Adsorption Equilibrium of Heavy Metals on Natural Zeolites

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Abstract—Prior to equilibrium experiments, a clinoptilolite-type Korean natural zeolite was pretreated with HCl, NaOH, and NaCl to improve the ion-exchange capacity for heavy metals. Single- and multi-species equilibrium data of heavy metals such as copper, cadmium, cesium, and lead on treated and untreated natural zeolites were measured experimentally. For single-species equilibrium data, one of the conventional adsorption isotherms, the Sips equation, was used to fit them and then multi-species equilibrium data were predicted by using the loading ratio correlation (LRC), the ideal adsorbed solution (IAS) theory, and the real adsorbed solution (RAS) theory based on the Sips equation. In applying the RAS theory, we used the Wilson equation for fitting activity coefficients of metal ions in the ion-exchanger phase. It was proven that basic adsorption models except the LRC model could describe multi-species ion-exchange equilibrium for heavy metals/natural zeolite systems well.

Key words: Korean Natural Zeolite, Heavy Metals, Ion Exchange, Multi-Species Equilibrium

INTRODUCTION

The ion-exchange process using natural zeolites has recently become known as an improved means for isolating heavy metals from contaminated surface and ground waters, because it has the advantage of saving energy and having no secondary pollution [Blanchard et al., 1984; Ouki and Kabanagh, 1997; Pansini, 1996]. Since various types of natural zeolites such as chabazite, clinoptilolite, and modenite are widely distributed all over the world and they can be modified cheaply and easily, they would be very attractive ion-exchanging media for removing toxic heavy metals from water streams [Biskup and Subotic, 1998; Colella, 1996; Curkovic et al., 1997; Kim et al., 1995].

In zeolites, the exchange of ions arises from the presence of extra-framework cations, located in the regular array of channels and cages, which constitute the rigid anionic framework [Perona, 1993]. Cations are bound to the lattice and the water molecules, which normally fill the zeolite micropores. When the zeolite comes into contact with an electrolytic solution, the cations in zeolites can be removed from their sites and replaced by other cations from the solution. Substitution of ions is stoichiometric, and it can cover the entire cation-exchange capacity (CEC), unless partial or total exclusion occurs in the case of the inaccessibility of specific exchange sites. Actually, there are commonly various cation sites in zeolite structures, which are different in framework positions and in bond energies together. This may affect both the extent and kinetics of cation sieving. It is due to cation size both in diameter and volume, being incompatible with the channel dimensions or with the space available in the specific site. Cation sieving may also occur due to the inability of the negative charge distribution on the zeolite structure to accommodate a given cation [Colella, 1996].

The selectivity of exchange on inorganic ion-exchangers has been explained by many theories [Mehablia et al., 1994; Perona, 1993],

but no unified hypothesis has been drawn up yet. Some authors have stated that the selectivity is given primarily by the magnitude of the hydration energy of the exchanged ion, charge density on the ion-exchanger lattice, and its structure. For example, the greatest lattice charge density is exhibited by zeolites with low Si/Al ratios, low internal water contents, and higher affinity for small ions. In general, the selectivity of ion-exchangers has been determined not only by the diameter of these windows, but also by their ability to adapt to the size of the entering ions. The ions are dehydrated during sorption and are bonded very strongly inside the six-membered ring of the zeolite. A similar mechanism of increased selectivity is valid in a more marked form for zeolites whose structure contains an eight-membered ring, e.g., chabazite, erionite, and clinoptilolite.

In one of our previous works [Lee et al., 1999], a clinoptilolite-type Korean natural zeolite was pretreated with HCl, NaOH, and NaCl to assess the effect of such pretreatments on the ion-exchange capacity for heavy metals. From experimental results based on chemical analyses, X-ray diffraction, and BET experiments, it was proven that pretreatment with NaCl gave the best ion-exchange capacity for all heavy metal ions encountered. Such a result has encouraged our further work on this subject since the treatment with NaCl is economically cheap and does not create any serious environmental problems. As a further work, the ion-exchange equilibrium of each heavy metal on treated and untreated natural zeolites was studied. In order to study practical and dynamic behavior of an ion-exchange process, it might be necessary to have information on ion-exchange equilibrium.

When an ion-exchanger is in contact with the surrounding fluid with a certain composition of an ion, ion exchange occurs inside ion-exchanger particles [Breeuwsma and Lyklema, 1973]. Ion exchange is a kind of reversible chemical adsorption since it involves a chemical reaction of which the heat of reaction approaches the value of chemical bonds. Ionic species can be exchanged stoichiometrically with those of the same sign of charge in a surrounding aqueous solution. When an ion-exchanger containing mobile ions is placed in water containing different ions of the same charge sign,

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an equilibrium state can be achieved, as the thermodynamic chemical potential for each ion becomes the same inside and outside the ion-exchanger, after a sufficient long time [Harjula et al., 1992; Perona, 1993; Suzuki, 1990]. The equilibrium state can be determined by a large number of factors and it is not so easy to fit experimental data satisfactorily because solid and aqueous phases must be highly nonideal.

The binary distribution of two ions, A and B, of the same sign at ion-exchange equilibrium can be obtained by maintaining electroneutrality of each ion [Harjula et al., 1992; Tien, 1994]. The most important property for an ion-exchanger is the selectivity for an ion to others at equilibrium state. The measured selectivity depends on the system to separate objective ions from the bulk solution to the ion-exchanger phase. In this work, single- and multi-species equilibrium experiments for heavy metals, such as lead, cadmium, and copper, on treated and untreated natural zeolites were conducted isothermally in a batch system to assess the selectivity of each zeolite for heavy metal ions to others.

In general, an ion-exchange process has been simply considered as an adsorption [Ha, 1987; Slater, 1991]. Therefore the Sips equation was used to fit experimental data for single-species ion exchange, and the IAS and RAS theories were used in predicting multi-species equilibrium. In treating an ion-exchange process, one of difficult problems is to estimate the activity coefficients of ions accurately, which are a function of concentration and temperature, for real systems containing different ions. In applying the RAS theory, we utilized the Wilson equation in fitting activity coefficients for binary systems in the ion-exchanger phase [Wilson, 1964]. Final results on equilibrium will be applied in predicting and simulating the dynamic behavior of heavy metals in column separators charged with ion-exchange particles in future.

