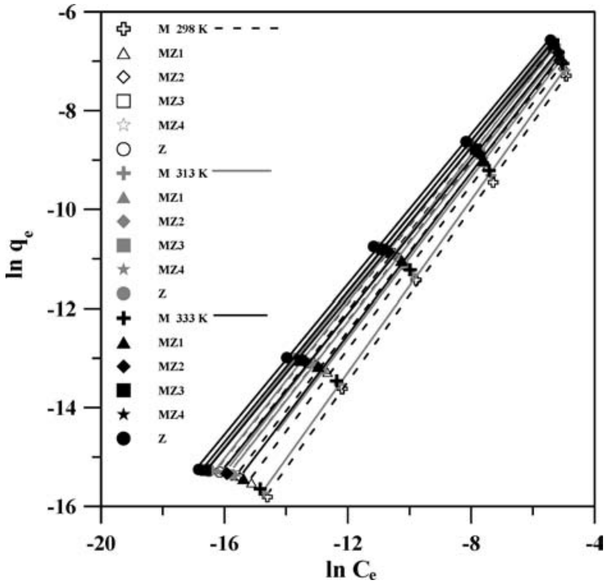

Figure 2. Freundlich adsorption isotherms for Sr adsorption onto montmorillonite, zeolite, and their mixtures at different temperatures in the presence of 10^{-2} M NaCl.

calculated according to eq 9 by giving q values chosen arbitrarily from both sides of q_{max}.[39]

$$\frac{m_{(q)}}{m_{max}} = \frac{2\cos(\pi n)\exp[n(q_m - q)] + 2\exp[n(q_m - q)]}{1 + 2\cos(\pi n)\exp[n(q_m - q)] + \exp[2n(q_m - q)]} \tag{9}$$

where m_q/m_{max} is the ratio of the number of sites of class q to the value of $m_{(q)}$ at its maximum. The parameter q, representing the class of adsorption sites, is defined as

$$q = \ln(K_I/K_{II}) \tag{10}$$

K_I and K_{II} are the affinity parameters for the competing species I and II (I: Sr^{2+} and II: Na^+); and q_{max} is the value of q when $m_q = m_{max}$ and calculated with the equation

$$q_{max} = \frac{1}{n}\ln(kC_{II}^n/M) \tag{11}$$

where M is the total number of adsorption sites corresponding to the CEC (in equiv·g^{-1}), and C_{II} is the average concentration of species II.

The site distribution functions for motmorillonite[9] and zeolite minerals are compared in Figure 3 for 298 K (as being representative). The ratio of the area under the positive section of the curves to the negative region is a relative measure of the affinity of competing ions for exchange sites. The larger area under the positive section is related to the number of sites that have higher affinity for the first component in the Sr/Na exchange system, whereas surface sites having a higher affinity for the second component correspond to the negative peak area. The larger peak area in the negative region for montmorillonite indicates that most of the exchange sites have a higher affinity for Na^+ ions, whereas the affinity of exchange sites on the zeolite surface is greater for Sr^{2+} ions. The sign of q_{max} is also an indication of surface affinity for exchanging ions. The more positive values of q_{max} for mineral mixtures indicate that the affinity of adsorbents for Sr^{2+} ions increases with zeolite fraction. It can be deduced from the values of q_{max} presented in Table 4 that the affinity for Sr^{2+} ions becomes greater as the temperature increases.

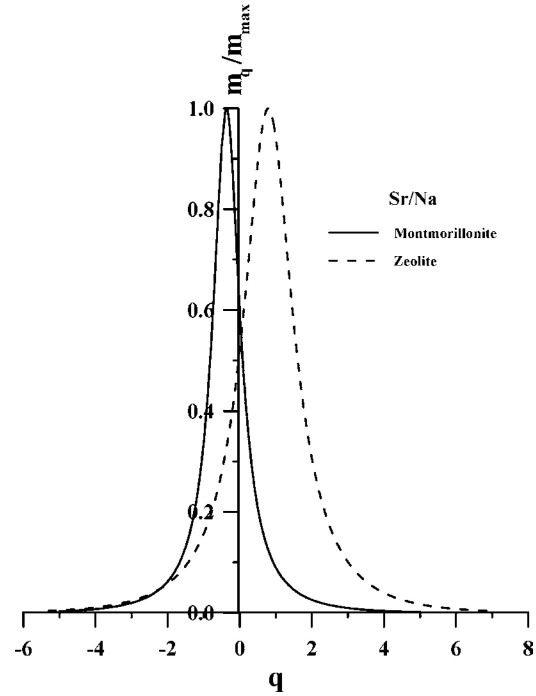

Figure 3. Site distribution functions on montmorillonite and zeolite for Sr and Na at 298 K.

