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ABSTRACT

Cation fixation is of great importance to agricultural productivity and to the chemical and physical properties of soils. Reduction of Fe(III) to Fe(II) in clay minerals is known to enhance the potential for K⁺ fixation on drying, but further studies are needed to determine whether K⁺ fixation also increased when reduction occurs without drying, and to measure the potential for fixation of other cations. The objective of this study was to address these questions. The effect of Fe oxidation state on cation fixation was determined by chemically reducing aqueous suspensions of a ferruginous smectite and a montmorillonite with Na₂S₂O₄, then saturating the exchange complex with either K⁺, Ca²⁺, Cu²⁺, or Zn²⁺ using inert-atmosphere techniques. The amount of fixed cation was calculated as the difference between the total and the exchangeable (relative to Mg²⁺) amounts. Both smectites displayed substantial capacity to fix interlayer cations (without drying) as the level of Fe(II) increased in their structures, depending on the cation and the Fe(II) content. For a given Fe(II) content, the amount of cation fixation increased in the order Cu²⁺ < Zn²⁺ < Ca²⁺ < K⁺, which follows precisely the inverse of the hydration energies (ΔH_{hyd}) of the cations and suggests that reduction

of octahedral Fe encourages dehydration of the interlayer region. In both clays, the amount of exchangeable K⁺ was largely independent of Fe(II) content, but virtually all additional negative charge due to Fe reduction was reflected in the nonexchangeable K⁺ fraction.

A HIGH CATION-EXCHANGE CAPACITY (CEC) is one of the characteristics that distinguishes smectites from other clay minerals, and is a principal basis for their beneficial contribution to the properties of soils and sediments. Studies have shown that the oxidation state of structural Fe is a controlling factor in determining the magnitude of the negative charge of clay layers (Stucki et al., 1984b; Lear and Stucki, 1985, 1989). But studies have also shown that such changes in layer charge increase the potential for cation fixation (Chen et al., 1987; Lear and Stucki, 1989). The exchangeability of interlayer cations may, therefore, be hindered as the total layer charge increases. Chen et al. (1987) reported that the chemical reduction of structural Fe in standard reference clays and in several Indiana soil clays increased the amount of K⁺ fixation on drying by as much as 40 cmol_c kg⁻¹ clay; Lear and Stucki (1989) found that, even without drying, the

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chemical reduction of Fe in nontronite increased the amount of nonexchangeable Na⁺, in spite of a concomitant increase in both layer charge and CEC. These results suggest that cations other than K⁺ also become nonexchangeable in the nontronite mineral matrix as a result of Fe reduction.

While increased layer charge of soil and clay minerals may generally be viewed as a beneficial process, the true benefit is defined more precisely by the distribution of charge between exchangeable and nonexchangeable fractions, and by the impact of mineral properties on the intended land-use project. For example, a high cation-fixation capacity would be detrimental to the agricultural use of a soil because valuable nutrients, such as K⁺, Ca²⁺, and various micronutrients, could be prevented from reaching plant roots; whereas, in a landfill, this attribute would enable the surrounding soils, sediments, and clay barriers to trap hazardous cations and thereby retard their movement. These are only two examples of soil and land uses that could benefit enormously by a more complete understanding of the behavior of soil systems in response to changes in redox conditions. With such knowledge, methods may be devised for modifying cation exchange and fixation properties in situ.

The objectives of our study were to determine the effect of Fe reduction on the fixation of both uni- and divalent cations, and to compare the fixation capacities of low- and high-Fe smectites in order to define further the scope of cation fixation that may be induced by the reduction of structural Fe in smectites.