ADSORPTION EQUILIBRIUM

1. Single-species Equilibrium

The ion-exchange mechanism is a bit complex; therefore, it is very difficult to find a simple and accurate ion-exchange isotherm. However, considering that an ion-exchange process is reversible in terms of ionic concentration, one of the conventional adsorption isotherms could be utilized in treating ion-exchange equilibrium data reasonably even if it is a kind of chemical reaction [Slater, 1991]. There are many kinds of isotherm equations for single-species adsorption systems. The Langmuir equation has been applied to adequately describe adsorptions in many instances [Langmuir, 1918]. However, the Langmuir equation is not generally useful in describing adsorption in heterogeneous systems because of its intrinsic assumptions. The other well-known isotherm, the Freundlich equation, assumes that there is no association or dissociation of the molecules after they are adsorbed on the surface and chemisorption is completely absent [Freundlich, 1926]. Although this equation is simple and convenient, it does not always accurately reproduce experimental data over a wide range of concentrations. According to the Freundlich equation, the amount adsorbed increases infinitely with increasing concentration. Therefore, this equation is unsatisfactory for high coverage. On the other hand, Sips introduced the suggestion that a Gaussian-like statistical function could represent the distribution of site-solute interactions [Sips, 1948]. This

isotherm, which is based on the assumption of localized adsorption without interaction among sites, has three parameters. It looks like a combined empirical expansion of the Langmuir and Freundlich equations. Among many isotherms, the Sips equation will be used to fit single-species data in this work because it is more accurate than other isotherms with two adjusting parameters.

$$q = \frac{q_m C^{1/n}}{1 + K_s C^{1/n}} \tag{1}$$

2. Multi-species Equilibrium

When two or more ions exist with the possibility of occupying the same ion-exchange sites, equilibrium relationships become more complex. The simplest is the extension of the Langmuir isotherm by assuming no interaction between adsorbing molecules [Ruthven, 1984; Yang, 1986]. This equation enables quick estimation of equilibrium relations of multi-species adsorption from Langmuir parameters determined from the single-species isotherm of each ion. However, it is not proper to use this simple model for the heavy metal ions encountered here. In this work, the extension of the Sips equation, called loading ratio correlation (LRC), was used [Ruthven, 1984].

$$q_i = \frac{q_{mi} C^{1/n_i}}{1 + \sum_{j=1}^{N} K_{Sj} C^{1/n_j}} \tag{2}$$

One of the most widely used thermodynamic models is the IAS theory of Myers and Prausnitz [1965]. The IAS theory is based on the assumption that the adsorbed phase follows ideal behavior. The IAS theory has several assumptions: (i) The ion-exchanger phase is a thermodynamically inert ion-exchanger, (ii) the temperature is constant, (iii) The Gibbs surface model for adsorption can be applied, and (iv) the same surface area is available to all ions without any steric effect. Basic equations for the IAS theory are as follows:

$$q_i = q_T z_i \tag{3}$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i} \right]^{-1} \tag{4}$$

$$C_i = C_i^0(\pi_i, T) z_i \tag{5}$$

$$\Pi = \frac{RT}{\pi A} = \int_0^{C_i^*} \frac{q_i^0}{C_i^0} dC_i^0 \tag{6}$$

$$q_i = f(C_i^0, \pi_i) \tag{7}$$

$$\sum_{i=1}^{N} z_i = 1 \tag{8}$$

Calculation procedures for the IAS theory are given elsewhere [Tien, 1994]. However, the use of the IAS theory does not guarantee good accuracies in treating ion-exchange equilibrium data for real systems. In general, one may expect to improve the predictive accuracy of this theory by introducing adsorbed-phase activity coefficients as shown in Eq. (9).

$$C_i = \gamma_i C_i^0(\pi_i, T) z_i \tag{9}$$

This improved model, called the RAS theory, shows less error differences between the experimental and the calculated values than the IAS theory. In this model, the activity coefficients of heavy metals in the ion-exchanger phase may be obtained by the Wilson equation as shown in Eq. (10) [Wilson, 1964].

$$\ln\gamma_i = 1 - \ln\left(\sum_{j=1}^{N} y_j \Lambda_{ij}\right) - \sum_{k=1}^{N}\left(\frac{y_k \Lambda_{ki}}{\sum_{j=1}^{N} y_j \Lambda_{kj}}\right) \tag{10}$$

EXPERIMENTAL

A Korean natural zeolite and a synthetic chabazite (AW-500), supplied by Han-Doo Co. and Aldrich Co., respectively, were used as ion-exchangers in this study. The natural zeolite used was crushed and sieved to give the fraction of 16/30 mesh, using ASTM standard sieves. The average particle diameter of the natural zeolite was about 0.89×10^{-3} m. In addition, the natural zeolite was pretreated with 1 mol/L HCl, NaOH, and NaCl solutions prior to equilibrium experiments. The commercial chabazite, which is calcium-based and has a regularly arranged structure, was also used for comparison with treated and untreated natural zeolites in equilibrium studies.

Lead, copper and cadmium were used as heavy metals while cesium was used as a radionuclide [Kim et al., 1995]. All stock solutions were prepared from their nitrate and chloride salts. Equilibrium studies were conducted in the concentration range of 0.05-30 mol/m³ at 30 °C. In single-species equilibrium experiments, given amounts of natural zeolites were put in 300 ml vessels filled with 100 ml metallic solution. The vessels were located in a constant temperature shaker, in which temperature was maintained uniformly. They were shaken for two days, which was sufficient for the attainment of equilibrium under experimental conditions used. Natural zeolites and solutions were separated by centrifugation at 2,000 RPM for 15 min and the supernatants were then filtered through 0.45 μm membrane filters. The concentrations in the solutions were analyzed by AES-ICP (Liberty-220/Varian). The initial pH was controlled by hydrogen chloride and sodium hydroxide solutions and pH was measured by a pH-meter (Model 920A/Orion).

In binary systems, individual metal solutions were prepared by mixing two stock solutions and equilibrium tests were conducted similarly as the single-species system. In the ternary system of Pb²⁺/Cd²⁺/Cu²⁺, three kinds of mole ratios were prepared. The concentration of solutions or the weights of zeolites were varied and equilibrium concentrations of individual heavy metals were measured.

