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Carbonate Adsorption onto Goethite as a Function of pH and Ionic Strength

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Carbonate / Goethite / Adsorption / Isotherm

Abstract

The adsorption of carbonate onto goethite was studied as a function of both pH and ionic strength (NaClO₄ electrolyte) using ¹⁴C tracer. The pH ranged from 2.5 to 11.6. The ionic strength was controlled by varying the NaClO₄ concentration and ranged from 0.01 to 0.1 molar. The results indicate that carbonate is adsorbed on goethite as primarily an inner-sphere complex at pH values above the point of zero charge. This is inferred from the lack of dependence on ionic strength in the adsorption of carbonate. Below the point of zero charge carbonate is adsorbed by an additional outer-sphere mechanism. An adsorption isotherm was measured at pH 7.0 with an electrolyte concentration of 0.01M. Deconvolution of the isotherm proved that at least two sorption mechanisms exist. These mechanisms lead to large distribution coefficients at low pH. Thereby making the complete removal and exclusion of carbonate from an aqueous goethite system difficult, for the purpose of characterizing a "clean" goethite surface.

Introduction

The migration of radionuclides from a nuclear waste repository is expected to be retarded by sorption on minerals contained in the surrounding rock. Sorption being one of the interactions which make the geochemical barrier effective in preventing the release of radionuclides to the biosphere. Goethite, FeOOH, is an important mineral to study because it is known to have an affinity for actinides¹ and oxyanions^{2,3}. Most common minerals, including most clays and zeolites are cation exchangers at a pH typical of most groundwaters, (>6.5). Goethite typically has a point of zero charge of about pH 8.4⁴ and is therefore an anion sorber in many groundwaters. Chemisorption leads to sorption of many oxyanions (selenite⁵ for example) even at pHs above the point of zero charge. Iron oxides including goethite are common minerals in soil and rock. Carbonate has been found to adsorb on iron containing soils⁶. The adsorption of carbonate on goethite is of particular interest because carbon-14, a waste element contained in spent fuel, is not readily sorbed by more abundant minerals present in rocks. In addition the adsorption of carbon dioxide from the air by goethite is known to cause shifts on the point of zero charge for goethite determined by potentiometric titration⁷.

The adsorption of carbon dioxide on goethite surfaces has been studied by Russell et al. using infrared spectroscopy⁸. The author concluded that carbon dioxide was adsorbed at the C'-type oxygens⁹ which are exposed in the channels on the surfaces

which project onto the [100] plane. This crystallographic structure is illustrated in Fig. 1. The formal charge at the C'-type oxygen is -1/2. This charge is delocalized through the formation of a carbonate ligand and by hydrogen bonding with A-type hydroxyls on the goethite surface.

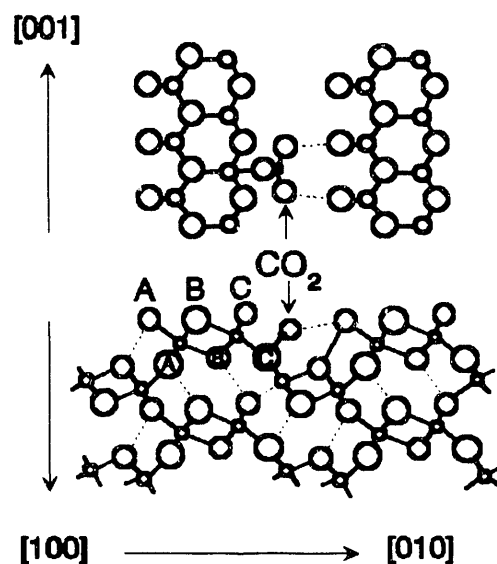


Figure 1. Crystallographic structure of Goethite showing position of adsorbed CO_2 (from Russell et al.⁸).

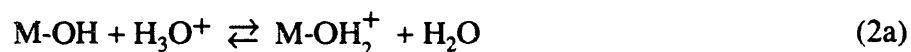
This paper will examine the adsorption of carbonate by radiochemically measuring the uptake of ^{14}C by goethite, as a function of pH, carbonate concentration, ionic strength, and time. The Carbonate adsorption isotherms will be analyzed using the deconvolution method^{10,11}.

