

Competitive Ion Exchange Behavior on Oxides

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ABSTRACT

Cation adsorption data using MnCl_2 and the proton isotherm of a Si oxide were compared with pH as the variable. The cation adsorption data quantitatively correlated with the proton isotherm analysis; the $\text{H}^+/\text{Mn}^{2+}$ exchange ratio was 6.0. The presence of adsorption plateaus are due to pH-dependent (step) reactions; this was suggested as the only reasonable explanation for adsorption isotherms covering several pH units. These plateaus are very important to surface adsorption modeling, and may be significant in determining experimental conditions for other soil and colloidal research. The proton isotherm obtained using the backtitration technique had some pH- and salt-dependent shifts that may involve competitive reaction mechanisms between the ions in solution and the oxide surface. Cation adsorption studies were also used to determine the total number of sites available; this resulted in an initial estimate of $13.6 \mu\text{mol m}^{-2}$. The authors review several topics related to ion exchange modeling and data interpretation; emphasis is placed on avoiding an oversimplified view of the chemical nature of the solid-aqueous phase.

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THE MAXIMUM NUMBER of sites (Γ_{max}) that a solid phase can support is an essential parameter for modeling ion adsorption. The Γ_{max} values can be determined based on potentiometric titration data (Huang, 1981); however, the mathematical manipulation of the data can be rather difficult. A problem with this method is that the proton isotherms obtained by the traditional potentiometric titration methods are not accurate due to the variable solubility effects of the solid phase. Schulthess and Sparks (1986) have developed a backtitration technique to correct for the pH-dependent solubility effects. From the resulting H^+ adsorption data, Γ_{max} values were determined by direct observation of the data without any further mathematical manipulations. Additionally, the cation exchange capacity (CEC) and anion exchange capacity (AEC) data, and the proton isotherm data (using the backtitration technique) both resulted quantitatively in the same adsorption isotherm values (Schulthess and Sparks, 1987).

The Langmuir (1918) equation has been used extensively in describing ion adsorption behavior, and the logical inclusion of a maximum adsorption limit makes it easy to use CEC and AEC data to estimate the Γ_{max} values. As is predicted by the Langmuir equation, the CEC or AEC values generally reach a max-

imum (the Γ_{\max} value) with increasing concentration of the exchanging ion. Additionally, the dependence of these values on pH has been described by Mattson (1931), Kurbatov et al. (1951), and many others. Subsequently, the CEC-AEC data are typically measured under specific pH conditions (e.g., soil pH or pH 7.00). If the CEC and AEC values are equal, the surface is assumed to have zero net charge. Thus, the highest ion adsorption values attainable are with high ion concentrations and at the extremely high or low pH values relative to the zero point of charge (ZPC).

For variable charge surfaces (e.g., oxides), traditional views state that CEC increases as pH increases because the solid phase (soil or colloid) has increased in negative charge. Similarly, AEC increases as pH decreases because the solid phase has increased in positive charge. Schematically, the surface charge reactions are



with surface-OH₂ existing at low pH values and adsorbing anions (high AEC), and surface-O⁻ existing at high pH values and adsorbing cations (high CEC). The adsorption phenomenon is predominantly an electrostatic attraction (nonspecific adsorption). However, cation and anion adsorption are also known to displace H⁺ cations and OH⁻ anions, respectively, from the surface. Thus, the concept of *exchange of bases* is extended to include the H⁺ and OH⁻ ions. Schematically, the ion exchange (specific adsorption) reactions



are in competition with the reactions in Eq. [1] and [2], where M⁺ = cation and L⁻ = anion. Equations [1] to [4] are commonly expressed for single site models; other similar equations have also been suggested (e.g., van Riemsdijk et al., 1987). The suggestion of a double protonation of surface sites (Bloom and Erich, 1987), or multiple ion adsorption bonds per surface metal site (Yariv and Cross, 1979, p. 249; Schulthess and Sparks, 1987), are relatively new concepts compared to multiple surface site models (Syers et al., 1973). It is generally assumed that the oxide surfaces consist of "clean" surface-OH groups; however, x-ray photoelectron spectroscopy (XPS) studies show increasing evidence of inorganic C contaminants existing on surfaces that have been exposed to air (Swift et al., 1983; Martin and Smart, 1987).