Selectivity Coefficients. The preference of an adsorbent for the Sr−Na binary system can be expressed by the selectivity coefficient, $K_{c(Sr-Na)}$[39]

$$K_{c(Sr-Na)} = \frac{\bar{E}_{Sr}(X_{Na})^2\gamma^4_{\pm NaCl}}{(\bar{E}_{Na})^2 X_{Sr}\gamma^3_{\pm SrCl_2}} \tag{12}$$

where $\bar{E}$ and X denote the equivalent fractions in the solid phase and the mole fractions in the solution phase, respectively, and $\gamma_\pm$ is the mean activity coefficient of the electrolytes in solution which is represented by the Debye−Hückel equation[40]

$$\log \gamma_\pm = -\frac{Az_+z_-I^{1/2}}{1 + Ba_iI^{1/2}} \tag{13}$$

where A and B are constants; z_+ and z_- are the charge number of the positive and negative ion, respectively; I is the ionic strength, given by $I = (1/2)\Sigma\, c_i z_i^2$ (mol·L^{-1}); and a_i is the closest distance of approach of ions. The values of A and B are 0.5115 L$^{1/2}$·mol$^{-1/2}$ and 3.29·10^7 L$^{1/2}$·cm^{-1}·mol$^{-1/2}$ at 298 K. The values of a_i for $SrCl_2$ and NaCl were taken to be (3.72·10^{-8} and 3.45·10^{-8}) cm, respectively.[41]

The thermodynamic equilibrium constant (K^0) can be calculated from the graphical integration of the $K_{c(Sr-Na)}$ vs $\bar{E}_{Sr}$ plot drawn according to the following relation[39]

$$\ln K = -1 + \int_0^1 \ln K_{c(Sr-Na)} d\bar{E}_{Sr} \tag{14}$$

The values of K^0 estimated by interpolating the value of ln $K_{c(Sr-Na)}$ at $\bar{E}_{Sr} = 0.5$ in Figure 4 were used in calculations of thermodynamic functions using the following well-known equations.

$$\Delta G^0 = -RT\ln K^0 \tag{15}$$

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{16}$$

where ΔG^0, ΔH^0, and ΔS^0 are free energy, enthalpy, and entropy changes, respectively.

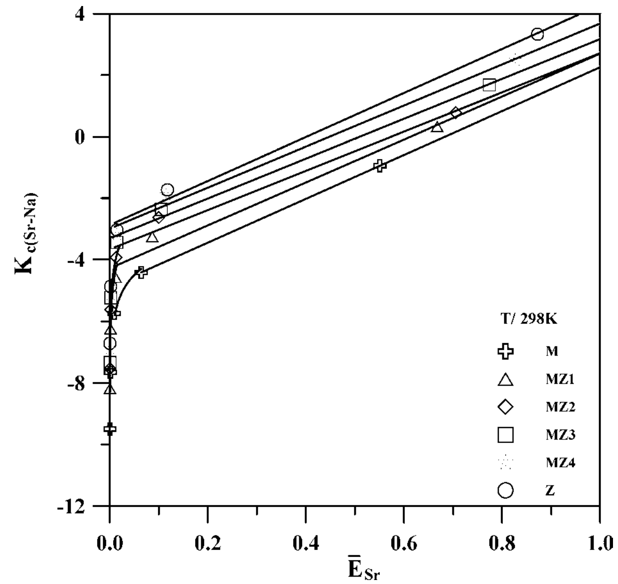

Figure 4. Change of selectivity coefficients with equivalent fraction of Sr on montmorillonite, zeolite, and their mixtures at 298 K.

Table 5. Thermodynamic Parameters for Sr Adsorption onto Single and Binary Mineral Mixtures

	K^0			ΔG^0 kJ·mol^{-1}			ΔH^0	ΔS^0	
T/K	298	313	333	298	313	333	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	r
M	0.10	0.12	0.19	5.71	5.35	4.62	16.71	36.29	0.97
MZ1	0.17	0.25	0.37	4.39	3.82	2.78	20.12	52.08	1.00
MZ2	0.23	0.37	0.58	3.64	2.83	1.49	23.86	67.19	1.00
MZ3	0.35	0.73	3.28	2.60	0.66	−3.29	62.44	197.38	0.96
MZ4	0.52	1.14	11.66	1.62	−1.01	−6.80	89.46	289.04	0.92
Z	0.75	1.75	15.68	0.71	−1.94	−7.62	86.96	284.03	0.93

As can be seen from $K^0 < 0$ and $\Delta G^0 > 0$ values in Table 5, Na adsorption is more favorable than Sr at 298 K, while Sr is more preferred at higher zeolite fractions and temperatures. The positive values of ΔH^0 indicate that overall Sr adsorption is an endothermic process. $\Delta H^0 > T\Delta S^0$ values for low temperature and high montmorillonite fractions correspond to an enthalpy-controlled adsorption process, whereas spontaneity of Sr adsorption is entropy-controlled at higher temperatures and zeolite fractions. These results are consistent with the reported studies for Sr adsorption onto clay minerals.[9,25]

Conclusion

The effects of initial strontium concentration, sodium chloride, and temperature on distribution coefficients of Sr have been studied depending on mineral fraction in montmorillonite−zeolite mixtures.

• Distribution coefficients increased with increasing zeolite fraction and temperature, whereas they decreased as initial Sr^{2+} concentration increased in the range of (10^{-6} to 10^{-2}) M.

• The decrease in distribution coefficients in the presence of 10^{-2} M NaCl indicated that Sr^{2+} ions could migrate in brines.

• Mathematically calculated distribution coefficients for single minerals and their mixtures are in agreement with those of experimental values.

• Mean energy values calculated from the D−R isotherm parameters confirmed that Sr adsorption is dominated by ion exchange mechanisms.

• The values of Freundlich exponents ($n < 1$) indicated that both pure and mixed adsorbents are heterogeneous in nature.

• Site distribution functions calculated using the Freundlich isotherm parameters showed that affinity for Sr decreases with increasing montmorillonite fraction when Sr^{2+} and Na^+ ions compete for the same exchange sites.

• Selectivity coefficients, thermodynamic equilibrium constants, and thermodynamic functions revealed that Sr adsorption is more spontaneous at higher temperatures.

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