RESULTS AND DISCUSSION

1. Adsorption Equilibrium

In this study, single-metal sorption isotherms for Pb²⁺, Cd²⁺, Cu²⁺, and Cs⁺ were measured and used to determine the capacity of adsorption on natural zeolites. The equilibrium amounts of Pb²⁺ on all natural zeolites are compared in the range of C_{eq}=0-3 mol/m³ at 30 °C as shown in Fig. 1. For each of the adsorbents such as NaCl-treated, NaOH-treated, HCl-treated, and untreated natural zeolites and a commercially available natural zeolite, chabazite, equilibrium data were fitted with the Sips Isotherm. The commercial cha-
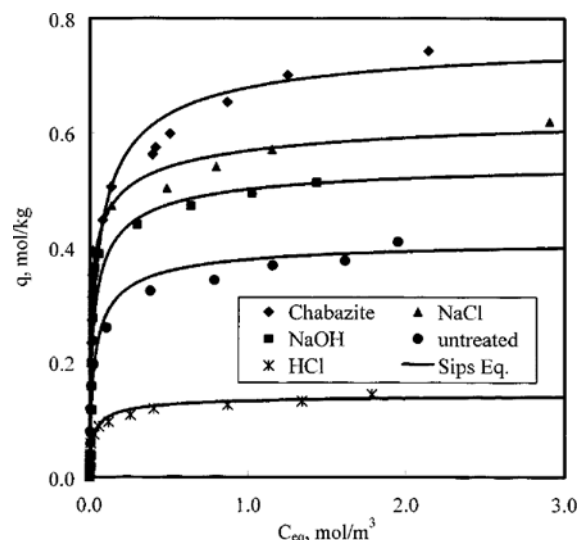

Fig. 1. Single-species adsorption isotherms for Pb²⁺ on several natural zeolites at 30 °C (In Figs. 1-4, chemicals in figures mean-treated, for example, HCl-treated).

bazite has the largest adsorption capacity for Pb²⁺ among all natural zeolites, coming with the order of NaCl-treated, NaOH-treated, untreated, HCl-treated natural zeolites.

The empirical parameters of the Sips equation and the average percent deviations between measured and calculated values are given in Table 1. The average percent deviations are mostly less than

Table 1. Sips empirical parameters and average percent differences between measured and predicted values in the system of metal ion natural zeolites

	Types	q_m (mol/kg)	K_S $(m^3/mol)^{1/n}$	n	Error (%)*
Pb²⁺	Chabazite	0.780	6.73	1.54	5.30
Pb²⁺	NaCl-treated	0.668	5.66	2.34	4.61
Pb²⁺	NaOH-treated	0.560	8.59	1.64	15.8
Pb²⁺	untreated	0.420	9.40	1.49	13.3
Pb²⁺	HCl-treated	0.147	9.58	1.61	8.41
Cd²⁺	Chabazite	0.459	3.02	2.01	7.36
Cd²⁺	NaCl-treated	0.470	3.28	2.44	3.86
Cd²⁺	NaOH-treated	0.251	10.9	1.09	2.45
Cd²⁺	untreated	0.198	0.594	1.14	8.85
Cd²⁺	HCl-treated	0.116	0.513	2.31	5.49
Cu²⁺	Chabazite	0.370	7.42	1.14	2.05
Cu²⁺	NaCl-treated	0.411	5.53	2.20	0.51
Cu²⁺	NaOH-treated	0.250	9.40	1.11	5.40
Cu²⁺	untreated	0.177	2.72	1.35	4.20
Cu²⁺	HCl-treated	0.100	0.354	2.39	7.67
Cs⁺	Chabazite	2.28	0.842	1.79	2.39
Cs⁺	NaCl-treated	1.49	1.14	2.08	3.37
Cs⁺	NaOH-treated	1.42	1.08	1.84	4.35
Cs⁺	untreated	1.25	0.935	2.06	3.27
Cs⁺	HCl-treated	1.38	0.486	4.19	2.01

$$*\text{Error (\%)} = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{q_{exp,i} - q_{cal,i}}{q_{exp,i}}\right]$$

10% when the Sips equation was used. This means the Sips equation is a proper isotherm in fitting single-species equilibrium data of heavy metals such as Pb^{2+}, Cd^{2+}, Cu^{2+}, and Cs^+ on natural zeolites encountered in this study.

Experimental equilibrium data are important to judge the feasibility of the adsorption process for a given application. Moreover, the isotherm plays a crucial role in predictive modeling procedure for analysis and design of heavy metal removal processes [Suzuki, 1990; Tien, 1994]. The equilibrium exchanged amounts of cadmium, copper and cesium are shown in Figs. 2-4. It should be noted that the NaCl-treated natural zeolite was more favorable than the commercial chabazite. The results showed that the adsorption capacity is in the order of NaCl-treated>chabazite>NaOH-treated>untreated>HCl-treated. The capacity for Cs^+, that is similar to that of Pb^{2+}, is in the order of chabazite>NaCl-treated>NaOH-treated>untreated>HCl-treated. It is shown that the natural zeolite treated
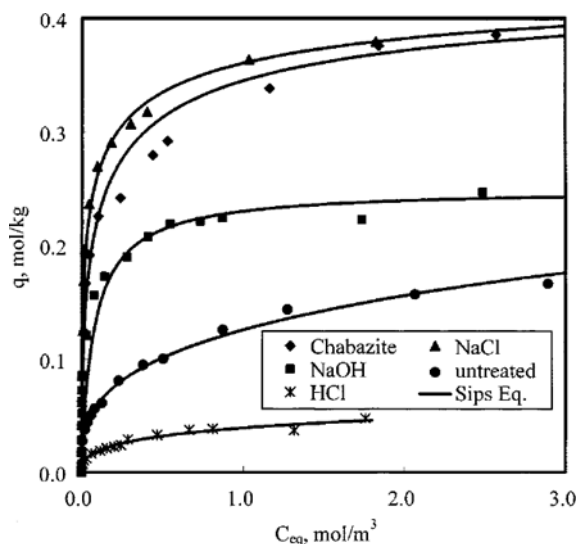