In traditional surface charge models, the specific adsorption of anions presumably decreases at high pH values due to the charge repulsion of the surface-O⁻ species, or to the reduced affinity for these sites. By comparing the Lewis base strengths of compounds, it is reasonable to suggest that if a ligand (L⁻) can replace an OH⁻ anion of the surface-OH species (Eq. [4]), then the same ligand would much more easily replace the H₂O molecule of the surface-OH₂ species. Instead, as the pH lowers, anion adsorption envelopes often show an adsorption maximum followed by an adsorption decrease (Hingston et al., 1967). The ligand exchange theory suggests that anion adsorption envelopes may be due to a decreased affinity for the sur-

face with increasing acidity of the aqueous ligand (Goldberg, 1985; Hingston et al., 1972; see also Sposito, 1984, p. 138–139). Hingston et al. (1972) correlated several pK_a values of conjugate acids with the pH of inflection; the only exception found was F⁻, which correlated well on goethite but poorly on gibbsite (the inflection was circa 1.5 pH units too high). An alternate theory for the observed adsorption envelopes of anions is a competitive ion exchange theory. Schulthess and Sparks (1988) suggested that models based on charge repulsion or attraction are not representative of the adsorption mechanism; instead, the surface was described as being always neutral. Thus, L⁻ anion adsorption envelopes are described in terms of OH⁻ anion competition at high pH values, and Cl⁻ anion (or conjugate base to the acid used for the acidic pH adjustments) competition at low pH values. Such a model applies to all anions; the ability for a given anion to compete with other anions depends on its concentration and Lewis base strength.

If there are two different ligands in the system, then there would undoubtedly be more reactions to consider. However, several adsorption studies on oxide surfaces have not considered significant the presence of the Cl⁻ anion introduced into various adsorption experiments by the pH adjustment procedure (addition of HCl). For example, Goldberg and Glaubig (1985) modeled B adsorption envelopes by several Al oxides at various pH values and did not consider the possibility of Cl⁻ anion competition at low pH; their acidic pH adjustments were made with HCl. Additionally, the aqueous species of B at low pH may have a reduced affinity for the oxide surfaces relative to the Cl⁻ anion. Adsorption of the Cl⁻ anion by Al surfaces is well documented (Hingston et al., 1972; Schulthess and Sparks, 1987). The exclusion of the Cl⁻ anion as a competitive species may be due to the assumption that nonspecifically adsorbed ions are generally non-competitive towards specifically adsorbed ions. For generating adsorption predictions, the principal issue should not be if the ions are specifically or nonspecifically adsorbed, but rather if the ions are competitive. Bingham and Page (1971) found the adsorption of B on the Ap horizon of a Hydric Dystrandepet was independent of SO₄²⁻ and PO₄³⁻ concentration but decreased slightly with Si. They further suggested that NO₃⁻ and Cl⁻ ions would probably show no competitive effects. We caution against making broad generalities between significantly different anions. The chemical behavior of sulfates is often difficult to interpret. For example, the presence of SO₄²⁻ ions increased the adsorption of another anion (SeO₃²⁻) by a Panhill (fine-loamy, mixed, thermic Typic Haplargid) soil (pH 6.5 to 8.5, Fig. 2 In Neal et al., 1987b). This may be suggestive of a "bridging" behavior of anions with other anions.

Specific and nonspecific adsorption have also been termed inner- and outer-sphere complexes (Hingston et al., 1967). An electrostatic attraction to the species in Eq. [1] and [2] by an ion would be considered an outer-sphere complex provided that at least one solvent molecule (e.g., H₂O) is present between the surface and the adsorbing ion (Sposito, 1984, p. 13). An inner-sphere complex would involve strong attractive forces and would be expected of ions that undergo

exchange reactions as illustrated by Eq. [3] and [4]. The presence of ligand exchange is generally considered sufficient evidence for the existence of an inner-sphere complex (rather than outer-sphere). In situ spectroscopic analyses offer more direct evidence for differentiating the inner- and outer-sphere surface complexes (Johnston and Sposito, 1987; Hayes et al., 1987). If the complex is inner-sphere, then the compounds involved should be included in mass action equations and rate laws (Stumm, 1986). However, outer-sphere complexes (or weakly adsorbing ions) should also be considered, at least as competitive ions, particularly at high concentrations. Schulthess and Sparks (1988) emphasized that both the hydrated outer-sphere and dehydrated inner-sphere adsorbed ions are successful in maintaining a net neutral surface charge; both are also involved in mass action equations.

The concepts of outer-sphere complexes and their assumed lack of competitiveness also "justify" the use of indifferent electrolytes. The identification of indifferent background electrolytes is based on potentiometric titration data as described by Lyklema (1984). If the pH of ZPC, as measured with a KNO_3 electrolyte, is shifted in the presence of another electrolyte, then the latter salt is considered specifically adsorbed; otherwise, the latter salt is considered an indifferent electrolyte. The KNO_3 electrolyte was assumed an indifferent electrolyte based on the equal compensation rule (Lyklema, 1984), which also assumed equal adsorption of the K^+ and NO_3^- ions when the surface is neutral. This procedure may be justified for determining the pH of ZPC (Schulthess and Sparks, 1987), but the equal compensation rule does not apply to the use of the indifferent electrolyte as an inert electrolyte. The use of an indifferent electrolyte to study surface charge behavior at various pH values overextends the basic assumptions of the equal compensation rule. That is, the indifferent electrolyte is indifferent only at a particular pH value; furthermore, it may behave competitively at all other pH values.

