

THE SURFACE CHEMISTRY OF IMOGOLITE

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Abstract—Imogolite is a tubular aluminosilicate which is common in Andosols and Spodosols. The high pH at point-of-zero charge at the outer parts of the tube and the anomalously high chloride adsorption of imogolite suggested that there may be structural charge associated with this mineral. The structural charge may arise because of changes in bond valence imposed by the incorporation of orthosilicate anions in a gibbsite-type sheet. By using a Basic Stern Model approach, it is shown that the surface charge properties of imogolite are explained if the mean Al–O bond valence of the outer $-Al_2OH$ groups is higher than the inner $-Al_2OHSiO_3$ groups. Hence, a weak positive charge is developed on the outer tube walls whereas a negative charge develops in the tubular pores. The best model fits were obtained where either one or two units of structural charge per unit cell of tube were assumed. The model may also explain why imogolite tubes are normally aggregated in large bundles in close hexagonal packing, because bound counterions may hold the tubes together. However, to arrive at good model descriptions, the deprotonation of $-Al_2OH$ groups must occur at a higher pH than that expected when assuming that all surface oxygens form two hydrogen bridges with H_2O . A more precise structure of imogolite is required to test fully this hypothesis.

Key Words—Adsorption, Basic Stern Model, Bond Valence, Chloride, Imogolite, Point-of-Zero Charge, Surface Charge.

INTRODUCTION

Imogolite, $HOSiO_3Al_2(OH)_3$, is a tubular 2:1 aluminosilicate first described by Yoshinaga and Aomine (1962). Later research found that imogolite has a widespread occurrence in Andosols and in the B horizon of Spodosols worldwide (Wada, 1989; Gustafsson *et al.*, 1999). It has a large surface area, in the order of $1000\text{ m}^2\text{ g}^{-1}$ as measured by ethylene glycol (Egashira and Aomine, 1974) and $\sim 300\text{--}400\text{ m}^2\text{ g}^{-1}$ as measured by BET (N_2) adsorption (Brunauer *et al.*, 1938) at elevated temperatures (Ackerman *et al.*, 1993; Pohl *et al.*, 1996). Furthermore, imogolite was shown to be reactive towards anions and cations (Farmer *et al.*, 1983; Wada, 1989). These properties make imogolite an important soil constituent in the soils where it occurs; unfortunately, the mechanisms of ion sorption to this mineral are not known in detail. To understand fully the surface chemistry of imogolite, it is necessary to analyze the crystal structure of imogolite.

Imogolite displays several unusual features that have not been satisfactorily explained from the present knowledge of the imogolite structure: (1) Imogolite never occurs as single fibers but always in bundles in close hexagonal packing (Farmer *et al.*, 1983; Pohl *et al.*, 1996; Hoshino *et al.*, 1996). (2) Although some imogolite samples have a very low reactivity towards phosphate, imogolite always sorbs chloride in appreciable amounts (Clark and McBride, 1984). In addition, chloride adsorption may be constant over a wide pH range and largely equimolar with sodium adsorption when NaCl is added (Clark and McBride, 1984; Su *et al.*, 1992). (3) Electrophoretic mobility studies suggest a very high point-of-zero charge (PZC) of the

outer parts of the imogolite tubes, *i.e.*, above pH 11 (Harsh *et al.*, 1992; Su and Harsh, 1993).

To explain (2), Clark and McBride (1984) suggested that intercalation of NaCl occurs. Harsh *et al.* (1992) speculated that imogolite carried a weak structural positive charge. It is clear that such a structural charge cannot involve substitutions such as Al for Si, because nuclear magnetic resonance (NMR) studies have shown imogolite to consist exclusively of hexavalent Al and unpolymerized, tetravalent Si (Goodman *et al.*, 1985; Ildefonse *et al.*, 1994). In this paper, I argue that differences in Al–O bond valences can explain why the outer walls of imogolite may develop a weak positive charge that is constant over a wide pH range, whereas the inner walls develop a weak negative charge. By using a Basic Stern Model approach inspired by the recent gibbsite investigations of Hiemstra *et al.* (1999), it is shown that this may provide explanations for the three phenomena given above.

