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HYDROXY-INTERLAYERS IN EXPANSIBLE LAYER SILICATES AND THEIR RELATION TO POTASSIUM FIXATION

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Abstract—Hydroxyaluminosilicate (HAS) and hydroxyaluminum (HyA) ionic solutions having final Al concentrations ranging from 3.74 to 4.00 m*M*; NaOH/Al molar ratios of 1.0, 2.0 and 2.5; and Si/Al molar ratios of 0.00, 0.27–0.30, 0.51–0.56 and 0.95–1.01 were prepared through the interaction of $AlCl_3$, orthosilicic acid and NaOH solutions. When these solutions reacted with <2 μm sized vermiculite (Vt) and montmorillonite (Mt), varying amounts of Al and Si were fixed on Vt and Mt clays. Potassium fixation and exchange capacities of HyA/HAS (OH/Al = 1.0, 2.0 and 2.5)-Vt and HyA/HAS (OH/Al = 2.0)-Mt complexes were compared with those of untreated Vt and Mt at added K levels ranging from 21 to 319 $cmol_c\ kg^{-1}$. The untreated Vt clay showed K fixation as high as 94 $cmol_c\ kg^{-1}$, in contrast to only 16 $cmol_c\ kg^{-1}$ exchangeable K. The untreated Mt fixed a maximum of 9 $cmol_c$ K kg^{-1} out of a total K adsorption capacity of 67 $cmol_c\ kg^{-1}$. In the HyA/HAS-Vt complexes, K fixation reduced drastically in comparison to untreated Vt, and ranged from 9 to 24 $cmol_c\ kg^{-1}$ out of their total K adsorption capacities of 61 to 81 $cmol_c\ kg^{-1}$. In the HyA/HAS-Mt complexes, too, the amount of K fixed reduced to a great extent in comparison to Mt and ranged from 1.48 to 1.84 $cmol_c\ kg^{-1}$. Potassium became more exchangeable due to the presence of hydroxy-interlayers in the clays. The reduction in CEC and the well-known propping effects of hydroxy-cations' islands in the interlayers might have hindered K fixation by the complexes. The relationships of maximum K fixing capacities of the HyA/HAS-Vt complexes with the amounts of Al, Si and Al + Si fixed on Vt were all exponential and negative. However, the amount of Al + Si or only Al fixed on Vt appeared to be the best indicator of K fixation capacities of hydroxy-interlayered Vt clay.

Key Words—Hydroxyaluminum, Hydroxyaluminosilicate, Montmorillonite, Potassium Fixation, Vermiculite.

INTRODUCTION

Fixation of certain cations in the interlayer position of vermiculite (Vt) and montmorillonite (Mt) clays is well established (Mackenzie 1963; Grim 1968). Out of these cations, K is of the greatest interest to most geologists and clay mineralogists (Inoue 1983). Numerous workers have studied K fixation in soils and clays and have explained that K fixation takes place by an irreversible adsorption of K at cation exchange sites followed by layer collapse (Page et al. 1967; Sawhney 1972). Kittrick (1966) indicated that ion fixation in clay interlayers could occur when the electrostatic attraction forces between the negatively charged silicate layers and the positively charged interlayer ions exceed the interlayer expanding forces resulting from ion hydration. Thus, fixation of large amounts of K (with low hydration energy) by Vt clays (with highly charged tetrahedral sheets) and also by vermiculitic soils has been frequently observed (Rich and Black 1964; Page et al. 1967; Inoue 1983).

Partially interlayered expansible phyllosilicates have been found in many soils and sediments (Jackson 1963; Rich 1968). Recent studies have reported the predominance of 2:1 to 2:1:1 layer silicate intergrades in some nonallophanic Andisols (Shoji et al. 1985, 1987; Bautista-Tulin and Inoue 1997) and also in Red-Yellow soils (Hapludaulfs and Hapludults) influenced by eolian dust (Bautista-Tulin and Inoue 1997). Based on higher soluble Si concentrations (such as 0.04–1.0, m*M*, as reported by Farmer et al. 1979) than Al (such as 0.02–0.2 m*M*, as reported by Manley et al. 1987) in solutions of acid soils, Lou and Huang (1994) indicated that a substantial portion of HyA is bound to react with monosilicic acid to form HAS ions before entering the interlayer spaces of expansible layer silicates. Experimental evidences have also shown that, in addition to HyA ions, the interlayer materials of natural chloritized Vt and 2:1 to 2:1:1 layer silicate intergrades are partially composed of HAS ions. Matsue and Wada (1988) reported that, in Dystrocrepts derived from Tertiary sediments, the interlayer materials dissolved by citrate treatment had Si/Al ratios ranging from 0.24 to 0.72, suggesting a hydroxy-Al sheet containing some Si tetrahedra as a possible model of the interlayer materials in partially interlayered Vt. Recently, Bautista-Tulin and Inoue (1997) observed predominance of hydroxy-interlayered Vt and Mt in 28 samples of Japanese loess-derived soils from 7 pedons classified as Hapludalfs, Hapludults or Melanudands. Based on selective dissolution analyses of these soil clays, they concluded that the interlayer ma-

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Table 1. The chemical composition and structural formula of vermiculite used in this study.†

Chemical composition											
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	LOI‡	Total
Oven-dry basis (%)											
41.50	14.50	10.30	0.82	0.06	0.30	20.42	3.90	3.90	0.07	4.24	99.51
Structural formula											
$K_{0.35}Na_{0.53}Ca_{0.02}(Al_{0.09}Fe_{0.54}Mg_{2.12})(Si_{2.90}Ti_{0.04}Al_{1.06})O_{10.00}(OH)_{2.00}$											

† Cited from Inoue and Satoh (1992).
‡ Loss on Ignition.

terials were composed not only of HyA ions but also HAS ions with Si/Al ratios ranging from 0.12 to 0.86.