Another misuse of the indifferent electrolyte concept includes adsorption studies. Adsorption experiments generally include an indifferent background electrolyte (such as NaClO_4 , KNO_3 , or NaCl) at various concentrations with the justification that these ions will adjust the ionic strength without undue complications in the analysis (i.e., the ions should behave essentially as an inert electrolyte and/or competitive reactions may be excluded). However, these ions are known to adsorb on oxide surfaces; they are, therefore, not inert and may possibly be competitive with other reactions being studied. Note that the competitive behavior of an aqueous species is affected not only by its affinity for the surface, but also by the aqueous concentration present. Schulthess and Sparks (1987) suggested that all the background electrolytes are directly involved in the surface chemical reactions by cation and anion exchange (Eq. [3] and [4]), and that surface charge equations (Eq. [1] and [2]) do not adequately describe the surface adsorption phenomenon (Schulthess and Sparks, 1988). To assume that some ions are inert or noncompetitive background electrolytes may easily result in erroneous conclusions.

The exchange reactions outlined in Eq. [3] and [4]

suggest that the changes in H^+ and OH^- concentrations should be stoichiometrically related to the changes in L^- anion and M^+ cation concentrations in the bulk solution. The H^+ /cation stoichiometry, or exchange ratio, is based on a comparison of potentiometric titration data with cation removal data. The potentiometric data offer, in theory, the amount of protons adsorbed or desorbed by the surface. Some values reviewed by Schindler (1981) and Kinniburgh and Jackson (1981) show a trend in the H^+ /cation stoichiometric ratio with respect to pH; the ratio often increases with pH. Few OH^- /anion stoichiometry have been directly measured (Rajan, 1979; Schulthess and Sparks, 1987), but the methods are essentially the same as for the H^+ /cation ratio determinations. One should keep in mind that the measurements on the concentration of H^+ and OH^- ions desorbed were most probably overestimated if the potentiometric titration method used did not account for the variable solubility of the solid phase (Schulthess and Sparks, 1986). The dissolution of the solid phase acts as a source (or sink) for the protons in the aqueous phase. Another source of error in determining exchange ratios may occur when the solid phase is incorrectly assumed to be clean of impurities. If, for example, Ca^{2+} cations not only exchange with H^+ in a given exchange study, but also with, say, Na^+ cations, then an oversight of the parallel Na-Ca exchange would result in low estimations of the $\text{H}^+/\text{Ca}^{2+}$ stoichiometric exchange ratio.

In this article, we wish to make additional comments on the interpretation of adsorption data. For this purpose, the adsorption isotherms of a Si oxide were investigated with NaCl and MnCl_2 electrolyte solutions and with the backtitration technique (Schulthess and Sparks, 1986). We were not able to model the pH-dependent behavior of the Si oxide; we were, however, able to (i) characterize the proton isotherm behavior of a Si oxide, (ii) study the pH effects on cation adsorption, and (iii) correlate the cation adsorption isotherm with the proton isotherm. The Mn^{2+} cation was chosen for this study because it does not appreciably hydrolyze before precipitation occurs at pH near 8 (Baes and Mesmer, 1976).

MATERIALS AND METHODS

The colloid studied was SiO_2 made by J.M. Huber Corp. (Havre de Grace, MD) under the name Zeothix® 265. The manufacturer's specifications on this oxide are shown in Table 1. The manufacturing procedure for this Si oxide was described by Wason (1978).

Table 1. Huber Corp. specifications on Zeothix® 265.

SiO_2	89–92%
Al_2O_3	0–0.9%
Na_2O	0.5–1.0%
Na_2SO_4	Maximum 1.5%
R_2O_3	0.04–0.12%
Loss on ignition (1173 K)	3.5–5.5%
Density (298 K)	2.0 g mL^{-1}
Average particle size	1.5–2.0 μm
BET surface area (source)†	200–300 m^2g^{-1}
BET surface area (source)‡	192.4 m^2g^{-1}
BET surface area (washed)§	139.6 m^2g^{-1}

† Original Si oxide, manufacturer's specifications.

‡ Original Si oxide (see text).

§ Washed Si oxide (see text).

The oxide was acid washed with HCl (pH = 3.22, conductivity = 0.26 S m^{-1}) followed by eight water washings to a final conductivity of $3860 \mu\text{S m}^{-1}$ (pH = 5.5). The water used was purified through an ultrapure D8902 cartridge (Barnstead Co., Newton, MA) and N_2 purged for at least 15 min before each use. With each wash the sample was agitated overnight on a reciprocating shaker, and separated for 20 min on an RC-5B Sorvall centrifuge (DuPont Co., Wilmington, DE) at $11000 \times g$. An N_2 atmosphere was maintained at all times, except during the removal of the oxide from the centrifuge tubes.

