Effect of pH on the cation exchange capacity of some halloysite nanotubes

NIA GRAY[1,*], DAVID G. LUMSDON[1] AND STEPHEN HILLIER[1,2]

[1] *The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, UK*
[2] *Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), Uppsala SE-75007, Sweden*

ABSTRACT: The cation exchange capacity (CEC) of seven well characterized halloysite nanotubes (HNTs) in the dehydrated 7 Å form has been measured using a method based on cobalt hexammine exchange. In addition to unbuffered measurements, which varied between 2.9 and 9.3 cmol(+)kg^{-1}, CECs were also determined over a wide pH range and proton titration measurements were conducted on two samples. The data were fitted using a constant capacitance model based on the presence of two sites: permanently charged sites and pH-dependent variable charged sites. Normalization of CEC to the average specific surface area (BET) of the halloysite samples reduces considerably the variation of CEC values for the different samples particularly over the intermediate pH range (5–9) with the average value at pH 7 equal to 8.5 cmol(+)kg^{-1} and a standard deviation of 1.17. Overall the CEC behaviour of the seven samples appears reasonably consistent throughout the set. Calculations based on proton titrations suggest a ratio of variable charge to basal sites for the dehydrated halloysite nanotubes of ~3:1.

KEYWORDS: Halloysite, Nanotube, HNT, Cation exchange capacity, pH, Constant Capacitance Model.

Halloysites are 1:1 layer dioctahedral aluminosilicate minerals belonging to the kaolin subgroup and in the fully hydrated (10 Å) state, in which they form, they have an ideal chemical composition of $Al_2(OH)_4Si_2O_5(2H_2O)$. Halloysite was first reported by Berthier (1826) and is found naturally in various commercially exploited deposits worldwide (Wilson & Keeling, 2016) as well as being widely distributed in weathered rocks and soils (Churchman & Lowe, 2012). Halloysite can be differentiated from the other kaolin minerals in the hydrated state by a variety of methods but primary among these is X-ray diffraction (XRD), because the presence of interlayer H_2O molecules in halloysite results in a basal spacing of ~10 Å, as opposed to the 7 Å basal spacing seen for kaolinite, dickite and nacrite. The irreversible dehydration of halloysite removes the weakly held interlayer H_2O molecules, and the resulting 7 Å form is not as readily distinguished from kaolinite without recourse to ancillary tests.

Halloysite also occurs in a variety of different habits including tubular, spherical and platy. Nonetheless, tubular morphologies appear to be the most common (Joussein *et al.*, 2005), indeed all commercially exploited deposits seem to be composed predominantly of halloysite nanotubes (Wilson & Keeling, 2016). In this form, naturally occurring 'eco-friendly nanotubes', often abbreviated as HNTs, have the advantage of being non-toxic (Kamble *et al.*, 2012). Moreover, increasingly halloysite has been the focus of a wide range of both industrial and research applications (Du *et al.*, 2010) profiting in part from its chemical similarity to kaolinite, a clay mineral that is already used in an immense array of materials and applications and with which regulatory bodies are already familiar.

Cation exchange capacity (CEC) measurements give information on the surface-charge properties of materials. Many previous studies have reported on the CEC of halloysites but the reviews of Bailey (1990)

*E-mail: nia.gray@hutton.ac.uk

and of Joussein *et al.* (2005) highlight the fact that many questions about the CEC of halloysites remain. Based on the literature cited in both of the aforementioned reviews there is a wide range of CECs reported and values of up to 50 cmol(+)kg^{-1} are not uncommon for some forms of halloysite. Bailey (1990) commented that the higher values are too large to be attributed solely to edge sites and postulated that exchangeable interlayer cations might be a driving force for the presence of interlayer H$_2$O molecules in halloysite; whilst also recognizing that impurities may explain some of the data. Indeed some explanation for the wide range of values (2–60 cmol(+)kg^{-1}) given by Joussein *et al.* (2005) may be related to the wide variety of halloysite types found in nature and/or unrecognized impurities in some samples. Intercalation of salts has also been identified as a source of erroneously high CEC values for hydrated halloysites (Garrett & Walker, 1959) although Norrish (1995) documented an as yet unexplained variation in CEC that may be related to the state of hydration of halloysite during the exchange reaction which did not appear to be due to the occlusion of salt.

By analogy with kaolinite, halloysite nanotubes are assumed to contain different types of surface functional groups the availability of which defines the material's CEC. The permanently charged basal sites of the siloxane surfaces are believed to arise due to minor substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet giving rise to a small net negative charge (Bailey, 1990). Previous work has shown that the pH-dependent basal hydroxyls and edge hydroxyls of the octahedral sheets along with edge sites of the tetrahedral sheets are overwhelmingly the main contributors to the CEC of kaolinites (Ma & Eggleton, 1999) and the same authors suggested that halloysite may display the same characteristics. The CEC of halloysite nanotubes for this study is therefore defined by two types of sites, namely permanently charged siloxane basal sites and pH-dependent variable charge sites, including tetrahedral sheet silanol edge sites (≡SiOH) and edge and basal aluminol (≡AlOH) sites from the octahedral sheet.