MATERIALS AND METHODS

Samples of ferruginous smectite (SWa-1, Source Clay Minerals Respository of the Clay Minerals Society, Columbia, MO) from Grant County, Washington, and Upton, WY, montmorillonite (API 25, Wards Natural Science Establishment, Rochester, NY) were initially Na⁺ saturated, fractionated to <2 μm, and freeze-dried. Subsequently, the <0.5-μm fraction was removed from sample SWa-1. Structural Fe was reduced in each sample by suspending 30 mg of the freeze-dried sample in 30 mL of sodium citrate-bicarbonate solution (Stucki et al., 1984a) using an inert-atmosphere, open-system reaction vessel as described by Komadel et al. (1990), heating to 70 °C, then adding 100 mg of Na₂S₂O₄ salt. The level of reduction was varied by controlling the reaction time, giving the initial levels of reduction in Table 1.

Table 2. Total layer charge (ν), cation-exchange capacity (ω), and fixation of interlayer cations ($\nu - \omega$) by unaltered (oxidized) and reduced (4-h treatment) smectite SWa-1 as measured with four different cations. Ionic (R_i) and hydrated (R_h) radii, with corresponding charge/radius ratios (ν_i/R) and hydration energies (ΔH_{hyd}) are also reported.

Cation	ΔH_{hyd} †	R_i ‡	R_h ‡	ν_i/R_i	ν_i/R_h	Oxidation state	ω	ν	$\nu - \omega$
K ⁺	321	0.133	0.331	7.52	3.02	Oxidized	76.2	79.8	3.6
						Reduced	77.9	108.0	30.1
Ca ²⁺	1650	0.099	0.412	20.20	4.85	Oxidized	74.7	82.2	7.5
						Reduced	81.7	97.6	15.9
Zn ²⁺	2050	0.074	0.430	27.03	4.65	Oxidized	66.3	72.4	6.2
						Reduced	90.8	100.8	10.0
Cu ²⁺	2100	0.072§	0.540§	27.78	3.70	Oxidized	77.3	79.9	2.6
						Reduced	99.7	106.3	6.6

† Atkins (1986, p. 824).

‡ Conway (1981, Table 8).

§ McBride et al. (1975).

Table 1. Levels of structural Fe(II) attained in smectites heated at 70 °C for different lengths of time in citrate-bicarbonate solution using 100 mg of Na₂S₂O₄.

Smectite	Time (h)	Fe(II)/Total Fe
SWA-1	0	0.0
	1	0.264
	2	0.718
	3	0.774
	4	0.813
Upton	0	0.0
	1	0.324
	2	0.441
	3	0.561
	4	0.690

Reduced suspensions were then washed four times with deoxygenated, 1 M solutions of the chloride salts of either K⁺, Ca²⁺, Cu²⁺, or Zn²⁺, using the methods described by Stucki et al. (1984a), followed by four washings with a deoxygenated, 0.005 M solution of the same salt. Amounts of exchangeable cations were measured by atomic absorption (Ca²⁺ at 423 nm; Cu²⁺, 325 nm; and Zn²⁺, 214 nm) or emission (K⁺ at 766 nm) analysis of supernatant solutions obtained from five subsequent washings with a deoxygenated, 0.5 M solution of MgCl₂·6H₂O. Total layer charge was determined similarly, except the sample was digested in HF-H₂SO₄, then analyzed by atomic absorption or emission for total interlayer cation, corrected for the amount of cation remaining in the outer solution of the clay gel, using methods described by Stucki et al. (1984b) and Lear and Stucki (1985, 1989). The amount of fixed cation was assumed to be the difference between the total and the exchangeable.

The ratio of Fe(II) to total Fe was measured in freshly washed (with deoxygenated 0.005 M NaCl solution) clay gels using the 1,10-phenanthroline photochemical method of Komadel and Stucki (1988).

RESULTS AND DISCUSSION

Total Layer Charge

Table 2 shows that the total layer charge (ν) of unaltered (oxidized) ferruginous smectite SWa-1, measured by either K⁺, Ca²⁺, Zn²⁺, or Cu²⁺, compared favorably with the value of 80.6 cmol.kg⁻¹ reported by Lear (1984) where Na⁺ was the interlayer cation. Similar agreement was found for the Upton montmorillonite, comparing the K⁺ (Table 2) with the Na⁺ (Stucki et al., 1984b) form.