Because of widespread occurrence of hydroxy-interlayers and their significant effects on many physicochemical and mineralogical properties of soils and clays, considerable efforts have been devoted to investigate the nature of hydroxy-interlayers and the processes of their formation. The HyA and HAS ions fixed on the clays are nonexchangeable, occupy cation exchange sites (Inoue et al. 1988; Lou and Huang 1988) and, as a consequence, cause a drastic reduction in permanent negative charge with a great increase in pH-dependent charge of both Vt and Mt (Inoue and Satoh 1992, 1993). The HyA/HAS-Vt complexes showed manifold higher phosphate adsorption abilities than untreated Vt, since hydroxy-materials residing in the interlayer spaces were actively involved in the adsorption processes (Saha and Inoue 1997). It has been reported that hydroxy-cations' islands in the interlayer spaces of clays could prevent K fixation through reduction of effective cation exchange capacity (CEC) and by their propping effects (Rich and Black 1964). Consequently, in the presence of hydroxy-interlayers, an increase in K/Ca cation exchange selectivity of Vt and K-depleted biotite was observed (Kozak and Huang 1971). However, information on the relationship between the degree of HyA and HAS interlayering in Vt and Mt clays and K fixing capacities of the resultant HyA/HAS-Vt/Mt complexes is not clear. This paper reports the evaluation of K fixation and exchange capacities of hydroxy-interlayered Vt and Mt clays in relation to degree of interlayer filling with Al and Si.

MATERIALS AND METHODS

Preparation of the Hydroxyaluminum- and Hydroxyaluminosilicate-Clay Complexes

Orthosilicic acid was prepared from tetraethyl orthosilicate (Farmer et al. 1979). The HyA and HAS ionic solutions having final Al concentrations ranging from 3.74 to 4.00 m*M*; NaOH/Al molar ratios of 1.0, 2.0 and 2.5; and Si/Al molar ratios of 0.00, 0.27–0.30, 0.51–0.56 and 0.95–1.01 were prepared through interaction of orthosilicic acid with $AlCl_3$ and NaOH solutions. The solutions were aged for 7 d at 20 °C. The pHs of the solutions were recorded and clear filtrates were obtained by passing through a Toyo Roshi cellulose NO_3 membrane filter (Toyo-Roshi Co., Tokyo) of 0.2 μm pore size to remove the solid particles of $Al(OH)_3$ or aluminosilicates formed.

The <2 μm fractions of Vt and Mt clays were collected from Zonolite (obtained from near Libby, Montana) and Hojun bentonite (Gunma, Japan), respectively, by repeated dispersion, sedimentation and siphoning techniques. The collected clay samples were then successively treated with dithionite-citrate (Mehra and Jackson 1960), 2% Na_2CO_3 (Jackson 1979) and 1 *M* CH_3 COONa +1 *M* NaCl (pH 5, 4 times), made Cl^--free by being washed with 80% methanol and acetone, air-dried and finally ground gently in an agate mortar. The Vt used in this study is a trioctahedral mineral containing a significant amount of interstratified biotite-vermiculite. The Mt clay contained a significant amount of cristobalite. The X-ray diffractograms (XRD) of these clays have been published elsewhere (Inoue and Satoh 1992, 1993). The chemical composition and structural formula of this Vt clay reported by Inoue and Satoh (1992) are given in Table 1. The CECs of the Mt and Vt clays determined by the method of Wada and Okamura (1980) were 57 and 95 $cmol_c\ kg^{-1}$, respectively, and showed negligible pH dependence (Inoue and Satoh 1992, 1993).

Four grams of Na-saturated clay specimens (Vt or Mt) were reacted with 200 mL of HyA or HAS ionic solution for 30 min repeatedly for 8 times. After every 30-min reaction period, the suspensions were centrifuged at 7500 × *g* for 10 min and the supernatants collected for Al and Si determinations. The resultant HyA/HAS-Vt/Mt complexes were made Cl^--free by being washed with 80% methanol and acetone and then air-dried, gently ground and passed through a 60-mesh sieve. The Al and Si contents of the initial HyA and HAS ionic solutions and of the supernatants were determined according to the methods reported by Davenport (1949) and Weaver et al. (1968), respectively. The amounts of Al and Si fixed on the Mt/Vt were estimated as the difference between that present in the solution initially and that remaining in the solution after reaction with the clays (Lou and Huang 1994). The preparation methods of the complexes used in the

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Table 2. Chemical characteristics of the parent HyA and HAS ionic solutions and the hydroxy materials fixed on Vt and Mt clays.

Characteristics of HyA and HAS parent solutions					Characteristics of the resultant complexes			
NaOH/Al ratio	pH	Si concentration m*M*	Al concentration m*M*	Si/Al ratio	Si fixed mmol g^{-1}	Al fixed mmol g^{-1}	Al + Si fixed mmol g^{-1}	Si/Al ratio
HyA/HAS-Vt complexes								
1.0	4.25	0.00	3.93	0.00	0.000	0.900	0.900	0.00
	4.01	1.06	4.00	0.27	0.085	0.716	0.801	0.12
	3.94	2.00	3.94	0.51	0.135	0.689	0.824	0.20
	3.91	3.98	3.96	1.01	0.180	0.761	0.941	0.24
2.0	4.64	0.00	3.89	0.00	0.000	0.932	0.932	0.00
	4.19	1.10	3.93	0.28	0.117	0.846	0.963	0.14
	4.02	2.17	3.94	0.55	0.220	0.927	1.147	0.24
	4.12	3.78	4.00	0.95	0.265	0.882	1.147	0.30
2.5	5.01	0.00	3.94	0.00	0.000	0.999	0.999	0.00
	4.48	1.03	3.74	0.28	0.113	0.774	0.887	0.15
	4.32	2.13	3.81	0.56	0.207	0.716	0.923	0.29
	4.09	3.97	3.93	1.01	0.531	1.100	1.631	0.48
HyA/HAS-Mt complexes								
2.0	4.48	0.00	3.85	0.00	0.000	1.130	1.130	0.00
	4.30	1.16	3.83	0.30	0.460	1.370	1.830	0.34
	4.03	1.99	3.82	0.52	0.530	1.350	1.880	0.39
	3.97	3.80	3.82	1.00	0.660	1.370	2.030	0.48

Key: HyA = hydroxyaluminum, HAS = hydroxyaluminosilicate, Vt = vermiculite, Mt = montmorillonite.

present study have been published elsewhere in greater detail (Inoue and Satoh 1992, 1993).