In order to gain an understanding of the adsorption occurring on the surface of the clay in CEC reactions, modelling simulations were undertaken. The Constant Capacitance Model (CCM) is a surface complexation model that can account for inner-sphere reactions. The model has been applied in a variety of forms to examine the adsorption of cations onto the surfaces of clay minerals. Huertas *et al.* (1998) concluded that three different surface sites affect the surface charge

with varying pH and Wieland & Stumm (1992) used a three-site CCM model to represent the adsorption sites on kaolinite. Further work successfully used a two-site CCM model to predict the adsorption of divalent metal cations onto a kaolinite surface over a wide pH range (Angove *et al.*, 1997; Ikhsan *et al.*, 1999; Peacock & Sherman, 2005; Gu & Evans, 2008). In this study a two site model was used as opposed to a three-site model so as to reduce the number of input parameters, where the two sites considered correspond to the various variable charged sites (≡SOH) described previously and to the permanently charged siloxane basal sites (≡X$^-$). The CCM can be used to determine a ratio of the two-site charge densities (variable charge:permanent charge) for example, fitting of the titration data for a previous kaolinite study determined this ratio as 6:1 (Gu & Evans, 2008).

In an attempt to begin to rationalize some of the conflicting reports on the CEC of halloysite the present investigation was designed to measure the CEC of a number of well characterized HNTs. All samples were examined in a dehydrated 7 Å form (oven dried overnight at 105°C). The effect of pH on the exchange capacity was also investigated and the data interpreted in terms of the CCM to assist in the evaluation of the relative roles of permanent *vs.* pH-dependent charge in determining the observed CECs of halloysite nanotubes. In addition, proton titration measurements were used to provide an independent evaluation of site charge densities and to derive the thermodynamic parameters and constraints required for the modelling of surface chemistry.

MATERIALS AND METHODS

Seven different halloysite nanotube samples all of relatively high phase purity were chosen for study based on mineralogical and physical characteristics given in full by Hillier *et al.* (2016), some of which are reproduced here in Table 1. Particular emphasis was placed on sample selection in relation to differences in specific surface area (BET equation using five points in the relative pressure range 0.05–0.20) which ranged from 30 to 80 m^2 g^{-1} (Table 1). Differences in surface area are directly correlated to variation in other mineralogical and physical characteristics of halloysite nanotubes as shown by Hillier *et al.* (2016).

CEC measurement

The CEC measurements were made using the cobalt hexamine trichloride method (Ciesielski &

TABLE 1. Sample information for halloysites used in the study.

Sample ID	BET (m^2/g)	Quartz	Alunite	Woodhouseite	Gibbsite	Cristobalite	Halloysite	Kaolinite	Total
4Ch	80	0.1	0.0	0.0	Trace	0.0	98.5	1.4	100
7Ch	70	0.0	0.0	0.0	1.1	0.0	98.9	0.0	100
8NZ	35	0.6	0.0	0.0	0.0	0.6	98.8	0.0	100
12Tu	61	4.0	1.9	Trace?	2.9	0.0	88.0	3.2	100
17US	30	0.4	0.1	Trace?	0.0	0.0	99.0	0.5	100
19US	36	0.6	Trace	0.0	0.0	0.0	98.8	0.6	100
20US	74	1.4	0.0	0.0	4.3	0.0	89.5	4.8	100

Quantitative XRPD analysis to give percentage mineral contents was conducted by a normalized full-pattern fitting reference intensity ratio (RIR) method.

Sterckeman, 1997b; Dohrmann & Kaufhold, 2009) which was initially developed for use on soils (ISO23470, 2007). The method is based on adding a solution of known concentration of cobalt hexammine trichloride to the sample and the CEC is calculated by the difference between the initial cobalt complex concentration and the amount of cobalt complex remaining in solution, *i.e.* that which has not adsorbed onto the surface of the mineral.

The cobalt complex concentrations are determined by spectrophotometry at a fixed wavelength of 480 nm where there is an assumed linearity between the concentration and the absorbance measured (Ciesielski & Sterckeman, 1997a; Aran *et al.*, 2008; Hadi *et al.*, 2016).

The method is an unbuffered one with respect to pH and whilst it has been described as redox sensitive (Hadi *et al.*, 2016) the chemical compositions of the halloysite nanotube samples show no obvious indications of iron-reducing species (Hillier *et al.*, 2016) so potential redox issues are assumed to be negligible. The cobalt hexammine ion is temperature stable up to 200°C (Wendlandt, 1963); the compound is light-sensitive however, so the reaction and adsorption measurement is carried out in the timeframe of 1 working day. Trials were run to measure the difference in absorbance between 1 working day and 4 working days after which point a total reduction of 3.1% in absorbance was seen. When measuring the CEC by this method one important parameter is the solid/solution ratio, *i.e.* the concentration of cobalt hexammine trichloride and mass of sample used must be appropriate for the degree of exchange occurring. To increase precision several experimental boundaries were employed in this method; Dohrmann & Kaufhold (2009) allowed for between 5 and 50% of cobalt

complex to be exchanged in solution whilst Ciesielski & Sterckeman (1997a) recommend repeat analysis to be conducted if the concentration of cobalt complex exchanged did not lie between 5 and 35%. In the present study the cobalt complex exchange concentration was between 5 and 50% for all samples in unbuffered conditions though during the pH adjustment one measurement for one sample (20US) was recorded with an exchange of 55% at the highest pH. A palygorskite (PFl-1), available from The Clay Minerals Society (www.clays.org) Source Clays Repository, was used to monitor precision and gave an average CEC of 15.4 cmol(+)kg^{-1} with a standard deviation of 0.4 ($n = 7$) over the course of the experiments.