THE STRUCTURE OF IMOGOLITE

The only effort to present a detailed structure for imogolite was made by Cradwick *et al.* (1972). Figure 1 shows a cross-section of a synthetic imogolite tube, as well as a sketch of the structure along the tube axis. The repeat distance between each tube unit along the tube axis is 8.4 \AA . The outer diameter of natural imogolite tubes is $\sim 20\text{ \AA}$, whereas the inner diameter is 10 \AA . For imogolite synthesized at 100°C , these distances are greater (*i.e.*, ~ 23 and 11 \AA) owing to the incorporation of more molecular imogolite units in one unit cell of the tube. The values given above are “average” values from several sources (Cradwick *et al.*, 1972; Farmer *et al.*, 1983; Wada, 1989; Pohl *et al.*,

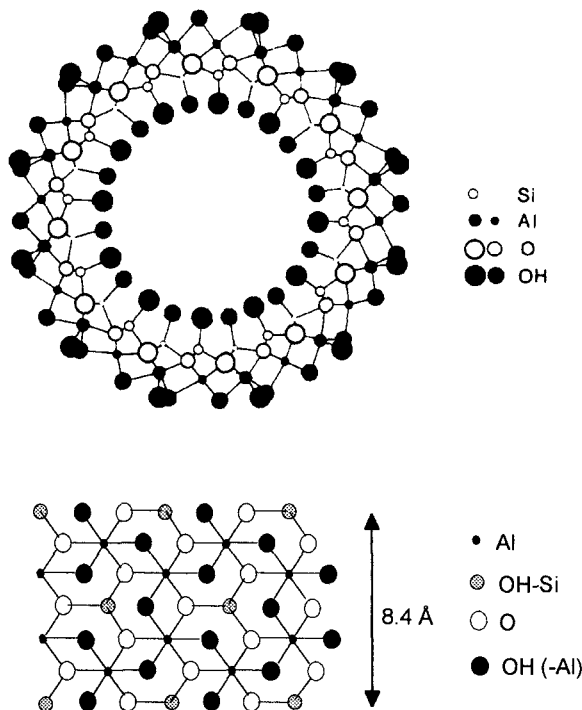
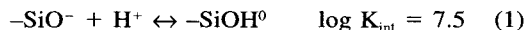


Figure 1. Top: A cross-section of the structure of a 14-molecular unit imogolite tube (from Goodman *et al.*, 1985). Bottom: Schematic view of the structure of the imogolite cylinder. Note that all hydroxyls bonded to Al are doubly coordinated; singly coordinated hydroxyls are found only on the tube-ends.

1996). A unit cell of a tube contains ten molecular units of imogolite (*i.e.*, ten Si atoms and 20 Al atoms) for natural imogolite (Cradwick *et al.*, 1972; Pohl *et al.*, 1996), whereas synthetic imogolite is thought to contain either 12 or 14 molecular units (Farmer *et al.*, 1983; Pohl *et al.*, 1996).

The formation of imogolite is believed to occur in a gibbsite sheet through the displacement of three hydroxyl groups surrounding a vacant octahedral site by an orthosilicate anion. This requires a considerable shortening of the O–O distances around the site (to <3 Å), which causes the gibbsite sheet to curl, and form a tube. Doubly coordinated $-\text{Al}_2\text{OH}$ groups are found on the outer tube walls, whereas the inner tube walls consist of $-\text{SiOH}$ groups.

In general, doubly coordinated $-\text{Al}_2\text{OH}$ groups occurring on Al oxide minerals are uncharged over a wide pH range (0–11.9). Moreover, surface complexation of ions by these groups is not considered possible. Consequently, it may be assumed that the outer tube walls are unreactive towards ions. On the other hand, the $-\text{SiOH}$ groups on the tube interior may develop negative charge at high pH, according to the following reaction valid for the surfaces of hydrated SiO_2 -type minerals (Hiemstra *et al.*, 1989):



where K_{int} is a surface acid-base constant which includes an electrostatic correction term. From the structure of Cradwick *et al.* (1972) imogolite would be expected to be predominantly negatively charged over a wide pH range, and unreactive towards anions. However, this is not the case. From electrolyte ion-adsorption data, the overall PZSE (point-of-zero salt effect) of imogolite has been estimated to be between pH 6–8 (Wada, 1989; Harsh *et al.*, 1992; Denaix *et al.*, 1999). Imogolite may also sorb phosphate strongly (Theng *et al.*, 1982; Clark and McBride, 1984). These observations may be at least partly explained by singly coordinated $-\text{AlOH}^{1/2-}$ groups on tube-ends and by any $\text{Al}(\text{OH})_3$ infillings. The $-\text{AlOH}^{1/2-}$ groups may protonate according to the following reaction:



where K_1 is the surface acid-base constant. The value of K_1 implies that $-\text{AlOH}_2^{1/2+}$ predominates below pH 10. This would also indicate that the PZC of the tube exterior (outer walls + ends) is at pH ~ 10 . This value is not far from the observed value of pH > 11 (Harsh *et al.*, 1992) but it is still clearly lower. In addition, the presence of the $-\text{AlOH}^{1/2-}$ groups in combination with uncharged $-\text{Al}_2\text{OH}$ groups does not explain why chloride sorption was substantially higher than phosphate sorption (in a NaCl matrix), as observed by Clark and McBride (1984).

