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THE CATION EXCHANGE CAPACITY OF SOME KAOLIN MINERALS

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Abstract

The variation of the cation exchange capacity (CEC) of some kaolin minerals with the nature of the exchanging cation, temperature, and pH has been studied. Cation exchange properties of kaolins originate largely from isomorphous substitution and pH-dependent surface charges but the exchange reaction was complicated by the presence of impurities on the clay surfaces and the tendency of kaolins to form intercalation complexes. The CEC apparently increases with increasing pH, halloysite showing a stronger pH–dependence than kaolinite. High-temperature studies were limited to temperatures below 100°C. The CEC's for all halloysites and a kaolinite were less than 10 meq/100g and the temperature effects were small and rather unpredictable.

Introduction

The cation exchange capacity (CEC) of clay minerals is believed to be largely due to broken bonds around the edges of the silica-alumina units, isomorphous substitution in the clay structure and, in some cases, replacement of the hydrogen of exposed hydroxyls[1]. CEC's are influenced. therefore, by factors such as chemical pretreatment, type of saturating cation, particle size, temperature and pH of the saturating solution.

Rivière[2] determined the cation exchange capacity of halloysite by treating the Ba^{2+}-exchanged clay with an ammonium chloride solution buffered at pH 7 and displacing the exchangeable NH_4^+ with Mg^{2+}, the liberated ammonia being absorbed in an acid and back-titrated. The results obtained for hydrated and dehydrated clays were, respectively, 50 and 5 meq/100g. The value for halloysite(10Å) was questioned by Garrett and Walker[3] who obtained a CEC value of 9.0–9.5 meq/100g for K^+ in an halloysite sample from the same locality. They argued in view of the ability of the clay to form intercalation complexes with certain salts and the possibility of incomplete removal of excess salt in Rivière's experiment that a CEC value of 50 meq/100g was too high. The CEC of halloysite(7Å) was comparable to that of kaolinite and could be related to similar charge densities of the clays[4].

Mitra and Prakash[5] studied the adsorption of potassium ion as a function of solution pH and concentration by some clay minerals including kaolinite and halloysite. It was found that the exchange capacity of halloysite was generally greater in an alkaline medium although some slight fluctuations of the results were observed. CEC values ranged from 13.86 meq/100g at pH 5.2 to 28.21 meq/100g at pH 11.8. The adsorption of potassium appeared to be related to the content of exchangeable calcium originally present. However no definite conclusions was made regarding the effect of pH on the exchange capacity.

The work of Wada[6] on the adsorption of some alkali halides on halloysite has suggested that adsorbed interlayer salts might be the cause of the high CEC's reported in literature[2]. It has been found[7] that the efficiency of the washing solvent used in removing excess salt from halloysite depends on the solubility of the salt in that solvent. The use of alcohols usually leads to partial dehydration of halloysite(10Å) and incomplete removal of the interlayer salts.

The dependence of the CEC on pH has been studied extensively[8-10]. Schofield[11] found that the negative charge on clay particles was partially dependent on pH, increasing with increasing alkalinity. The concepts of permanent and pH-dependent charges were developed by Coleman *et al.*[12] who also introduced the breakdown of the CEC into low-pH and high-pH components. The charge on kaolinite and halloysite is found to be largely pH-dependent[13] and arises from the release of protons from structural hydroxyl groups[14].

The effects of salt concentration and cation species on the CEC of clays were studied by Wada and Harada[15]. According to these investigators a solution concentration of 0.05 equiv dm^{-3} was suitable for saturation since the errors due to hydrolysis, non-Coulombic adsorption, and clay dispersion could be minimised. For halloysite, marked salt retention was indicated at solution concentrations higher than 0.1 equiv dm^{-3} and the exchange reaction depended strongly on the cation species. The CEC of halloysite ranged from 12 to ~30 meq/100g in the range of concentration used in their study.

In the present investigation the CEC of halloysites and kaolinite was measured using monovalent cations (NH_4^+ and K^+) and a divalent cation (Mn^{2+}). The variation of CEC's with the nature of the exchanged cation, temperature and pH has also been studied in an attempt to resolve discrepancies reported in literature. High temperature studies were first undertaken in the hope of obtaining information concerning transport and deposition of minerals. However ion exchange reactions at high temperatures were complicated by other reactions induced by the temperature increase and the CEC determinations were limited to temperatures below 100°C.