CEC measurement by cobalt hexammine trichloride as a function of pH

Samples were hand ground and sieved to <250 μm before being oven dried at 105°C overnight. The sample mass and solid to liquid ratio was kept constant over all samples. 1.2–1.5 g of sample was weighed into centrifuge tubes and 45 mL of ~3.3 × 10^{-3} M cobalt hexammine trichloride solution was added, where the exact concentration of the solution was known. 1 mL of various known concentrations of HCl (standardized against Na$_2$CO$_3$) or NaOH (standardized and carbonate-free) was then added immediately to each sample vial. Hadi *et al.* (2016) suggest that the extraction of exchangeable cations is complete in <30 min, whilst Aran *et al.* (2008) suggest that 1 h is the time required for the system to reach equilibrium. In the present study the pH-adjusted samples were roller shaken for 1 h and centrifuged down for 10 min at 2000 rpm. The pH was measured the same day using a Hanna 210 combination electrode and the remaining cobalt

complex left in solution was determined by colorimetric absorption at 480 nm using a Konelab 20XT clinical chemistry analyser. For each colorimetric measurement four repeat measurements of each supernatant solution were made so as to reduce any influence of instrumentation and measurement errors. These errors are expected to be low because the standard deviation of $n = 28$ blank samples run during the experiments is 0.0003.

To confirm that the molar extinction coefficient (ε) is not affected by changes in pH, solutions of cobalt hexammine trichloride with no sample present at pHs of 3.02, 5.03 and 10.72 were measured using spectrophotometry where four measurements of each sample were made *in situ*. The average molar extinction coefficient for the cobalt complex was 36.2 with a standard deviation of 0.3 for the 12 measurements. Parenthetically we note that the pH independence is in contrast to the behaviour of Cu trien as reported by Kaufhold & Dohrmann (2013).

Proton titration experiments

For the proton titration experiment, two of the purest halloysites, 4Ch and 17US, were selected to determine the proton binding constants over a range of pHs

($\sim$3–10). Twelve aliquots of 0.2 g of each halloysite were weighed into centrifuge vials and 1 mL of various known concentrations of HCl (standardized against Na_2CO_3) or NaOH (standardized and carbonate-free) was added along with 25 mL of deionized water, where the concentrations of the acid or base solutions varied along a gradient from acidic to basic. No background electrolyte was used and a blank check was included. The samples were rolled for 1 h to allow for equilibrium and the pH immediately measured. The kinetics of the titration reactions were considered by determining if a change in pH was recorded for the most acidic and basic samples over the 4 h of pH measurements; no significant change was noted.

RESULTS AND DISCUSSION

CEC and the effect of pH

Unbuffered CEC measurements for the seven halloysite samples ranged from 2.9 to 9.3 cmol(+) kg^{-1} (Fig. 1). In addition, as reported previously for smectite clay minerals (Kaufhold & Dohrmann, 2013; Delavernhe *et al.*, 2015) all samples behaved in a similar manner with respect to pH, showing increased
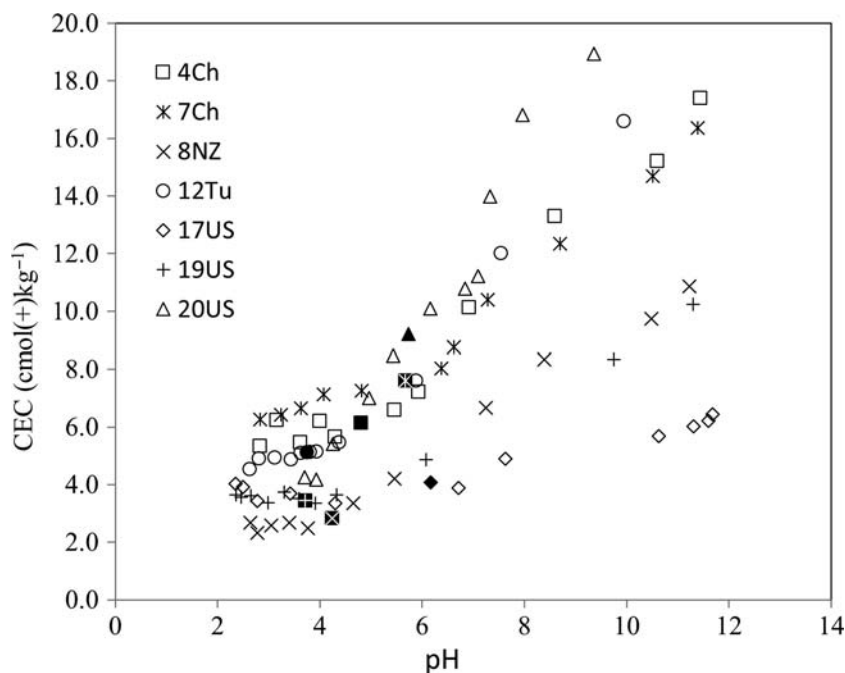

FIG. 1. Combined data of pH *vs.* measured CEC for all seven halloysite samples. Note unbuffered CEC values for each sample are shown as solid symbols.

CEC with increasing pH, which suggests the influence of pH-dependent binding sites. By analogy with kaolinite models previously reported (Angove *et al.*, 1997; Ikhsan *et al.*, 1999; Peacock & Sherman, 2005; Gu & Evans, 2008), at acidic conditions (pH 2–4) the adsorption contribution may be equated with permanently charged sites only as indicated by a region of little or no slope in the CEC data (Fig. 1). As the pH is increased (>pH 5) there is a pH-dependent variable-charge site contribution which results in observed increasing adsorption. Comparison of all the results on one graph shows some significant differences between the samples, particularly at higher pH. However, normalization of the data to the average specific surface area (BET) of all seven samples (55 m^2 g^{-1}) results in a considerable reduction in variability of the CEC (Fig. 2). In particular this can be seen over the intermediate pH range (5–8), where the curves for the samples become more or less coincident. Extrapolation of each sample curve gives an average CEC of 8.5 cmol(+)kg^{-1} with a standard deviation of 1.17 at pH 7. The effect of surface area normalization demonstrates the dependence of the measured CECs for the different samples on surface area, *i.e.* before normalization samples with the largest surface areas show the largest CEC values and the steepest slopes with respect to changes in CEC as a function of pH. It

might be suggested that some persistent scatter of the data at pH >9 in the surface-area normalized data could due to dissolution of the minerals as opposed to surface-area effects. From Figs 1 and 2 note that sample 20US has a steeper gradient of CEC, reduced basal-site contribution, and what appears to be additional adsorption in the pH curve at pH 7–9. These differences may be due to effects of some of the minor impurities it contains, including 4% of gibbsite. Alternatively, this effect may be less apparent, but present, in the remaining samples and it can be hypothesized that it is due to different binding stoichiometries of variable-charge sites by the cobalt complex. Confirmation of these various possibilities would require further investigation.

