

Boron and Silicon Adsorption on an Aluminum Oxide

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ABSTRACT

Boron and Si adsorption on the Al oxide, α -Al₂O₃, were investigated under changing conditions of pH, total solution anion concentration, reaction time, and order of anion addition. Boron adsorption increased at low pH, exhibited a peak near pH 8, and decreased at high pH. The constant capacitance model was successfully used to describe B adsorption over the pH range 5 to 9 and at initial B concentrations ranging from 0.185 to 1.85 mol m⁻³ using only one adjustable parameter, the B surface complexation constant. Silicon adsorption was much greater than B adsorption and exhibited a broad maximum extending from pH 6 to 10. Simultaneous B and Si adsorption produced a small, significant reduction in B adsorption but had no effect on Si adsorption, indicating that some of the sorption sites showed anion preference. The magnitudes of the adsorption maxima for B and Si remained essentially constant for total reaction times ranging from 10 min to 24 d. The Al oxide was very soluble, solutions were supersaturated with respect to gibbsite after 10 min at pH 4.6 to 5.7. We therefore recommend short reaction times (<2 h) for the study of adsorption reactions on α -Al₂O₃ and amorphous Al oxide.

Additional Index Words: anion adsorption, ligand exchange, surface chemistry, constant capacitance model, FITEQL.

BORON is an essential plant nutrient. Since the concentration range in which plants exhibit neither B deficiency nor B toxicity symptoms is narrow, careful study of the reactions governing B availability in soils is necessary (Keren and Bingham, 1985). The magnitude of B adsorption in soils is governed by a variety of soil constituents including clay mineral type and content, Al oxide and Fe oxide content, organic matter content, soil pH, and soil salinity (Keren and Bingham, 1985). A significant correlation between B sorption behavior and the Al₂O₃ content of four Mex-

ican and six Hawaiian soils was found by Bingham et al. (1971), indicating that Al oxides play an important role in B sorption.

The pH-dependent adsorption reaction of B on amorphous Al oxides, pseudoboehmite, gibbsite, and assorted aluminas has been investigated previously (Scharrer et al., 1956; Sims and Bingham, 1968; McPhail et al., 1972; Choi and Chen, 1979; Goldberg and Glaubig, 1985). Boron adsorption in these studies was found to increase at low pH, exhibit a peak between pH 6 and 8, and decrease at high pH. Ligand exchange with reactive surface hydroxyl groups has been suggested as the mechanism of specific B adsorption on Al oxide minerals (Sims and Bingham, 1968; McPhail et al., 1972). Boron adsorption produced shifts in the point of zero charge (PZC) of Al oxide minerals, which are indicative of specific adsorption (Fricke and Leonhardt, 1950; Alwitt, 1972; Beyrouy et al., 1984). The constant capacitance model, a chemical model using a ligand exchange mechanism to account for specific adsorption (Stumm et al., 1980), successfully described B adsorption on various Al oxides (Goldberg and Glaubig, 1985; Goldberg, 1986).

Silicon has a beneficial effect on plant growth. In dissolved form it plays an important role in soil development. The adsorption behavior of Si on Al hydroxide and gibbsite has been investigated previously (Beckwith and Reeve, 1963; Hingston and Raupach, 1967; Hingston, 1970). Silicon adsorption was also found to be pH dependent; increasing at low pH, exhibiting a peak at pH 9 to 10, and decreasing at higher pH. Ligand exchange with reactive surface hydroxyl groups has also been suggested as the mechanism of specific Si adsorption on Al oxides (McPhail et al., 1972; Parfitt, 1978). Hingston (1970) observed shifts in the PZC of gibbsite upon Si adsorption, again indicating specific adsorption. The constant capacitance model successfully described Si adsorption on amorphous Al oxide (Goldberg, 1986).