Fig. 4. Single-species adsorption isotherms for Cs^+ on several natural zeolites at 30 °C.
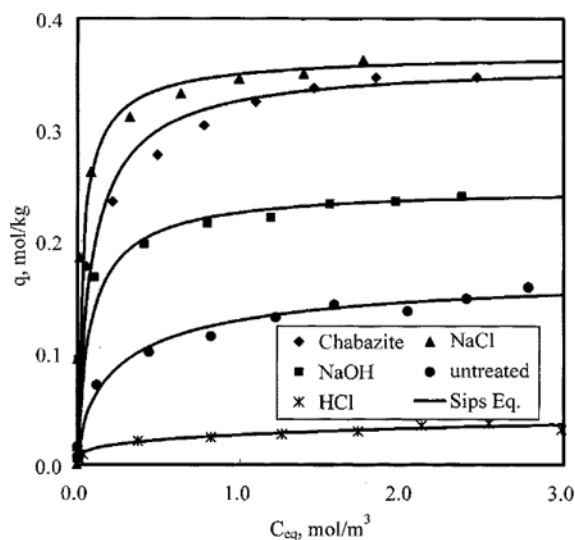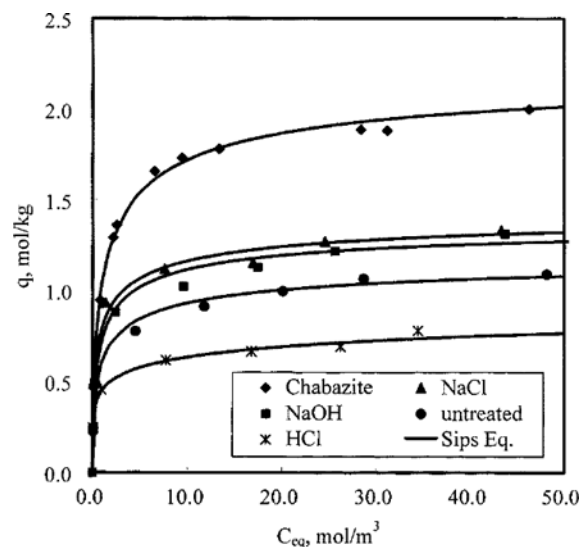
with NaCl is more appropriate than others. Considering that the natural zeolite is more cheap and abundant than the commercial chabazite and it can be easily modified by simple treatments, it will be a promising medium for removal of heavy metals from aqueous solutions.

According to BET adsorption data, the HCl-treated natural zeolite has the largest surface area but the adsorption amounts of heavy metals are low [Lee at al., 1999]. From this result, it is evident that the removal of metals by zeolites is not a physical adsorption but a chemical adsorption, namely an ion-exchange process. It will be shown in the next section that the removal mechanism of heavy metals by using natural zeolites follows fairly closely the ion-exchange reaction and a little, the physical interaction.

The selectivity of the NaCl-treated natural zeolite and the chabazite for heavy metals encountered here follows the order of $Cs^+>>$
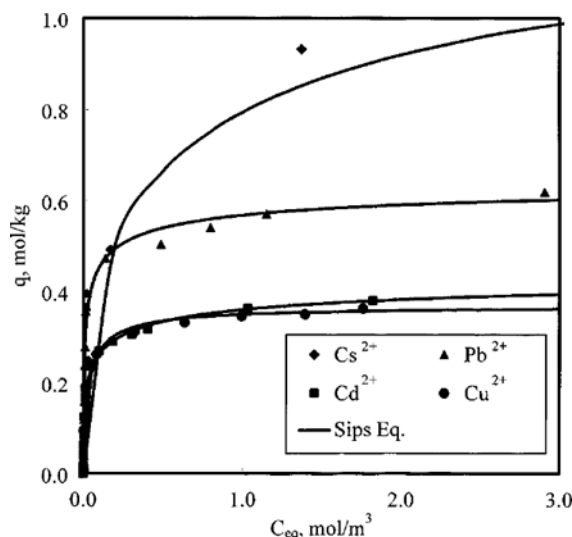

Fig. 2. Single-species adsorption isotherms for Cd^{2+} on several natural zeolites at 30 °C.

Fig. 3. Single-species adsorption isotherms for Cu^{2+} on several natural zeolites at 30 °C.

Fig. 5. Single-species adsorption isotherms for several metals on natural zeolite treated with 1 mol/L NaCl solution at 30 °C.
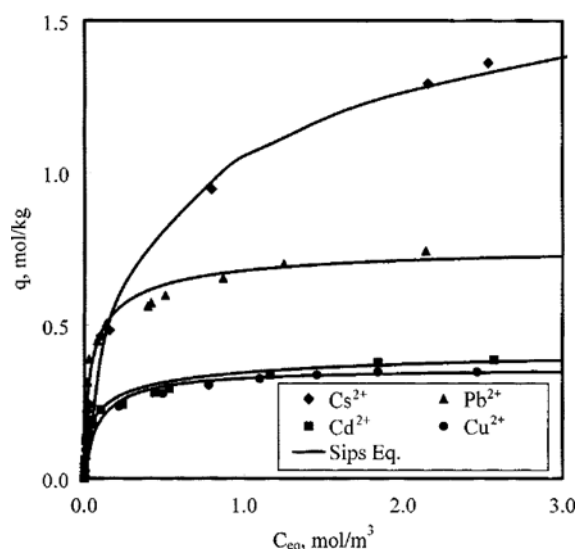
Fig. 6. Single-species adsorption isotherms for several metals on chabazite at 30 °C.
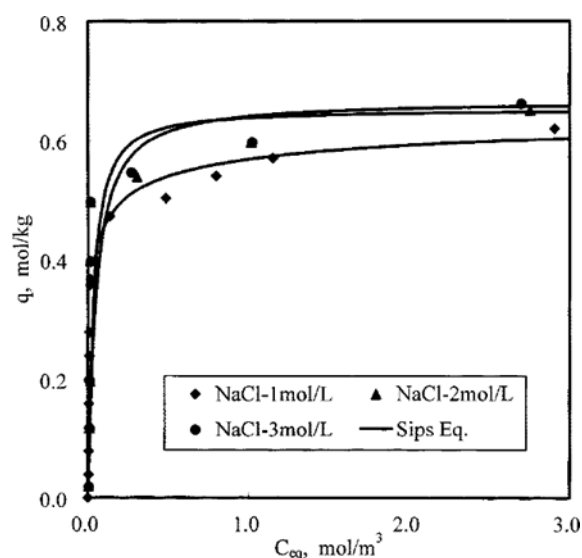

Fig. 7. Single-species adsorption isotherms for Pb²⁺ on natural zeo-lite treated with 1, 2, and 3 mol/L NaCl solutions at 30 °C.

$Pb^{2+}>Cd^{2+}\geq Cu^{2+}$ as shown in Figs. 5-6. This result is not matched with ion radii but fairly coincides with the reversed order of hy-drated ion radii as $Cs^+(3.30\,\text{Å})>Pb^{2+}(4.01)>Cu^{2+}(4.19)>Cd^{2+}(4.26)$ [Semmens and Seyfarth, 1978].

The effect of NaCl concentration in the treatment solution on ad-sorption capacity is not significant as shown in Fig. 7. When the natural zeolite was pretreated with 3 mol/L NaCl solution, it had slightly higher adsorption capacity than those pretreated with 1 and 2 mol/L NaCl solutions.