Modelling proton titration data

Previous work on kaolinite (Angove *et al.*, 1997; Ikhsan *et al.*, 1999; Peacock & Sherman, 2005; Gu & Evans, 2008) demonstrated that the surface-charge characteristics can be understood adequately in terms of two types of charge site, the permanent charge sites on the basal surface ($\equiv$X$^-$) and variably-charged sites ($\equiv$SOH) as discussed previously. We assume that this arrangement also applies to halloysite; therefore, the CCM developed for kaolinite (Gu & Evans, 2008) has been applied to the tubular halloysites in the present
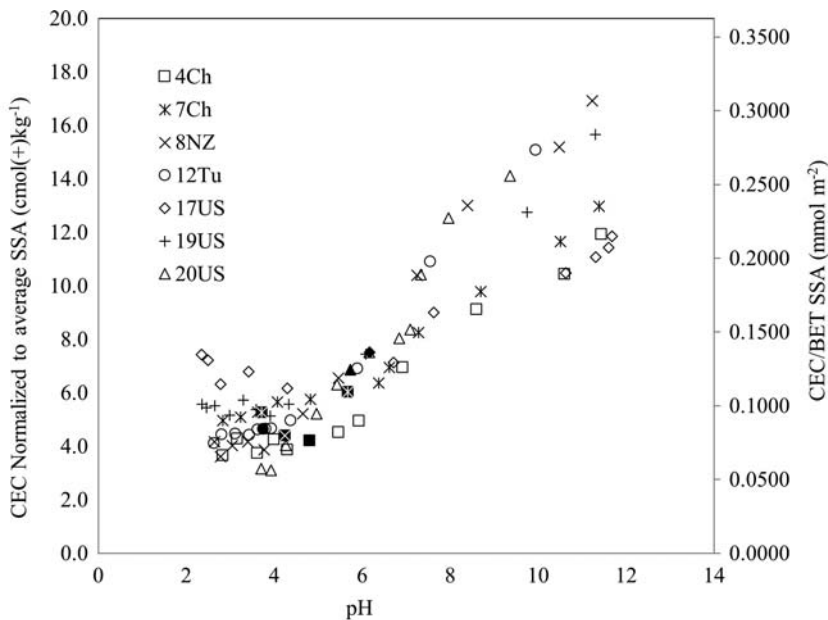

Fig. 2. pH *vs.* CEC normalized to average specific surface area of the samples (55 m^2 g^{-1}). Unbuffered CEC values are shown as solid symbols. As well as units of cmol(+)kg^{-1}, the vertical axis is also given in units of mmol m^{-2}.

study. To test whether the modelling approach used for kaolinite could be applied to halloysite, proton titration measurements of two of the purest halloysites (4Ch and 17US) were also performed.

Equilibrium constants used in the model for proton adsorption (including $\log K_{a1}$, $\log K_{a2}$, $\log K_{(Na,X)}$) and charge densities of the two surface sites ($\equiv X^-$, $\equiv SOH$) were either derived using the least-squares fitting program *FITEQL* 3.1 (Westall & Herbelin, 1994), or taken from Gu & Evans (2008) as listed in Table 2. The model fit of the data for the halloysites 4Ch and 17US is shown in Figs 3 and 4.
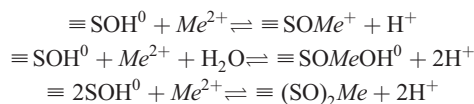
The *FITEQL* model fits indicate a permanent-charge site concentration and a variable-charge site concentration of 2.1 cmol(+)kg^{-1} and 7.05 cmol(+)kg^{-1}, respectively for 4Ch compared with 0.7 cmol(+)kg^{-1} and 2.4 cmol(+)kg^{-1} for 17US. Both give an approximate ratio of variable charge to permanent charge sites of 3:1. The sum of the basal and variable charge sites gives the total CEC of 9.15 cmol(+)kg^{-1} for sample 4Ch and 3.1 cmol(+)kg^{-1} for 17US. Both values are less than those obtained by the cobalt hexammine trichloride method, which were 15.2 cmol(+)kg^{-1} and 5.7 cmol(+)kg^{-1} (Fig. 1) at similar maximum pH ($\sim$pH 10). Possible reasons for these differences due to variable binding stoichiometries of the cobalt complex are considered and discussed later.

The model analysis of the proton titration data is consistent with a reactive surface containing two key types of adsorption site (Figs 3 and 4) within the specific pH range. In addition, the thermodynamic parameters

were very similar to those found for kaolinite (Gu & Evans, 2008) as shown in Table 2. On this basis we surmise that the two-site CCM is a reasonable model to interpret the cobalt complex adsorption data.