Potassium Fixation Studies

Potassium fixation behavior of some selected HyA/HAS-Vt complexes formed at NaOH/Al ratios of 1.0, 2.0 and 2.5 and of HyA/HAS-Mt complexes formed at a NaOH/Al ratio of 2.0 were evaluated in comparison to untreated Vt and Mt, respectively. The method adopted for this study was essentially that of Rich and Obenshain (1955) with some modifications. Potassium as KCl solution was added to 50-mg clay samples at 7 different targeted amounts of 20, 40, 60, 100, 150, 200 and 300 $cmol_c\ kg^{-1}$. For this purpose, 1 mL of 10, 20, 30, 50, 75, 100 or 150 m*M* KCl solution was added and mixed well with a fine mixer and kept overnight for equilibration with occasional mixing. A blank sample was also prepared by adding 300 $cmol_c\ kg^{-1}$ Na as NaCl solution and equilibrated in the same way. The specimens were then dried for 24 h 3 times in an oven at 110 °C with intervening wettings. Wetting was performed by adding 1 mL deionized water to the dried specimens followed by mixing well and keeping them under wet condition for 6 h with occasional mixing before starting the next drying cycle. After completion of 3 alternate wetting and drying cycles which ended with the third drying, the specimens were washed once with 6 mL deionized water and thrice with 6 mL 80% (v/v) methanol by adopting the centrifuge-decantation technique, and the supernatants were collected (Extracts A) for determination of K. Later on, 6 mL of 1 *M* CH_3COONH_4 (pH 7) was added to the specimens, mixed well, kept overnight for equilibration with occasional mixing, centrifuged and the supernatants collected. Washing with 6 mL of 1 *M* CH_3COONH_4 was repeated 5 more times, omitting only overnight equilibration. All the CH_3COONH_4 extracts were also collected (Extracts B) for K determination. The K contents of the extracts A and B were determined by a Perkin-Elmer Atomic Absorption Spectrophotometer 3300. The K contents of the added KCl solutions were also standardized by atomic absorption spectrophotometry (AAS) and used for calculating the exact amount of K added at the beginning of the fixation experiments.

The amount of K recovered in extract A ($K_{Ext\ A}$) of the samples, including blank, and the amounts of added K (K_{Added}) were used to calculate the amount of total K adsorbed ($K_{Total\ Ads}$) as follows:

$$K_{Total\ Ads} = K_{Added} + K_{Ext\ A\ (blank)} - K_{Ext\ A\ (sample)} \quad [1]$$

Later on, using the amount of K recovered in extract B ($K_{Ext\ B}$), it was possible to calculate exchangeable K (K_{Ex}) and fixed K (K_{Fix}) as follows:

$$K_{Ex} = K_{Ext\ B\ (sample)} - K_{Ext\ B\ (blank)} \quad [2]$$

$$K_{Fix} = K_{Total\ Ads} - K_{Ex} \quad [3]$$

All categories of K in the above 3 equations were considered as $cmol_c\ kg^{-1}$.

RESULTS AND DISCUSSION

Hydroxyaluminum- and Hydroxyaluminosilicate-Clay Complexes

Table 2 shows the pertinent chemical characteristics of the HyA/HAS parent solutions and also of the re-

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sultant HyA/HAS-Vt/Mt complexes. The pHs of the parent solutions were mostly within the range of 3.9 to 5.0. The concentration of Al ranged from 3.74 to 4.00 m*M*. The Si/Al ratios varied from 0.00 to 1.01.

The interactions of both Vt and Mt clays with HyA and HAS ionic solutions showed removal of Al and Si from the solutions, suggesting fixation of HyA and HAS ionic species on the clays. The amount of Al fixed on Vt ranged from 0.76 to 0.90, 0.85 to 0.93 and from 0.72 to 1.10 mmol g^{-1} for the HyA and HAS ionic solutions with OH/Al ratios of 1.0, 2.0 and 2.5, respectively. The amount of Al fixed on Mt was substantially higher for the HAS ions than for the HyA ions. However, for the HAS-Mt complexes with different Si/Al ratios, the amounts of Al fixation were almost identical. The amount of Si fixed on Vt and Mt increased with Si/Al ratios of the interacting HyA and HAS ionic solutions. A higher OH/Al ratio of the parent solutions also resulted in a higher amount of Si fixed on Vt. The amount of Si fixed on Vt ranged from 0.09 to 0.18, 0.12 to 0.27 and 0.11 to 0.53 mmol g^{-1} for the HAS ions with varying degrees of silication formed at OH/Al ratios of 1.0, 2.0 and 2.5, respectively. On Mt, the amount of Si fixed ranged from 0.46 to 0.66 mmol g^{-1} for the parent solutions with Si/Al ratios ranging from 0.30 to 1.0.

The Si/Al ratios of the HAS ions fixed on Vt and Mt increased with Si/Al ratios of the parent HAS ionic solutions. Increased OH/Al ratios of the parent HAS solutions also increased Si/Al ratios of the HAS ions fixed on Vt. After reaction of HAS ionic solutions (OH/Al = 2.0) having Si/Al ratios of 0.30, 0.52 and 1.00, the Si/Al ratios of the HAS ions fixed on Mt were 0.34, 0.39 and 0.48, respectively.

Hydrolysis and polymerization reactions of aqueous Al in partially neutralized solutions and the resultant reaction products have been extensively studied (Bertsch and Parker 1996). Hsu (1989) proposed a polymerization scheme consisting of single $[Al_6(OH)_{12}{}^{6+}]$ or double $[Al_{10}(OH)_{22}{}^{8+}]$ gibbsite-like rings at OH/Al ratio lower than 2.1. A further increase in OH/Al ratio (2.2 to 2.7) transforms these cyclic derivatives in larger polymers through $[Al_{13}(OH)_{30}{}^{9+}\cdot 18H_2O]$ and $[Al_{24}(OH)_{60}{}^{12+}\cdot 24H_2O\ ]$ to $[Al_{54}(OH)_{144}{}^{9+}\cdot 36H_2O\ ]$ with a reduced net positive charge per Al atom but with ionic charge remaining positive until OH/Al = 3. A more recently proposed model of Al polynucleation includes tridecameric Al_{13} polynuclear species $[AlO_4Al_{12}(OH)_{24}(H_2O\ )_{12}{}^{7+}]$ and larger condensed unit of this basic structure, usually in combination with a minimum of other species, such as dimer $[Al_2(OH)_2{}^{4+}]$ and/or trimer $[Al_3(OH)_4{}^{5+}]$ (Bottero et al. 1980; Akitt and Farthing 1981; Bertsch et al. 1986). Parker and Bertsch (1992) proposed a conceptual model wherein the sum of polynuclear forms of Al are a simple linear function of OH/Al ratio up to a maximum of 2.46 with a consequent decrease in monomeric Al fraction. Wada and Wada (1980) also reported that, during the formation of HyA and HAS ions, incorporation of Al into polymer ions is a simple linear function of OH/Al ratio of the solution and the proportions of polymeric Al were around 40, 75 and 90% for the OH/Al ratios of 1.0, 2.0 and 2.5, respectively.