HYPOTHESIS: TUBE WALLS MAY HAVE STRUCTURAL CHARGE

The observed surface properties are explained with a model that allows the outer tube walls to have a weak positive charge, which is constant over a wide pH range. This may be the case if the mean bond valence of the Al–O bonds of the $-\text{Al}_2\text{OH}$ groups is >0.5, which is the expected value if these groups are uncharged in the pH range of 0–11.9 (Hiemstra *et al.*, 1999). High bond valences may result from the Al–O bond lengths being affected by the incorporation of orthosilicate anions in the gibbsite sheet. The shortening of the O–O distances and the decreased repeat distance between adjacent tube units along the tube axis cause substantial changes of the bond angles of the Al octahedra that form the outer part of the imogolite tubes. The bond lengths may also be affected.

As shown in Table 1, the calculation method of Brown and Altermatt (1985) results in surprisingly small errors in the bond valence sums if a ten-molecular unit cell of the tube is assumed. These data do not indicate any structural charge. In the calculations, all surface oxygens were assumed to form two hydrogen bonds with H_2O , so that the mean bond valence (in electrostatic valency units, esu) of O–H bonds plus O...H bonds was approximated to 1 esu (0.80 + 0.20).

Table 1. Bond lengths (Å), the corresponding bond valences¹, and bond valence sums (BVS) for the imogolite structure (ten-molecular unit cell of the tube) of Cradwick *et al.* (1972).

Atoms	Bond lengths (Å)	Bond valences
Si–O(H)	1.62	1.011
Si–O	1.72; 1.58; 1.58	0.771; 1.126; 1.126
Al–O	1.86; 1.89; 2.00	0.568; 0.510; 0.389
Al–O(H)	1.83; 1.96; 1.96	0.616; 0.434; 0.434
BVS (Al)		2.952
BVS (Si)		4.035
BVS (O) ²		1.987
BVS [O(H)] ³		1.989

¹ Calculated from: bond valence = $\exp[(\text{bond length} - R_0)/0.37]$ using the R_0 values of Brown and Altermatt (1985).

² Mean bond valence sum for the O atoms that bridge Si to Al.

³ Mean bond valence sum for the O atoms of the doubly coordinated $-\text{Al}_2\text{OH}$.

When a 12-molecular unit cell of the tube was assumed, the calculated bond valence sums deviated considerably from the ion valences (data not shown); this suggests that this model is unlikely for natural imogolite. However, Ildefonse *et al.* (1994) showed that the Al–O bond lengths of imogolite are probably much less diverse than those proposed by Cradwick *et al.* (1972), and therefore it seems likely that the ten-molecular unit cell model should be modified.

In the absence of more precise data for the imogolite structure, any alternative model for the bond angles and bond lengths is speculative. However, the most plausible scenario is that the mean Al–O bond length is slightly longer for the Al–O–Al bonds bridging the Si tetrahedra, as compared with the outer Al–OH–Al bonds. This produces bond angles for the Al–OH–Al bonds that are more in agreement with those of gibbsite; in addition, longer Al–O–Al bonds may be more energetically favorable to bridge the comparably small Si tetrahedra. If this is correct, the inner Al–O bonds have a mean bond valence of <0.5 esu, whereas the outer Al–O bond valence would be >0.5 esu, so that the sum is 3 esu. This, in turn, would cause a slight oxygen oversaturation on the outer $-\text{Al}_2\text{OH}$ groups (*i.e.*, the bond valence sum around the O atom is greater than the value of the oxygen valence of -2.0 esu) and a weak positive charge is created. To ensure a bond valence sum of 2 esu around each bridging O atom and 4 esu around each Si atom, the Si–O bonds which bridge Si to Al become shorter, whereas the innermost Si–O bond (of the $-\text{SiOH}$ group) is stretched, so that a negative charge is developed on the inner tube walls.

Any surface charge developed in this way must be neutralized by counterions in the diffuse and Stern layers. It is assumed that the surface charges always sum to an integer value, at least for each unit cell within the tube. In the modeling (see below), it was found that charges of 3 per unit cell of the tube required very

Table 2. Mean bond valences (in esu) resulting from the implementation of Model 1 and Model 2.

Bond	No. of bonds/ tube unit cell	Bond valence			
		Model 1		Model 2	
		$n = 10$	$n = 14$	$n = 10$	$n = 14$
Si–O(H)	n	0.9	0.928	0.8	0.856
Si–O	$3n$	1.033	1.024	1.067	1.048
Al–O	$6n$	0.483	0.488	0.467	0.476
Al–O(H)	$6n$	0.517	0.512	0.533	0.524

¹ n = Number of molecular imogolite units per tube unit cell.