Modelling cobalt complex adsorption data

Previous studies have looked at modelling the surface complexation of divalent transition metal cations such as Cd^{2+}, Zn^{2+} and Cu^{2+}, amongst others (Angove *et al.*, 1997; Ikhsan *et al.*, 1999; Gu & Evans, 2008) on the surface of kaolinite clay minerals. The studies reported reaction stoichiometries for monodentate and bidentate binding to the variable charge sites as shown below:

$$\equiv SOH^0 + Me^{2+} \rightleftharpoons \equiv SOMe^+ + H^+$$
$$\equiv SOH^0 + Me^{2+} + H_2O \rightleftharpoons \equiv SOMeOH^0 + 2H^+$$
$$\equiv 2SOH^0 + Me^{2+} \rightleftharpoons (SO)_2Me + 2H^+$$

where Me^{2+} indicates a divalent metal cation.

For exchange on the permanently charged, *i.e.* siloxane basal sites, it is assumed that each divalent cation reacts with two of the sites ($\equiv X^-$).

$$2 \equiv X^- \cdot H^+ + Me^{2+} \rightleftharpoons \equiv X_2^- \cdot Me^{2+} + 2H^+$$
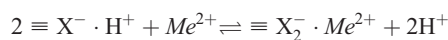
However, there is little published information as to how interactions with a trivalent cation should be represented in modelling studies. Considering the large ionic radius of cobalt hexammine (3.25 Å) sterically it is possible for one cobalt complex to bridge three

TABLE 2. Proton and other parameters used in the model for proton adsorption by 4Ch and 17US halloysite.

Surface acidity reactions	Equilibrium constants	
	4Ch	17US
$\equiv SOH^0 + H^+ \rightleftharpoons \equiv SOH^{2+}$	Log $K_{a_1} = 5.45$[a]	Log $K_{a_2} = 6.05$[a]
$\equiv SOH^0 \rightleftharpoons \equiv SO^- + H^+$	Log $K_{a_2} = -6.92$[a]	Log $K_{a_2} = -7.54$[a]
$\equiv X^- \cdot H^+ + Na^+ \rightleftharpoons \equiv X^- \cdot Na^+ + H^+$	Log $K_{(Na,X)} = 2.02$[b]	Log $K_{(Na,X)} = -2.02$[b]
Other parameters	4Ch	17US
Site density $[\equiv X^-]_T$ (cmol(+)kg^{-1})	2.1[a]	0.7[a]
Site density $[\equiv SOH]_T$ (cmol(+)kg^{-1})	7.05[a]	2.4[a]
Specific capacitance, κ (F m^{-2})	1.2[b]	1.2[b]
Ss (m^2 g^{-1})	80[c]	30[c]
Sd (g L^{-1})	7.91	7.69

[a]Optimized from *FITEQL*.
[b]Assumed from Gu & Evans (2008).
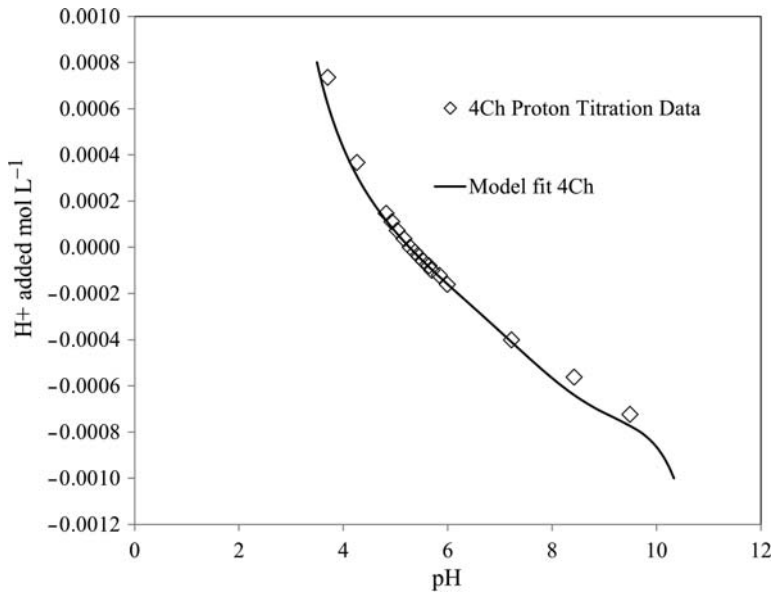[c]Measured by the BET/N$_2$ method.

FIG. 3. Proton batch titration results and modelled data for sample 4Ch halloysite. The model parameters derived from the proton titration are given in Table 2.

variable charge sites on the surface of halloysite nanotubes (Fig. 5). The exact binding sites remain unspecified as no previous work has been conducted for trivalent cations as far as the authors are aware. For the permanently charged basal sites of kaolinite, Sposito (1984) suggested that aluminium substitution for silicon in the tetrahedral sheets could be up to 0.012 per unit cell. For the halloysite sample 4Ch, where the permanent charge is taken as 2.1 cmol(+)kg^{-1} from the proton titration measurements, the site density can be
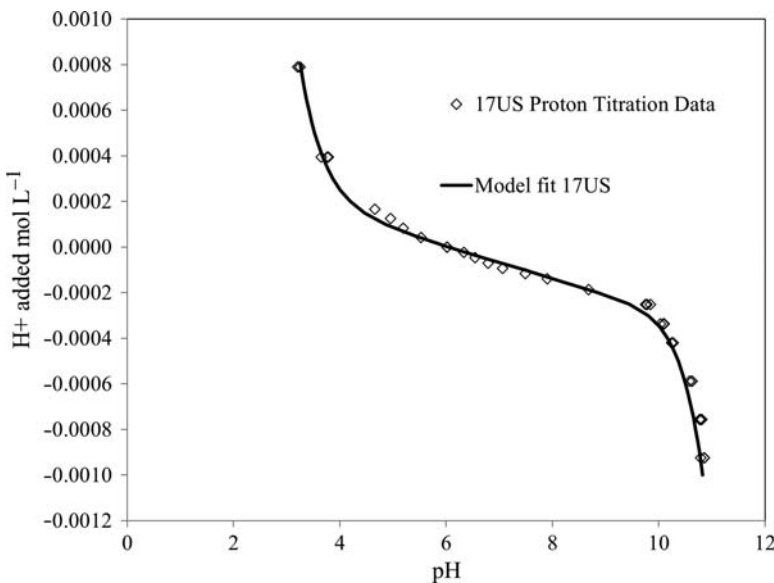

