

SELECTIVE ADSORPTION OF ZINC ON HALLOYSITE

KOJI WADA AND YASUKO KAKUTO

Faculty of Agriculture, Kyushu University 46, Fukuoka 812, Japan

Abstract—Zn- and Ca-adsorption equilibria of five Ca-saturated halloysite samples were measured at equilibrium Zn concentrations up to 10^{-2} M in 10^{-4} to 10^{-2} M CaCl_2 . The results were interpreted on $K_{\text{Ca}}^{\text{Zn}}$ vs. $[\text{Zn}]/\text{CEC}$ (%) plots, where $K_{\text{Ca}}^{\text{Zn}}$ is the selectivity coefficient ($=[\text{Zn}][\text{Ca}]/[\text{Ca}][\text{Zn}]$), Zn and Ca represent the adsorbed species, and CEC is the cation-exchange capacity. All Zn adsorption occurred at cation-exchange sites, and 0.77 to 36.0 meq Zn/100 g clay, which constitutes 9 to 83% of the CEC, was adsorbed with “high selectivities” ($K_{\text{Ca}}^{\text{Zn}} > 10$). The higher values were found for two spherical and one “filmy” halloysites, whereas the lower values were found for two tubular halloysites. The magnitude of their 001 intensity, hydration in interlayer space, CEC, and “free” iron oxide content did not correlate with the selective Zn adsorption, but a good correlation was found between the proportion of “high selectivity” sites for Zn and proportion of “high affinity” sites for H^+ . The adsorption of Zn at the “high selectivity” sites was not completely reversible, and $K_{\text{Ca}}^{\text{Zn}}$ values > 1000 were recorded in 0.5 M CaCl_2 for Zn which occupied 10–40% of the exchange sites. Selective Zn adsorption decreased with decreasing pH, and all adsorbed Zn was extracted with 0.1 M HCl.

Key Words—Adsorption, Cation exchange, Halloysite, Selectivity, Zinc.

INTRODUCTION

Heavy metals, such as Cu, Pb, Zn, and Cd, are found only in traces in soils but are concentrated under some circumstances with or without intention. Their deficiency or excess can have considerable effect on plants, animals, and human beings. The adsorption of heavy metals by clays moderates the partition of such metals between solid and aqueous phases in soils and controls their availability to plants and their concentration in aquifers.

In an earlier study (Wada and Abd-Elfattah, 1979) on Zn adsorption by soils which differ in their major cation-exchange materials, halloysite was found to be a very selective adsorbent for Zn. Halloysite and kaolinite are widespread products of hydrothermal alteration and weathering and are common constituents of soils and sediments. The cation-exchange capacity (CEC) of halloysite varies, but it is generally higher than that of kaolinite. The present paper reports the results of studies on Zn adsorption by halloysite samples that are formed by weathering but which have different origins. Their adsorption capacities for Zn with specified selectivities were evaluated and compared with those of montmorillonite, kaolinite, and allophanes. Both the adsorption and desorption equilibria of Zn in the presence of CaCl_2 were analyzed. Adsorbed Zn was also extracted with 1 M NaCl, 1 M NH_4Cl , and 0.1 M HCl.

MATERIALS AND METHODS

Clay samples listed in Table 1 were used after saturation with Ca and air-drying. Ca-saturation was carried out by successive washing with 1 M NaCH_3COO – CH_3COOH (pH 5.0), 0.5 M CaCl_2 , 0.005 M CaCl_2 , and acetone, where the pH of the sample suspension in 0.5

M CaCl_2 was adjusted to 7.0 with $\text{Ca}(\text{OH})_2$. Each Ca-saturated sample contained a small amount of CaCl_2 .

The adsorption of Zn was measured by adding 7 ml of ZnCl_2 solution containing different concentrations of Zn (0 to 10^{-2} M) to 0.1 or 0.2 g of the samples. In these suspensions, CaCl_2 was present at a concentration between 3.5×10^{-4} and 2×10^{-2} M. The suspension was shaken on a reciprocating shaker for 2 hr and allowed to stand for 24 hr at 25°C. The supernatant liquid obtained after centrifugation was analyzed for Zn and Ca by atomic absorption spectrophotometry. The equilibrium pH was also determined using the remaining supernatant liquid. The amounts of adsorbed Zn and desorbed Ca were calculated as the differences between the amounts of Zn and Ca present initially in the solution and those remaining after equilibration. In this calculation, the Zn and Ca extractable with 1 M $\text{NH}_4\text{CH}_3\text{COO}$ (pH 4.8) + 10^{-2} M EDTA from the sample were assumed to be involved in an adsorption equilibrium.

