

Retention of Na⁺ Cations in Nanopores and Its Implications to Sodic Soils

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Abstract

The management of sodic soils often involves the addition of Ca²⁺ cations because it is believed that these divalent cations will easily desorb the Na⁺ cations from the soil solid phase. However, the adsorption of cations in the interstitial region of minerals is counterintuitive, particularly if the diameter of the interstitial region is less than 1 nanometer. These very small dimensions are common in many soil minerals. Using zeolites, the ideal cation for treating sodic soils may be another monovalent cation, such as K⁺, rather than Ca²⁺. The reasons for this reversal of selectivity in nanopore regions of minerals may be due to a NISE (nanopore inner-sphere enhancement) effect. An enhanced liquid-phase stability of the Na⁺ ion in the presence of K⁺ ions may also be involved.

Key Words

Cation adsorption, nanopores, zeolite, ion hydration, sodium retention

Introduction

In the US, saline soils are found primarily in the arid Midwest and along the coastal states in the eastern and southern parts of the country. The greatest concentration of saline soils are in North Dakota, South Dakota, Michigan, and Colorado. The Natural Resources Conservation Service (NRCS) estimates that there are 500,000 to 725,000 hectares of saline soils in North Dakota's Red River Valley alone. These predominantly affect prime farmland and result in a loss of \$50-\$90 million in production each year to the state (NRCS 2007).

Saline soils are also problematic in East Asia. China alone is estimated to have 99.1 million hectares of saline soil (Matsumoto *et al.* 1998). Australia currently has 975,000 hectares of saline soils and another 4.5 million hectares are in danger of becoming saline (McFarlane *et al.* 2004). Saline soils can be an even more serious issue for low lying island countries such as Myanmar. The damage from the tsunami that struck Myanmar in May of 2008 was measured in terms of the number of fatalities and destroyed homes. But the salt intrusion onto agricultural lands due to the inundation by the ocean water was also damaging. Sodic soils are a subset of saline soils, where the salt present is high in sodium (Na⁺). Sodium is, for the most part, considered an indifferent electrolyte and adsorbs weakly in typical soils. It is usually desorbed quite easily by competing ions. The current view on how sodic soils are formed is that a constant source of sodium, such as a sodium rich bedrock, releases Na⁺ ions into the soil or groundwater. Only because of the constant release of sodium, according to this theory, does sodium build up in sodic soils. The most common method of remediating sodic soils is either through the management of the irrigation water (namely, by leaching the Na⁺ out of the soil profile) or through ion exchange of sodium with calcium through the use of gypsum (CaSO₄·2H₂O) (Oster 1982). Lime (CaCO₃) can also be added, but this is less common since sodic soils are typically already alkaline. Calcium, being divalent, is expected to be able to easily desorb Na⁺ from the exchange sites on the mineral surfaces. Also, gypsum and lime are plentiful, cheap, and easily obtained in most parts of the world. The retention of Na⁺ by soil minerals is known to be weak in most cases. However, recent studies by Schulthess *et al.* (2010) have found that the retention strength of ions in the nanopore interstitial region of soil minerals is much stronger than on their external surface sites. In some cases, for example, Na⁺ adsorption is much stronger than the adsorption of divalent cations, such as Ca²⁺ and Ni²⁺. Curiously, other monovalent cations are also held very strongly in the interstitial regions, such as K⁺ which is held even more strongly than the Na⁺ ions. The proposed explanation for this phenomenon is tentative at the present time, but it appears to be closely related to the ionic diameter of the adsorbing species, the pore diameter of the interstitial spaces in the mineral, and the amount of space remaining for the hydrating water molecules in the interstitial spaces.

Our understanding of the Na⁺ adsorption processes and that of other ions are closely tied to our management of sodic soils. The objectives of this study were to compare the retention of several cations on zeolite

minerals with interstitial cavities of different sizes, and to find a cation that can effectively desorb sodium cations better than calcium cations. The basic premise of this research is based on the theories presented by Schulthess *et al.* (2010), which we coin the nanopore inner-sphere enhancement (NISE) effect. Basically, small pores have the potential of reversing the adsorption selectivity observed on macropores or on external surface sites.