Given that both B and Si adsorb on Al oxides by

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ligand exchange with reactive surface hydroxyl groups, investigations of their competitive adsorption are of interest. McPhail et al. (1972) found that increasing prior Si adsorption progressively decreased the B adsorption capacity of an amorphous Al oxide. From these results, the authors postulated that B and Si adsorb via ligand exchange with the same set of surface hydroxyl groups and that many of these sorption sites had been inactivated for B adsorption by prior Si adsorption. In contrast, Bingham and Page (1971) found that total B adsorption of an allophanic soil was affected only slightly by prior Si adsorption even when adsorption of Si equalled four times that of B. These authors concluded that B adsorption was unaffected by Si adsorption because it occurred on a set of sites specific to B.

Keren and Talpaz (1984) suggested that, similar to its adsorption mechanism on Al oxides, B is adsorbed via ligand exchange with reactive surface hydroxyl groups on the broken edges of clay minerals. In a previous paper (Goldberg and Glaubig, 1986), we studied the competitive adsorption of B and Si on the clay minerals kaolinite and montmorillonite from solutions containing both ions. Results showed that substantial Si adsorption affected the magnitude of B adsorption on kaolinite only slightly, whereas B adsorption on montmorillonite was unaffected by Si adsorption. We suggested that Si was able to adsorb on a set of sites unavailable for B adsorption and that the majority of B sorbing sites were specific to B.

Because of the contradictory nature of the available data and the uncertainty inherent in extrapolation of competitive adsorption results from soil and clay minerals, additional investigation of the competitive adsorption reaction of B and Si on Al oxide is warranted. The present study was conducted to obtain detailed data for the competitive adsorption reaction of B and Si on an Al oxide under changing conditions of pH, total solution anion concentration, reaction time, and order of anion addition. The constant capacitance model will be tested for its ability to describe the adsorption reactions.

MATERIALS AND METHODS

The Al oxide used in our study was a fumed alumina, alon, obtained from Cabot Corp. This material was identified as δ -Al₂O₃ using x-ray diffraction analysis. Specific surface area of the alon was 69.6 m² g⁻¹. This value was obtained from a multipoint Brunauer-Emmett-Teller (BET) N₂ adsorption isotherm determined using a Cahn electrobalance model RG and outgassing at 110 °C. The PZC of the alon was pH 9.7. This value was obtained by microelectrophoresis using a Zeta-Meter 3.0 system and a suspension containing 0.01% alon in 0.01 M NaCl.

Adsorption experiments were carried out in batch systems. Subsamples of 0.250 g of alon were added to 50-mL polypropylene centrifuge tubes and equilibrated with 25.0 mL of a 0.1 M NaCl solution by shaking for 20 min, 2, 4, or 20 h on a reciprocating shaker. This solution contained either B or Si at concentrations of 0.185, 0.463, 0.925, or 1.85 mol m⁻³ and had been adjusted to the desired pH using 1 M HCl or 1 M NaOH. Optimal additions of acid or base had been determined in preliminary analyses and produced <2% changes in total volume. The samples were centrifuged in a Servall superspeed centrifuge at 12 500 rpm for 30 min. Competitive adsorption studies were carried out with so-

lutions containing 0.925 mol Si m⁻³ in addition to the above B concentrations or containing 0.185 mol Si m⁻³ and 0.925 mol B m⁻³. Boron and Si were also added consecutively to study the order of anion addition and its effect on adsorption.

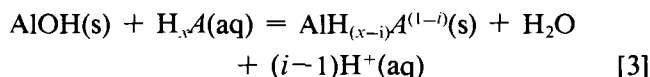
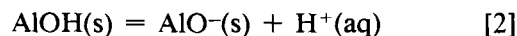
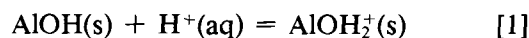
The decantates were analyzed for pH, filtered, and analyzed for B and Si concentration using a Technicon Auto Analyzer II. Boron was determined using the Azomethine-H method described by Bingham (1982), whereas Si was measured with the heteropoly blue method (American Public Health Association, 1976) using ascorbic acid as the reducing agent (Technicon Auto Analyzer II Industrial Method no. 105-71W/B).