The results were interpreted on $K_{\text{Ca}}^{\text{Zn}}$ vs. $[\text{Zn}]$ plots, where $K_{\text{Ca}}^{\text{Zn}}$ is the selectivity coefficient defined by the equation

$$K_{\text{Ca}}^{\text{Zn}} = \frac{[\text{Zn}][\text{Ca}]}{[\text{Ca}][\text{Zn}]}, \quad (1)$$

$[\text{Zn}]$ and $[\text{Ca}]$ are the amounts of Zn and Ca adsorbed (meq/100 g), and $[\text{Zn}]$ and $[\text{Ca}]$ are the concentrations of Zn and Ca in the equilibrium solution (M). $[\text{Zn}]$ and $[\text{Ca}]$ are expressed on an oven-dry clay basis, assuming that they are present only as divalent cations.

In determination of the desorption equilibrium, 7 ml of 0.5 M CaCl_2 was added to the sample remaining in the centrifuge tube in the adsorption measurement. The mixture was shaken for 2 hr, allowed to stand for 24 hr

Table 1. List of clay samples.

Clay mineral	Locality	Particle size (μm)	CEC ¹ (meq/100 g)	"Free" ² Fe ₂ O ₃ (%)
Halloysite	Choyo, Kumamoto	<2	43.3	3.76
Halloysite	Maui, Hawaii	<100	6.6	0.11
Halloysite	Uenae, Hokkaido	<2	56.7	2.17
Halloysite	Yoake, Oita	<100	14.2	0.75
Halloysite	Naegi, Gifu	<2	7.7	0.91
Kaolinite	Ibusuki, Kagoshima	<2	7.1	0.26
Montmorillonite	Hojun, Gunma	<2	69.0	2.13
Allophane	Kitakami, Iwate	<0.2	24.2	4.02
Allophane	Choyo, Kumamoto	<0.2	51.5	7.10

¹ The average value of $[Zn + Ca]$ values measured at different adsorption equilibria for each sample saturated with Ca at pH 7.0.

² Dithionite-citrate extractable (Mehra and Jackson, 1960).

at 25°C, and centrifuged. The amount of Zn in the supernatant liquid was determined. The amount of desorbed Zn was estimated taking into consideration the amount of Zn in the solution remaining in the centrifuge tube after the adsorption measurement. In calculating the K_{Ca}^{Zn} value, $[Ca]$ was approximated as 0.5 M and $[Ca]$ was equated with the $[Ca]$ measured at the adsorption equilibrium minus the amount of desorbed Zn.

The extraction of adsorbed Zn and Ca was studied using 1 M NaCl, 1 M NH₄Cl, and 0.1 M HCl. The experimental procedure used for extraction and determination was the same as that used for determination of the desorption equilibrium. The effect of H⁺ on the Zn adsorption was further studied by adding 7 ml of ZnCl₂ solutions containing an appropriate amount of Zn (Choyo, 10 μeq ; Maui, 1.24 μeq ; Uenae, 12.5 μeq ; Yoake, 0.5 μeq ; Naegi, 0.5 μeq ; Gunma, 1 μeq) and different amounts of HCl to 0.2 g of the samples and determining their Zn adsorption. The experimental procedure was the same as that used for determination of the adsorption equilibrium.

EXPERIMENTAL RESULTS

Figure 1 shows the K_{Ca}^{Zn} vs. $[Zn]/\text{CEC}$ (%) plots of two halloysites, one kaolinite, one montmorillonite, and two allophane samples. The equilibrium pH, 7.1–5.9, decreased with increasing Zn addition. The high $[Zn]$ values (4.2×10^{-3} M to 12.5×10^{-4} M) associated with the low equilibrium pH values (5.9–6.6). The latter pH was probably controlled by the hydrolysis of excess Zn²⁺. The $[Zn + Ca]$ values measured at different adsorption equilibria were constant within $\pm 5\%$ of the average value (CEC in Table 1) for all samples, indicating that most of the adsorbed Zn²⁺ is present on cation-exchange sites.