FIG. 4. Proton batch titration results and modelled data for sample 17US halloysite. The model parameters derived from the proton titration are given in Table 2.
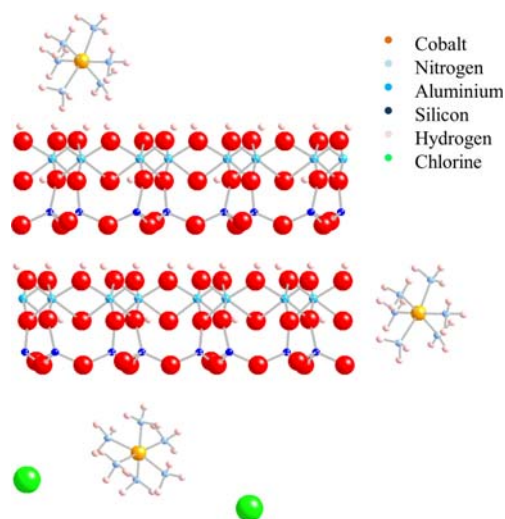
FIG. 5. Schematic representation (to scale) of 7 Å halloysite structure and cobalt hexammine ions in proximity to various surface sites. The ion in proximity to the siloxane surface illustrates monodentate adsorption so is shown with two associated Cl⁻ ions.

bridging would seem less likely for siloxane basal sites unless the assumed aluminium substitution is highly localized.

Implicit to the cobalt hexammine method of determining CEC is the assumption that the adsorption of 1 mole of cobalt hexammine ion equates to 3 moles of negative charge on the surface of the clay, *i.e.* tridendate adsorption. Measurement of the cobalt complex adsorbed, therefore, is not necessarily a direct measure of the total concentration of surface sites ($\equiv X^-$ plus $\equiv SOH$). If the adsorption stoichiometry is <1:3, it may instead provide an overestimated measurement of the surface sites.

In an attempt to determine the occupation of available sites on the halloysite nanotubes by the cobalt complex ions and to account for the disparity between the proton titration data and the cobalt complex adsorption data up to ~pH 10, a CCM was constructed for samples 4CH and 17US. The model tested whether the measured cobalt complex adsorption data could be modelled using a lesser density of permanently charged surface sites, *i.e.* commensurate with the proton titration data. The fits of the data for this model are shown in Figs 6 and 7 where the total site density was assumed by reference to the titration data. To obtain these fits a 1:1 stoichiometry of cobalt ions to available sites on the permanent charge sites and a 1:3 stoichiometry on variable charge sites was considered where the proposed reactions are

calculated as 0.16 sites nm^{-2} or 0.07 sites per unit cell and for 17US the values are 0.14 sites nm^{-2} or 0.06 sites per unit cell where the permanent charge is 0.7 cmol(+)kg^{-1}. Sterically, therefore, multidentate
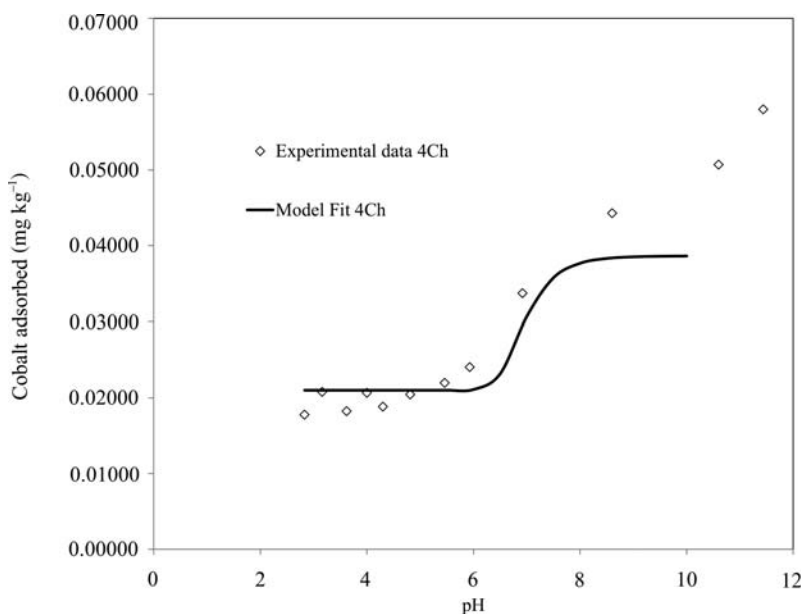