low surface areas for the outer tube walls in the model ($<250 \text{ m}^2 \text{ g}^{-1}$), which was considered unlikely because of the higher surface areas that are inferred from theoretical grounds ($\sim 1300\text{--}1400 \text{ m}^2 \text{ g}^{-1}$) or from surface area measurements. The best results were therefore obtained when the charge of the outer tube wall was set at either +1 or +2 esu per cell, whereas the charge of the inside walls was symmetric (*i.e.*, -1 or -2 esu per cell). Because there are 30 $-\text{Al}_2\text{OH}$ groups and ten $-\text{SiOH}$ groups in each ten-molecular unit cell, this indicates that each $-\text{Al}_2\text{OH}$ group carries a charge of +0.033 or +0.067 esu, whereas each $-\text{SiOH}$ group has a formal charge of -0.1 or -0.2 esu. For a 14-molecular unit cell, the charges for each $-\text{Al}_2\text{OH}$ group are +0.024 or +0.048 esu, and for each $-\text{SiOH}$ group they are -0.072 or -0.144 esu. The bond valences that result from these two alternative models (henceforth referred to as Model 1 and Model 2) are presented in Table 2. No effort was made to calculate individual bond lengths.

One or even two anions cannot balance the collective positive charge from 30 or 42 surface groups that are distributed around the tube circumference, particularly because the imogolite tubes occur in closely packed bundles. Each anion is likely to bind to parts of several adjacent tubes. Following the structure of imogolite bundles determined by Hoshino *et al.* (1996) and Pohl *et al.* (1996), the most plausible arrangement is that each monovalent anion binds to 1/6 of two unit cells of three adjacent tubes, for Model 1. For Model 2, the anion will instead bind to 1/6 of one unit cell of three adjacent tubes. This may provide a possible explanation of why imogolite tubes are aligned in bundles, because diffuse anion binding would act to hold the tubes together.

METHODS

Modeling surface charge

For the modeling, the chemical equilibrium program Visual MINTEQ was used (Gustafsson, unpubl.). This program was modified from the MINTEQA2 code (Allison *et al.*, 1991) to include the Basic Stern Model (BSM) as described by Venema *et al.* (1996) and by Rietra *et al.* (1999). The ability to handle fractional

charges, and a routine for calculating concentrations of ions of the diffuse layers from the counterion charge density, were included. In the BSM, the charge-potential relationship of the surface (*o*) plane is given by:

$$\sigma_o = C(\Psi_o - \Psi_d) \quad (3)$$

where σ_o is the surface charge density in the *o*-plane (C m^{-2}), C is the Stern layer capacitance (F m^{-2}) whereas Ψ_o is the surface potential (V), and Ψ_d is the potential in the *d*-plane (*i.e.*, the head-end of the diffuse layer). The Stern layer capacitance for the tube-ends and outer tube walls was assumed to be the same as for gibbsite, *i.e.*, 0.9 F m^{-2} (Hiemstra *et al.*, 1999).

In the *d*-plane, the charge-potential relationship is given by the difference between the diffuse-layer charge and the *o*-plane charge. For the former, the Poisson-Boltzmann equation results in the well-known Gouy-Chapman equation in the case of a flat plane. The charge-potential relationship therefore becomes:

$$\sigma_d = \sqrt{8000RTc\epsilon_0 D} \sin h\left(\frac{F\Psi_d}{2RT}\right) - \sigma_o \quad (4)$$

where σ_d is the surface charge density in the *d*-plane (C m^{-2}), c is the concentration of a 1:1 background electrolyte, ϵ_0 is the permittivity of vacuum, D is the dielectric constant of water, F is the Faraday constant, R is the gas constant, and T is the absolute temperature (K). I assume that the tube-ends, with their singly coordinated $-\text{AlOH}^{1/2-}$ groups, can be viewed as flat planes. For the tube walls the situation is clearly different. For the cylindrically shaped outer tube walls, approximation of the Poisson-Boltzmann equation (Ohshima, 1998) results in the following expressions for σ_d :

$$\sigma_d = A\sqrt{8000RTc\epsilon_0 D} \sin h\left(\frac{F\Psi_d}{2RT}\right) - \sigma_o \quad (5)$$

$$A = \sqrt{1 + \left(\frac{1}{\left(\frac{K_0(\kappa r)}{K_1(\kappa r)}\right)^2} - 1\right) \frac{1}{\cos h^2\left(\frac{F\Psi_d}{4RT}\right)}} \quad (6)$$

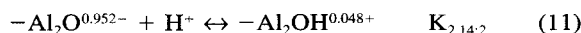
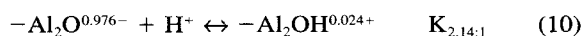
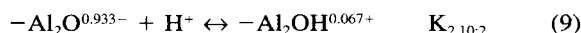
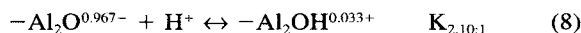
where K_0 and K_1 are modified Bessel functions of the second kind of the 0th and 1st order, respectively, r is the radius of the imogolite tube, and κ is the Debye-Hückel parameter which is defined as:

$$\kappa = \left(\frac{2000F^2c}{D\epsilon_0RT}\right)^{0.5} \quad (7)$$

For the inner tube walls, the description is extremely complex. In part, the complexity is related to the specific shape (rounded pores), which demands a numerical solution to the Poisson-Boltzmann equation. Also, the complexity is related to the extent counterions can freely diffuse in and out from these pores because of, *e.g.*, $\text{Al}(\text{OH})_3$ infillings on the tube-ends (Farmer *et al.*, 1983). Consequently, the surface charge properties of the $-\text{SiOH}$ groups were not modeled.