The K_{Ca}^{Zn} value as defined by the Eq. (1) measures the tendency of the clay to adsorb Zn in preference to Ca from a solution containing equal concentrations of Zn and Ca. Generally, the K_{Ca}^{Zn} value decreased with in-

creasing amounts of Zn adsorbed, where the $[Zn + Ca]$ value was nearly constant for each clay. It is considered that Zn is adsorbed at first on sites with "higher selectivity" and then on sites with "lower selectivity." The proportion of "high" and "low" selectivity sites differ from clay to clay, and their differences broadly parallel those between the soils containing these clays as major cation-exchange materials (Wada and Abd-Elfattah, 1979). However, some soils tend to adsorb Zn more

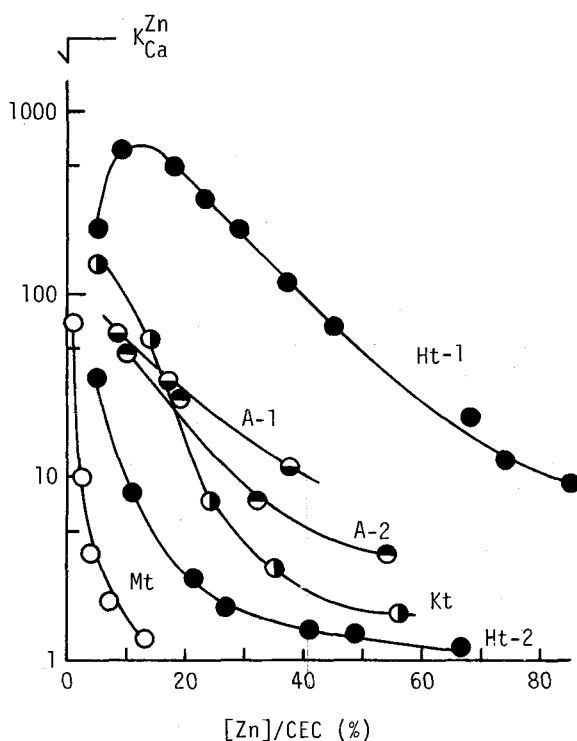


Figure 1. The K_{Ca}^{Zn} vs. $[Zn]/\text{CEC}$ relationships for halloysite (Ht-1. Choyo; Ht-2. Naegi), kaolinite (kt), montmorillonite (Mt), and allophane (A-1. Kitakami; A-2. Choyo) samples.

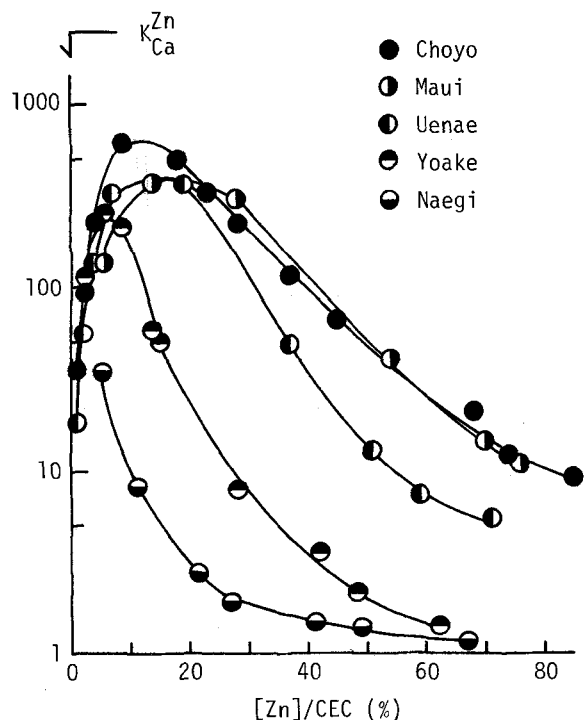


Figure 2. The K_{Ca}^{Zn} vs. $[Zn]/CEC$ relationships for halloysite samples.

selectively than do the corresponding clays, probably due to the presence of iron oxides in the former. A remarkable difference between the two halloysite samples suggested that the adsorption of Zn on halloysites of different origins be examined.