After the eight water washings, the sample was again resuspended in water and used as the stock Si oxide suspension for all experiments; the stock suspension was maintained under an N_2 atmosphere at all times. Approximately 1 L of stock solution was prepared and found to have a suspension concentration of 141.2 g L^{-1} . The objective of these washings was to obtain a Si oxide suspension that was free of impurities, particularly CO_2 and Na_2SO_4 . Based on the observations discussed later in this article, this objective was not well met.

The adsorption behavior of H^+ ions on the Si oxide was determined by mass balance as outlined in the backtitration technique of Schulthess and Sparks (1986). The procedure was modified by adding 5 mL of Si oxide suspension to 30 mL of deionized water preadjusted to various pH values and electrolyte concentrations. The pH was adjusted with known quantities of either 0.24 M HCl or 0.24 M NaOH; the electrolyte used was NaCl. Some samples had 1.000 mL of 1.75 M or 0.0175 M MnCl_2 solution added instead of the NaCl; thus, these samples had an initial MnCl_2 concentration of 0.053 M or $5.3 \times 10^{-4} \text{ M}$. The total volume of each sample was 35 mL. The exclusion volume was estimated to be 0.353 mL. After equilibrating overnight, centrifuging, and filtering through 0.2- μm GA-8 Gelman filter paper, the weighed supernatant was backtitrated with either 0.03 M NaOH or 0.03 M HCl. The end point pH varied from 4.7 to 8.0 depending on the Si solubility. The highly soluble alkaline suspensions (pH > 8.8) had end points at pH ≤ 5.0 . The low solubility concentrations under acidic conditions (pH < 8) had end points at pH 8.0. The BET surface area (see Brunauer et al., 1938) of the Si oxide was determined with a Quantachrome Corporation (Syosset, NY) model QS-7 using N_2 and He gas mixtures; the samples were degassed overnight at 388 °K. The surface area of the original unwashed sample and the washed sample are shown in Table 1.

Prior to backtitrating, some samples were analyzed for Mn^{2+} concentration remaining in solution with a Perkin Elmer (Norwalk, CT) PE 5000 Atomic Absorption spectrometer. These samples were diluted with 2% CaCl_2 solution to minimize Si interferences. Several portions of each experiment were repeated to enhance the detail of the resulting curves. Ion chromatography (IC) analyses were also done for Cl^- and SO_4^{2-} concentrations in the presence of MnCl_2 at low concentrations ($5.3 \times 10^{-4} \text{ M}$) with a Waters (Milford, MA) IC-PAK anion column, a Waters 430 conductivity detector, and a borate-gluconate eluant buffer. On a Si oxide suspension at pH 6.00, the aqueous Na^+ concentration was measured with a glass Orion (Boston, MA) 86-11BN Na^+ ion selective combination electrode before and after addition of the MnCl_2 . No NaCl was added; the conditions were the same as those described above for the low MnCl_2 assays, except the equilibration time was approximately 10 min.

Propagation of error analyses were done on all the data. An error bar accompanies each symbol on the figures if the error spread was larger than the symbol drawn.

RESULTS AND DISCUSSION

Figure 1 combines data from two independent experiments: proton adsorption data and Mn^{2+} adsorption data. The Mn^{2+} adsorption data are on a different

scale (exactly one-sixth the proton isotherm scale); the percent removal scale for Mn^{2+} is included to allow for comparison with figures to be discussed later; and the Mn^{2+} data are offset relative to the proton adsorption data. No NaCl electrolyte was added in either of these experiments. The Mn^{2+} isotherm has boundary limits of 0 to 100%. The H^+ isotherm does continue to desorb to much larger values at pH > 7 (not shown); it also may continue to adsorb at pH < 2, limited only by the surface exchange capacity. Equivalent values of the adsorption axes in Fig. 1 are: 0% $\text{Mn}(\text{II})$ removal = $0 \mu\text{mol Mn}(\text{II}) \text{ m}^{-2}$ = $0.85 \mu\text{mol H}^+ \text{ m}^{-2}$ and 100% $\text{Mn}(\text{II})$ removal = $0.19 \mu\text{mol Mn}(\text{II}) \text{ m}^{-2}$ = $-0.28 \mu\text{mol H}^+ \text{ m}^{-2}$. The close match of these two sets of data from the two independent experiments reconfirms the idea that cation (Mn^{2+}) adsorption occurs as a stoichiometric exchange reaction (ratio = 6.0) with the surface cations (H^+ and all other surface species that induce an apparent H^+ exchange). The closeness-of-fit of these two independent experiments over a wide range in pH has been observed before by Schulthess and Sparks (1987) for the H^+ and Cl^- adsorption isotherms on an Al oxide. We emphasize that the use of the traditional potentiometric titration method, which does not consider the pH-dependent solubility of the solid phase, results in an erroneous set of proton adsorption data; that is, the consistent 6.0 exchange ratio over a wide pH range would not have been apparent.