FIG. 6. Adsorption of trivalent cobalt hexammine cation on 4Ch halloysite as a function of pH.
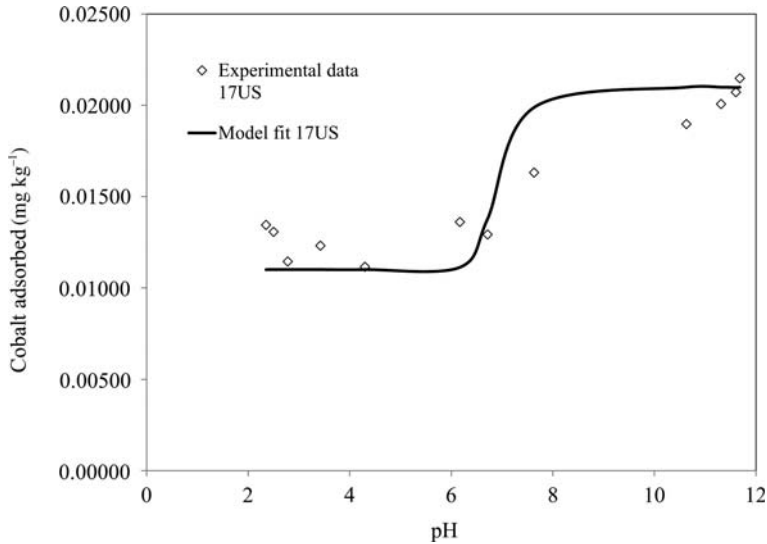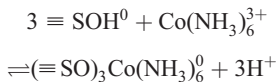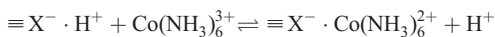
F<small>IG</small>. 7. Adsorption of trivalent cobalt hexammine cation on 17US halloysite as a function of pH.

shown below. The stoichiometric coefficients for these reactions are detailed in Table 3.

Variable charge sites:

$$3 \equiv SOH^0 + Co(NH_3)_6^{3+}$$
$$\rightleftharpoons (\equiv SO)_3 Co(NH_3)_6^0 + 3H^+$$

Permanently charged sites:

$$\equiv X^- \cdot H^+ + Co(NH_3)_6^{3+} \rightleftharpoons \equiv X^- \cdot Co(NH_3)_6^{2+} + H^+$$

The proposed fits in the model are consistent with the steric considerations for the different site types as discussed above and Figs 6 and 7 demonstrate a reasonable fit of the two site model between cobalt complex experimental data and model simulations using parameters derived from the proton titration reactions. Above pH 9 there is an observed split between the model curve and the cobalt complex experimental curve which may be rationalized as being due to the constraints of the proton titration data in terms of the number of available sites.

From previous studies it is known that multi-dentate metal complexes can occur with variable charge sites, *e.g.* cadmium adsorption on goethite, where the $\equiv FeOH$ sites form bi- and tridentate complexes (Venema *et al.*, 1996). The possibility of multi-dentate complexes with the cobalt ion complex has not been investigated here nor has the consideration that the cobalt complex may have variable charge with changes in pH which could result in different binding

T<small>ABLE</small> 3. Proton and metal surface complexes for halloysite and reaction stoichiometry used for *FITEQL* input.

| Surface species | Stoichiometric coefficients | | | | | | Log K | |
	$\equiv SOH$	$e(-F\psi/RT)$	$\equiv X^- \cdot H^+$	Co^{3+}	Na^+	H^+	4Ch	17US
$\equiv SOH^0$	1	0	0	0	0	0	0	0
$\equiv SOH_2^+$	1	1	0	0	0	1	5.45	6.05
$\equiv SO^-$	1	−1	0	0	0	−1	−6.92	−7.54
$\equiv (SO)_3 Co^0$	3	0	0	1	0	−3	17.3	17.3
$\equiv X^- \cdot H^+$	0	0	1	0	0	0	0	0
$\equiv X^- \cdot Na^+$	0	0	1	0	1	−1	−2.02	−2.02
$\equiv X_3^- \, Co^{3+}$	0	0	1	1	0	−3	1	1

stoichiometries. These considerations should not be ruled out and would require further study (*e.g.* by spectroscopic methods).

In summary this modelling work has shown that the adsorption behaviour of cations on the surface of 7 Å halloysite nanotubes appears similar to kaolinite and is consistent with adsorption on essentially two types of binding site, which can be equated with variable charge sites and permanently charged sites. A reasonable fit to the experimental cobalt complex data is obtained with a model which highlights that the adsorption on the permanently charged basal sites may be non-stoichiometric. The model also allows us to rationalize the apparent discrepancy between the proton titration data and the cobalt hexammine data, when the cobalt hexammine method implicit stoichiometry of one trivalent cobalt complex adsorbed to three negatively charged surface sites is assumed.

CONCLUSION

Measurements of the CEC of seven halloysite nanotube samples in the 7 Å dehydrated form determined by cobalt hexammine trichloride over a pH range of 2.63–11.4 vary from 3.4 to 18.9 cmol(+) kg^{-1}. Unbuffered CEC values for all seven samples cover a smaller range from 2.9 to 9.3 cmol(+)kg^{-1} and normalized to average specific surface area and at neutral pH the CEC of 7 Å halloysite nanotubes is 8.5 ± 1.17 cmol(+)kg^{-1}. The work also demonstrates that the variable-charge sites are the main contributors to the CEC of halloysite nanotubes, a point which has also been emphasized for the origin of the CEC of kaolinite (Ma & Eggleton, 1999). The adsorption of the trivalent cobalt complex was rationalized by a two-site constant capacitance model where the assumption was made that one cobalt ion complex occupies three charged sites for variable charged sites and one charged site for the permanently charged basal sites. Proton adsorption on the surface of two of the purest samples of halloysite was examined by titration curves from which the proton binding constants were determined. From both the experimental observations and modelling work conducted in this paper a tentative estimate of the variable charge to basal site ratio for the 7 Å halloysite nanotubes can be given at ~3:1.