Figure 2 shows the K_{Ca}^{Zn} vs. $[Zn]/CEC$ (%) plots of five halloysite samples derived from different materials by weathering (Table 2). The equilibrium pH was 7.1–6.1, and the $[Zn + Ca]$ values were constant within $\pm 5\%$ of the average value (CEC in Table 1) for each clay, except the Uenae halloysite for which the value decreased from 57.3 to 55.7 meq/100 g with increasing Zn addition. The proportion of cation-exchange sites with

“high selectivities” for Zn generally decreases in the order: Choyo = Maui > Uenae > Yoake > Naegi. On the other hand, the amounts of Zn adsorbed above a selectivity coefficient of $K_{Ca}^{Zn} > 10$ are 36.0, 31.2, 5.5, 4.0, and 0.77 meq/100 g for the Choyo, Uenae, Maui, Yoake, and Naegi halloysites, respectively. A broad parallel relationship between 001 intensity (Table 2), hydration in interlayer space (Table 2), and CEC (Table 1) was found. The 001 intensity decreased and the hydration and CEC increased in the order, Naegi, Maui, Yoake, Choyo, Uenae. This order does not correlate with that found for the proportion of “selective” Zn adsorption sites, nor does the content of “free” iron oxide (Table 1) correlate with the “selective” Zn adsorption. One physical characteristic which may be related to the Zn adsorption is the morphology of halloysite particles. Differences in morphology are possibly associated with differences in their genesis (Table 2). The proportion of “selective” Zn adsorption sites was high for the spherical halloysites, intermediate for the filmy halloysite, and low for the tubular halloysites.

Figure 2 shows that the K_{Ca}^{Zn} value decreases with increasing amounts of adsorbed Zn, and an anomalous decrease of the K_{Ca}^{Zn} value at very low amounts of adsorbed Zn. The relationships between the K_{Ca}^{Zn} , $[Zn]$, and $[Zn]$ values derived from each of the adsorption and desorption equilibria for four halloysite samples are shown in Figure 3. These data indicate that the anomalous K_{Ca}^{Zn} decrease occurs mostly at $[Zn] < 10^{-6}$ M. This level of $[Zn]$ maintained at the equilibrium pH values ranging from 7.1 to 6.3 is much lower than that expected in the presence of $Zn(OH)_2$, whose solubility product is 10^{-16} – 10^{-17} (Sillén and Martell, 1964). Possibly, Zn dissolves from more difficultly soluble compounds in the sample, and a slow equilibration at such low Zn concentrations results in the $[Zn]$ increase over that predicted from the cation-exchange equilibrium.

The K_{Ca}^{Zn} value derived from the desorption equilibrium was higher than that derived from the adsorption equilibrium, particularly at low $[Zn]/CEC$ values (Figure 3). Aside from the effect of the anomaly described above, this difference indicates that the Zn adsorption

Table 2. Description of halloysite samples.

Sample	Parent material	001 intensity (I) ¹		Morphology	Reference
		air-dried 110 Å/17.5 Å	heated at 300°C 17.2–7.4 Å		
Choyo	Pumice	23/0	28	Sphere	Aomine and Wada (1962), Wada <i>et al.</i> (1977)
Maui	Mugearite	15/19	60	Sphere	Nakamura and Sherman (1965)
Uenae	Pumice	8/0	10	Film	Wada and Mizota (1979)
Yoake	Andesitic agglomerate	12/10	43	Tube	Aomine and Higashi (1955)
Naegi	Granite	14/28	73	Tube	Nagasawa (1978)

¹ The 001 intensity was measured for the powder sample mounted in the cavity of a glass slide using an X-ray diffractometer.

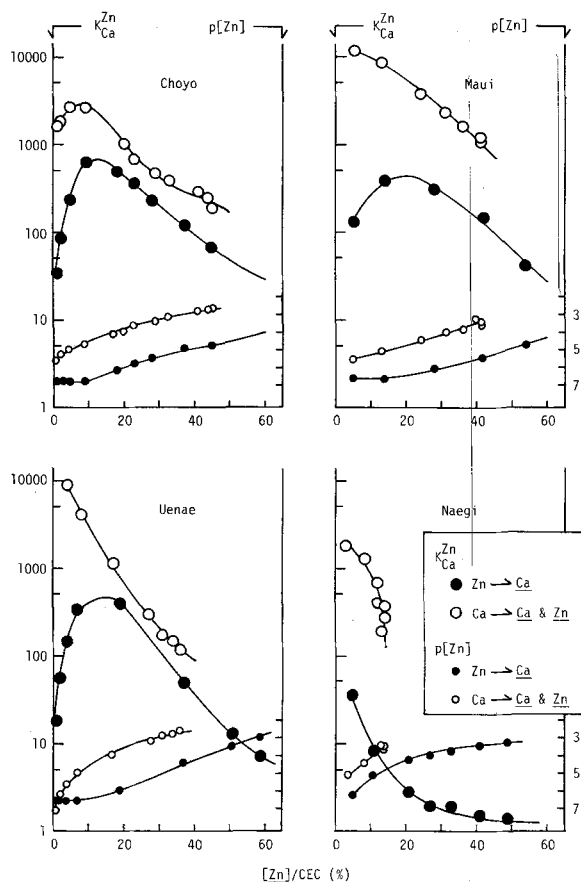


Figure 3. The adsorption equilibria of Zn for halloysite samples saturated with Ca ($Zn \rightarrow Ca$ in the legend) and desorption equilibria of Zn for halloysite samples which adsorbed Zn and Ca ($Ca \rightarrow Ca \& Zn$ in the legend).