2. Ion-exchanged Metal Amounts

Equivalent metal concentrations in the solution were compared before and after the experiment to check which metal ion domi-nantly contributes to the ion-exchange process. After Pb^{2+} uptake experiments in a batch system were finished, the amounts of metals extracted out of the zeolite into the solution were listed in Tables

Table 2. Exchanged metal amounts in the ion-exchange process of Pb^{2+}

(1) NaCl-treated natural zeolite

C_{iPb2+} (mol/m³)	Pb^{2+}_{eq} (N/m³)	Na^+ (N/m³)	Ca^{2+} (N/m³)	K^+ (N/m³)	Mg^{2+} (N/m³)	M_T (N/m³)
2.00	3.95	3.71	0.03	0.01	0.04	3.78
2.50	4.73	4.30	0.08	0.01	0.07	4.47
3.00	5.03	4.32	0.15	0.02	0.10	4.59
3.50	5.41	4.58	0.19	0.03	0.11	4.91
4.00	5.63	4.72	0.22	0.03	0.11	5.08

※ Al^{2+}, Fe^{3+} amounts are very small. M_T: Na^+, Ca^{2+}, K^+, Mg^{2+}, and others except Pb^{2+}.

(2) NaOH-treated natural zeolite

C_{iPb2+} (mol/m³)	Pb^{2+}_{eq} (N/m³)	Na^+ (N/m³)	Ca^{2+} (N/m³)	K^+ (N/m³)	Mg^{2+} (N/m³)	M_T (N/m³)
2.0	3.85	2.68	0.65	0.10	0.34	3.77
2.5	4.40	2.89	0.84	0.12	0.40	4.25
3.0	4.73	2.98	0.89	0.13	0.43	4.42
3.5	4.95	3.07	0.93	0.13	0.44	4.58
4.0	5.02	3.11	0.95	0.13	0.46	4.64

(3) HCl-treated natural zeolite

C_{iPb2+} (mol/m³)	Pb^{2+}_{eq} (N/m³)	Na^+ (N/m³)	Ca^{2+} (N/m³)	K^+ (N/m³)	Mg^{2+} (N/m³)	M_T (N/m³)
0.50	0.84	0.01	0.21	0.02	0.09	0.33
1.50	1.25	0.01	0.28	0.03	0.11	0.44
2.00	1.32	0.03	0.32	0.03	0.13	0.51
2.50	1.44	0.02	0.31	0.03	0.12	0.49

(4) untreated natural zeolite

C_{iPb2+} (mol/m³)	Pb^{2+}_{eq} (N/m³)	Na^+ (N/m³)	Ca^{2+} (N/m³)	K^+ (N/m³)	Mg^{2+} (N/m³)	M_T (N/m³)
1.00	1.95	0.84	0.69	0.15	0.14	1.82
2.00	3.15	1.04	1.32	0.28	0.19	2.82
2.50	3.43	1.05	1.49	0.30	0.20	3.04
3.00	3.69	1.10	1.55	0.33	0.21	3.18
3.50	3.78	1.07	1.61	0.33	0.21	3.22
4.00	3.92	1.07	1.63	0.34	0.20	3.23

2.1-2.4. In the case of the NaCl-treated zeolite, sodium was the main material exchanged with heavy metals in the solution since other alkali earth metals such as calcium, magnesium in zeolite were ex-changed with sodium when it was pretreated with sodium chloride solution. The contribution of sodium participating in the ion-ex-change process among all the exchanged metals was 93-98% in the case of the NaCl-treated natural zeolite, and 67-71%, and 33-46% in the case of NaOH-treated and untreated natural zeolites, respectively. The amounts of lead exchanged are slightly more than the sum of Na^+, Ca^{2+}, K^+, and Mg^{2+} ions released from the NaCl-treated, NaOH-treated, and untreated zeolites as shown in Tables 2.1-2.2. and 2.4. However, the equivalent amount of lead exchang-ed by the HCl-treated zeolite is larger than the sum of all metal ions released during the ion-exchange process, which is shown in Table 2.3. It is noted that the ion-exchange equilibrium of Cd^{2+} also has a

Table 3. Exchanged metal amounts in the ion-exchange process of Cd^{2+}

(1) NaCl-treated natural zeolite

C_{iCd2+} (mol/m³)	Cd^{2+}_{eq} (N/m³)	Ca^{2+} (N/m³)	Mg^{2+} (N/m³)	Na^+ (N/m³)	K^+ (N/m³)	M_T (N/m³)
1.0	1.98	0.01	0.02	2.00	0.00	2.03
1.5	2.97	0.02	0.01	2.76	0.00	2.79
2.0	3.40	0.00	0.03	3.17	0.01	3.21
3.0	3.93	0.02	0.05	3.53	0.02	3.62
4.0	4.35	0.03	0.06	3.66	0.02	3.77

※ Al^{2+}, Fe^{3+} amounts are very small to be ignored.

(2) NaOH-treated natural zeolite

C_{iCd2+} (mol/m³)	Cd^{2+}_{eq} (N/m³)	Ca^{2+} (N/m³)	Mg^{2+} (N/m³)	Na^+ (N/m³)	K^+ (N/m³)	Fe^{2+} (N/m³)	Al^{3+} (N/m³)	M_T (N/m³)
1.0	1.60	0.19	0.03	1.47	0.01	0.01	0.00	1.71
1.5	2.01	0.30	0.03	1.59	0.01	0.00	0.01	1.94
2.0	2.26	0.36	0.03	1.66	0.01	0.00	0.00	2.06
3.0	2.52	0.47	0.04	1.72	0.00	0.00	0.00	2.23
4.0	3.02	0.54	0.05	1.78	0.01	0.00	0.00	2.39

(3) HCl-treated natural zeolite

C_{iCd2+} (mol/m³)	Cd^{2+}_{eq} (N/m³)	Ca^{2+} (N/m³)	Mg^{2+} (N/m³)	Na^+ (N/m³)	K^+ (N/m³)	Fe^{2+} (N/m³)	Al^{3+} (N/m³)	M_T (N/m³)
0.2	0.17	0.03	0.02	0.01	0.01	0.00	0.12	0.18
0.5	0.24	0.04	0.02	0.01	0.01	0.00	0.01	0.09
1.0	0.30	0.03	0.02	0.00	0.00	0.00	0.04	0.10
1.5	0.37	0.04	0.02	0.01	0.01	0.00	0.12	0.20
2.0	0.48	0.04	0.02	0.00	0.01	0.00	0.08	0.15