The model which we will use to interpret the results of our experiments is the triple layer surface complexation model¹². The most important difference between this model and conventional chemical equilibria is the effect of surface charge on the activity of ions in the triple layer. This effect is calculated by multiplying the bulk solution concentration by a Boltzman factor,

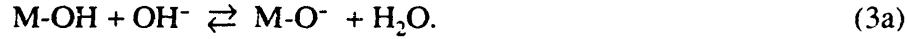
$$[\text{M}^+] = [\text{M}^+]_{\text{Bulk}} e^{-\left(\frac{e\psi_0}{kT}\right)}, \quad (1)$$

where, k is the boltzman constant, e is electronic charge, T is the temperature, and ψ_0 is the potential of the ion in the inner Helmholtz layer.

The charge on the metal oxide surface is produced by the amphoteric reaction of the metal oxide surface with acids and bases. The basic charge-producing reactions are with Bronsted acids and bases,

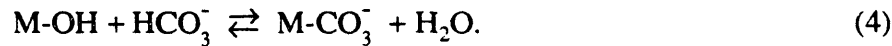


$$K_{a1}^{int} = \frac{[M-OH_2^+]}{[M-OH][H_3O^+]} e^{\left(\frac{e\psi_0}{kT}\right)} \quad (2b)$$

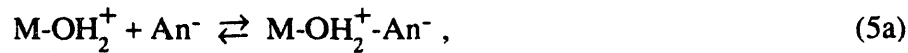


$$K_{a2}^{int} = \frac{[M-O^-]}{[M-OH][OH^-]} e^{\left(\frac{-e\psi_0}{kT}\right)} \quad (3b)$$

The surface charge can also be affected by the exchange or adsorption of Lewis acids or bases, (inner-sphere complexation). An inner-sphere complex is formed when the adsorbed ion is bonded in the inner Helmholtz layer. Inner-sphere complexes are strongly bonded and not affected by changes in the concentration of the background electrolyte. For example, we can postulate that bicarbonate oxygen replaces an oxygen on the metal oxide surface. The reaction describing this equilibrium is,



This reaction produces net negative charge on the surface. Cations and anions can interact with the electric field near the metal oxide surface by forming outer-sphere complexes. Ions can also be repelled from the aqueous phase near the metal oxide surface, as illustrated by eqn. 1. This can lead to the observation of negative distribution coefficients, K_{ds} . Negative K_{ds} are entirely realistic and lead to the correct prediction of more rapid migration of excluded tracer with respect to tritiated water, i.e., retardation factors less than 1.0. Outer-sphere complexation is represented in the following two equations,



$$K_{anion}^{int} = \frac{[M-OH_2^+-An^-]}{[M-OH_2^+][An^-]} e^{\left(\frac{-e\psi_\beta}{kT}\right)} \quad (5b)$$



$$K_{cation}^{int} = \frac{[M-O^--Cat^+]}{[M-O^-][Cat^+]} e^{\left(\frac{e\psi_\beta}{kT}\right)}, \quad (6b)$$

where ψ_{β} is the potential of the ion in the outer Helmholtz layer. The ions adsorbed in the outer layer can be exchanged for other ions. The ion exchange process would be expected to have selectivity differences due to factors such as ion size.

Experimental

Goethite was prepared according to a method of Atkinson et al.¹³ as described in more detail by Machesky and Anderson¹⁴. The goethite was prepared from A.R. quality reagents using a OH/Fe ratio of 2 in the preliminary aging step. The goethite was repeatedly washed with >16 megaOhm water until the conductivity no longer decreased with further washing. The conductivity of the rinse water in the last washing was less than or equal to 30 microSiemens (measured with a Philips PW-9529 conductivity meter). The N₂ BET surface area was 76 m²/g. Suspensions were prepared as needed from freeze-dried solid.