Experiments to determine the effect of reaction time on adsorption were carried out in large batch systems. Subsamples of 4.0 g of alon were added to 500-mL polypropylene centrifuge bottles, equilibrated with 400.0 mL of a 0.1 M NaCl solution containing either 0.925 mol m⁻³ of B, Si, or both (pH adjustment as above) by shaking on a reciprocating shaker. After each reaction time (10, 20, and 40 min, 2, 4, 7, and 20 h, and 1, 2, 4, 8, 16, and 20 d), a 10-mL subsample of each suspension was pipetted into a 50-mL centrifuge tube, centrifuged, analyzed for pH, filtered, and analyzed for B and Si concentration as above.

Stability of the alon was evaluated by reacting it in the 0.1 M NaCl background electrolyte for 10 and 20 min. The decantates were analyzed for pH, filtered through a 0.1- μ m Nucleopore filter, and analyzed for soluble monomeric Al using the colorimetric method of May et al. (1979a).

The constant capacitance model is a surface complexation model that describes specific adsorption of ions by ligand exchange at the oxide-solution interface (Stumm et al., 1980). The model assumes that all surface complexes, including those formed with protons and hydroxyl ions, are inner-sphere and located in the same surface plane of adsorption. Formation of complexes with ions from the background electrolyte is not considered. A linear relationship between the surface charge, σ , and the surface potential, ψ , is assumed.

In the present model application, the following surface reactions are defined:



where AlOH represents 1 mol of reactive surface hydroxyls bound to an Al³⁺ ion in the mineral, x is the number of protons present in the undissociated form of the acid ($x = 3$ for B or $x = 4$ for Si), A is the completely dissociated form of the acid (BO₃³⁻ or SiO₄⁴⁻), and $1 \leq i \leq n$ where n is the number of anion surface complexes and is equal to the number of dissociations undergone by the acid ($n = 1$ for B or $n = 2$ for Si). The above reactions are represented by the following intrinsic conditional equilibrium constants:

$$K_+(\text{int}) = \frac{[\text{AlOH}_2^+]}{[\text{AlOH}][\text{H}^+]} \exp(F\psi/RT) \quad [4]$$

$$K_-(\text{int}) = \frac{[\text{AlO}^-][\text{H}^+]}{[\text{AlOH}]} \exp(-F\psi/RT) \quad [5]$$

$$K_L^i(\text{int}) = \frac{[\text{AlH}_{(x-i)}\text{A}^{(1-i)}][\text{H}^+]^{(i-1)}}{[\text{AlOH}][\text{H}_x\text{A}]} \exp[(1-i)F\psi/RT] \quad [6]$$

where F is the Faraday constant, ψ is the surface potential (V), R is the molar gas constant, T is the absolute temperature, square brackets represent concentrations (mol m⁻³),

and L is the adsorbing anion (B or Si). The mass balance for the surface functional group, AlOH , is

$$[\text{AlOH}]_T = [\text{AlOH}] + [\text{AlOH}_2^+] + [\text{AlO}^-] + \sum_i^n [\text{AlH}_{(x-i)}\text{A}^{(1-i)}] \quad [7]$$

and the charge balance expression is

$$\sigma = [\text{AlOH}_2^+] - [\text{AlO}^-] - \sum_i^n (i - 1) [\text{AlH}_{(x-i)}\text{A}^{(1-i)}] \quad [8]$$

where the net surface charge, σ , also has units of moles per cubic meter.

The computer program FITEQL (Westall, 1982) containing the constant capacitance model was used to fit intrinsic anion surface complexation constants to the experimental adsorption data. The intrinsic protonation-dissociation constants, $\log K_+(\text{int}) = 7.20$ and $\log K_-(\text{int}) = -9.50$, and the number of Si reactive surface hydroxyls, $[\text{AlOH}]_T = 0.25 \text{ mol kg}^{-1}$, for alon were obtained experimentally by Hohl and Stumm (1976). The number of B reactive surface hydroxyls, $[\text{AlOH}]_T = 0.137 \text{ mol kg}^{-1}$, and the capacitance density, $C = 1.06 \text{ F m}^{-2}$, had been obtained by FITEQL optimization (Morel et al., 1981) of the experimental titration data of Hohl and Stumm (1976).