In the models, the influence of the diffuse layer overlapping from adjacent tubes was neglected. Although consideration of this effect would probably lead to more precise results, the mathematical problem is complex even in the relatively simple case of two adjacent planes (Behrens and Borkovec, 1999).

In accordance with the suggested surface charging (and with Hiemstra *et al.*, 1999), the acid-base equilibrium of Equation (2) was used for the singly coordinated $-\text{AlOH}^{1/2-}$ groups. For the $-\text{Al}_2\text{OH}$ groups of the outer tube walls, the following acid-base equilibria are defined:



where K_2 is the equilibrium surface acid-base constant and, for example, the subscript 10:1 is for the ten-unit cell having +1 charge per tube unit. To estimate values for these constants, the method of Hiemstra *et al.* (1996) and Venema *et al.* (1998) was initially followed. Hence the magnitude of the constants was estimated from:

$$\log K = -19.8\left(-2 + ms_H + n(1 - s_H) + \sum_i^{n_{st}} s_{i,st}\right) \quad (12)$$

in which m is the number of donating hydrogen bridges with adsorbed H_2O , n is the number of accepting hydrogen bridges, n_{st} is the total number structural bonds, $S_{i,st}$ is the bond valence of the i th structural Me-O or H-O bond, and s_H is the bond valence for an adsorbed proton. Assuming that each oxygen ligand can form two hydrogen bonds with solution (similar to the case for gibbsite), $m = 0$ and $n = 2$ and thus the values of $\log K_2$ were calculated to be 11.23, 10.55, 11.4, and 10.93, respectively. However, these values resulted in poor fits for the Cl^- adsorption data at high pH, and also in PZC values that were too low.

For the purpose of modeling, the $\log K_2$ values were increased by 1.3 (for Model 1, *i.e.*, the reactions involving +1 charge per unit cell of tube) or by 1.9 (Model 2) to obtain satisfactory fits. This is equivalent to $\log K_2$ values of 13.2 or 13.8, respectively, for the deprotonation of *uncharged* $-\text{Al}_2\text{OH}$ groups. The discrepancy in value between the calculated $\log K_2$ vs. the fitted values may be explained by any of the three following possibilities: (1) The model assumptions regarding the imogolite structure are incorrect. (2) Equation (12) does not adequately describe the deprotonation reaction of $-\text{Al}_2\text{OH}$. Indeed, very few data are available to test Equation (12) in the relevant pH range. (3) Part of the surface oxygen orbitals may not

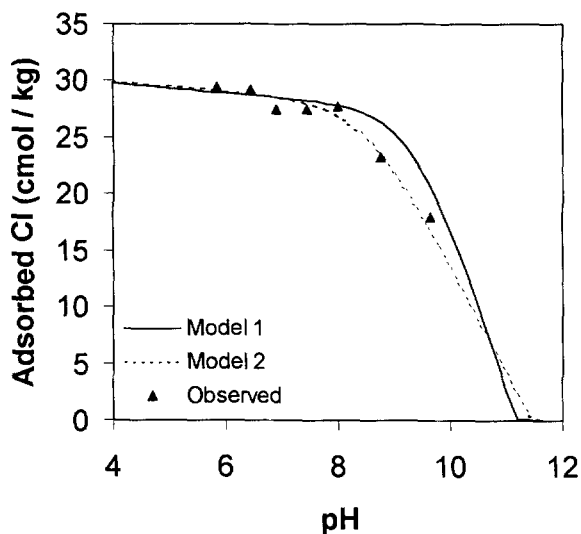


Figure 2. Measured chloride sorption from 0.1 M NaCl to KiG-imogolite (points; Clark and McBride, 1984) and fitted models. For model parameters, see Table 3. Suspension density: 20 g L⁻¹

be able to interact with H₂O, resulting in a higher log K₂ of Equation (12). Possibly, this may be related to the lack of H₂O in the intertubular pores, in combination with the hydration shell of the sorbed anion, which limits the availability of H₂O for bonding. Also, O...H bonds may form between adjacent surface oxygen atoms, thus reducing the available orbitals. If, for example, 1/3 of the -Al₂OH oxygen atoms are involved in such hydrogen bonding, Equation (12) predicts log K₂ values identical to those used in Model 1.