Traced solutions were prepared from a Amersham CF2 sodium [¹⁴C] carbonate stock solution. The sorption measurements were made holding a 0.01M ionic strength with a sodium perchlorate electrolyte. The pH was adjusted by adding perchloric acid or sodium hydroxide. The suspensions were made to a concentration of 0.2 grams of goethite per 10 ml. The solutions were contacted with goethite for 2 days before phase separation. The solid phase was separated by centrifugation at 12000 RPM for 1 hour using a Beckman model J2-21 centrifuge with a type JA-20.1 rotor. The aqueous phase was sampled by taking a 1 ml aliquot immediately after centrifugation. The solid phase was sampled by adding a 5 ml of a 1M sodium phosphate solution to the goethite and shaking. The phosphate displaces the carbonate from the goethite surface. After centrifugation the sodium phosphate is sampled and assayed. Solution concentrations were determined adding a 1 ml aliquot to 18 ml of Packard ULTIMA GOLD liquid scintillation cocktail. The activity was then measured in a liquid scintillation detector (Intertech SL-30, France).

The distribution ratio, K_d between the goethite (solid phase) and carbonate solutions were determined by two methods. One method utilized the solution concentration, only. The solid phase concentration was determined by the difference between the initial activity and the final activity, i.e., mass balance. The other method used the solid phase concentration as determined after treatment with sodium phosphate. Agreement between the two methods is required. The recovery of all initial tracer activity was also monitored and noted, particularly in the low pH measurements. Each measurement of K_d was performed using triple samples. Each measurement of radioactivity was made in triplicate to ensure the quality of measurements.

The measurement of K_d using the solid phase measurements is represented by the following formula,

$$K_d = \frac{(q_r - V_r c)}{c}, \quad (7)$$

where q_r is the wet solid phase specific activity, V_r is the residual water (determined by weight difference after drying solid sample), and c is the aqueous specific activity. If ion exclusion had occurred the concentration in the residual water would be less than the bulk aqueous concentration. The second method of calculating the distribution coefficient utilizes only the aqueous concentration.

$$K_d = \frac{(Vc_0 - Vc)}{mc}, \quad (8)$$

where c_0 is the initial aqueous concentrations, V is aqueous phase volume, and m is the mass of the dry solid phase. This approach is consistent with that in eqn. 7 and will also yield negative values if ion exclusion occurs.

Results and Discussion

The adsorption model for carbonate suggested by Russell⁸ et al. implies the possibility slow adsorption kinetics because the carbon dioxide molecules lies in a crystallographic channel somewhat below the goethite surface. If the carbonate is sterically hindered in entering the channel the kinetics could be affected. The distribution ratio for carbonate was measured as a function of time at a pH of 7.0. This pH was chosen because it is close to the equilibrium pH for a sodium bicarbonate solution in equilibrium with the air, thereby minimizing the loss or gain of atmospheric carbon dioxide. The K_d was measured in duplicate after 1, 2, 7, and 14 days, respectively. The pH remained constant at 7.01 ± 0.03 . The total ^{14}C was also monitored and a loss of nearly 10 percent was observed after 7 days and 25 percent after 14 days. The data are shown in Fig. 2. The data would appear to support slow kinetics if the isotherm were linear. When the data is corrected for loss of carbonate using the sorption isotherm the kinetics appears to be more rapid with full equilibration occurring within two days. The kinetics may therefore be slower than diffusion-limited but fast enough to allow sorption measurements after a two day contact time.

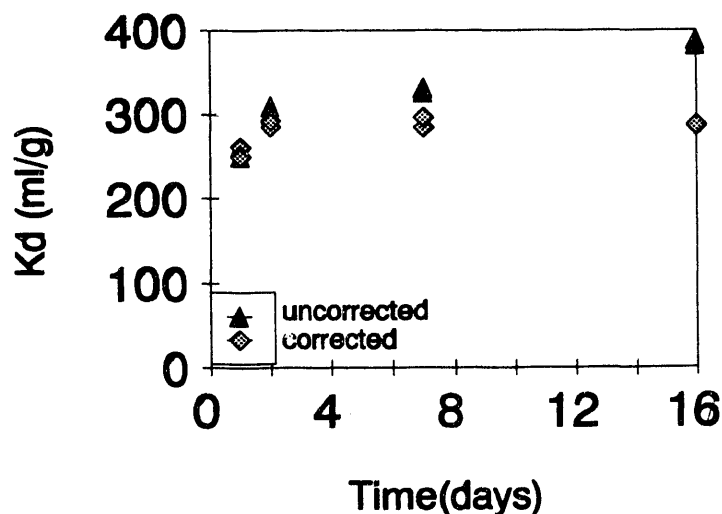


Figure 2. Time dependence of carbonate sorption. Data represented as diamonds were corrected for loss of carbon dioxide to the atmosphere.