at cation-exchange sites with "high selectivities" is not completely reversible. The difference between the adsorption and desorption equilibria is more manifest in the Maui and Naegi halloysites. A sharp difference in the selectivity between the "high" and "low" selectivity sites is also suggested for the Naegi halloysite. The fact that about 20, 40, and 20% of cation-exchange sites in the Choyo, Maui, and Uenae halloysites retain adsorbed Zn very strongly ($K_{Ca}^{Zn} = 1000\text{--}10,000$) in the presence of a large excess of Ca deserves attention when one considers the removal of Zn from aqueous solutions.

Table 3 shows the extraction of adsorbed Zn and Ca with different reagents. The difference in extractability between the adsorbed Zn and Ca is indicated by extraction with 1 M NaCl. The Zn adsorbed on "high selectivity" sites is difficultly exchanged with Na as well as Ca. A higher proportion of adsorbed Zn and Ca is extracted by NH_4Cl , where the pH values of the NaCl, $CaCl_2$, and NH_4Cl extracts were 5.9–6.2. The differ-

Table 3. Extraction of adsorbed Zn and Ca.

Extractant	Sample			
	Choyo ¹		Yoake ²	
	Zn	Ca	Zn	Ca
1 M NaCl	23	90	21	79
0.5 M $CaCl_2$	29	— ⁴	19	— ⁴
1 M NH_4Cl	46	100	62	85
0.1 M HCl	101	92	103	73

¹ $[Zn] = 17.9$ meq/100 g; $[Ca] = 24.5$ meq/100 g; $K_{Ca}^{Zn} = 68$. $[Zn]/CEC$ (%) = 41.3.

² $[Zn] = 1.77$ meq/100 g; $[Ca] = 12.7$ meq/100 g; $K_{Ca}^{Zn} = 80$. $[Zn]/CEC$ (%) = 12.5.

³ Percentage of $[Zn]$ and $[Ca]$.

⁴ Not determined.

ence between Na and NH_4 is attributed to high affinity of NH_4^+ to cation-exchange sites on halloysite (Okamura and Wada, 1979). All adsorbed Zn is recovered in 0.1 M HCl, indicating that H^+ replaces Zn^{2+} very effectively. On the other hand, the amount of Ca replaced in 0.1 M HCl is equal to or even smaller than that replaced in 1 M NaCl, though the reason for this is not clear. The extraction with 0.1 M HCl has been used to assess the availability of soil Zn to plants. The result indicates that the test can not distinguish between Zn adsorbed on "high" and on "low" selectivity sites, at least in halloysite under weakly acid to neutral conditions.

Figure 4 shows the adsorption of Zn by two samples of Choyo and Yoake halloysites; one was air-dried, and the other was dried at 105°C. Heating at 105°C resulted in a decrease in the CEC from 43.3 to 36.0 meq/100 g for the Choyo halloysite; the proportion of the cation-exchange sites with "high selectivity" for Zn also decreased, though some remaining exchange sites still strongly adsorbed Zn. The heating resulted in a CEC decrease from 14.5 to 11.3 meq/100 g for the Yoake halloysite, but the difference in the Zn adsorption between the two samples was small. Apparently exchange sites in the interlayer space are not a primary cause for the high selectivity for Zn.

Effects of successive dithionite-citrate and 2% Na_2CO_3 treatments for removal of "free" oxides (Wada and Greenland, 1970) on Zn adsorption were also studied on the Choyo halloysite containing the largest amount of "free" Fe_2O_3 (Table 1). The treatments resulted in about 5% CEC decrease and a K_{Ca}^{Zn} decrease at $[Zn]/CEC \geq 20$. The magnitude of the K_{Ca}^{Zn} decrease was comparable with that found for the sample dried at 105°C (Figure 4). The results indicate that "free" oxides affect and contribute to Zn adsorption by the Choyo halloysite but are not the main cause of its high selectivity for Zn.