The models also included ion-pair formation with electrolyte ions. The ion-pair constant for Na sorption, K_{Na}, was set at 10^{0.2}, whereas a K_{Cl} value of 10^{-0.2} was used for Cl⁻ sorption (Hiemstra *et al.*, 1999). According to the model simulations, most Cl⁻ was adsorbed through diffuse-layer sorption except at pH < 5 in the synthetic imogolite data sets, where >50% was adsorbed as an ion pair to the -AlOH^{1/2-} groups.

Site densities for the -Al₂OH groups of the walls were calculated by assuming that the diameter for the ten-molecular cells of natural imogolite tubes was 20 Å whereas a value of 23 Å was used for the 14-molecular cells of synthetic imogolite. The calculated values were 5.68 and 6.92 sites nm⁻², respectively. On the tube-ends, the surface structure is not well known. From the imogolite structure, it may be assumed that there are ten or 14 singly coordinated -AlOH^{1/2-} groups on each end face, which results in a low site density (<4 sites nm⁻²). However, if there are any Al(OH)₃ inclusions, this number may be larger. In the modeling, a site density of 4 sites nm⁻² was used throughout for the -AlOH^{1/2-} groups.

Data selection

The following data sets were considered: (1) Cl adsorption, 0.1 M NaCl, KiG-imogolite (Clark and McBride, 1984); (2) Cl adsorption, 0.1 M NaCl, synthetic imogolite (Clark and McBride, 1984); (3) Cl adsorption, 0.01 M NaCl, synthetic imogolite (Su *et al.*, 1992); and (4) electrophoretic mobility, 0.01 M NaCl, synthetic imogolite (Harsh *et al.*, 1992)

The 0.01-M NaCl data of Clark and McBride (1984) were not used owing to insufficient information on the experimental conditions. The 0.1-M NaCl data of Su *et al.* (1992) were also not used because only ~1% of the Cl⁻ ions were adsorbed; this may have caused unreasonably large uncertainties in the solid-solution partitioning step.

RESULTS

KiG-imogolite

Because KiG-imogolite is a natural imogolite, a ten-molecular cell structure was assumed. Close agreement between model results and the observations of Clark and McBride (1984) were obtained for both structural models (Figure 2). The very weak pH dependence of Cl⁻ sorption below pH 9 compared well to the models. Table 3 summarizes the surface areas for the outer tube walls and tube-ends that resulted from fitting the data. Note that Model 1 required a total outer surface area of 837 m² g⁻¹, whereas Model 2 used an area of 445 m² g⁻¹. Only 10 m² g⁻¹ was assumed to be related to the -AlOH^{1/2-} groups located on the tube-ends. Areas for these groups in the range of 5–15 m² g⁻¹ caused little change in the fits, however.

The predicted value for the -AlOH^{1/2-} site concentration was compared with the PO₄ adsorption capacity measured in an equilibrium PO₄ concentration of 0.13 mmol L⁻¹ (values from Clark and McBride, 1984), and in 0.01 M CaCl₂. The equilibrium pH was not given, but is probably between pH 4.5–6 for this method (Theng *et al.*, 1982). Because PO₄ adsorbs to singly coordinated groups, but not to doubly coordinated groups, the -AlOH^{1/2-} site concentration should be comparable to the PO₄ adsorption capacity. In fact, the modeled -AlOH^{1/2-} site concentration was >2 times higher than the measured PO₄ adsorption, which is reasonable if most of the PO₄ adsorbs as bidentate complexes (*i.e.*, binding to two surface sites) and that full surface saturation was not obtained.

Synthetic imogolite

For synthetic imogolite, a 14-molecular cell structure was used. Synthetic imogolites often contain large amounts of non-tubular material, such as allophane, silica, *etc.* (Farmer *et al.*, 1983; Ackerman *et al.*, 1994). These impurities are probably why the concentration of the -AlOH^{1/2-} sites was much higher than

Table 3. Selected parameters of the models used, and PO₄ adsorption of Clark and McBride (1984).

	log K _s	Total surface area (m ² g ⁻¹)	Surface area, outer walls (m ² g ⁻¹)	Site conc., outer walls (mol kg ⁻¹)	Surface area, tube-ends (m ² g ⁻¹)	Site conc., tube-ends (mol kg ⁻¹)	PO ₄ adsorption ¹ (mol kg ⁻¹)
KiG-imogolite							
Model 1	12.53	837	827	7.8	10	0.066	0.032
Model 2	12.45	445	435	4.1	10	0.066	0.032
Synthetic imogolite (Clark and McBride, 1984)							
Model 1	12.7	940	765	8.79	165	1.10	0.30
Model 2	12.83	580	425	4.88	155	1.03	0.30
Synthetic imogolite (Su <i>et al.</i> , 1992)							
Model 1	12.7	940	810	9.31	130	0.86	—
Model 2	12.83	580	460	5.29	120	0.80	—

¹ Phosphate adsorption in 0.01 M CaCl₂, at an equilibrium PO₄ concentration of 0.13 mmol L⁻¹ P (Clark and McBride, 1984).

for KiG-imogolite to properly simulate the Cl sorption data (Figure 3) of Clark and McBride (1984). Reasonably good fits could be produced using both models, although Cl⁻ sorption at the highest pH (pH 9.8) was not well described. For the data (Figure 4) of Su *et al.* (1992), both models provided similar fits when a slightly smaller proportion of -AlOH^{1/2-} sites was used. Again, Cl⁻ sorption at the highest pH (pH 11.5) was underestimated with the model. The fits at high pH may be improved if the K_{Cl} ion-pair constant, in combination with the site density of the -AlOH^{1/2-} groups, was allowed to increase (data not shown). However, owing to the small amount of experimental data, it is possible that the model deviation was coincidental.