The H^+ /cation ratio determined from the data in Fig. 1 is 6.0 protons removed per Mn^{2+} adsorbed. This does not necessarily indicate that one Mn^{2+} occupies six proton sites. Such a conclusion would imply an electroneutrality imbalance. We analyzed the aqueous Cl^- concentration since it was introduced with the HCl and MnCl_2 additions; no removal of aqueous Cl^- was detected. Sulfate-dependent reactions may be considered significant to the surface exchange reactions based on the information in Table 1. We observed a small increase in aqueous SO_4^{2-} concentration with decreasing pH (0.254 mM at pH 4.50 to 0.371 mM at pH

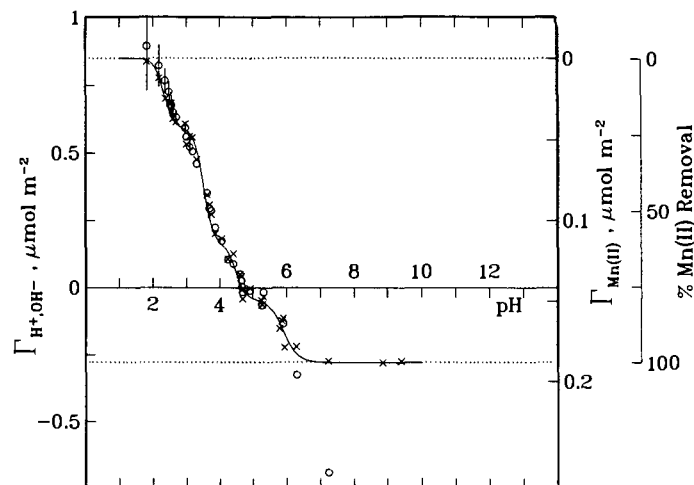


Fig. 1. Proton adsorption and $\text{Mn}(\text{II})$ adsorption isotherms. Initial $[\text{MnCl}_2] = 5.3 \times 10^{-4} \text{ M}$; no NaCl was added. Symbols (O) are for the proton isotherm data and are read by the adsorption values on the left vertical axis. Symbols (X) are for the $\text{Mn}(\text{II})$ adsorption data and are read by either the adsorption or percent removal values on the right vertical axes.

1.85). Since this trend was expected for increasing pH values, this behavior remains poorly understood at this time. We suggest that our SO_4^{2-} data may be a result of complex ion interactions. Our emphasis here, however, is not to prove that a particular equation(s) accurately represents the surface chemical reaction(s), but rather to state that proton/cation exchange ratios based on aqueous phase cation exchange data may sometimes be *apparent surface cation exchange ratios*. We are also suggesting that cations do not necessarily have to exchange directly with protons (or other cations), but may also exchange indirectly via anion-dependent mechanisms.

A pH-dependent reaction in a completely aqueous solution generally occurs within a narrow pH range (≤ 2 pH units); one should keep in mind that each pH unit corresponds to a 10-fold change in H^+ (or OH^-) concentration. Consequently, the occurrence of a single pH-dependent reaction that spans five pH units (equivalent to a 10^5 -fold change in H^+ concentration), is nearly impossible to conceptualize. The answer lies in the phenomena being most probably a result of several pH-dependent reactions. A similar rationale applies to solid-aqueous phase reactions, like the Mn^{2+} adsorption reaction observed in Fig. 1 that spans five pH units. If the solid-aqueous phase is subject to several pH-dependent reactions (or step reactions), then the adsorption isotherm patterns would also show several pH-dependent steps (or plateaus) and thus span several pH units. Figure 1 shows that at least three plateaus may be present (at pH 2.9, 4.0, and 5.2). The solid line drawn in Fig. 1 merely highlights these plateaus; it is not the adsorption prediction of any particular surface speciation model.

Each plateau (or step) in Fig. 1 corresponds to a transition zone between two chemical reactions; i.e., the completion of one type of reaction, and initiation of another type of reaction. From classical titration theory and interpretation of titration curves, each pH-dependent reaction is 50% completed (or 50% titrated) at the pH value between the plateaus. These are not due to an electrostatic sequence of reactions between a charged surface and the counterions in the bulk solution (Schulthess and Sparks, 1988). Instead, each sequence of the surface exchange reactions varies in its affinity for the H^+ or OH^- ions and, consequently, also varies in the pH values (or range) where H^+ buffering is observed. Thus, Fig. 1 shows that the pH-dependent Mn^{2+} adsorption on Si oxide involves several pH-dependent reactions. From a modeling viewpoint, it is not reasonable to suggest that a single reaction (expressed graphically as a single line with no plateaus or kinks) can span 5 pH units. One should realize that use of exponential correction terms for surface adsorption modeling is also not easily justified (Schulthess and Sparks, 1988).