Thus, it might be assumed that, for the HyA-Vt/Mt complexes formed at a higher OH/Al ratio, larger sized HyA polymers were adsorbed on Vt. Aluminum polymers formed from hexameric ring structure $[Al_6(OH)_{12}{}^{6+}]$ might dominate over Al_{13} in the Vt and Mt interlayers, because the former has been reported to be preferentially adsorbed over the latter in the clay interlayers (Hsu 1992). Hsu (1992) suggested that some of the Al_{13} polymers might be depolymerized to monomeric Al in presence of clay. The monomeric Al, in turn, entered the clay interlayer and polymerized *in situ*. Evidence from ^{27}Al nuclear magnetic resonance (NMR) spectroscopic examination of HAS solutions suggests that concentration of Al_{13} decreased rapidly with increasing Si/Al molar ratio and became nondetectable with Si/Al $\geq$ 0.28. There was also a significant increase in the proportion of Al_{NON} (nonsymmetric Al) that includes both HyA and HAS polymers which are electrically asymmetric (S. Hiradate, personal communication, 1997). Table 2 indicates that substantial amounts of Al and Si were removed from the HAS solutions during interaction with Vt and Mt. Lou and Huang (1988) observed that adsorption of orthosilicic acid on the 2:1 expansible clays did not occur at pH < 7. The present results therefore show that fixation of Si on Vt and Mt occurred in the form of HAS ions. Lou and Huang (1994) reported that HAS ions adsorbed in the interlayer spaces of Mt from HAS parent solutions of varying Al and Si concentrations had a similar Si/Al ratio of 0.485 $\pm$ 0.009, which is consistent with the theoretical Si/Al molar ratio of protoimogolite (0.5) that possesses a positive charge under acidic conditions (Farmer 1981). The soluble protoimogolite was also termed as HAS ions by Wada and Wada (1980). In our case, the hydroxy-materials adsorbed on Vt and Mt in some of the HAS-Vt and HAS-Mt complexes show Si/Al ratios (calculated from the amounts of Al and Si fixed) substantially less than 0.5. In such cases, the interlayer materials may comprise both HyA and HAS ions, the latter having a protoimogolite structure with Si/Al molar ratio around 0.5. A higher Si/Al molar ratio (but <0.5) of the fixed hydroxy-materials indicates the occurrence of HAS ions in a greater proportion. The Si/Al ratios of the hydroxy-materials fixed on Vt and Mt were close to 0.5 in some cases where almost all of the interlayer materials might be HAS ions having a protoimogolite-like structure.

The charge characteristics of these HyA/HAS-Vt/Mt complexes have been extensively studied by Inoue and Satoh (1992, 1993). Their findings reveal that hy-

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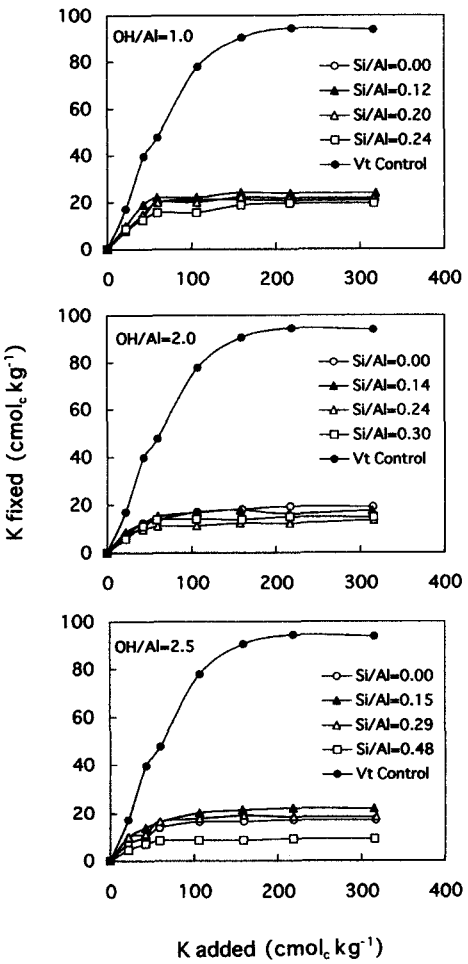


Figure 1. Potassium fixation patterns of different HyA/HAS-Vt complexes and untreated Vt in relation to added K.

droxy-interlayering in both Vt and Mt caused a great reduction in effective CEC with a significant increase in pH-dependent negative charge.

Fixation of K as Related to Added K

Potassium fixation behavior of HyA/HAS-Vt/Mt complexes was evaluated in relation to added K at different amounts ranging from 21.2 to 318.7 cmol$_c$ kg^{-1}. The plots of K fixation versus added K for the HyA/HAS-Vt and HyA/HAS-Mt complexes and also that for Vt and Mt (control) are shown in Figures 1 and 2, respectively.