RESULTS AND DISCUSSION

Boron adsorption as a function of pH is shown in Fig. 1a for four initial B concentrations. All four adsorption curves exhibit adsorption maxima near pH 8. Figure 1b similarly shows Si adsorption as a function of pH for four initial Si concentrations. The amount of Si adsorption was large; >90% of the initial Si was adsorbed over most of the pH range. Silicon adsorption curves exhibiting a similar degree of flatness have been observed previously for goethite (Sigg and Stumm, 1981). Silicon adsorption was nearly three times as high as B adsorption from initial solutions of identical molar anion concentration indicating that Si was adsorbed on alon with much greater affinity than B.

The effect of simultaneous Si adsorption on B adsorption is shown in Fig. 1c. Boron adsorption was significantly reduced by the presence of added Si; however, the amount of Si adsorbed was much greater than the reduction in B adsorption. On the other hand, simultaneous B adsorption had no effect on Si adsorption (Fig. 1b). The magnitude of Si adsorption was unaffected even in initial solutions having a B/Si ratio of 4:1 (data not shown). These results suggest that the majority of anion adsorption occurs on sites preferential to one of the anions. Evidence for non-uniform adsorption sites on alon has been presented previously (Benjamin and Leckie, 1980).

Additional evidence for the site-preference sorption hypothesis follows from Fig. 2, which shows the effect of the order of anion addition on B adsorption. Boron adsorption was greatest when B was added alone or before Si. The fact that B adsorption was similar for these systems indicates that once B is adsorbed on some of the sites it cannot subsequently be displaced by Si. Only slightly less B is displaced by a 0.1 M NaCl solution than by Si, indicating that B desorption is