The desorption of bicarbonate from goethite was monitored by bubbling inert gas through a traced goethite suspension and recovering carbon dioxide by bubbling the effluent gas through a sodium hydroxide solution. The goethite suspension of 20 g of goethite per liter was traced with ^{14}C . The suspension was acidified by adding 23.6 ml of 0.1 N perchloric acid to the suspension. The resulting pH was approximately 3. After bubbling for 7.9 days 93 percent of the traced carbonate had desorbed.

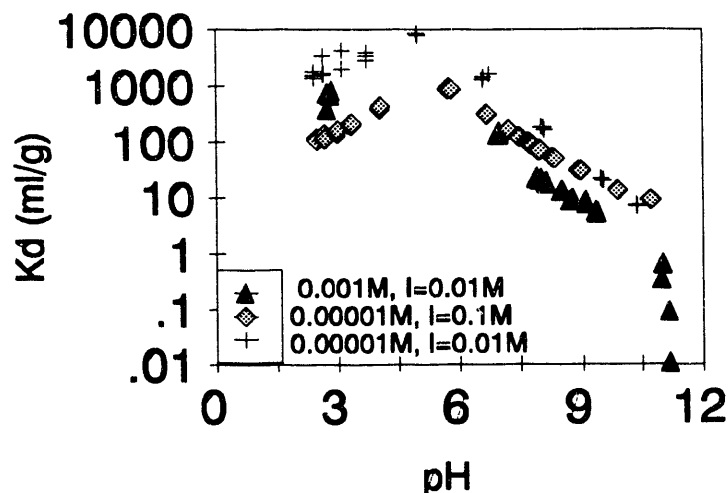
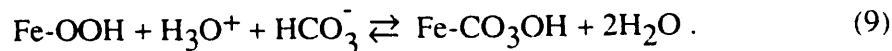


Figure 3. The pH and ionic strength dependence of carbonate adsorption.

The pH dependence of carbonate sorption was determined at two electrolyte concentrations 0.1M, and 0.01M. The initial carbonate concentrations were set to 0.001M and 0.00001M and the electrolyte concentration was adjusted with sodium perchlorate. The results are shown in figure 3. Significant sorption is observed even at pH values well above the point of zero charge, PZC, 9.3 (determined by potentiometric titration for the goethite used in this work). The distribution coefficients for 0.00001M carbonate concentration at both electrolyte concentrations are the same at pH values above the PZC. This is consistent with an inner-sphere sorption mechanism. The dependence of the distribution ratio on pH should reveal the stoichiometry of the surface complexation. This is unfortunately complicated by the surface charge dependence of the bicarbonate concentration in the solution nearest the goethite surface. This dependence is represented in equation 1. If the K_d s are less than 100 ml/g the surface charge should not be significantly affected by the adsorbed bicarbonate given an initial concentration of 0.01M and the solution to solid ratio used. This allows a relatively simple analysis of the pH dependence. It is possible to imagine two different stoichiometries which differ in pH dependence; the one based on the mechanism suggested by Russell⁸ et al., does not produce new surface charge; and the other similar to that postulated by Hayes⁵ et al. for selenite sorption produces negative charge on the goethite surface, i.e., lowers the point of zero charge.

The first mechanism is equivalent to adsorbing carbon dioxide on the C-type oxygen of the goethite surface and leads to the expression,



This reaction has the equilibrium expression,

$$K_{\text{ads}} = \frac{[\text{Fe-CO}_3\text{OH}]}{[\text{Fe-OOH}][\text{HCO}_3^-][\text{H}_3\text{O}^+]} , \quad (10)$$

which can be rewritten to show that the K_d is proportional to the hydrogen ion concentration,

$$K_d = \frac{[\text{Fe-CO}_3\text{OH}]}{[\text{HCO}_3^-]} = K_{\text{ads}} [\text{Fe-OOH}] [\text{H}_3\text{O}^+] . \quad (11)$$