Vermiculite (control) clay showed quite a high K fixation capacity (Figure 1). Fixation of K by Vt increased progressively with added K until 150 cmol$_c$ kg^{-1}, when its fixation capacity was more or less satisfied. Abrupt changes in K fixation patterns were experienced with the HyA/HAS-Vt complexes. In the complexes, a drastic reduction in K fixation in comparison to Vt was clearly delineated. Fixation of K

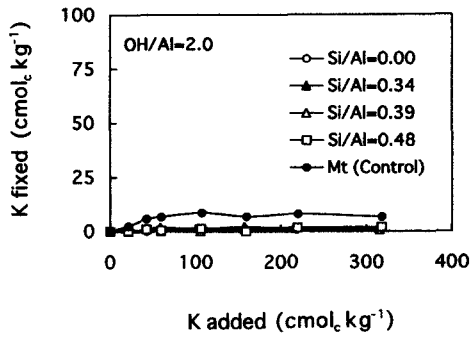


Figure 2. Potassium fixation patterns of different HyA/HAS-Mt complexes and untreated Mt in relation to added K.

reached the saturation point just after addition of about 60 cmol$_c$ K kg^{-1} in most cases, although in some of the complexes, when more than 60 cmol$_c$ K kg^{-1} was added, only a slight further increase in K fixation was noticed. Vermiculite sample showed a maximum K fixation of 94.4 cmol$_c$ kg^{-1}. On the contrary, the maximum K fixation capacities of different HyA/HAS-Vt complexes ranged from 9.2 to 23.9 cmol$_c$ kg^{-1} only. Thus, the findings clearly indicated that the presence of HyA or HAS islands in the interlayer spaces of Vt had a strong inhibitory effect on fixation of K.

The Mt fixed a much lower amount of K in comparison to Vt. The maximum K fixation capacity as shown by Mt was only 8.6 cmol$_c$ kg^{-1}. In the HyA/HAS-Mt complexes, the amounts of K fixed were very low and ranged from 1.48 to 1.84 cmol$_c$ kg^{-1}.

It has been established that at least 3 factors are important for fixation of cations within the ditrigonal cavities of highly charged 2:1 clay minerals (Barnhisel and Bertsch 1989). These factors are 1) low hydration energy of the cation, 2) appropriate size of the cation and 3) sufficient tetrahedral charge on the layer silicates. The orientation of OH, substitution of OH by F and stacking nature of adjacent silicate layers may also affect cation fixing properties of the clays. The K ion, due to its appropriate size, fits well in the ditrigonal cavities of basal oxygen planes of the adjacent silicate layers (Page and Baver 1940; Barshad 1948, 1950; Stanford 1948; Wear and White 1951) and, due to its low hydration energy, prevents interlayer expansion (Kittrick 1966; Shainberg and Kemper 1966) and thus could be fixed easily by highly charged 2:1 clays. The Vt had a higher density of negative charge per unit cell than the Mt. The predominant source of negative charge in the Vt is in the tetrahedral position, while that in the Mt is in the octahedral position. Wear and White (1951) reported that the distance from the center of the K ion to the source of the deep-seated octahedral charge is twice as great as that implied for the K ion and the source of the deep-seated tetrahedral charge. Since the electrostatic valence rule is satisfied over a shorter distance in case of a K ion in the inter-

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Table 3. Distribution of K at exchangeable and fixation sites of HyA/HAS-Vt complexes at low and high rates of K addition.

Sample†	Si/Al ratio	K added ($cmol_c\ kg^{-1}$)	K adsorbed ($cmol_c\ kg^{-1}$)‡		
			Nonexchangeable K	Exchangeable K	Total
Vt (Control)	—	42.7	39.6 (93)	3.0 (7)	42.6 (100)
		218.7	93.9 (84)	17.4 (16)	111.3 (100)
OH/Al = 1.0					
HyA-Vt	0.00	42.5	13.7 (44)	17.1 (56)	30.8 (100)
		218.2	20.7 (34)	40.6 (66)	61.3 (100)
HAS-Vt	0.12	42.5	18.9 (54)	16.1 (46)	35.0 (100)
		217.3	23.8 (36)	41.5 (64)	65.3 (100)
HAS-Vt	0.20	42.0	14.7 (45)	17.8 (55)	32.5 (100)
		215.6	21.7 (34)	42.1 (66)	63.8 (100)
HAS-Vt	0.24	42.2	12.4 (39)	19.1 (61)	31.5 (100)
		216.2	19.5 (29)	47.6 (71)	67.1 (100)
OH/Al = 2.0					
HyA-Vt	0.00	42.0	12.6 (43)	16.8 (57)	29.4 (100)
		216.9	19.3 (28)	50.8 (72)	70.1 (100)
HAS-Vt	0.14	42.1	12.5 (41)	18.3 (59)	30.8 (100)
		215.3	16.3 (23)	54.7 (77)	71.0 (100)
HAS-Vt	0.24	42.4	9.8 (31)	21.3 (69)	31.1 (100)
		216.3	12.3 (17)	60.5 (83)	72.8 (100)
HAS-Vt	0.30	42.4	11.2 (36)	19.9 (64)	31.1 (100)
		216.2	15.1 (20)	60.4 (80)	75.5 (100)
OH/Al = 2.5					
HyA-Vt	0.00	42.4	9.8 (32)	20.9 (68)	30.7 (100)
		218.8	17.0 (22)	61.6 (78)	78.6 (100)
HAS-Vt	0.15	42.4	13.7 (47)	15.7 (53)	29.4 (100)
		218.2	22.2 (29)	53.6 (71)	75.8 (100)
HAS-Vt	0.29	42.3	11.1 (32)	23.4 (68)	34.5 (100)
		219.0	18.4 (23)	62.9 (77)	81.3 (100)
HAS-Vt	0.48	42.2	7.2 (20)	28.5 (80)	35.7 (100)
		218.3	9.2 (12)	68.0 (88)	77.2 (100)

† HyA = hydroxyaluminum, HAS = hydroxyaluminosilicate, Vt = vermiculite.
‡ Figures in the parentheses indicate percentage of total K adsorbed.

layer position of Vt, so the attractive force between the interlayer K ion and the adjacent silicate layers might be much stronger in the case of Vt than Mt (Wear and White 1951). Hence, a substantially higher K fixing capacity of Vt in comparison to that of Mt might have been observed. The previous studies concerned with charge characteristics of these HyA/HAS-Vt/Mt complexes revealed that the presence of interlayered hydroxy-materials caused a significant reduction of effective CEC (Inoue and Satoh 1992, 1993). In the present study, significant inhibition of K fixation by the complexes might be attributed to reduction of effective CEC, presence of exchangeable Al (Rich and Lutz 1965; Somasiri and Huang 1974; Nagasawa et al. 1974) and propped-open effects of the hydroxy-cation islands in interlayers, which inhibit layer collapse about K ions (Rich 1960; Rich and Black 1964; Rich 1968).