(4) untreated natural zeolite

C_{iCd2+} (mol/m³)	Cd^{2+}_{eq} (N/m³)	Ca^{2+} (N/m³)	Mg^{2+} (N/m³)	Na^+ (N/m³)	K^+ (N/m³)	Fe^{2+} (N/m³)	Al^{3+} (N/m³)	M_T (N/m³)
1.0	1.07	0.37	0.09	0.46	0.03	0.00	0.02	0.97
1.5	1.60	0.49	0.11	0.49	0.03	0.00	0.01	1.13
2.0	1.46	0.55	0.11	0.48	0.07	0.00	0.00	1.22
3.0	1.86	0.68	0.13	0.52	0.04	0.00	0.01	1.38
4.0	2.22	0.72	0.13	0.57	0.04	0.00	0.01	1.48

similar tendency as shown in Tables 3.1-3.4. In the case of the HCl-treated natural zeolite, about 40% of metal ions in the solution were exchanged with metal ions in the ion-exchanger phase. According to experimental results above, it may be concluded that a considerable portion of heavy metals could be physically adsorbed when the HCl-exchanged natural zeolite was used. Although a similar amount can be physically adsorbed in other cases, it was not clearly found since the contribution of a physically adsorbed amount is much less than that of the ion-exchanged amount. As it was experimentally proven in the previous work [Lee et al., 1999], the pretreatment with HCl destroys the skeletal structure by dissolving a considerable amount of metals including aluminum. Therefore, it lost many of the exchangeable cations that can participate in the ion-exchange process.

On the other hand, the above result may be partially explained by exchanging of metal ions with protons in the zeolite phase since Na^+ can be replaced by H^+ during their pretreatment processes, in particular, with HCl solution. Although it cannot be confirmed clearly, the decrease in pH during ion-exchanging as shown in Fig. 9 shows an indirect clue for this fact.

3. Effects of pH, Temperature, and Other Factors

The initial pH values of Pb^{2+}, Cd^{2+}, and Cu^{2+} stock solutions were in the range of 5-6. On the other hand, the final values of pH after equilibrium experiments were in the range of 4.2-8.0 according to the pretreatment types. This implies that the solution pH can affect the ion-exchange process. Therefore, the pH dependency on the removal efficiency of heavy metals was examined after equilibrium experiments at different pH values from 2.0 to 12.0, as shown in Fig. 8.

The removal efficiency of Pb^{2+}, Cd^{2+}, and Cu^{2+} by natural zeolites encountered here was almost over 99.5% in the range of pH 4-10 when initial concentration was 1 mole/m³. However, the removal efficiency significantly decreased at pH values below 4 or over 10. According to experiments the final solution pH value was slightly changed in all the range for Pb^{2+} adsorption system, while it was a little bit shifted to the lower value for Cd^{2+} and Cu^{2+} adsorption systems as shown in Fig. 9. This extent of change in pH will not reduce the removal efficiency of heavy metals during ion-exchange processes.

As mentioned in the previous section, the removal process of heavy metals by natural zeolites is a kind of chemical adsorption and it is expected that its activity may be increased with tempera-
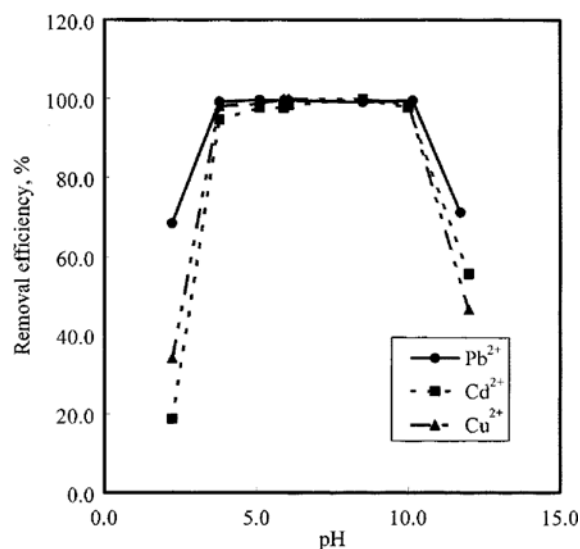
Fig. 8. Effect of pH on removal of heavy metals by NaCl-treated natural zeolite in initial concentration of 1 mol/m³ lead nitrate solution.
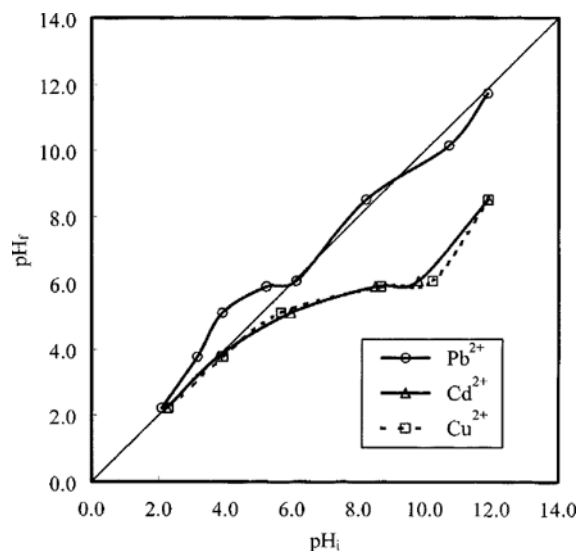

Fig. 10. Effects of temperature on Pb^{2+} adsorption on NaCl-treated natural zeolite.

Fig. 9. Comparison of initial and final pH values of solution after equilibrium experiments.

Fig. 11. Measured and predicted adsorption amounts of Pb^{2+}/Cd^{2+} onto NaCl-treated natural zeolite in binary mixture at $C_0 = 2$ mol/m³.

ture. Fig. 10 shows the effect of temperature on the adsorption amount of Pb^{2+} on the NaCl-treated natural zeolite.