Halloysites from three localities viz. Te Puke, Kauri Mountain, and Matauri Bay, New Zealand, and a kaolinite from Bang Rin, Ranong, were used. All halloysites were almost fully hydrated. The Kauri clay was essentially free from impurities whereas quartz was present in both the Matauri Bay and Te Puke samples while the latter contained a little cristobalite, traces of iron and some organic matter[16]. The Te Puke clay consisted of mainly tabular particles but some rolled material was present[17,18]. Electron microscope examination indicated the presence of many tubular particles in the Kauri and Matauri Bay samples. The Bang Rin kaolinite was X-ray pure with irregular morphology[19]. The presence of some tubular particles was revealed by scanning electron microscope examination.

All samples were not sized prior to CEC determinations.

Methods

1. Room-Temperature CEC

1.1 The ammonium ion method

Each clay sample was washed once, shaking and centrifuging, with an ammonium acetate solution (1 mol dm^{-3}) buffered at pH 3 with acetic acid, to remove exchangeable aluminium ions. The sample was subsequently washed five times with a 1 mol dm^{-3} ammonium acetate solution (self-buffered at pH 7), shaking and centrifuging as before. All washings were discarded. The hydrated NH_4^+-exchanged sample was stored in a 76.5% R.H. atmosphere to prevent spontaneous dehydration in air while the dehydrated clay was stored in air.

Prior to the ammonium ion determination, the excess salt was removed by washing the exchanged clay repeatedly with absolute ethanol on a Buchner funnel until the washings were free of ammonium ions. After air drying the sample was transferred to a distillation flask and digested with a boiling 10% solution of sodium hydroxide. The ammonia liberated was absorbed by a 2% boric acid solution and titrated against a standard hydrochloric acid solution.

The dry weight of the clay was determined by washing a small portion of the air dried sample once with distilled water, heating at 110°C overnight and weighing at room temperature.

1.2 The manganese ion method

Saturation of the clay with Mn^{2+} ions was accomplished by washing with a 0.5 mol dm^{-3} manganese(II) chloride solution and employing the usual shaking and centrifuging procedure. The treatment was repeated four times and all washings were discarded. Excess manganese ions on the clay samples were removed by successive wahings with absolute alcohol until the washings were chloride free.

The exchangeable manganese ions were displaced by treating the clay with five successive portions of ammonium acetate solution (1 mol dm^{-3}), shaking and centrifuging. The washings were collected and the amount of manganese in the solution was determined colorimetrically[20].

2. High-Temperature CEC

The manganese ion method was used and involved Mn^{2+} ion saturation and excess Mn^{2+} removal a 70°C. However exchangeable Mn^{2+} ions were displaced at room temperature.

A sample of clay was shaken with a 0.5 mol. dm^{-3} manganese (II) chloride solution. The suspension was centrifuged and the supernatant liquid discarded. The washing was then repeated four times using a hot Mn^{2+} solution, holding and stirring the clay-solution mixture in a 70°C water bath for five minutes. The suspension was quickly centrifuged and the solution discarded.

Removal of excess salt was effected by washing the clay with hot absolute alcohol (70°C) and holding the mixture at 70°C as before. The treatment was repeated until the washings were chloride free. The sample was then allowed to cool to room temperature.

Displacement of exchangeable Mn^{2+} ions with ammonium acetate and the colorimetric determination of Mn^{2+} were carried out as in 1.2.

3. pH-Dependent CEC

All samples were converted to the Na^+–exchanged form using a 1 mol dm^{-3} sodium chloride solution and a saturation method similar to that described for Mn^{2+}. Excess Na^+ ions were removed by washing once with distilled water.

Saturation of the clay with potassium ions was done by washing with aqueous solutions of potassium salts adjusted to pH's ranging from 2 to 12. The compositions of the buffer solutions were taken from the Handbook of Chemistry and Physics, 54th ed., Chem. Rubber Pub. Co., D-113(1973), replacing sodium hydroxide with potassium hydroxide.

Samples of the Na^+–exchange clays were washed five time with the appropriate buffer solution employing the usual washing procedure. Excess potassium ions were removed from the clay by washing five times with the buffer solution diluted 100 times. The loss of exchangeable potassium ions by hydrolysis was thus avoided[21].

Exchangeable potassium ions were extracted from the clay with a 1 mol dm^{-3} ammonium acetate solution and determined flame-photometrically. The CEC was then calculated in meq/100g dry clay.