Plateaus of this nature have gone unnoticed by many researchers. A particularly significant study by James and Healy (1972) reported similar data with Co(II) , Cr(III) , and Fe(III) removal by a Si oxide. However, they did not allude to the existence of plateaus even though their data showed plateaus nearly 1 pH unit wide for both Cr(III) and Co(II) . Furthermore, their data could easily be sectioned into discrete pH-independent regions. Other examples of plateaus in cation

removal vs. pH data include: NH_4^+ by a Chernozemic soil (Wada and Okamura, 1980), Na^+ by alkali soils (Gupta et al., 1985) and by kaolinite (Ferris and Jepsen, 1975; Bolland et al., 1976), Pb^{2+} by Al oxide (Hohl and Stumm, 1976), and Cu^{2+} by Fe oxide (Wang and Stumm *In* Stumm, 1986). These observations are not unique to cations; anion adsorption isotherms also display very clear plateaus, including: PO_4^{3-} , SiO_4^{4-} , and SeO_3^{2-} by goethite (Hingston, 1970 *In* Goldberg, 1985), SeO_3^{2-} by several alluvial soils (Neal et al., 1987a,b), and Cl^- by Al oxide (Schulthess and Sparks, 1987).

In all the observations cited above, the recognition that a plateau is present seems to depend on its size. Small plateaus (even 1 pH unit wide) can be ignored without excessive error or deviation from model generated predictions. However, the transitions between these plateaus are fingerprint images of the pH-dependent surface-aqueous phase chemical reactions. To free-draw a smooth curve while ignoring a series of plateaus (or steps) is most inappropriate. If such curves are model generated, then the model may be considered incomplete. Overly simplistic adsorption models often assume that the surface is clean, that the competitive nature of other ions is negligible, or that solubility phenomena are inconsequential. We strongly encourage that these complicating conditions be fully considered whenever surface adsorption modeling becomes the primary objective.

Undoubtedly, a large set of data is needed to locate the plateaus on a pH-dependent cation adsorption isotherm. Determining the location or pH value of these plateaus is important for surface adsorption modeling and various other research objectives. To illustrate this, imagine the isotherm in Fig. 1 for low Mn^{2+} concentrations with only five or six data points. One would probably have no hint of the existence of these plateaus, and consequently draw a line covering 5 pH units connecting the data. Firstly, from a modeling point of view, no single chemical reaction could justify such a broad pH range behavior. Secondly, it is easy to see how this may lead to further misinformation if the same researcher also performs experiments that

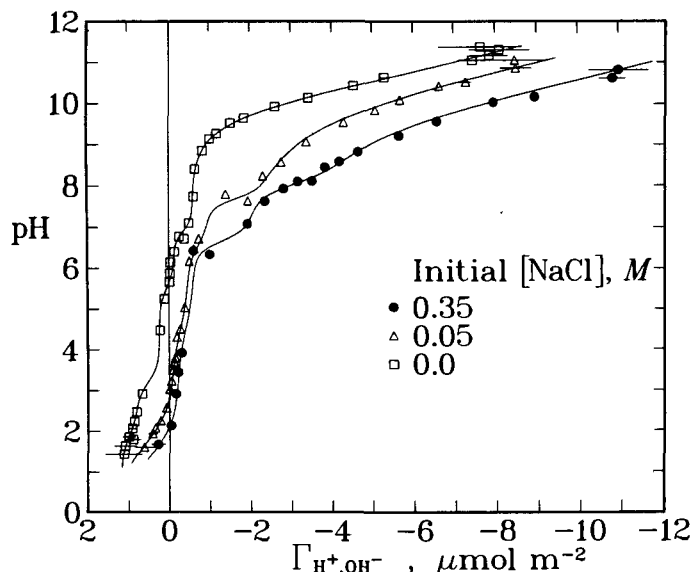


Fig. 2. Backtitration analysis of Si oxide at various NaCl concentrations.

are pH sensitive, e.g., rate of dissolution or adsorption experiments at an improperly selected fixed pH value. Note that at some pH values in Fig. 1, very small pH alterations result in large changes in the amount of cation removed; on the other hand, if the pH values are fixed at the location of the plateaus, then perhaps even moderate pH deviations may be tolerated without affecting the surface chemical characteristics.