4. Multi-species Systems

In binary adsorption systems, the equilibrium amounts of heavy metals by the NaCl-treated natural zeolite are predicted and compared with experimental amounts adsorbed. Three multi-species adsorption isotherms such as the LRC, the IAS theory, and the RAS theory were used to predict those binary data. As shown in Figs. 11-13, three binary experiments for Pb^{2+}/Cd^{2+}, Pb^{2+}/Cu^{2+}, and Cd^{2+}/Cu^{2+} systems were performed under the conditions that $C_o = 2$-5 mol/m³, contact time=48 h, and temperature=30 °C. The LRC model gave considerable deviation between calculated and predicted amounts particularly in the Pb^{2+}/Cd^{2+} and Pb^{2+}/Cu^{2+} systems. However, the data of Cd^{2+}/Cu^{2+} binary system were fitted well by all three models. Among the three models, the RAS theory gave the best fit
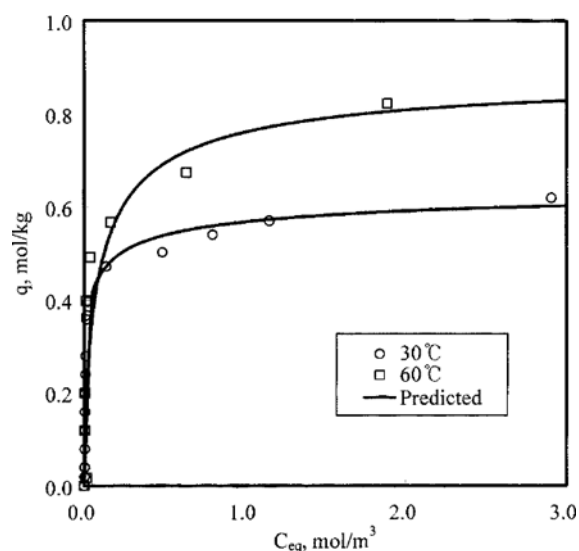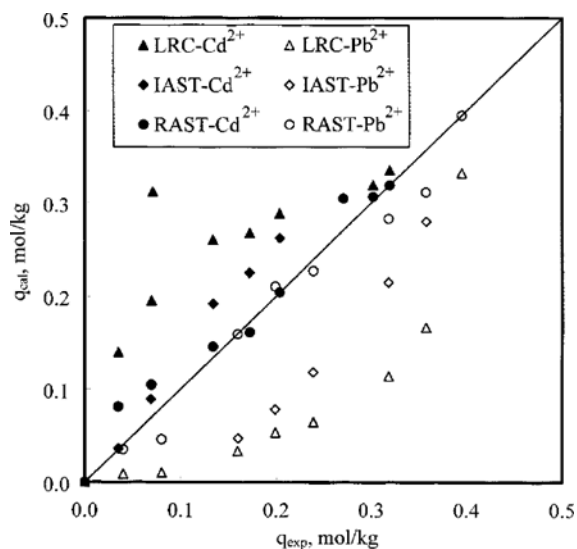
to all data in three binary systems because solid phase activity coefficients were taken into account. This result is not a surprising one. The result by the RAS theory is a kind of fitting rather than prediction since the activity coefficients of metals in the ion-exchanger phase were calculated from binary data themselves. According to calculated results, the simple LRC model is not proper in treating the multi-species ion-exchange equilibrium encountered here. The reason why the Cd^{2+}/Cu^{2+} system was fitted well by all models may be that Cu^{2+} and Cd^{2+} have similar properties in hydrated ionic radius, valence, and ion-exchange affinity.

In dilute solutions such as the case applied here, it is considered that (i) dielectric strength between two components can be ignored, and (ii) spreading pressure is not changed much when a single ion is mixed with other ions to be adsorbed. Therefore, the IAS theory may be a favorable theory adaptable to this kind of removal pro-
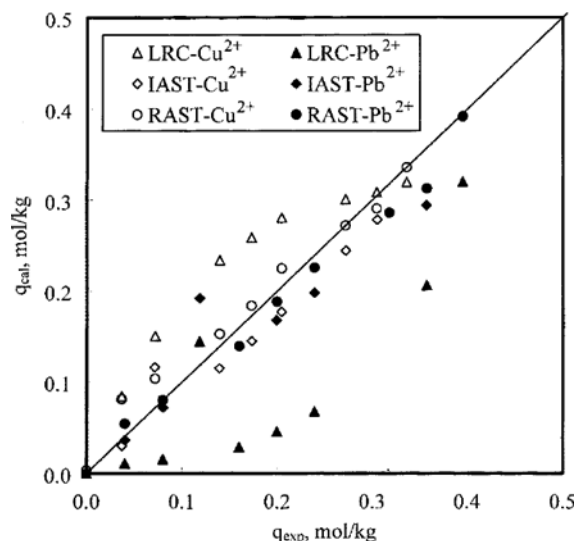
Fig. 12. Measured and predicted adsorption amounts of Pb^{2+}/Cu^{2+} onto NaCl-treated natural zeolite in binary mixture at $C_0 = 2$ mol/m³.
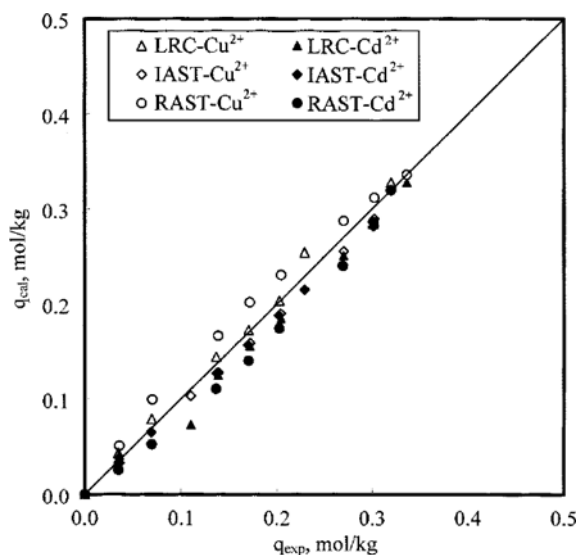

Fig. 13. Measured and predicted adsorption amounts of Cd^{2+}/Cu^{2+} onto NaCl-treated natural zeolite in binary mixture at $C_0 = 2$ mol/m³.

Table 4. Ion-exchanger phase activity coefficients obtained for the RAS theory

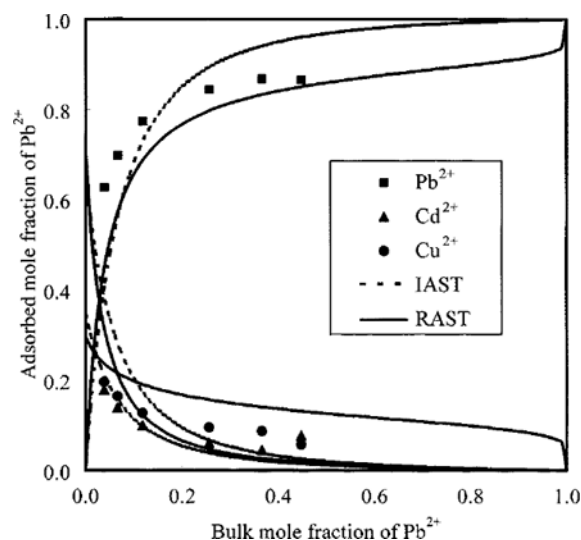| Items	Pb^{2+}-Cd^{2+}		Pb^{2+}-Cu^{2+}		Cu^{2+}-Cd^{2+}	
Wilson parameter	Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}
Value	25	0.1	25	0.15	1.5	1.1
Error (%)	2.55		2.67		0.01	