Materials and Methods

Two zeolite materials were used for this study: ZSM-5 and zeolite-Y. The ZSM-5 zeolite has interconnected pores with dimensions of 0.55×0.51 nm and 0.56×0.53 nm. The zeolite-Y has interconnected pores that are 0.74 nm in diameter. Slurries of these zeolites were prepared in a closed reactor and purged with N₂ gas to remove any adsorbed inorganic-C present. These zeolites do contain a large amount of adsorbed inorganic-C and the purging of this contaminant takes several days to complete. Batch adsorption experiments were performed with these zeolites as a function of pH. Mixtures were prepared in 50-mL nominal centrifuge tubes consisting of zeolite slurry, NaOH, HCl, and other salt solutions as needed. The amount of Na⁺ cations present in each reaction container was kept constant by adding a fixed quantity of NaOH solution to each sample and adjusting the pH with variable quantities of a HCl solution. The added salt solutions included KCl, MgCl₂, CaCl₂, and BaCl₂. The samples were then centrifuged and the supernatant solutions were analyzed for pH and remaining cations present using inductively coupled plasma optical emission spectroscopy (ICP-OES). The amount of cations adsorbed by the zeolites are based on the amount added minus the amount remaining in solution.

Results

The adsorption of sodium (Na⁺) cations on zeolite minerals is surprisingly strong. However, there are marked differences in adsorption strength observed among different zeolites. Figure 1 shows a strong retention of Na⁺ ions on ZSM-5 zeolite. The presence of equimolar concentrations of K⁺ ions has a very strong desorption effect on Na⁺, whereas an equimolar concentration of Ca²⁺ has a very weak effect (Figure 1). Figure 2 shows that the retention of K⁺ on ZSM-5 is very strong, but the retention of Ca²⁺ is very weak. The fact that Ca²⁺ ions have a minor impact on Na⁺ retention, but K⁺ ions have a large impact, is counterintuitive and very significant to our understanding of how these ions are stabilized in the interstitial region of minerals.

Adsorption on zeolite-Y was much weaker, but still noteworthy (Figure 3). The impact of equimolar concentrations of Ca²⁺ and K⁺ on Na⁺ adsorption was similar to the effects observed in Figure 1. Figures 3 and 4 show that the retention of Na⁺, K⁺, and Ca²⁺ are all relatively weak on zeolite-Y, but all are nearly the same strength. Once again, the fact that Ca²⁺ ions have a minor impact on Na⁺ retention, but K⁺ ions have a large impact, is counterintuitive and very significant to our understanding of how these ions are stabilized in the interstitial region of minerals.

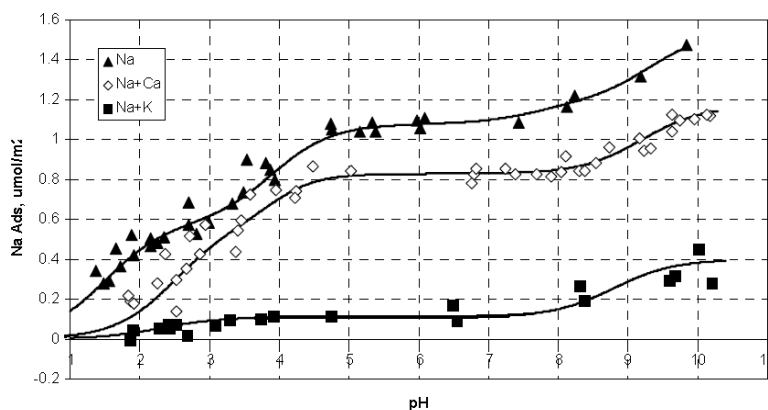


Figure 1. Adsorption ($\mu\text{mol}/\text{m}^2$) of Na⁺ cations on ZSM-5 (medium nanopores present) as a function of pH in the presence and absence of Ca²⁺ and K⁺ cations.