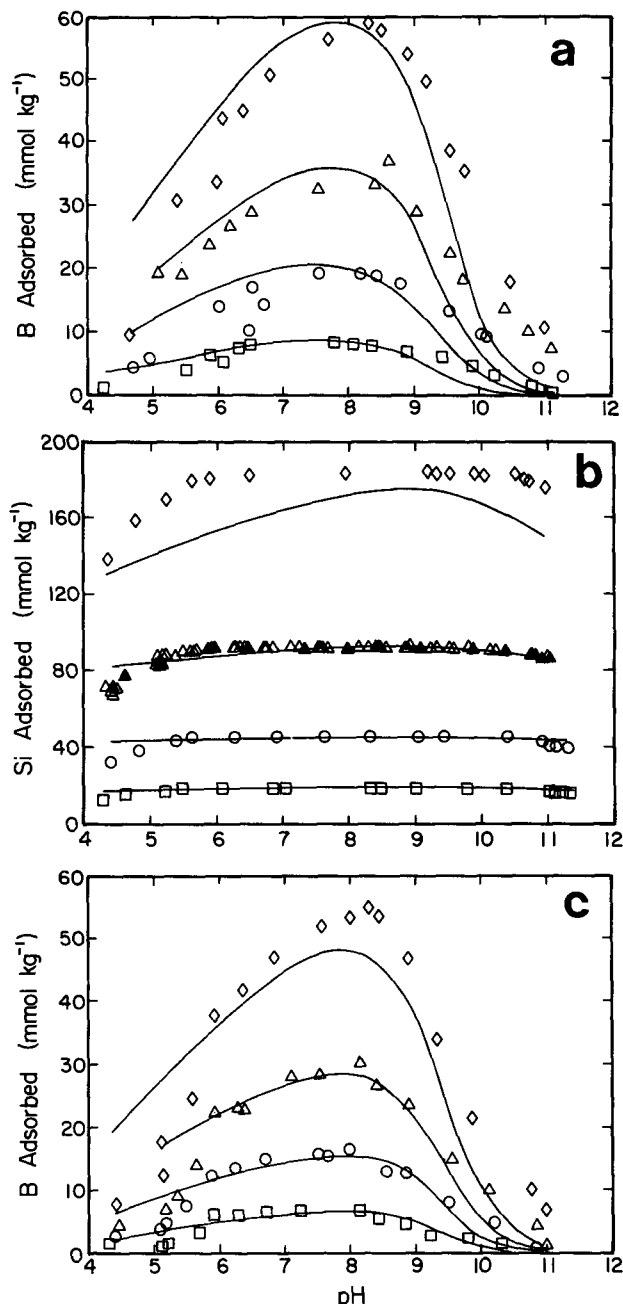


Fig. 1. Anion adsorption on alon: (a) B without added Si, (b) Si in the absence and presence of added B, and (c) B in the presence of 0.925 mol m^{-3} added Si. Symbols represent experimental data: squares B_7 or $Si_7 = 0.185 \text{ mol m}^{-3}$; circles $B_7 = 0.463 \text{ mol m}^{-3}$ (experimental data from Goldberg and Glaubig, 1985) or $Si_7 = 0.463 \text{ mol m}^{-3}$; open triangles $B_7 = 0.925 \text{ mol m}^{-3}$; closed triangles $Si_7 = 0.925 \text{ mol m}^{-3}$; diamonds B_7 or $Si_7 = 1.85 \text{ mol m}^{-3}$. Model results are represented by solid lines. Reaction time = 20 h.

slow (data not shown). Concomitant B and Si adsorption results in slightly lower B adsorption than in the aforementioned systems. The lowest amount of B adsorption is obtained when it follows Si adsorption. This result suggests that B cannot displace Si from some sites for which it can compete effectively in the presence of Si. Nevertheless, the effect of the order is small, indicating that some of the sorption sites prefer one or the other anion.

The constant capacitance model was able to de-

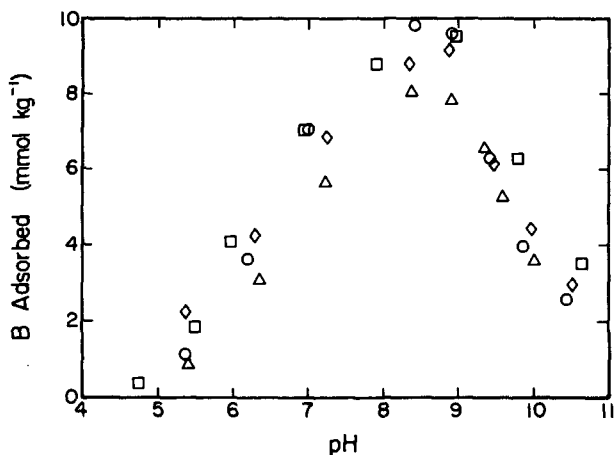


Fig. 2. Boron adsorption on alon. Squares represent B without Si addition. Circles represent B with subsequent Si addition. Triangles represent B with prior Si addition. Diamonds represent concomitant B and Si addition. $B_T = Si_T = 0.463 \text{ mol m}^{-3}$. Reaction time with each different solution was 2 h.

scribe B adsorption over most of the pH range and for most of the initial B concentrations (Fig. 1a and 1c). The same set of constants were used to describe adsorption at all four initial B concentrations. Under these conditions, $\log K_B(\text{int})$, the B surface complexation constant, was the only parameter that was optimized by the FITEQL program. Values of $\log K_B(\text{int})$ were 2.87 in the absence of added Si and 2.71 in the presence of added Si. This decrease in $\log K_B(\text{int})$ reflects the lower B adsorption in the presence of Si. The fit of the constant capacitance model to Si adsorption was not as good as for B (Fig. 1b). We believe that this difficulty is due to the broad, flat nature of the Si adsorption curves resulting from the high degree of Si adsorption over most of the pH range. Values of the Si surface complexation constants obtained for alon, $\log K_{Si}^1(\text{int}) = 4.14$ and $\log K_{Si}^2(\text{int}) = -3.17$, were in excellent agreement with those obtained by Sigg and Stumm (1981) for goethite, $\log K_{Si}^1(\text{int}) = 4.1$ and $\log K_{Si}^2(\text{int}) = -3.3$.

The effect of reaction time (10 min to 24 d) on the B, Si, and competitive adsorption reactions was studied in detail. The magnitude of the adsorption maxima over this time period remained essentially constant and the values were therefore averaged. Maximum adsorption in millimoles per kilogram was: 33.1 ± 1.0 for B alone, 26.9 ± 1.7 for B in the presence of Si, 94.7 ± 0.36 for Si alone, and 94.7 ± 0.53 for Si in the presence of B. The decrease in B adsorption maximum in the presence of Si was statistically significant at the 99% level of confidence; Si adsorption was unaffected by the presence of B.