The higher -AlOH^{1/2-} site concentration for synthetic imogolite agrees with the PO₄ adsorption data of Clark and McBride (1984) (see Table 3). In this

case, the site concentration was between three and four times higher than the molar concentration of sorbed PO₄.

Figure 5 shows electrophoretic mobility (EM) data (Harsh *et al.*, 1992) for synthetic imogolite. These data are thought to reflect the zeta potential, located in the shear plane outside the imogolite tube; therefore, it is only the surface charge of the outer tube walls and tube-ends that contributes to the EM. The zeta potential cannot be directly compared to the model results, because it is not directly proportional to any model parameter, although it has some relationship with Ψ_d (Dzombak and Morel, 1990). Nevertheless, it is useful to compare the PZC for the outer tube walls + ends (from Figure 5 this value is estimated at pH 11 or slightly higher, where the EM is 0) to the modeled surface-charge data for this system. As seen in Figure

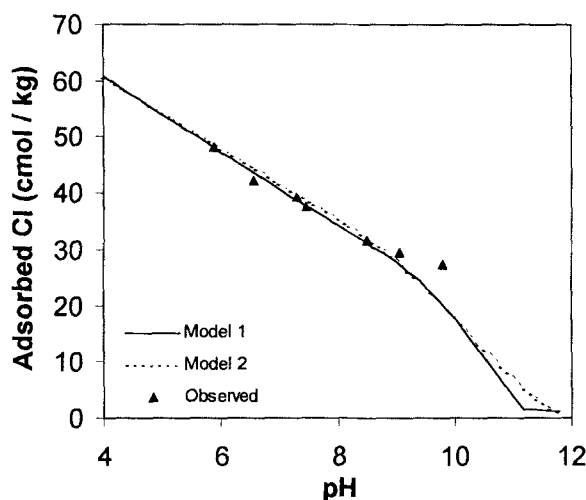


Figure 3. Measured chloride sorption from 0.1 M NaCl to synthetic imogolite (points; Clark and McBride, 1984) and fitted models. For model parameters, see Table 3. Suspension density: 20 g L⁻¹.

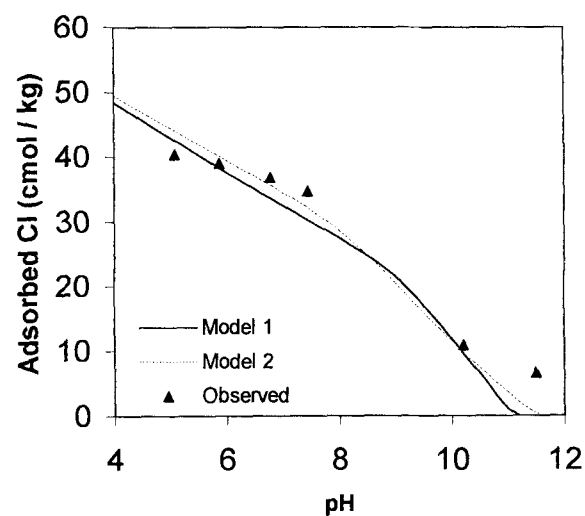


Figure 4. Measured chloride sorption from 0.01 M NaCl to synthetic imogolite (points; Su *et al.*, 1992) and fitted models. For model parameters, see Table 3. Suspension density: 2.5 g L⁻¹.

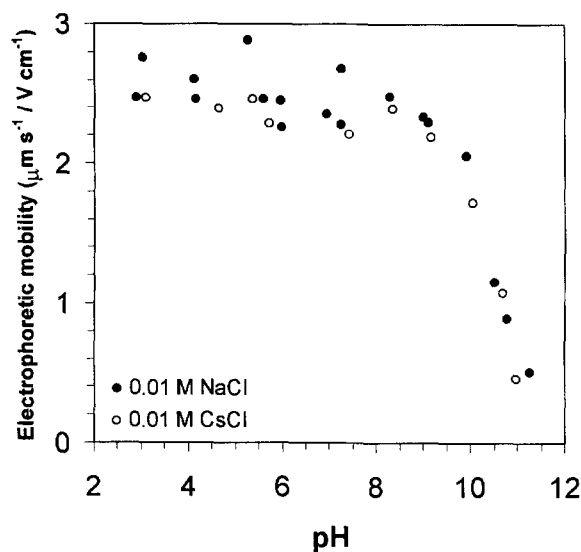


Figure 5. Electrophoretic mobilities for synthetic imogolite, measured by Harsh *et al.* (1992) in 0.01 M NaCl and 0.01 M CsCl. Suspension density: 0.1 g L⁻¹.