Distribution of Exchangeable K and Fixed K

Distribution of K at exchangeable and fixation sites with added K levels around 40 (low) and 200 (high) $cmol_c\ kg^{-1}$ for Vt and Mt control samples and for different HyA/HAS-Vt and HyA/HAS-Mt complexes are shown in Tables 3 and 4, respectively.

In the case of Vt, the amounts of total K adsorbed were 43 and 111 $cmol_c\ kg^{-1}$ for low and high amounts of K addition, respectively, and a vast majority of the total adsorption took place at the fixation sites at both levels of added K (93 and 84%, respectively). The total amounts of K adsorbed by different HyA/HAS-Vt complexes were noticeably lower than Vt at both low (29 to 36 $cmol_c\ kg^{-1}$) and high (61 to 81 $cmol_c\ kg^{-1}$) amounts of K addition. This was due to their lower CEC than that of Vt (Inoue and Satoh 1992). However, it is remarkable that a substantial portion of total K adsorbed by the complexes occurred at the exchangeable sites at both low (46 to 80%) and high (64 to 88%) levels of added K (Table 3). The data also show that as the amounts of K addition increased, the proportion of total K adsorbed at the fixation sites gradually decreased and that of total K adsorbed at the exchangeable sites increased (data for all the amounts of K addition are not shown). This trend was true for Vt and for different HyA/HAS-Vt complexes, as well.

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Table 4. Distribution of K at exchangeable and fixation sites of HyA/HAS-Mt complexes at low and high rates of K addition.

Sample†	Si/Al ratio	K added ($cmol_c\ kg^{-1}$)	K adsorbed ($cmol_c\ kg^{-1}$)‡		
			Nonexchangeable K	Exchangeable K	Total
Mt (Control)		42.5	6.0 (24)	19.0 (76)	25.0 (100)
		220.1	8.2 (13)	57.4 (87)	65.6 (100)
HyA-Mt	0.00	42.8	0.1 (1)	20.6 (99)	20.7 (100)
		218.5	0.9 (2)	51.2 (98)	52.1 (100)
HAS-Mt	0.34	42.1	1.1 (5)	23.6 (95)	24.7 (100)
		216.2	1.7 (3)	54.6 (97)	56.3 (100)
HAS-Mt	0.39	42.2	1.1 (4)	26.2 (96)	27.3 (100)
		216.2	1.7 (3)	48.4 (97)	50.1 (100)
HAS-Mt	0.48	42.7	1.1 (4)	26.5 (96)	27.6 (100)
		219.6	1.7 (3)	49.2 (97)	50.9 (100)

† HyA = hydroxyaluminum, HAS = hydroxyaluminosilicate, Mt = montmorillonite.
‡ Figures in the parentheses indicate percentage of total K adsorbed.

The amounts of total K adsorbed by Mt were 25 $cmol_c\ kg^{-1}$ at low and 66 $cmol_c\ kg^{-1}$ at high amounts of added K. At low and high amounts of K addition, the proportions of total K adsorbed at the fixation sites were 24 and 76%, and, at the exchangeable sites, 13 and 87%. Like the HyA/HAS-Vt complexes, the total amounts of K adsorbed by the HyA/HAS-Mt complexes were also lower than Mt for the same reason (Inoue and Satoh 1993). The amount of K adsorbed at the exchangeable sites was always more than 95% for different HyA/HAS-Mt complexes at both low and high amounts of K addition. Consequently, K fixation never exceeded 5% of total K adsorption (Table 4).

The exchangeable nature of a larger proportion (64 to 88%) of total K adsorbed by the HyA/HAS-Vt complexes as observed in the present study might be explained by the fact that complexation of Vt with HyA/HAS ions caused a significant reduction of permanent negative charge and a substantial increase in pH-dependent negative charge (Inoue and Satoh 1992) and made the interlayer spaces propped open. The K adsorbed at the pH dependent charge sites might be fairly exchangeable. In addition, the hydroxy-cations' islands in the interlayers, through their propping effects, favor K exchange involving permanent charge sites (Kozak and Huang 1971), which could otherwise be involved in K fixation. Rich and Black (1964) observed that only 2.8 $cmol_c\ kg^{-1}$ of K could be displaced from Ca-K-saturated Libby vermiculite by CH_3COONH_4 extraction, the remainder being fixed between the collapsed interlayers. In contrast, after synthesis of Al interlayers in that vermiculite, 23.2 $cmol_c\ kg^{-1}$ of K were exchanged by CH_3COONH_4, suggesting that K fixation was nearly eliminated by the Al interlayer formation (Rich and Black 1964).

Relationship of K Fixation with Si/Al Ratio of the Interlayered Hydroxy-Materials

Potassium fixing capacities of the HyA/HAS-Vt complexes did not follow any definite trend with the Si/Al ratio of their interlayer hydroxy-materials. At OH/Al ratio of 1.0, K fixing capacities of the complexes were in the order of HAS (Si/Al = 0.12)-Vt > HAS (Si/Al = 0.20)-Vt ≥ HyA (Si/Al = 0.00)-Vt ≥ HAS (Si/Al = 0.24)-Vt. Potassium fixing capacities followed the trend of HyA (Si/Al = 0.00)-Vt > HAS (Si/Al = 0.14)-Vt > HAS (Si/Al = 0.30)-Vt ≥HAS (Si/Al = 0.24)-Vt for the complexes carrying interlayer hydroxy-materials with OH/Al = 2.0. At OH/Al ratio of 2.5, the HAS (Si/Al = 0.15)-Vt complex showed the highest K fixing ability, which was followed by HAS (Si/Al = 0.29)-Vt, HyA (Si/Al = 0.00)-Vt and HAS (Si/Al = 0.48)-Vt complexes, respectively.

Like HyA/HAS-Vt complexes, K fixing capacities of the HyA/HAS-Mt complexes also did not follow any definite trend with the Si/Al ratio of their interlayer hydroxy-materials. In addition, K fixing capacities of the HyA/HAS-Mt complexes were low and varied within a narrow range of 1.48 to 1.84 $cmol_c\ kg^{-1}$.