Figure 3 indicates the effect of time on B adsorption as a function of pH for representative reaction times from the shortest to the longest. The location of the B adsorption maximum shifts to progressively lower pH values over time. We believe that this effect is due to the dissolution of alon and the precipitation of amorphous Al hydroxide or gibbsite over the course of the experiment. Previous results indicated that amorphous Al oxide and the poorly crystalline Al oxide, pseudoboehmite, exhibit a B adsorption maximum located about 1 pH unit below that of alon

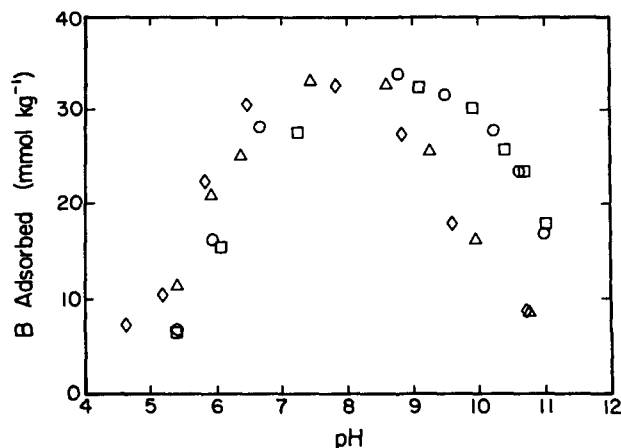


Fig. 3. Boron adsorption on alon. Squares represent 10 min; circles, 2-h; triangles, 1-d; and diamonds, 24-d reaction times. $B_T = 0.925 \text{ mol m}^{-3}$.

(Goldberg and Glaubig, 1985). Over the course of our experiments, the location of the B adsorption maximum shifted downward by about 1 pH unit, suggesting that a less soluble Al hydroxide might have formed.

Furrer and Stumm (1986) determined the reaction rate from pH 3.5 to 6.0 for the dissolution of aluminium oxide C. This material is also a $\delta\text{-Al}_2\text{O}_3$ and is very similar to alon in specific surface area and particle size. Using the reaction rates of Furrer and Stumm (1986), we calculated the length of time required for a sample of $\delta\text{-Al}_2\text{O}_3$ to release sufficient Al to produce a solution saturated with respect to gibbsite. Aluminum concentrations in equilibrium with gibbsite at pH values 3.5 to 11.0 in a 0.1 M NaCl background electrolyte were calculated using the chemical speciation program, WATEQ (Truesdell and Jones, 1974). We calculated that a suspension of $\delta\text{-Al}_2\text{O}_3$ becomes supersaturated with respect to gibbsite after 14 d at pH 4.5, 27 h at pH 5.0, 4.9 h at pH 5.5, and 2.4 h at pH 6.0.

Furrer and Stumm (1986) soaked their $\delta\text{-Al}_2\text{O}_3$ in dilute HF for 2 h before use. This treatment resulted in dissolution of about 40% of the initial material. Stumm et al. (1983) found that unwashed $\delta\text{-Al}_2\text{O}_3$ contained partially amorphous surface layers and thus exhibited a much higher dissolution rate than did washed $\delta\text{-Al}_2\text{O}_3$. Since we did not pretreat our alon material, the dissolution rates in our experiments should be much higher than those calculated above. Indeed, our alon sample was so soluble that solutions at pH values of 4.6, 4.9, and 5.7 were supersaturated with respect to gibbsite after 10 min. Solutions at pH values of 6.3, 7.4, 8.1, 9.2, and 10 were undersaturated after 20 min. We therefore recommend that $\delta\text{-Al}_2\text{O}_3$ be washed before use to reduce its dissolution. If the above solutions had contained Si in the initial concentrations of our experiments, they would also have been supersaturated with respect to kaolinite. We consider kaolinite precipitation to be unlikely after such short time periods. Aluminum must be present as a sixfold coordinated complex in solution for kaolinite precipitation to be possible at room temperature (Linares and Huertas, 1971).