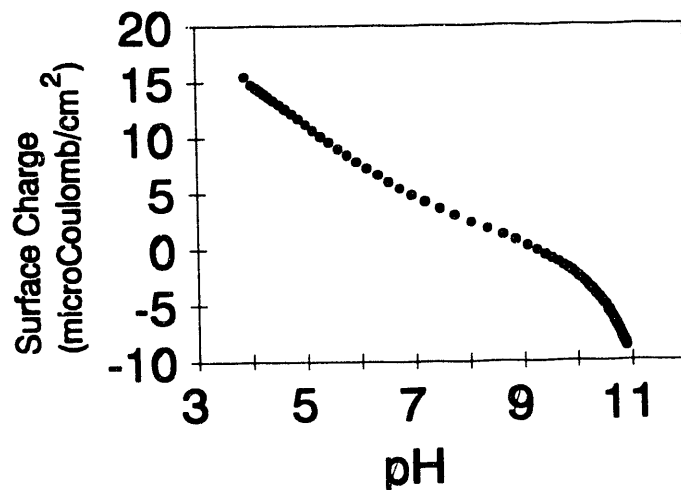
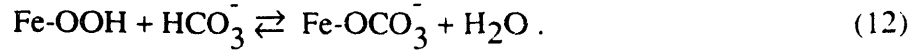


Figure 4. Surface charge of goethite in the absence of CO_2 as a function of pH at an electrolyte concentration of 0.01M derived from potentiometric titration data.

Several alternative mechanisms can be written which yield the same equilibrium expression as eqn. 10. For example, if bicarbonate underwent ion-exchange replacing a surface hydroxide instead of complexing as carbon dioxide the equilibrium expression would still be eqn. 10. We could say therefore that eqn. 9 actually represents a class of reactions which have the common characteristic of binding bicarbonate to goethite without changing the surface charge.

The second mechanism is the formation of a carbonate ligand with the accompanying release of a water. This mechanism places negative charge on the goethite surface because a proton is lost from the bicarbonate ion. The expression for this reaction is,



This reaction has the equilibrium expression,

$$K_{\text{ads}} = \frac{[\text{Fe-OCO}_3^-]}{[\text{Fe-COH}][\text{HCO}_3^-]} e^{\left(\frac{-e\psi}{kT}\right)} , \quad (13)$$

which can be rewritten to show that the K_d is proportional Boltzman factor as in equation 1,

$$K_d = \frac{[\text{Fe-CO}_3\text{OH}]}{[\text{HCO}_3^-]} = K_{\text{ads}} [\text{Fe-OOH}] e^{\left(\frac{e\psi}{kT}\right)} . \quad (14)$$

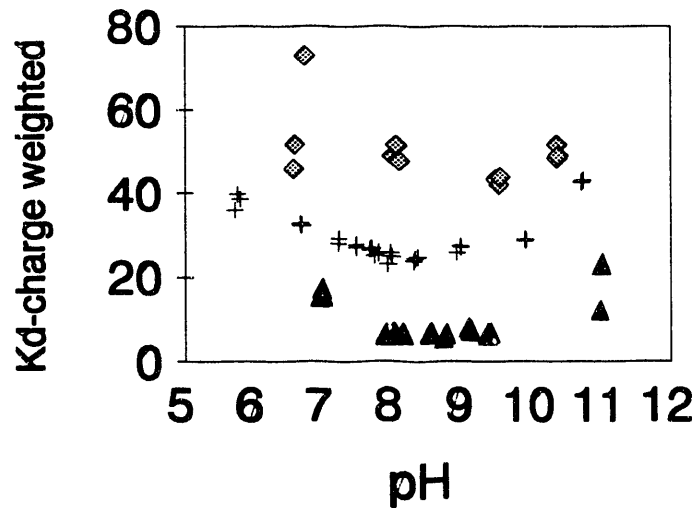


Figure 5. Distribution coefficients corrected to the point of zero charge by dividing by the Boltzman factor. The diamond and cross symbols represent data taken with a bicarbonate concentration of 0.00001 M. The triangle symbols represent data taken with a bicarbonate concentration of 0.001 M. The data represented by the crosses were taken at a background electrolyte concentration of 0.1 M the others at 0.01 M.