Altered K fixation patterns of the HyA/HAS-Vt/Mt complexes relative to untreated Vt and Mt have been observed, probably due to irreversible occupancy of the cation exchange sites by the HyA and HAS ions and their propping effects in the Vt and Mt interlayers. A higher positive charge of the interlayer hydroxy-materials inactivates CEC of Vt and Mt in a greater magnitude which could, otherwise, be involved in K fixation and/or exchange reactions. In case of larger amounts of Al and Si fixation, the size of the individual unit of interlayer hydroxy-material increases with a concomitant decrease in the average positive charge per Al atom. Still, the total positive charge of the interlayer hydroxy-materials and, hence, the magnitude of CEC inactivation is higher when larger amounts of Al and Si are fixed in the interlayers. Again, when larger amounts of Al and Si are fixed in the clay interlayers, the propping action which also hinders K fixation by inhibiting layer collapse could be increased due to increased number and/or enlarged size of the props. Thus, the major factor controlling the K fixing

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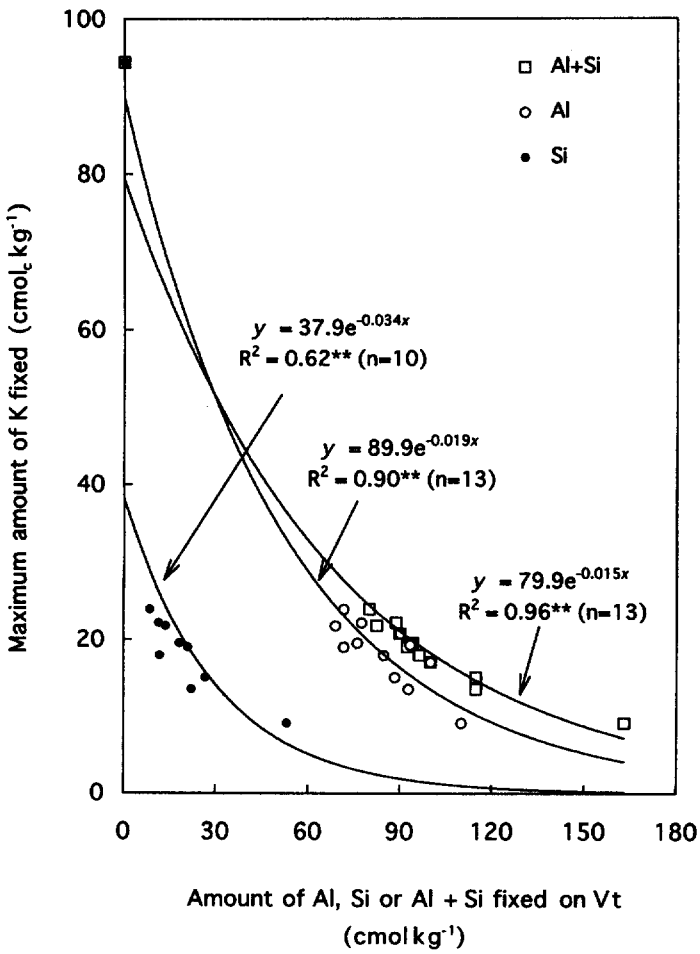


Figure 3. Relationships of maximum K fixing capacities of HyA/HAS-Vt complexes with the amounts of Al and/or Si residing as HyA/HAS islands in the interlayer spaces of Vt.

capacities of the HyA/HAS-Vt/Mt complexes might be the total amounts of Al and Si rather than Si/Al ratio of the interlayer hydroxy-materials, since the former one determines both propping action and CEC inactivation ability of the interlayered hydroxy-materials. As a result, it was hardly possible to establish any definite relationship between K fixation and Si/Al ratios of the hydroxy-materials fixed on Vt and Mt, even though the HyA/HAS-Vt/Mt complexes had very wide Si/Al ratios ranging from 0.00 to 0.48.

Relationship of K Fixation with Degree of Interlayering in Vermiculite

The observation of a distinct reduction in K fixation capacities of the HyA/HAS-Vt complexes caused by reduction in effective CEC and propping effect of HyA and HAS cations residing in the interlayer positions gave the cause to investigate the relationships (if any) between the K fixing capacities of clays (including Vt and HyA/HAS-Vt complexes) and the amounts of Al and Si fixed on Vt clay during interaction with HyA/HAS ions. The plots of maximum observed K fixation versus the amounts of Al, Si and Al + Si fixed on Vt are shown in Figure 3. All the plots show that as the amounts of Al and Si fixation increased, the K fixing capacities of the complexes decreased. Hence, very clear negative relationships exist between K fixing capacities of the complexes and the amounts of Al, Si or Al + Si taken up by Vt clay during complex formation. A higher adsorption of HyA or HAS polymers could logically cause a greater reduction in K fixing capacity of Vt clay. When the HyA or HAS polymers are more abundant in the interlayer spaces, the propping effects retarding layer collapse and favoring K exchange could be increased (Kozak and Huang 1971).

These relationships could be best described by the exponential equations shown in Figure 3. The values of the coefficient of determination (R^2) for all the equations are significant at the 99% confidence inter-

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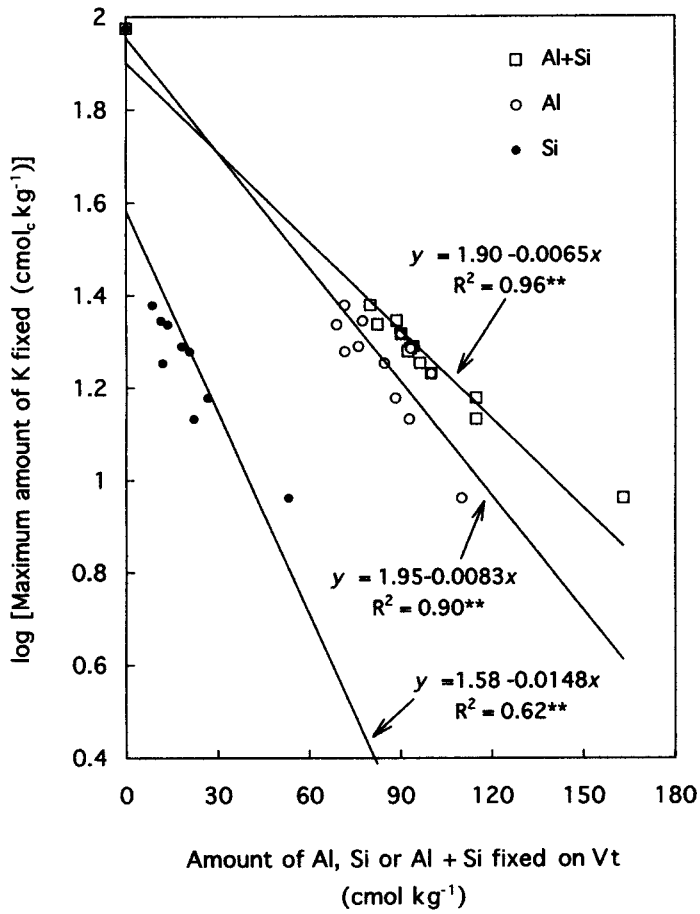