Precipitation of gibbsite from supersaturated suspensions in the pH ranges 6 to 7 is not kinetically

hindered; convergence with the solubility line occurs within 2 h (May et al., 1979b). The rapidity with which δ - Al_2O_3 dissolves and gibbsite precipitates necessitates a short reaction time for adsorption studies, preferably <2 h. Our results indicate that the adsorption maxima for B and Si are constant after 10 min of reaction time. We consider a reaction time of 10 min to 2 h to be appropriate for future adsorption studies with δ - Al_2O_3 . We discourage the use of longer reaction times (such as the popular 1- and 2-d reaction periods) because of the danger of precipitation. We believe that our results are applicable to amorphous Al oxide, that, despite being less soluble than δ - Al_2O_3 , is also unstable relative to gibbsite. We therefore also recommend reaction times of 10 min to 2 h for the study of adsorption reactions on amorphous Al oxide. Short reaction times have been used previously for the study of Ca adsorption on hydrous γ - Al_2O_3 (Huang and Stumm, 1973, 15 min), acetate adsorption on montmorillonite (Bingham et al., 1965, 1 h), and adsorption of assorted metals and the anions selenite (Benjamin et al., 1982, 1 h), selenate, chromate (Benjamin, 1983, 2 h), sulfate, and thiosulfate (Davis and Leckie, 1978, 2 h) on amorphous Fe hydroxide.