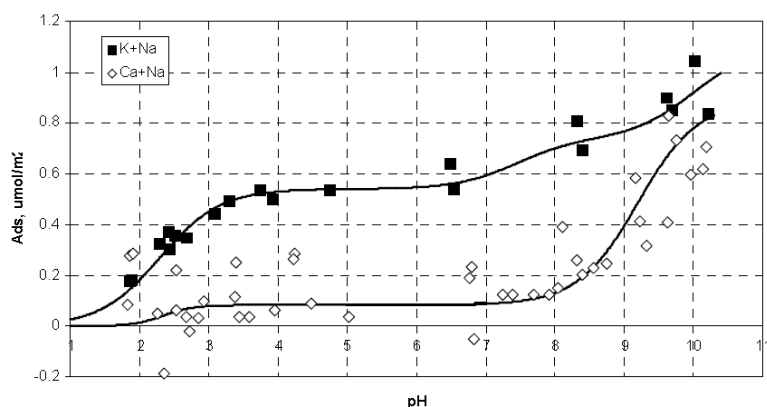


Figure 2. Adsorption ($\mu\text{mol}/\text{m}^2$) of Ca^{2+} and K^+ cations on ZSM-5 (medium nanopores present) as a function of pH in the presence of Na^+ .

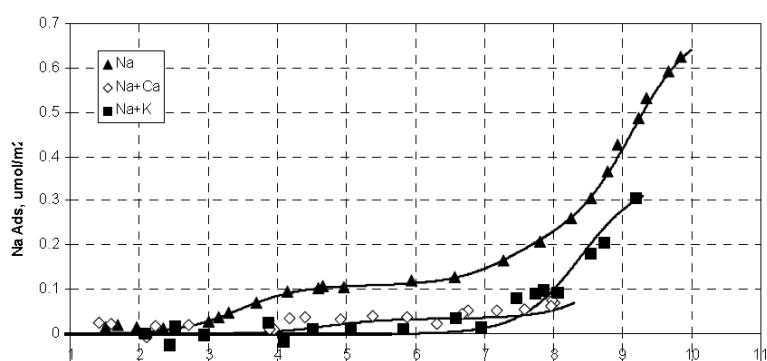


Figure 3. Adsorption ($\mu\text{mol}/\text{m}^2$) of Na^+ cations on zeolite Y (large nanopores present) as a function of pH in the presence and absence of Ca^{2+} and K^+ cations.

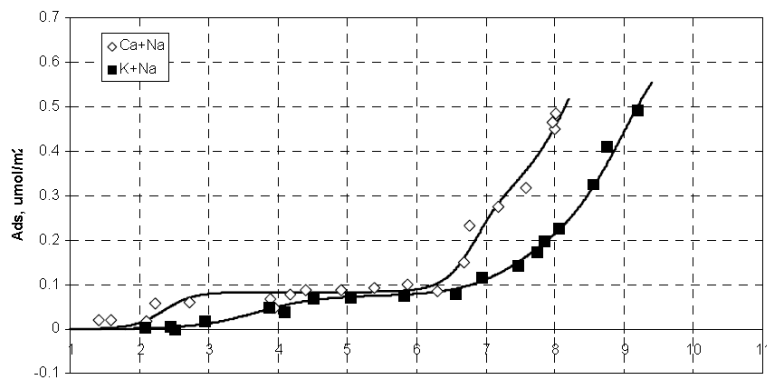


Figure 4. Adsorption ($\mu\text{mol}/\text{m}^2$) of Ca^{2+} and K^+ cations on zeolite Y (large nanopores present) as a function of pH in the presence of Na^+ .

Conclusions

The retention of Na^+ cations by porous minerals, specifically those with interstitial spacing in the subnanometer diameter range, is much stronger than previously anticipated. The desorption of this cation by other cations is possible, but it is wrong to assume that divalent cations are more effective than monovalent cations. The stability of the ion in the liquid phase versus in the nanopore regions of the mineral should be evaluated carefully if a full understanding of the processes involved are to be understood. This can have significant implications on how sodic soils are managed in the field.

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