Figure 4. Linear relationships between log [maximum K fixation] and the amounts of Al and/or Si residing as HyA/HAS islands in the interlayer spaces of Vt.

val. However, considering the R^2 values, the equations derived for the plots of K fixed versus the amounts of Al + Si, Al and Si fixed on Vt could represent 96, 90 and 62%, respectively of the variation in the K fixing capacities existing therein. It may be noted that all the 3 equations have the general form:

$$y = a\ e^{-bx} \qquad [4]$$

where y is the maximum K fixing capacity (cmol$_c$ kg^{-1}), x is the amount of Al, Si or Al + Si fixed on Vt (cmol kg^{-1}) and a and b are the constants.

Taking logarithm on both sides of Equation [4], the following relationship can be obtained:

$$\log y = \log a - (b \log e)\ x \qquad [5]$$

Equation [5] indicates that a plot of log y versus x is a straight line whose intercept is given by log a and slope by $-b$ log e. This relationship could be more useful for easier estimation of the parameters a and b for prediction purposes. Such plots using the amount of Al, Si, or Al + Si fixed on Vt are shown in Figure 4.

Again for the control Vt sample (when $x = 0$), Equation [4] becomes $y_0 = a$, hence the extent of reduction in K fixation ($y_0 - y$) as a consequence of hydroxy-interlayering can be written as:

$$y_0 - y = a - a\ e^{-bx} \qquad [6]$$

A differential of ($y_0 - y$) with respect to x can be used for the estimation of the rate of reduction in K fixing capacities of the complexes per unit amount of Al, Si or Al + Si fixed on Vt. This can be given by:

$$d(y_0 - y)/dx = ab\ e^{-bx} \qquad [7]$$

The plots of the rates of reduction in K fixation capacities estimated from the 3 equations given in Figure 3 versus the corresponding observed rates are presented in Figure 5. The estimated and observed rates of reduction in K fixation show very high correlation (r = 0.998 and 0.992) when the estimation was performed using the amounts of Al or Al + Si fixed on Vt as independent variable. This correlation was remarkably weaker (r = 0.687) when the rates of reduc-

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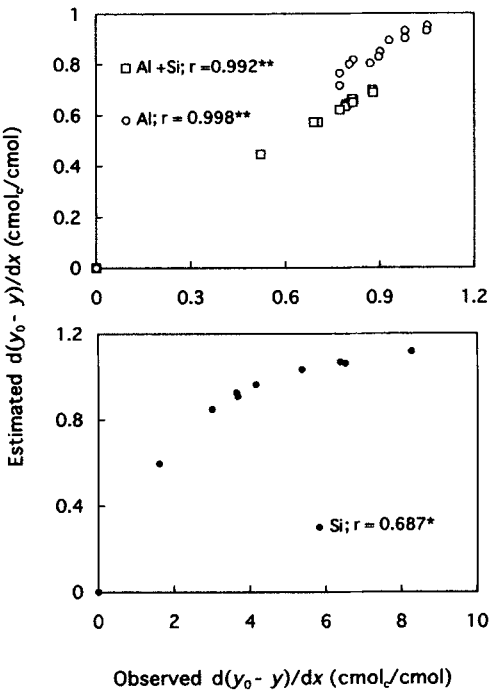


Figure 5. Relationships of the rates of reduction in maximum K fixation estimated using the amounts of Al and/or Si residing as HyA/HAS islands in the interlayer spaces of Vt as independent variables with the observed rates.

tion in K fixing capacities were estimated based on the amounts of Si fixed Vt. Thus, the results indicate that deposition of both Al and Si as HyA and HAS cations in the interlayer of Vt led to the reduction in maximum K fixing capacities in HyA/HAS-Vt complexes. However, the amount of Al residing in the Vt interlayers alone also appears to be a useful independent variable for predicting K fixing capacities of the hydroxy-interlayered Vt. This is probably due to the fact that Al represents the major interlayer component in most of the HyA/HAS-Vt complexes.

CONCLUSIONS

This study demonstrates that hydroxy-interlayers in 2:1 expansible clays exert a distinct inhibitory effect on K fixation but a favorable effect on K exchange, resulting in a drastic reduction of K fixing capacities of both Vt and Mt clays. The relationships of maximum K fixing capacities of the HyA/HAS-Vt complexes with the amounts of Al, Si and Al + Si residing as HyA/HAS ions in the Vt interlayers were all exponential and negative. However, the amounts of Al or Al + Si residing in the Vt interlayers show great promise in predicting the K fixing abilities of hydroxy-interlayered Vt clays.

PRACTICAL IMPLICATIONS

Hydroxy-interlayered vermiculites and montmorillonites are important components of soil colloidal complexes in some nonallophanic Andisols (Shoji et al. 1985, 1987; Bautista-Tulin and Inoue 1997) and in Red-Yellow soils (Hapludults and Hapludalfs) influenced by eolian dust (Bautista-Tulin and Inoue 1997) where these clays could play a significant role in regulating dynamics and hence availabilities of cationic and anionic plant nutrients. Results of K fixation and exchange behavior of these clays accomplished in the present study might be of considerable significance in better understanding the K dynamics in soils with a predominance of 2:1 to 2:1:1 layer silicate intergrades.

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