Table 4 shows the effect of HCl addition on the adsorption of Zn and Ca by halloysite and montmorillon-

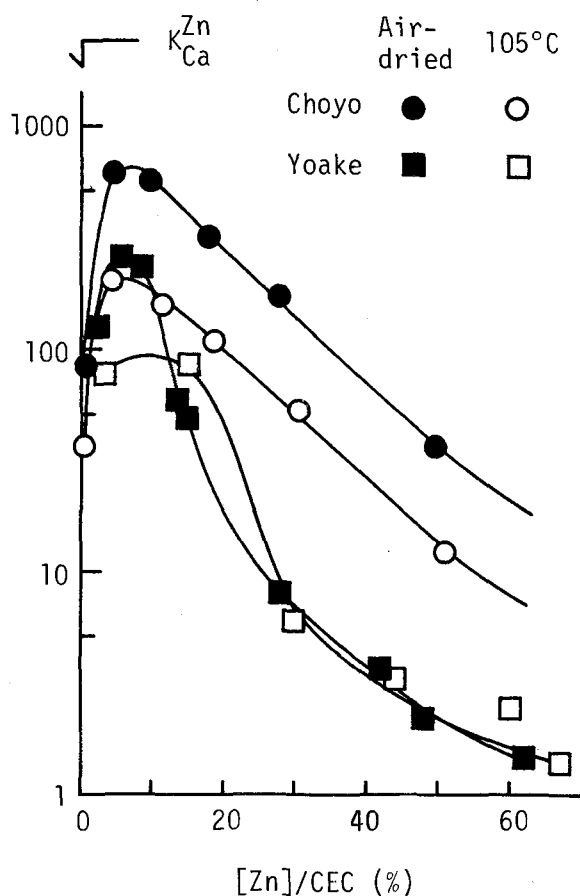


Figure 4. The K_{Ca}^{Zn} vs. $[Zn]/CEC$ relationships for halloysite samples air-dried and heated at $105^{\circ}C$.

ite. The addition of HCl resulted in decrease of $[Zn + Ca]$ by a preferential adsorption of H^+ , and possibly in development of positive charge on the Choyo and Uenae halloysites. The $[Zn + Ca]$ decrease with decreasing pH follows the order Maui > Choyo, Uenae > Yoake > Naegi, which parallels the order in which the proportion of cation-exchange sites with "high selectivities" for Zn decreases. The $[Zn]/[Zn + Ca]$ ratio increases or decreases slightly, but the associated K_{Ca}^{Zn} values are much lower than those given in Figure 2. The results indicate that the charge sites showing high affinities for H^+ are responsible for the selective Zn adsorption by halloysite. In the montmorillonite, the proportion of the exchange sites showing high affinities for H^+ is very small, yet those developed at pH 6.9 exhibit "high" selectivity for Zn. These exchange sites are most probably edge OH groups. The exchange sites due to ionic substitution exhibit little preference for Zn over Ca.

DISCUSSION

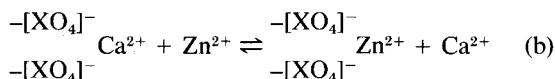
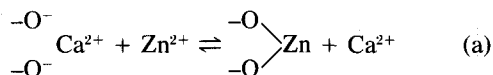
Adsorption of cations on oxides has been discussed in terms of two different reactions, namely "non-specific" and "specific" adsorption. The "non-specific" adsorption refers to adsorption of cations by simple coulombic interaction in the diffuse electric double layer. On the other hand, the "specific" adsorption refers to adsorption of cations in the inner layer forming bonds to surface Al or Fe atoms via O atoms or OH groups (Bowden *et al.*, 1977; Schwertman and Taylor, 1977). Cations are classified into two groups, "non-specifically" adsorbing cations, such as most alkali and alkaline earth cations, and "specifically" adsorbing cations, such as Zn^{2+} , Cu^{2+} , and Pb^{2+} .

Table 4. Effects of HCl addition on Zn and Ca adsorption by halloysite and montmorillonite.