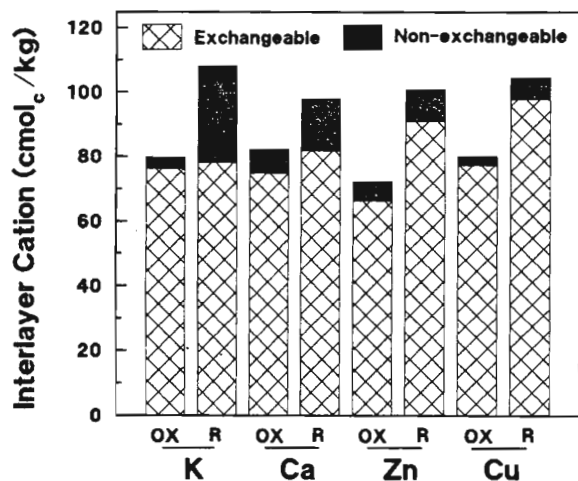


Fig. 1. Exchangeable and nonexchangeable K⁺, Ca²⁺, Zn²⁺, and Cu²⁺ in oxidized (OX) and 4-h reduced (R) smectite SWa-1.

The value of ν for sample SWa-1 increased with Fe reduction (Table 2, Fig. 1), as expected, based on previous studies (Stucki and Roth, 1977; Stucki et al., 1984b; Lear and Stucki, 1985), regardless of which interlayer cation was present. But the values of ν for reduced SWa-1 obtained using the various interlayer cations (Table 2) agreed only qualitatively with one another because the value depends on the Fe(II) content, and results were not normalized with respect to Fe(II). In fact, the absolute coincidence of these values would have been rather fortuitous because achieving and preserving the same level of reduction in all reaction vessels during the many washing steps required for ion exchange and analysis is difficult, even with stricter controls than those used in these experiments. Determination of Fe(II) in the final state of the sample was omitted due to the necessity of digesting the sample to determine the total amount of exchanged cation.

Exchangeable vs. Nonexchangeable Fractions

The distributions of total layer charge between exchangeable and nonexchangeable fractions of ferruginous smectite SWa-1 in various oxidation states are reported in Fig. 1 and 2 and in Table 2, and for Upton montmorillonite in Fig. 3. In sample SWa-1, differences occurred in the relative fractions of exchangeable vs. nonexchangeable cations, depending on whether the interlayer cation was K⁺, Ca²⁺, Cu²⁺, or Zn²⁺ (Fig. 1, Table 2). Note also that, in each clay, the reduction of structural Fe increased both the CEC (ω) and the cation fixation capacity ($\nu - \omega$) regardless of the interlayer cation. The only exception is that the amount of exchangeable K⁺ increased only slightly (Fig. 2 and 3). All reduced samples contained a greater portion of exchangeable relative to nonexchangeable cations, using Mg²⁺ as the exchanging ion, but the nonexchangeable or fixed fraction was substantial (6–30%) in all cases.

The extent of fixation in sample SWa-1 increased in the order Cu²⁺ < Zn²⁺ < Ca²⁺ < K⁺, which follows precisely the inverse of ΔH_{hyd} of the cations (Fig. 4; Table 2), and the sequence is also consistent with the cation charge/ratios as they probably exist in a clay-