6, both models predict a PZC value of pH \geq 11 (11.0 in Model 1 and 11.4 in Model 2). To produce Figure 6, the modeled surface charges for the tube walls and for the tube-ends, which in themselves are the sums of the *o*- and *d*-plane surface-charge densities σ_o and σ_d , were expressed relative to the total surface area. The contributions from the two surfaces were then combined to yield the overall surface charge. Note that the tube walls had a nearly constant surface charge below pH 9, whereas the surface charge of the tube-ends decreased steadily with increasing pH.

DISCUSSION

From modeling alone, it is not possible to determine whether Model 1 or Model 2 is the better description of reality. Both models are able to provide reasonably good fits to the data where the modified log K_2 values are used. Model 2 seems to provide a better description for the KiG-imogolite (Figure 2). On the other hand, Model 1, which involves only one charge unit (esu) per unit cell of tube, may seem more probable where the modeled surface area is concerned; this agrees better with surface area measurements with ethylene glycol and with theoretical surface areas. In addition, the mean bond valences predicted by Model 1 depart less from the bond valences in the structure (Cradwick *et al.*, 1972) for the ten-molecular unit cells.

The model has been kept simple to describe the major trends of imogolite surface charge. It is quite possible that the true situation is more complex. For example, some singly coordinated $-\text{AlOH}^{1/2-}$ groups also may exist in defects or steps of the outer-wall struc-

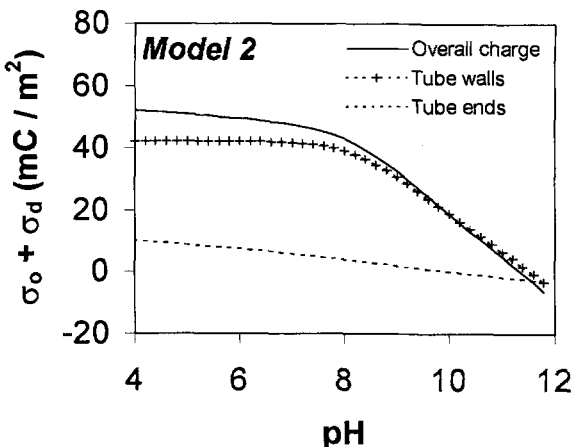
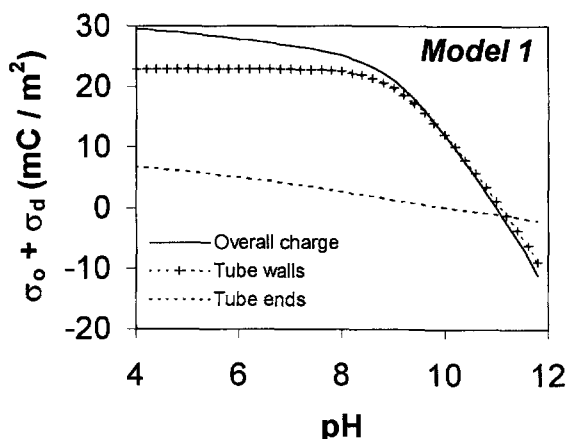


Figure 6. Modeled surface charge ($\sigma_o + \sigma_d$) for the synthetic imogolite data of Figure 5. Model parameters were the same as for the synthetic imogolite of Su *et al.* (1992), see Table 3.

ture. The presence of such groups would affect, for example, the pH dependence of the surface charging and the surface complexation of phosphate and sulfate ions. However, as emphasized above, singly coordinated $-\text{AlOH}^{1/2-}$ groups cannot be the only source of charge on the tube walls, because they do not explain the anomalously high PZC and the extremely low phosphate adsorption (as compared to chloride sorption) of some imogolites.

CONCLUSIONS

This paper suggests one possible hypothesis to explain the surface chemistry of imogolite; the models suggest the existence of doubly coordinated $-\text{Al}_2\text{OH}$ groups along the tube walls having a weak positive charge, whereas the $-\text{SiOH}$ groups on the tube interior may develop a negative charge. Despite the apparent

success of this approach, the model is clearly speculative and there are many uncertainties and assumptions involved. The amount of quality data against which the model may be tested is small. Therefore, the hypothesis may prove to be wrong. To test this hypothesis thoroughly, the following information would be desirable: (1) a more detailed structural analysis of imogolite, (2) more sorption experiments involving electrolyte ions, and (3) a more thorough understanding of the behavior of the surface oxygen atoms in the intra- and intertubular pores.

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