Results and Discussion

1. Room-Temperature CEC

The ammonium ion exchange capacities of the halloysites were found to fluctuate considerably and the ranges are as follows:

Te Puke halloysite (7Å) CEC 8.5 – 13.9(± 0.1) meq/100g
Te Puke halloysite (10Å) CEC 24.3 – 29.8(± 0.1) meq/100g
Kauri halloysite (7Å) CEC 5.2 – 6.2(± 0.1) meq/100g
Kauri halloysite (10Å) CEC 28.7 – 30.3(± 0.1) meq/100g

At least 10 individual samples were included in each of the four ranges of results which are given in milliequivalents (meq) of the cation in 100g of clay dried at 110°C for at least 10 hours. The CEC's for the hydrated clays are excessively high compared to the values obtained for the dehydrated clays. The discrepancies between the two sets of results and the wide variations can be attributed to the ability of halloysite(10Å) to form an intercalation complex with ammonium acetate[3, 22] and the incomplete removal of the intercalated salt by absolute ethanol[7]. Thus, it appears that this method may not be suitable for halloysite(10Å) although it is a more or less standard method for determining the CEC of many clays[23, 24]

With Mn^{2+} as the exchangeable cation smaller variations were found in the CEC results (Table 1). Since X-ray diffraction evidence showed that the intercalation of Mn^{2+} or its chloride salt did not occur it is not surprising that lower CEC's were obtained for both hydrated and dehydrated clays (cf. NH$_4^+$ exchange capacities).

TABLE 1. ROOM-TEMPERATURE Mn^{2+}–EXCHANGE CAPACITY

Sample	CEC, meq/100g dry clay	
	Hydrated clay	Dehydrated clay
Te Puke halloysite	8.5 ± 0.2	5.1 ± 0.2
Kauri halloysite	8.4 ± 0.2	4.5 ± 0.2
Matauri Bay halloysite	5.2 ± 0.2	2.5 ± 0.2
Bang Rin kaolinite	–	3.0 ± 0.2

Experimental results were reproducible within limits of error. Halloysiste (10Å) showed a higher CEC than the dehydrated form although all CEC values are relatively low and are of the same order of magnitude as the value for kaolinite. Differences in exchange capacities between individual samples are usually attributable to variations in particle size, sample morphology, and the types and amounts of impurities present in the clay samples which, in this study, were not sized. However there was little correlation between the tubular Kauri and Matauri Bay samples and the tabular Te Puke clay. X-ray diffraction data indicated that halloysite from the Matauri Bay deposits contained quartz and the original sample was partially dehydrated. Hence the low CEC may be caused by dilution with the non-exchanging material. No attempt was made to determine the amount of highly disordered or amorphous material (allophane) which is usually present in halloysite samples[25].

Although a direct comparison cannot be made between the NH$_4^+$ ion and Mn^{2+} ion exchange capacities obtained for halloysites(10Å) the CEC values for the dehydrated samples may be compared. The average NH_4^+ exchange capacities were found to be considerably higher than the corresponding Mn^{2+} values, This was probably due to the difference in the solubilities of ammonium acetate and manganese chloride in ethanol which was used to remove surplus salt prior to the cation determinations. On the other hand, Weiss[26] noted that the adsorption of monovalent cations at exchange sites is energetically favourable if the discrete negative charges are fixed to the surface and not uniformly distributed. On low-charge surfaces the adsorption of divalent cations is an 'equimolar' and not 'equivalent' exchange reaction. This suggested mechanism could lead to a higher CEC for divalent cations. However such is not the case with halloysites used in the present study.

2. High-Temperature CEC

The Mn^{2+} exchange capacities of the clays at 70°C are as follows:

Te Puke halloysite	(7Å)	CEC	5.6 ± 0.2 meq/100g
Te Puke halloysite	(10Å)	CEC	11.3 ± 0.2 meq/100g
Kauri halloysite	(7Å)	CEC	5.0 ± 0.2 meq/100g
Kauri halloysite	(10Å)	CEC	7.4 ± 0.2 meq/100g
Bang Rin kaolinite		CEC	5.4 ± 0.2 meq/100g

Comparison of the above results with the room-temperature CEC's (Table 1) show that, with the exception of Kauri halloysite (10Å), the CEC increases with temperature. The difference in high-temperature behaviour may be explained on the morphological basis. Evidence from electron microscopy[16, 27] indicated tabular and tubular morphology for Te Puke and Kauri halloysites, respectively. Similar changes in CEC with temperature found for Te Puke halloysite and Florida kaolinite possibly suggest a correlation between clay morphology and the high-temperature cation exchange behaviour.