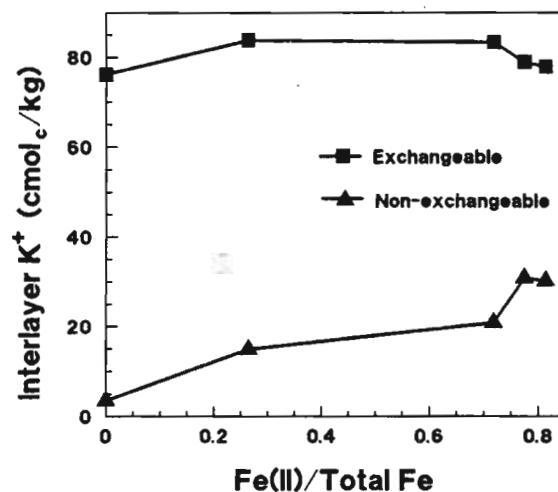


Fig. 2. Effect of Fe(II) on exchangeable and nonexchangeable K⁺ in smectite SWa-1.

water system (Table 2), i.e., the divalent cations being hydrated and K⁺ being largely unhydrated. Such an inverse relationship between cation fixation and hydration state is not surprising because fixed cations logically would be unhydrated.

The intriguing question, however, is why the change in oxidation state invokes the fixation of an appreciable number of highly hydrated interlayer cations. Vermiculite and illite are well known for their ability to fix K⁺, which is customarily attributed to their high layer charge (Barshad, 1954; Grim, 1968). In this sense, Fe reduction causes the smectite to behave somewhat like either an illite or a vermiculite. Consistent with common belief regarding the driving force behind illitization or vermiculitization, the increased charge on reduced smectite layers could explain the greater cation fixation.

The inverse relationship with ΔH_{hyd} , however, indicates that the fixation mechanism in reduced smectite may be more complex than simply an increase in electrostatic attraction between the clay surface and the interlayer cation. Stucki et al. (1984c) and Lear and Stucki (1989) showed that reduction of structural Fe in smectites produces a less hydrated environment in the clay interlayer region (i.e., a lower affinity of the clay surface for water), decreases the specific surface area, and yields a high correlation between the amount of fixed interlayer Na⁺ and the fraction of totally collapsed layers in the system. Mulla (1983) reported a significant statistical correlation between specific surface area and Fe(II) content of smectites. But Mulla (1983) also showed that no statistical correlation exists between octahedral Mg(II) content and either the specific surface area or swelling in water, inferring that no relationship exists with cation fixation either. Since Mg(II) has the same charge and about the same ionic radius as Fe(II), but fails to induce similar effects on the properties of smectites, one must regard the principal force underlying these effects to be noncoulombic. The dehydration and increased attractive forces between planar clay surfaces imposed uniquely by structural Fe(II) could thus cause partial dehydration of the clay surface and of the interlayer cation.

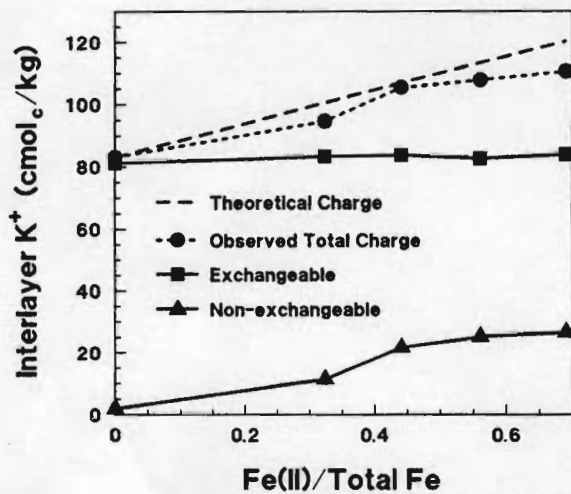


Fig. 3. Effect of Fe(II) on exchangeable and nonexchangeable K^+ in Upton montmorillonite (API 25). Also shown are the observed total layer charge and the theoretical value based on a 1:1 relationship between Fe(II) content and layer charge.