ACKNOWLEDGEMENTS

REFERENCES

Angove M.J., Johnson B.B. & Wells J.D. (1997) Adsorption of cadmium(II) on kaolinite. *Colloids and Surfaces A – Physicochemical and Engineering Aspects*, **126**, 137–147.

Aran D., Maul A. & Masfaraud J.F. (2008) A spectrophotometric measurement of soil cation exchange capacity based on cobaltihexamine chloride absorbance. *Comptes Rendus Geoscience*, **340**, 865–871.

Bailey S.W. (1990) Halloysite – a critical assessment. *Sciences Geologiques-Memoires*, **86**, 89–98.

Berthier P. (1826) Analyse de l'halloysite. *Annali di chimica Physical*, **32**, 332–335.

Churchman G.J. & Lowe D.J. (2012) Alteration, formation and occurence of minerals in soils. Pp. 20.21–20.72 in: *Handbook of Soil Sciences. Properties and Processes, Second Edition* (P.M. Huang, Y. Li & M.E. Sumner, editors). CRC Press, Boca Raton, Florida, USA.

Ciesielski H. & Sterckeman T. (1997a) A comparison between three methods for the determination of cation exchange capacity and exchangeable cations in soils. *Agronomie*, **17**, 9–16.

Ciesielski H. & Sterckeman T. (1997b) Determination of cation exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions. *Agronomie*, **17**, 1–7.

Delavernhe L., Steudel A., Darbha G.K., Schäfer T., Schuhmann R., Wöll C., Geckeis H. & Emmerich K. (2015) Influence of mineralogical and morphological properties on the cation exchange behavior of dioctahedral smectites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **481**, 591–599.

Dohrmann R. & Kaufhold S. (2009) Three new, quick CEC methods for determining the amounts of exchangeable calcium cations in calcareous clays. *Clays and Clay Minerals*, **57**, 338–352.

Du M.L., Guo B.C. & Jia D.M. (2010) Newly emerging applications of halloysite nanotubes: a review. *Polymer International*, **59**, 574–582.

Garrett W. & Walker G. (1959) The cation-exchange capacity of hydrated halloysite and the formation of halloysite-salt complexes. *Clay Minerals Bulletin*, **4**, 75–80.

Gu X.Y. & Evans L.J. (2008) Surface complexation modelling of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption onto kaolinite. *Geochimica et Cosmochimica Acta*, **72**, 267–276.

Hadi J., Tournassat C. & Lerouge C. (2016) Pitfalls in using the hexaamminecobalt method for cation exchange capacity measurements on clay minerals

and clay-rocks: Redox interferences between the cationic dye and the sample. *Applied Clay Science*, **119**, 393–400.

Hillier S., Brydson R., Delbos E., Fraser T., Gray N., Pendlowski H., Phillips I., Robertson J. & Wilson I. (2016) Correlations among the mineralogical and physical properties of halloysite nanotubes (HNTs). *Clay Minerals*, **51**, 325–350.

Huertas F.J., Chou L. & Wollast R. (1998) Mechanism of kaolinite dissolution at room temperature and pressure: part 1. Surface speciation. *Geochimica et Cosmochimica Acta*, **62**, 417–431.

Ikhsan J., Johnson B.B. & Wells J.D. (1999) A comparative study of the adsorption of transition metals on kaolinite. *Journal of Colloid and Interface Science*, **217**, 403–410.

ISO23470 (2007) Determination of effective cation exchange capacity (CEC) and exchangeable cations using a hexammine trichloride solution.

Joussein E., Petit S., Churchman J., Theng B., Righi D. & Delvaux B. (2005) Halloysite clay minerals – A review. *Clay Minerals*, **40**, 383–426.

Kamble R., Ghag M., Gaikawad S. & Panda B.K. (2012) Halloysite nanotubes and applications: a review. *Journal of Advanced Scientific Research*, **2**, 25–29.

Kaufhold S. & Dohrmann R. (2013) The variable charge of dioctahedral smectites. *Journal of Colloid and Interface Science*, **390**, 225–233.

Ma C. & Eggleton R.A. (1999) Cation exchange capacity of kaolinite. *Clays and Clay Minerals*, **47**, 174–180.

Norrish K. (1995) An inusual fibrous halloysite. Pp. 275–284 in: *Clays Control the Environment – Proceedings of the 10th Internatiopnal Clay Conference, Adelaide 1993* (G.J. Churchman, R.W. Fitzpatrick & R.A. Eggleton, editors). CSIRO Publishing, Melbourne, Australia.

Peacock C.L. & Sherman D.M. (2005) Surface complexation model for multisite adsorption of copper(II) onto kaolinite. *Geochimica et Cosmochimica Acta*, **69**, 3733–3745.

Sposito G. (1984) *The Surface Chemistry of Soils.* Pp. 234. Oxford University Press, New York.

Venema P., Hiemstra T. & VanRiemsdijk W.H. (1996) Multisite adsorption of cadmium on goethite. *Journal of Colloid and Interface Science*, **183**, 515–527.

Wendlandt W.W. (1963) Thermal decomposition of metal complexes .3. stoicheiometry of the thermal dissociation of some hexamminecobalt (III) complexes. *Journal of Inorganic and Nuclear Chemistry*, **25**, 545–551.

Westall J.C. & Herbelin A.L. (1994) *FITEQL : A Program for Determination of Chemical Equilibrium Constants From Experimental Data. Version 3.1.* Oregon State University, Corvallis, Or.

Wieland E. & Stumm W. (1992) Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C. *Geochimica et Cosmochimica Acta*, **56**, 3339–3355.

Wilson I. & Keeling. (2016) Global occurrence and geology of halloysite. *Clay Minerals*, **51**, 309–324.