

Cation exchange of cesium and cation selectivity of natural zeolites: Chabazite, stilbite, and heulandite



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ABSTRACT

The sorption characteristics of Cs and competitive ion exchange with other alkali cations and Sr on three natural zeolites, chabazite, stilbite, and heulandite, were investigated. Chabazite showed the most rapid sorption of Cs, followed by heulandite and then stilbite, and this was closely related to its high cation exchange capacity (CEC) and low Si/Al ratio. The kinetic data for all zeolites were best explained by a pseudo-second-order rate model. The sorption process involved multiple steps and is influenced by the CEC values of the zeolites. The equilibrium adsorption isotherms of the three zeolites were best fitted by both the Langmuir and Freundlich models. The exchange isotherms of Cs and the other investigated cations clearly showed that chabazite showed higher selectivity for Cs than for the others. At lower equivalent fractions of Cs in solution, the selectivities for the other cations showed the following trend: Na > Li > Sr > K > Rb. However, for stilbite and heulandite, the selectivity for Cs is only higher at lower equivalent fractions, and isotherms show sigmoidal shapes mainly because there are more than two sorption sites for Cs while chabazite has one site. Those trends were confirmed by Kielland plots.

1. Introduction

Zeolites have framework structures with tectosilicates composed of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ coordination polyhedra. Isomorphous substitution of Al^{3+} for Si^{4+} in the polyhedra causes negative charges in the framework that can be balanced by exchangeable alkali or alkaline earth metal cations present within a zeolite structure. These structures contain channels and cages, and as a result, the cations are hydrated and can be exchanged easily. The number of exchangeable cations depends on the number of $[\text{AlO}_4]^{5-}$ tetrahedra in the zeolite framework. Each zeolite has unique features such as molecular sieve and ion exchange capabilities owing to their different building units and forms and sizes of pores. For this reason, zeolites can be used for a variety of applications such as petrochemical cracking, waste and wastewater treatment, and the separation and removal of gases and solvents [1–5]. They can also be applied for agriculture and construction [6].

Among the various types of applications, environmental applications are some of the most widely investigated. Zeolites have been used successfully as adsorbents of heavy metals [7–10]. Erdem et al. [7] and Kocaoba et al. [9] used clinoptilolite for ion exchange experiments with heavy metals using a batch method and concluded that natural zeolite can be used effectively for the removal of heavy metals from wastewater. Natural zeolites have also been reported to be effective in

immobilizing heavy metals in soils [10].

Radiogenic isotopes such as ^{137}Cs , which are also harmful to the environment, can be introduced to natural environments via nuclear accidents, which was the case after the Fukushima Dai-ichi Nuclear Power Plant accident in Japan [11,12]. Therefore, controlling these isotopes in soils and waters is critical for the prevention of their migration. Finding the most suitable materials for the treatment of nuclear waste is also important, and many different materials have been tested as effective adsorbents of radiogenic isotopes [13,14]. Some studies have shown that natural and synthetic zeolites are some of the most effective materials for the exchange of nuclear elements in nuclear waste and waters [15–17]. However, those studies normally used synthetic zeolites or zeolitic rocks containing not only natural zeolites formed through alteration or diagenesis, but also other minerals. Natural zeolite can be used as a cost-effective adsorbent for radionuclides. However, most zeolitic rocks used as low-cost adsorbents contain impurities, and therefore, information on the sorption characteristics of pure natural zeolites is necessary for the quantitative estimation of the sorption behaviors of those rocks. In natural environments, many different cations, including alkali metal cations, compete with radionuclides and affect the sorption behaviors of natural zeolites. Therefore, the sorption behaviors of radionuclides such as Cs in competition with other cations should also be evaluated in order to understand Cs

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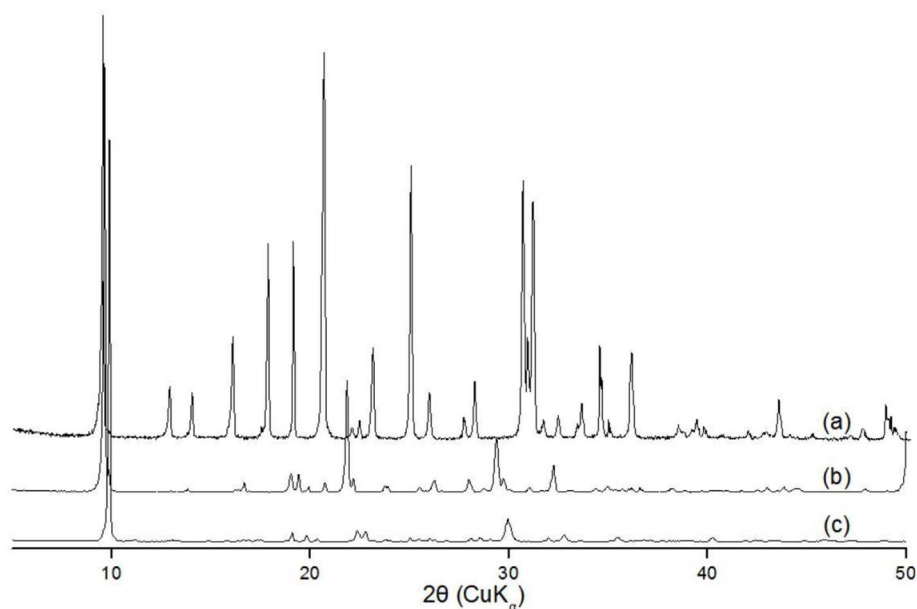


Fig. 1. XRD patterns of the zeolites used in this study: (a) chabazite, (b) stilbite, (c) heulandite.

sorption on zeolites in natural environments. The objective of this study was to investigate the sorption kinetics and analyze the isotherms of Cs with three different natural zeolites: chabazite, stilbite, and heulandite. In addition, experiments were carried out in order to understand the sorption behaviors of Cs in the presence of Sr and other alkali metals.