Ion exchange is an exothermic reaction and usually involves the evolution of a small amount of heat, of the order of 0 kJ mol^{-1}[28]. An increase in temperature would therefore be expected to lower the CEC of the clays although the effect may generally be small[29]. A reduction in CEC with increasing temperature has been observed for montmorillonite and bentonite but was attributed to migration of cations into the clay structure[30]. Fixation of Mn^{2+} ion in halloysite has been observed[31] and could be enhanced at high temperatures, resulting in a lower CEC. On the other hand, there has been evidence[32] that the exchange reaction is somewhat accelerated when the temperature is raised. Increasing temperature enhances vibrations in the clay structure and presumably opens up exchange sites normally inaccessible to the exchanging cation. The cations themselves are provided with more translational energy to reach these sites. Consequently, a higher CEC would result.

The fact that the CEC of halloysite(10Å) is normally greater than that for the dehydrated form may be explained in terms of extra adsorption sites at the crystal edges due to the larger c-dimension of the expanded mineral. These additional sites may be sterically hindered from the exchanging cations when the mineral is dehydrated and the structure collapses.

3. pH-Dependent CEC

Experimental results are tabulated in Table 2. CEC's appear to increase with increasing pH. The difference in the CEC's of kaolinite at the two extreme pH's is markedly smaller than for both halloysite(10Å) and halloysite(7Å). At all pH's the CEC of halloysite(10Å) was greater than for the dehydrated form. All results were satisfactorily reproducible. Figure 1 shows the plot of the CEC of the clays vs. pH of the saturating solution.

TABLE 2. pH-DEPENDENT CEC

Sample	CEC, meq/100g dry clay				
	pH 2.00	pH 4.00	pH 7.00	pH 10.00	pH 12.00
Matauri Bay halloysite(10Å)	2.38 ± 0.06	3.7 ± 0.1	5.4 ± 0.2	6.9 ± 0.2	8.5 ± 0.3
Matauri Bay halloysite(7Å)	1.93 ± 0.05	2.34 ± 0.06	3.9 ± 0.1	4.6 ± 0.2	5.2 ± 0.2
Bang Rin kaolinite	2.5 ± 0.1	2.6 ± 0.1	2.9 ± 0.1	2.9 ± 0.2	3.0 ± 0.2

At low pH the exchange capacity of the clay may be reduced either by destruction of its structure through acid attack or by clogging of the exchang positions by migrating octahedral aluminium ions[33]. Low CEC values were therefore expected. Also, assuming that the negative charge in the clay structure arises from isomorphous substitution[34] and broken bonds at the crystal edges[35], a reduction in pH would cause neutralisation of the edge charges by protons and consequently lower the CEC. Helling *et al.*[36] observed a linear relationship between the CEC of clays and pH of the saturating solution. This was partly attributed to the presence of allophane which may develop a positive or negative charge under acidic or alkaline conditions, respectively. Thus the pH-dependence may be related, at least in part, to the content of allophane. However, according to Coleman and Thomas[37] the pH-dependent CEC has two components viz. weakly dissociated acid groups of organic matter and sesquioxide coatings on the clay surfaces. Sawhney *et al.*[14] also arrived at the same conclusion and it was stated that the contribution from sesquioxides to pH-dependent CEC was negligible compared to that from organic matter. In the case of the halloysites used in this investigation the content of organic impurities is negligibly small. Thus it appears unlikely that the contribution from the organic matter would be significant. Exposed hydroxyl groups in the clay structure should also contribute to the pH-dependent CEC since replacement of the hydrogen with the exchanging cation occurs more easily when the pH of the solution is raised.

Distinction between permanent and pH-dependent CEC's has not been possible since the extent to which the layer structure of the clays is affected by acidic and alkaline environments is not known. In addition, the presence and formation of amorphous colloids such as allophane, iron and aluminium oxides, and organic impurities may further complicate the exchange reaction. Nevertheless CEC values at low pH's may be an indication that the permanent negative charge presumably originating from isomor-