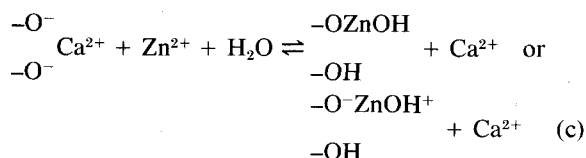
Sample	HCl added (meq/100 g)	pH	$[Zn]$ (μM)	$[Ca]$ (mM)	$[Zn + Ca]^1$ (meq/100 g)	$[Zn]/[Zn + Ca]$ (%)	K_{Ca}^{Zn}
Halloysite							
Maui	0	7.0	0.15	0.44	6.70 (1.00)	9.9	310
	4	6.4	9	0.85	3.62 (0.54)	16.6	19
	6	4.9	38.5	1.02	2.13 (0.32)	17.8	5.7
Choyo	0	6.9	0.6	1.05	44.2 (1.00)	3.6	260
	20	5.1	135	3.5	24.3 (0.53)	19.8	6.4
Uenae	0	7.0	0.9	1.44	56.8 (1.00)	13.2	243
	20	5.9	49.5	3.91	35.8 (0.63)	19.7	19
	30	4.7	285	5.0	25.7 (0.45)	24.2	11
Yoake	0	6.8	0.1	0.28	12.0 (1.00)	2.3	86
	4	6.0	0.3	0.72	8.64 (0.72)	3.0	73
	6	5.3	1.75	0.94	6.98 (0.58)	3.7	21
Naegi	0	6.7	0.45	0.39	7.29 (1.00)	3.6	31
	2	6.1	12.5	0.50	6.39 (0.88)	2.7	1.1
Montmorillonite							
Gunma	0	6.9	0.25	4.45	69.0 (1.00)	0.81	158
	7.5	4.9	20.5	5.05	64.0 (0.93)	0.77	1.5

¹ The values in parentheses give the ratio to the highest value.

The findings in the present and previous studies (Wada and Abd-Elfattah, 1978, 1979) indicate that the adsorption sites for the "specifically" and "non-specifically" adsorbing cations, i.e., Zn and Ca, are not different at least in clay minerals, and that their pH-dependent cation-exchange sites can be potential adsorption sites showing "high" selectivities for Zn. The reactions studied can be formulated as follows:



where Ca^{2+} and Zn^{2+} represent hydrated species, Zn represents dehydrated species, and -O^- and $\text{-[XO}_4\text{]}^-$ represent exchange sites due to ionized surface OH group and ionic substitution, respectively. The stability of the Zn complex formed involving deprotonated OH groups as ligands can be greater than that of the Ca and Zn ion-exchange complexes. The stability of these complexes will differ depending on the nature of surface OH groups and the kinds of ionic substitution and the sterical relationships between neighboring cation-exchange sites. The first hydrolysis constant of Zn^{2+} , $10^{-8.96}$ – $10^{-9.36}$ (Sillén and Martell, 1964) suggests that ZnOH^+ contributes significantly only above pH 7 in solution, but the surface reaction



can not be excluded. Any of the reactions (a), (b), or (c) can explain the observed stoichiometry. The complex formation of various metals with deprotonated surface OH groups as bidentate and monodentate ligands has been reported for silica and other oxides by several investigators (e.g., Davis and Leckie, 1978).

The origin of cation-exchange sites in halloysite has not been established (Dixon, 1977). Yoshida (1970) and Wada and Okamura (1977) estimated that 80–85% of the cation-exchange sites in halloysite are due to permanent negative charge, using Al^{3+} or NH_4^+ as an index cation. The differences in the affinity of the cation-exchange sites for Zn^{2+} (Figure 2) and H^+ (Table 4) between the halloysite samples is interesting in suggesting that the mechanism of charge development is different, possibly depending on their genesis.

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Резюме—Измерялись адсорбционные равновесия Zn и Ca в пяти образцах галлуазита, насыщенного Ca при равновесных концентрациях Zn до 10^{-2} M в 10^{-4} – 10^{-2} M CaCl₂. Результаты анализировались с помощью графиков зависимости K_{Ca}^{Zn} и $[Zn]/КОС$ (%), где K_{Ca}^{Zn} = это коэффициент селективности (= $[Zn][Ca]/[Ca][Zn]$); Zn и Ca представляют адсорбированные разновидности, а КОС = катионная обменная способность. Вся адсорбция Zn происходила в местах обмена катионов, и от 0,77 до 36,0 мэк Zn/100 г глины, что составляет от 9 до 83% КОС, было адсорбировано с “высокими селективностями” ($K_{Ca}^{Zn} > 10$). Более высокие величины были обнаружены для двух сферических и одного “пленочного” галлуазита и более низкие величины— для двух трубчатых галлуазитов. Величина их интенсивности 001, гидротация в межслойном пространстве, КОС, и содержание “свободной” окиси железа не согласуются с селективной адсорбцией Zn, но была установлена хорошая корреляция между пропорцией мест “высокой селективности” для Zn и пропорцией мест “высокого” сродства для H⁺. Адсорбция Zn в местах “высокой селективности” не была полностью обратимой, а величины $K_{Ca}^{Zn} > 1000$ были обнаружены в 0,5 M CaCl₂ для Zn, который занимал 10–40% мест обмена. Селективная адсорбция Zn уменьшалась с понижением pH, и весь адсорбированный Zn был извлечен с помощью 0,1 M HCl. [N.R.]