2. Experimental

2.1. Sample preparation and characterization

The chabazite, stilbite, and heulandite samples were obtained from Nova Scotia, Canada, and Nasik and Maharashtra, India, respectively. These samples were ground using a bowl mill grinder, and samples with particle sizes between 150 and 355 μm were selected by using sieves. The samples were washed with deionized water three times and dried at 40 $^{\circ}\text{C}$ in an oven. The mineral species of the zeolites were confirmed using X-ray diffraction (XRD; Philips, X'pert APD) analysis with a Philips X-ray diffractometer with Ni-filtered Cu-K α radiation at 40 kV and 30 mA at the Daegu Center of the Korea Basic Science Institute. The data were collected in the 2θ range from 5 $^{\circ}$ to 50 $^{\circ}$ with 0.02 $^{\circ}$ intervals and a counting time of 1 s per step. The chemical compositions of the zeolites were determined using electronic probe microanalysis (EPMA; Shimadzu, EPMA1610) at the Korea Basic Science Institute.

The cation exchange capacity (CEC) was measured using the BaCl $_2$ compulsive exchange method suggested by Gillman and Sumpter [18].

2.2. Sorption experiments

Kinetic experiments were carried out by mixing 0.5 g of each zeolite sample with 50 mL of 1.00×10^{-4} M CsCl solutions in high-density polyethylene bottles at 25 $^{\circ}\text{C}$ in a water bath. The bath was shaken at 175 rpm for reaction times ranging from 10 min to 10 d. At the end of the reactions, the solutions were separated from the solid samples by centrifugation at 2000 rpm for 10 min. The solutions were filtered through a 0.45 μm membrane filter. The Cs concentrations of the separated solutions were determined using inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer, ELAN 6100) at the Seoul Center of the Korea Basic Science Institute. The amount of Cs sorbed on the zeolites was calculated using the following equation:

$$q = \frac{C_0 - C_e}{m} \times V$$

where C_0 and C_e (mg/L) are the initial and equilibrium Cs concentrations, respectively, and m and V are the mass of zeolite used (g) and volume of the solution (L), respectively.

Sorption experiments were also carried out with different Cs concentrations. Solution concentrations ranging from 3.0×10^{-6} to 2.0×10^{-2} M were used for four days under the same experimental conditions as those in the kinetic experiments. After the reactions, the solutions were separated and analyzed using the same method as that in the kinetic experiments.

To investigate the effects of other alkali cations and Sr in the solution on the sorption of Cs on these zeolites, sorption experiment solutions were prepared by mixing the CsCl solution with alkali chloride solutions and a SrCl $_2$ solution at different ratios. The final concentrations of the solutions were 4.00×10^{-3} N. The mixed solutions (50 mL) were mixed with 0.5 g of each zeolite sample and the resulting mixtures were reacted at 25 $^{\circ}\text{C}$ in a water bath that was shaken at 175 rpm for four days. After the reaction, the solutions were separated from the solid samples by centrifugation and filtration. ICP-MS (ELAN DRC II, Perkin Elmer) was used for the analysis of Li, Rb, Sr, and Cs, and ICP-optical emission spectroscopy (OES) (ICP-OES Ultima 2, Horiba Jobin Yvon) was used for Na and K at the Seoul Center of the Korea Basic Science Institute.

3. Results and discussion

3.1. Characterization of samples

The XRD patterns clearly show that the samples we used were pure chabazite, stilbite, and heulandite (Fig. 1). No other mineral phases were identified. The chemical compositions of the zeolites were determined using EPMA. The chemical compositions calculated based on the results were Ca $_{1.15}$ Na $_{0.99}$ K $_{1.20}$ Mg $_{0.01}$ Ba $_{0.16}$ Al $_{4.79}$ Si $_{7.21}$ O $_{24}$ for chabazite, Ca $_{0.04}$ Na $_{1.06}$ K $_{0.22}$ Ba $_{0.01}$ Mg $_{0.01}$ Al $_{4.11}$ Si $_{14.30}$ O $_{36}$ for heulandite, and Na $_{0.34}$ Ca $_{2.41}$ Al $_{7.49}$ Si $_{29.08}$ O $_{72}$ for stilbite. Ca is the major exchangeable cation in stilbite and heulandite, while chabazite does not have any dominant cations but contains high amounts of Ca and K. The calculated Si/Al ratios were 1.50, 3.88, and 3.48 for chabazite, stilbite, and heulandite, respectively.

The CECs measured using the BaCl $_2$ method were 238.1, 139.4, and 151.9 meq/100 g for chabazite, stilbite, and heulandite, respectively. Chabazite, which showed the lowest Si/Al ratio, has the highest CEC. The negative charges in zeolites that are balanced by exchangeable

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