The proton isotherm of the Si oxide is shown in Fig. 2 at various initial NaCl concentrations. A significant observation is that there are three salt-dependent shifts at pH 8.5, 7.0, and <6.0. The latter salt-dependent shift is composed of several small transitions from pH 1.5 (and perhaps lower) to 6.0. This implies the existence of salt-dependent and competitive reactions similar to those hypothesized for Al oxide (Schulthess and Sparks, 1987). The isotherms observed in Fig. 2 are believed to be due predominantly to the Si surface. The major reported metal impurity is Al (Table 1), yet the proton isotherms shown do not exhibit the isotherm patterns studied earlier for Al oxide (Schulthess and Sparks, 1987). That is, if Al impurities were significant, then several plateaus would be expected; namely at pH values near 2, 4, 7.5, and 9 (Schulthess and Sparks, 1987). The plateau at pH 7.5 is observed, but the others are missing; thus, the plateau at pH 7.5 is believed to be due to Si oxide. Furthermore, the salt-dependent shift at pH 8.5 was very small for Al oxide, whereas here, it is rather significant in magnitude. One may also argue that if Al were present in a significant quantity, the point of zero salt effect (PZSE) would probably be raised to higher pH values.

Another significant observation is that there is no PZSE present in Fig. 2; however, a PZSE may exist at very low pH values. Parks (1965) reports an average ZPC at pH 2.0 for Si oxides based on electrokinetic data. Schulthess and Sparks (1987) hypothesized that positive PZSE shifts on the proton isotherm data may be due to cation impurities present on the oxide prior to the titration analysis. Thus, this oxide may also have some cation impurities (e.g., surface-ONa groups) initially present in spite of the acid and water wash-

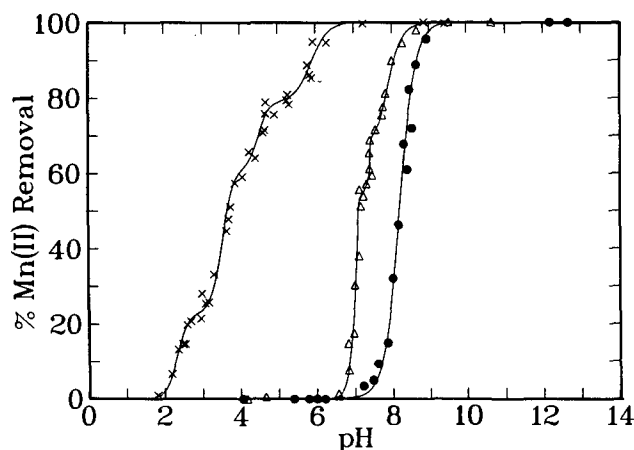


Fig. 3. Percent Mn(II) removal vs. pH. Symbols (x) and (Δ) are with Si oxide present; (●) are precipitation analyses in the absence of Si oxide. Initial $[MnCl_2] = 5.3 \times 10^{-4} M$ (x), and $0.053 M$ (Δ and ●). The low $MnCl_2$ concentration data are the same as those shown in Fig. 1. No NaCl was added to any of these experiments.

ings. This is consistent with the data shown in Fig. 1; i.e., a Na-Mn exchange would show no H^+ release by the surface. At pH 5.0 (the average equilibrium pH without acid or base additions), Fig. 1 shows 78.8% Mn(II) removal with almost no H^+ concentration change. The aqueous Na^+ cation concentration measured at pH 6.00 indicated $0.145 \mu mol m^{-2}$ desorption of Na^+ after addition of $MnCl_2$, while Fig. 1 shows $0.173 \mu mol m^{-2}$ of Mn(II) adsorbs at pH 6.00. Since the Na^+ desorbed accounts for only 42% of the charge balance, additional reactions must be occurring. It is clear, however, that the Si oxide surface was not properly cleaned of unknown impurities as was intended by the washing procedure.

The backtitration technique gives an accurate proton isotherm due to the correction for the pH-dependent solubility effects of the analysis. This is particularly important with Si oxide because of its extremely high solubility at the alkaline pH values; so much so, that nearly 1.0 mmol of NaOH is needed for the suspension to reach pH 10.5 (compared to 0.011 mmol for a blank). The excess NaOH added is consumed in forming aqueous species such as $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, $Si_4O_8(OH)_4^{4-}$, and $Si_4O_8(OH)_6^{2-}$ from the dissolved aqueous $Si(OH)_4$ species (Baes and Mesmer, 1976). This made it very difficult to raise the pH of the suspension while maintaining low propagation of error in the analysis. Consequently, the maximum adsorption value in the alkaline region was not observed due to the large solubility-induced buffering just described.