Fig. 14. Prediction of adsorbed mole fraction along Pb^{2+} for ternary mixture, Pb^{2+}-Cd^{2+}-Cu^{2+} (2:1:1) onto NaCl-treated natural zeolite at $C_0 = 3$ mol/m³.

the initial mole ratio was 2:1:1 for Pb^{2+} : Cd^{2+} : Cu^{2+}, and temperature was 30 °C. Two multi-species models, the IAS theory and the RAS theory, were applied to predict those equilibrium data. The result shown in Fig. 14 indicated that both models suitably predict them. However, it was proven that the RAS theory gives better predictions than the IAS theory as expected. Furthermore, it was noted that the ternary curves predicted by the RAS theory showed an azeotropic condition in the high mole fraction range of Pb^{2+}. That came from the non-ideality of ions in the ion-exchanger phase.

CONCLUSIONS

Single-species adsorption of metals onto the natural zeolite pretreated with NaCl solution showed the best result compared with other treatments. This result may come from the contribution of sodium that was exchanged with other alkali metals in natural zeolites during the pretreatment process. It was experimentally confirmed by analyzing metal concentrations before and after ion-exchange experiments. It should be noted that the equilibrium amounts of cadmium and copper on the NaCl-treated natural zeolite were larger than those of a commercial natural zeolite, chabazite (AW-500), which was chosen as a reference. Experiments also showed that the concentration of NaCl solution did not affect the amount adsorbed much when the concentration was over 1 mol/m³. From the results on equilibrium, it may be concluded that the pretreatment of the Korean zeolite with NaCl will be a promising technology, considering that it is economical and environmentally com-

cess for heavy metals using natural zeolites. There are some discrepancies between predicted and observed data when the IAS theory is applied as shown in Fig. 11. Those originate mainly from the solid phase non-ideality and non-uniformity rather than the liquid phase non-ideality of electrolytes. However, the IAS theory may be a fairly useful theory in predicting heavy metal/zeolite systems, considering that the RAS theory is a complicated and time-consuming model in simulating breakthrough behavior of column operations. Wilson parameters, which are used to predict multi-specie equilibrium data using the RAS theory, were determined by using an optimization routine, the Levenberg-Marquardt algorithm, and their values are listed in Table 4.

A ternary adsorption system of $Pb^{2+}/Cd^{2+}/Cu^{2+}$ was also carried out under the conditions that the total concentration was 3 mol/m³,

patible.

The Sips equation was applied to fit single-species equilibrium data of heavy metals on treated and untreated natural zeolites. The selectivity of the HCl-treated natural zeolite to these metals follows the order of $Cs^+>Pb^{2+}>Cu^{2+}\geq Cd^{2+}$. This result is very similar to the reversed order of the hydrated cation radii. For all heavy metals, the amount exchanged greatly depends on the content of sodium in zeolites. The contribution of sodium during ion-exchange processes were about 93-98%, 67-71%, and 33-46% for NaCl-treated, NaOH-treated, and untreated zeolites, respectively. When the natural zeolite was pretreated with HCl, below 40% of the total exchanged amount seems to have been achieved by ion exchange itself according to chemical analyses before and after equilibrium experiments, and the other portion may have been removed by physical adsorption or exchanging with protons. In other cases such as the NaCl-treated and NaOH-treated natural zeolites, similar amounts of physical adsorption of metals are expected, but this was not confirmed clearly because the contribution of physical adsorption was relatively small compared with the total amount. However, it can be conjectured from the fact that the sum of equivalent amounts exchanged with major metal ions, Na^+, Ca^{2+}, K^+, and Mg^{2+}, in most equilibrium runs are slightly smaller that the equivalent amount of heavy metals.

When the initial concentration is 1 mol/m^3, the removal efficiency of Pb^{2+}, Cd^{2+}, and Cu^{2+}, by the NaCl-treated natural zeolite was almost over 99.5% in the range of pH 4-10. According to experiments, the final value of solution pH was slightly changed in all the range for metal adsorption systems even if it was a little bit shifted to the lower value for Cd^{2+} and Cu^{2+} adsorption systems. This extent of change in pH will not reduce the removal efficiency of heavy metals much during ion-exchange processes. The effect of temperature on metal sorption by treated and untreated zeolites was that the adsorption amount increased with temperature. This implies that this ion-exchange process is a kind of chemical process.

In Pb^{2+}/Cd^{2+} and Pb^{2+}/Cu^{2+} binary systems, the simple LRC model gave large discrepancies between measured and predicted amounts of metals, while the IAS theory and the RAS theory describe all binary equilibrium data well. As expected, the RAS theory gave the best fit to the data because the non-ideality in the ion-exchanger phase was taken into account.

For a $Pb^{2+}/Cd^{2+}/Cu^{2+}$ ternary system, both models suitably predicted ternary equilibrium data. However, the RAS theory gave better predictions than the IAS theory as expected. It was also noted that the ternary curves predicted by the RAS theory showed an azeotropic condition in the high mole fraction of Pb^{2+} because of the non-ideality of ions in the ion-exchanger phase.

ACKNOWLEDGEMENT

NOMENCLATURE

A   : surface area per unit mass of adsorbent [m^2]
cal   : calculated or predicted
C   : concentration in liquid phase [mol/m^3]

C^0 : single-species concentration in mixture [mol/m^3]
C_0 : initial concentration in liquid phase [mol/m^3]
C_{eq} : equilibrium concentration in liquid phase [mol/m^3]
exp   : experimental
f   : isotherm function defined in Eq. (7)
i, j, k : species index such as i, j, and k
K_s : equilibrium parameter of Sips equation [$(m^3/mol)^{1/n}$]
n   : reciprocal value of the exponent of Sips equation
N   : total number of species
q   : amount adsorbed [mol/kg]
q_m : monolayer amount adsorption for Sips equation [mol/kg]
q_T : total amount adsorbed [mol/kg]
R   : gas constant [J/K mol]
T   : temperature [K]
z   : mole fraction in ion-exchanger phase

Greek Letters

γ : activity coefficient in ion-exchanger phase
Λ : Wilson parameters
π : spreading pressure
Π : modified spreading pressure defined in Eq. (6)

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