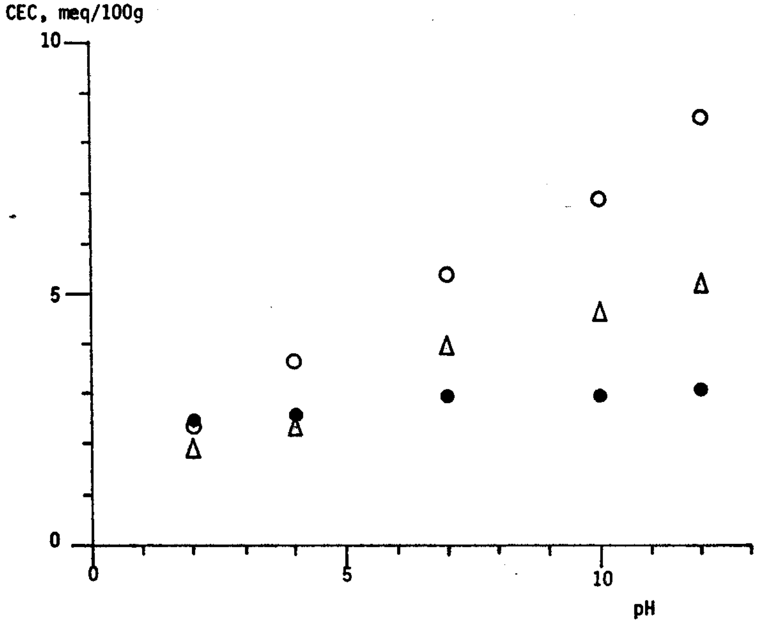

Fig. 1. Variation of CEC with pH

○ Matauri Bay Halloysite(10Å)

△ Matauri Bay Halloysite(7Å)

● Bang Rin Kaolinite

phous substitutions is higher in Bang Rin kaolinite than in Matauri Bay halloysite. On the other hand, both forms of halloysite showed a stronger dependence on pH than did kaolinite, suggesting probably an easier destruction of the layer structure of halloysite in acidic environment. The halloysite structure, because of its disordered nature, would be expected to be more vulnerable to acid attack than the more highly-ordered kaolinite.

That cation exchange properties of clays are a function of permanent and pH–dependent surface charges has been critically examined by Ferris and Jepson[38] who found no evidence for isomorphous substitution. Using the method of isotopic labelling they obtained results indicating that the CEC of kaolinite is zero at pH ≤ 2 and discussed the nature of cation exchange reactions in terms of the presence of aluminosilicate gel coating on the clay surface. Results of the present study, however, show that the CEC decreases with decreasing pH but does not diminish completely. Hence, the concept of isomorphous replacement cannot be discarded.

It can be concluded that the cation exchange properties of halloysite and kaolinite originate primarily from isomorphous replacement in the clay structure and the ionisable silanol groups, —Si–OH, at the edges of the clay particles. The presence of amorphous colloids such as allophanic aluminosilicates and hydrous iron and aluminium oxides also directly or indirectly affect the magnitude of the pH-dependent CEC.

The effects of temperature on CEC's are relatively small in the temperature range below 100°C. The results suggest a tendency towards a small increase in exchange capacity with increasing temperature. Since the observed effects are small, no definite conclusions can be drawn without more information at higher temperatures.

The CEC's of halloysite and kaolinite have been found to vary with the type of saturating cation and the method employed in CEC determination. The occurrence of reactions other than cation exchange between halloysite(10Å) and certain salts has been noted and has produced misleading results.

Finally, the chemical and structural nature of the clays has some influence on the ion exchange behaviour, e.g. stability with respect to pH and temperature.

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บทคัดย่อ

งานวิจัยนี้เกี่ยวกับการศึกษาความสามารถในการแลกเปลี่ยนไอออนบวก (cation exchange capacity) ของแร่ดินขาวบางชนิดภายใต้สภาวะต่าง ๆ กัน คือ ใช้ไอออนต่างชนิดกัน แปรอุณหภูมิ และ pH ของสารละลายที่ใช้ สมบัติการแลกเปลี่ยนไอออนนี้ มีสาเหตุมาจากการที่ไอออนต่างชนิดที่มีขนาดเท่า ๆ กัน แทนที่กันได้ในโครงสร้างของแร่ดินขาว แต่สิ่งมลทินบนพื้นผิวและการที่แร่ดินขาวมีความโน้มเอียงที่จะเกิดสารประกอบเชิงซ้อนระหว่างชั้น (intercalation complex) ก็อาจทำให้ปฏิกิริยาการแลกเปลี่ยนไอออนยุ่งยากซับซ้อนได้ ความสามารถของแร่ดินขาวในการแลกเปลี่ยนไอออนบวกจะสูงขึ้นตาม pH ของสารละลายที่ใช้ การเพิ่มอุณหภูมิของสารละลายที่ใช้ไม่ค่อยมีผลต่อการแลกเปลี่ยนไอออนนัก และผลลัพธ์ที่ได้จากการทดลองก็ไม่ให้ข้อมูลที่ตีความได้ชัดเจนเท่าที่ควร ทั้งนี้อาจเป็นเพราะอุณหภูมิเปลี่ยนแปลงน้อยเกินไป