REFERENCES

- Alwitt, R.S. 1972. The point of zero change of pseudoboehmite. *J. Colloid Interface Sci.* 40:195-198.
- American Public Health Association. 1976. Standard methods for the examination of water and wastewater. 14th ed. Amer. Public Health Assoc., New York. p. 490-495.
- Beckwith, R.S., and R. Reeve. 1963. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. *Aust. J. Soil Res.* 1:157-168.
- Benjamin, M.M. 1983. Adsorption and surface precipitation of metals on amorphous iron oxyhydroxide. *Environ. Sci. Technol.* 17:686-692.
- Benjamin, M.M., K.F. Hayes, and J.O. Leckie. 1982. Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation. *J. Water Pollut. Control Fed.* 54:1472-1481.
- Benjamin, M.M., and J.O. Leckie. 1980. Adsorption of metals at oxide interfaces: Effects of the concentrations of adsorbate and competing metals. p. 305-322. *In* R.A. Baker (ed.) Contaminants and sediments, Vol. 2, analysis, chemistry, biology. Ann Arbor Science, Ann Arbor, MI.
- Beyrouly, C.A., G.E. van Scoyoc, and J.R. Feldkamp. 1984. Evidence supporting specific adsorption of boron on synthetic aluminum hydroxides. *Soil Sci. Soc. Am. J.* 48:284-287.
- Bingham, F.T. 1982. Boron. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agronomy 9:431-447.
- Bingham, F.T., and A.L. Page. 1971. Specific character of boron adsorption by an amorphous soil. *Soil Sci. Soc. Am. J.* 35:892-893.
- Bingham, F.T., A.L. Page, N.T. Coleman, and K. Flach. 1971. Boron adsorption characteristics of selected amorphous soils from Mexico and Hawaii. *Soil Sci. Soc. Am. J.* 35:546-550.
- Bingham, F.T., J.R. Sims, and A.L. Page. 1965. Retention of acetate by montmorillonite. *Soil Sci. Soc. Am. J.* 29:670-672.
- Choi, W.W., and K.Y. Chen. 1979. Evaluation of boron removal by adsorption on solids. *Environ. Sci. Technol.* 13:189-196.
- Davis, J.A., and J.O. Leckie. 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environ. Sci. Technol.* 12:1309-1315.
- Fricke, R., and I. Leonhardt. 1950. Isoelektrischer Punkt und Pufferloesung. *Die Naturwissenschaften* 37:428.
- Furrer, G., and W. Stumm. 1986. The coordination chemistry of weathering: I. Dissolution kinetics of δ - Al_2O_3 and BeO. *Geochim. Cosmochim. Acta* 50:1847-1860.
- Goldberg, S. 1986. Chemical modeling of specific anion adsorption on oxides, clay minerals, and soils. p. 671-688. *In* P. Zannetti (ed.) Envirosoft 86. Proc. Int. Conf. Development and Application of Computer Techniques to Environ. Studies. 19-21 November. CML Publications, Southampton, England.
- Goldberg, S., and R.A. Glaubig. 1985. Boron adsorption on aluminum and iron oxide minerals. *Soil Sci. Soc. Am. J.* 49:1374-1379.
- Goldberg, S., and R.A. Glaubig. 1986. Boron adsorption and silicon release by the clay minerals kaolinite, montmorillonite, and illite. *Soil Sci. Soc. Am. J.* 50:1442-1448.
- Hingston, F.J. 1970. Specific adsorption of anions on goethite and gibbsite. Ph.D. diss. Univ. of West Australia, Nedlands.
- Hingston, F.J., and M. Raupach. 1967. The reaction between monosilicic acid and aluminum hydroxide. I. Kinetics of adsorption of silicic acid by aluminum hydroxide. *Aust. J. Soil Res.* 5:295-309.
- Hohl, H., and W. Stumm. 1976. Interaction of Pb^{2+} with hydrous γ - Al_2O_3 . *J. Colloid Interface Sci.* 55:281-288.
- Huang, C.-P., and W. Stumm. 1973. Specific adsorption of cations on hydrous γ - Al_2O_3 . *J. Colloid Interface Sci.* 43:409-420.
- Keren, R., and F.T. Bingham. 1985. Boron in water, soils, and plants. *J. Adv. Soil Sci.* 1:229-276.
- Keren, R., and H. Talpaz. 1984. Boron adsorption by montmorillonite as affected by particle size. *Soil Sci. Soc. Am. J.* 48:555-559.
- Linares, J., and F. Huertas. 1971. Kaolinite: Synthesis at room temperature. *Science* (Washington, DC) 171:896-897.
- May, H.M., P.A. Helmke, and M.L. Jackson. 1979a. Determination of mononuclear dissolved aluminum in near neutral waters. *Chem. Geol.* 24:259-269.
- May, H.M., P.A. Helmke, and M.L. Jackson. 1979b. Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C. *Geochim. Cosmochim. Acta* 43:861-868.
- McPhail, M., A.L. Page, and F.T. Bingham. 1972. Adsorption interactions of monosilicic and boric acid on hydrous oxides of iron and aluminum. *Soil Sci. Soc. Am. J.* 36:510-514.
- Morel, F.M.M., J.G. Yeasted, and J.C. Westall. 1981. Adsorption models: A mathematical analysis in the framework of general equilibrium calculations. p. 263-294. *In* M.A. Anderson, and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science, Ann Arbor, MI.
- Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. *Adv. Agron.* 30:1-50.
- Scharrer, K., H. Kuehn, and J. Luettmmer. 1956. Untersuchungen ueber die Bindung des Bors durch anorganische Bodenbestandteile. *Z. Pflanzenernaehr. Dueng. Bodenkd.* 73:40-48.
- Sigg, L., and W. Stumm. 1981. The interaction of anions and weak acids with the hydrous goethite (α - FeOOH) surface. *Colloids Surf.* 2:101-117.
- Sims, J.R., and F.T. Bingham. 1968. Retention of boron by layer silicates, sesquioxides, and soil materials: II. Sesquioxides. *Soil Sci. Soc. Am. J.* 32:364-369.
- Stumm, W., G. Furrer, and B. Kunz. 1983. The role of surface coordination in precipitation and dissolution of mineral surfaces. *Croat. Chem. Acta* 56:593-611.
- Stumm, W., R. Kummert, and L. Sigg. 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croat. Chem. Acta* 53:291-312.
- Truesdell, A.H., and B.F. Jones. 1974. Wateq, a computer program for calculating chemical equilibria of natural waters. *J. Res. U.S. Geol. Surv.* 2:233-248.
- Westall, J.C. 1982. FITEQL: A computer program for determination of chemical equilibrium constants from experimental data. Dep. of Chemistry, Rep. 82-01. Oregon State Univ., Corvallis.