An attempt was made to determine, at least tentatively, the maximum number of sites (Γ_{max}) on the Si oxide using cation (Mn^{2+}) adsorption data rather than proton adsorption data. Figure 3 shows removal of $0.053 M Mn^{2+}$ by precipitation (Si oxide solid phase is absent) from pH 7 to 9 with 50% removal at pH 8.25. In the presence of Si oxide, removal began at pH 6.5 and showed a slight plateau at pH 7.3 (55% removal) and 7.6 (73% removal). Note that the data shown are from several different experimental assays. Since the system is poorly buffered, the pH readings must be done within minutes of opening each container to minimize atmospheric CO_2 contamination that tends to lower the pH readings. No NaCl electrolyte was added during these experiments. It is suggested that these plateaus correspond to maximum cation adsorption (i.e., Γ_{max}). At these pH values, the dominant aqueous metal species is $MnOH^+$; thus, the cation exchange is expected to behave as a monovalent exchange process. If each Mn^{2+} adsorbed occupies one site (surface- $OMnOH$), the estimated maximum adsorption capacities for 55 and 73% removal are 10.2 and $13.6 \mu mol m^{-2}$, respectively. The latter value seems to be realistic with respect to the data shown in Fig. 2. These are equivalent to 6.1 and 8.2 surface-OH sites per nm^2 ; these values compare well to the 5 surface-OH groups per nm^2 value for a silica gel reported by Yariv and Cross (1979, p. 253) based on a maximum adsorption of Na^+ cations at pH 10.5 to 10.6. A fully hydrated silica gel holds about 7.9 surface-OH groups per nm^2 based on crystallographic surface models and two -OH groups per surface-Si (Armistead et al., 1969; Iler, 1979, p. 636).

Peri and Hensley (1968) suggested that the possi-

bility of more than two -OH groups per surface-Si was "highly unlikely." The Mn(II) adsorption data (Fig. 3) would then correspond to 3.0 or 4.1 surface-Si per nm². It is conceivable that each surface-Si, with a valence of +4, may support as many as three -OH groups and still remain bonded to the solid phase; the surface-Si(OH)₃ species may be stable under extreme conditions, e.g., at very high pH values where extensive dissolution reactions readily occur. This may result in the backtitration technique showing larger desorption values than anticipated. That is, if the pH of the Si oxide suspension were raised to extremely high values, the backtitration technique may result in desorption values circa 20.4 μmol m⁻² in Fig. 2 corresponding to a surface-Si(OM)₃ species (where M = exchanging cation, e.g., Na).

The interpretation of the Γ_{\max} value from these plateaus (Fig. 3) is merely tentative at this time. It is believed that the initiation of precipitation as Mn(OH)₂(s) would result in increased (more pronounced) cation removal rather than the observed plateaus. Additionally, with increased cation removal by adsorption and lower cation concentration remaining in solution, the initiation of the precipitation reaction should be shifted to slightly higher pH values. Thus, these plateaus may correspond to a saturation of surface sites (i.e., the Γ_{\max} value). A complication with this type of analysis is that Na⁺ cation competition may be significant. At pH 7.3 and 7.6 the concentrations of Na⁺ cations, introduced as NaOH alkaline pH adjustments, were 0.054 and 0.071 M, respectively. Thus, these plateaus may be underestimating the Γ_{\max} value. One must not assume that the Mn²⁺ and MnOH⁺ cations can out compete the Na⁺ cations for the Si oxide surface sites at all possible concentrations. Additionally, if clustering occurs as was suggested by Bleam and McBride (1985), then the Γ_{\max} values would be overestimated. Nevertheless, the values obtained using this method were reasonable.

CONCLUSIONS

The proton isotherm behavior of the Si oxide showed pH and salt-dependent shifts. Modeling this Si oxide may involve competitive reactions similar to those discussed for Al oxide by the authors (Schulthess and Sparks, 1987); however, the available data are too incomplete to properly formulate a model at this time. The proton isotherm was relatively stable at pH < 6 compared to the alkaline conditions.

A tentative attempt to determine the total number of sites present, based on Mn²⁺ adsorption data at high concentrations, resulted in 10.2 and 13.6 μmol m⁻²; the latter value is believed to be more accurate. This is equivalent to 8.2 sites nm⁻² or 4.1 surface-Si nm⁻² if each Si is assumed to support two surface-OH groups.

The Mn²⁺ cation isotherm correlated extremely well with the proton isotherm analyses with a cation exchange ratio of 6.0 over a broad pH range. It is strongly suggested that the presence of plateaus be considered significant when studying cation (and anion) adsorption data. Surface adsorption models should at least be able to suggest the reactions involved to the left and right of each of the plateaus. Finally, stoichiometric exchange ratios may involve complex reaction

sequences that can result in erroneous conclusions if interpreted without mass balancing all the ions present in the system. All ions should be considered potentially competitive.

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