Regardless of the driving force, however, these observations demonstrate that cation fixation occurs readily in reduced samples without drying, and are thus consistent with earlier observations of Na^+ fixation reported by Lear and Stucki (1989) in undried Garfield nontronite (API 33a) and ferruginous smectite (SWa-1). The high tendency of the clay to fix K^+ is also consistent with observations by Chen et al. (1987). The phenomenon appears to be general for all interlayer cations, with ΔH_{hyd} being the differentiating factor. The potential for exploiting these phenomena to solve practical problems is tremendous. For example, the oxidation state could be utilized to promote the fixation of trace elements in clay-liner barriers for landfills and hazardous-waste disposal sites. The levels of fixation will vary with extent of Fe(II) formation, but even the smallest level of fixation reported here after Fe reduction (6 $cmol_c kg^{-1}$) translates into about 2 g $Zn^{2+} kg^{-1}$ of clay material.

Potassium Fixation

Of the four interlayer cations studied, K^+ exhibited the most extreme behavior with respect to fixation and exchangeability. While the amount of fixed K^+ in SWa-1 was twice that of the next-highest cation (Ca^{2+}) and the total layer charge increased by almost 40%, the level of exchangeable K^+ remained virtually the same even though more than 80% of the structural Fe was reduced to Fe(II) (Fig. 2). This suggests that reducing conditions will increase the amount of fixed K^+ rather than increasing the total available nutrient pool. But following reoxidation, the reservoir of fixed K^+ will be released to the surrounding solution. This has tremendous implications toward understanding the widely fluctuating test results observed for K^+ in soils.

Figure 3 shows that the response of K^+ fixation to changes in Fe oxidation state in Upton montmorillonite is similar to that observed in sample SWa-1, indicating that such fixation is not unique to Fe-rich smectites. These results also reveal the potential significance of this phenomenon in soils. For example,

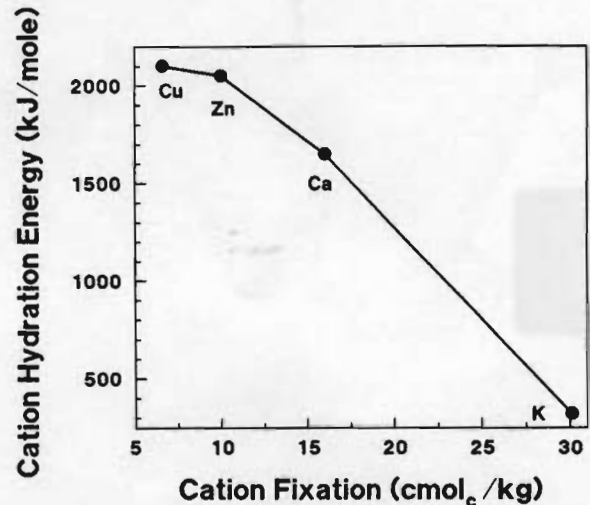


Fig. 4. Relation between cation hydration energy and fixation in smectite SWa-1 after a 4-h reduction treatment.

if the smectite in a medium-textured soil (consisting of 10% smectite by weight) were reduced to only 20%, the resulting increase in K^+ fixation, according to Fig. 3, would be about 10 $cmol_c kg^{-1}$. This is equal to a fixation capacity of 878 kg K per ha-plow layer of soil. Such a result indicates that, if K^+ fertilizer were added during a reducing cycle, most could become fixed, but then would be subject to release later under reoxidizing conditions.

SUMMARY AND CONCLUSION

The chemical reduction of structural Fe(III) to Fe(II) in the octahedral sheet of dioctahedral smectites causes an increase in fixation of interlayer cations in the order $Cu^{2+} < Zn^{2+} < Ca^{2+} < K^+$, which follows the inverse of the cation ΔH_{hyd} . Reduction also produces an increased ω and ν . In the case of K^+ -exchanged clay, the amount of exchangeable cation is largely independent of Fe(II) content. Cation fixation occurs in wet systems in the absence of drying, indicating that strong interlayer forces, which ultimately arise from Fe reduction, cause layers to collapse, thus trapping many interlayer cations.

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