Resümee—Die Zn- und Ca-Adsorptionsgleichgewichte fünf Ca-gesättigter Halloysitproben wurden bei Zinkgleichgewichtskonzentrationen bis zu 10^{-2} M in 10^{-4} bis 10^{-2} M CaCl₂ gemessen. Die Ergebnisse wurden in Diagrammen, in denen K_{Ca}^{Zn} gegen $[Zn]/CEC$ (%) aufgetragen ist, interpretiert, wobei K_{Ca}^{Zn} der Selektivitätskoeffizient (= $[Zn][Ca]/[Ca][Zn]$) ist, Zn und Ca die adsorbierte Ionenart darstellt, und CEC die Kationenaustauschkapazität ist. Jede Zn-Adsorption findet an Kationenaustauschplätzen statt, und 0,77 bis 0,36 mÄq Zn/100 g Ton, die 9 bis 83% der CEC ausmachen, wurden mit “hoher Selektivität” ($K_{Ca}^{Zn} > 10$) adsorbiert. Die höheren Werte wurden bei zwei kugelförmigen und einem “filmy” Halloysit gefunden, die niedrigeren Werte hingegen bei zwei röhrenförmigen Halloysiten. Die Größe ihrer 001-Intensität, die Hydratation im Zwischenschichtraum, die CEC, und der “freie” Eisenoxidgehalt korreliert nicht mit der selektiven Zn-Adsorption. Eine gute Korrelation wurde jedoch zwischen dem Verhältnis von Plätzen mit “hoher Selektivität” für Zink und dem Verhältnis von Plätzen mit “hoher Selektivität” für H⁺ gefunden. Die Adsorption von Zn an die Plätze “hoher Selektivität” war nicht vollständig reversibel. K_{Ca}^{Zn} -Werte > 1000 wurden für Zn in 0,5 M CaCl₂ verzeichnet, das 10–40% der Austauschplätze besetzt. Die selektive Adsorption von Zn nimmt mit abnehmendem pH ab. Alles adsorbierte Zn wurde mit 0,1 M HCl extrahiert. [U.W.]

Résumé—Les équilibres d'adsorption-Zn et -Ca de cinq échantillons d'halloysite saturés de Ca ont été mesurés à des concentrations d'équilibre Zn jusqu'à 10^{-2} M dans 10^{-4} à 10^{-2} M CaCl₂. Les résultats ont été interprétés sur des diagrammes K_{Ca}^{Zn} vs. $[Zn]/CEC$ (%), où K_{Ca}^{Zn} est le coefficient de sélectivité (= $[Zn][Ca]/[Ca][Zn]$), Zn et Ca représentant les espèces adsorbées, et CEC est la capacité d'échange de cations. Toute l'adsorption Zn s'est passée sur des sites d'échange de cations, et de 0,77 à 36,0 meq Zn/100 g d'argile, ce qui constitue de 9 à 83% de la CEC, ont été adsorbées à de “hautes sélectivités” ($K_{Ca}^{Zn} > 10$). Les valeurs les plus hautes ont été trouvées pour deux halloysites sphériques et une halloysite “recouverte d'un film,” tandis que les valeurs les plus basses ont été trouvées pour deux halloysites tubulaires. La magnitude de leur intensité 001, l'hydratation dans l'espace inter-couche, la CEC, et le contenu en oxide de fer “libre” n'ont montré aucune corrélation avec l'adsorption sélective Zn, mais une bonne corrélation a été trouvée entre la proportion de sites à “haute sélectivité” de Zn et la proportion de sites à “haute affinité” pour H⁺. L'adsorption de Zn aux sites de “haute sélectivité” n'était pas complètement réversible, et des valeurs $K_{Ca}^{Zn} > 1000$ ont été observées dans 0,5 M CaCl₂ pour Zn qui se trouvaient dans 10–40% des sites d'échange. L'adsorption sélective Zn a diminué à mesure que le pH décroissait, et tout le Zn adsorbé a été extrait par 0.1 M HCl. [D.J.]