The sorption distribution coefficients as a function of pH are shown in Fig. 3. The trend of K_d vs. pH does not support the first mechanism. The K_d rather than varying linearly with pH seems to vary with nearly the square root of pH. This dependence seems to be due to the Boltzman factor and is consistent with the second mechanism. The dependence of surface charge, σ , on pH shown in Fig. 4 is taken from the potentiometric titration data. The electrostatic potential of the bicarbonate ion was calculated from the surface charge by assuming an capacitance of $220 \mu\text{C}/\text{cm}^2$. This

is larger than the inner-sphere capacitance used for hydrogen ion, usually near $110 \mu\text{C}/\text{cm}^2$. When this surface charge function is inserted into the Boltzman factor as shown in eqn. 14 the K_d becomes a nearly linear function of the Boltzman factor, over the pH range from 6 to 11, as shown in figure 5. Therefore the bicarbonate ion appears to form the surface complex shown in eqn. 12. This is similar to the selenite complex studied by Hayes and coworkers⁵. There is some residual curvature in the data shown in Fig. 5. This could be due to the shift from a predominantly inner-sphere complex to an outer-sphere complex as the pH decreases. The capacitance for the outer Helmholtz layer is much less than the inner layer.

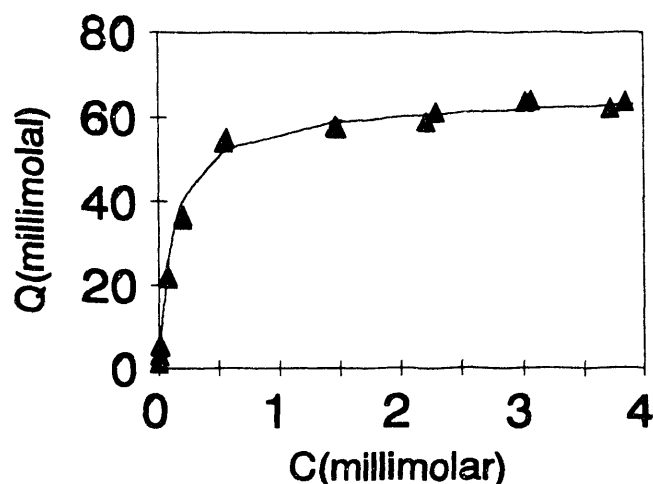


Figure 6. Carbonate adsorption isotherm at pH 7.0. Solid curve is the fit to a two-site mechanism.

A sorption isotherm was measured at an ionic strength of 0.01M and the results are shown in Fig. 6. These data can not be fit to a single Langmuir Isotherm. The solid phase concentration is treated as the sum of concentrations of carbonate in each site (each site following a Langmuir isotherm, eqn. 8). The equations are:

$$q_2^i = \frac{K^i Q^i \gamma_2 C_2}{C_0 \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2}, \quad (15)$$

$$q_2 = \sum_{i=0}^n q_2^i = \sum_{i=1}^n \frac{K^i Q^i \gamma_2 C_2}{C_0 \gamma_1 + (K^i \gamma_2 - \gamma_1) C_2}, \quad (16)$$

where K_i is the selectivity for carbonate in site i , Q^i is the concentration of sites of type i , C_2 is the concentration of carbonate in solution, C_0 is the concentration of the competing anion, γ_2 and γ_1 are the activity coefficients for the carbonate and

competing anion, respectively, q_2^i is the solid phase concentration of carbonate at site i , and q_2 is the total solid phase concentration of carbonate. If the deconvolution method¹⁰ is applied the distribution function shows two peaks. One at a selectivity of 0.1 and another with a selectivity 90. The quality of fit is only fair, however. The reason for the poorer performance for the deconvolution method is readily explained in view of the conclusions derived from the pH dependence. The deconvolution method assumes that ion-exchange is the sorption mechanism and that the kernel in the integral equation which describes ion-exchange at multiple sites is of the form represented by eqn. 16. The assumption of this hypothesis (hypothesis A) is that the bicarbonate ion competes with the perchlorate ion for sites as represented the following equation,



The preferred mechanism should be based on the interpretation of the pH dependence as represented by eqn. 12. The inner-sphere mechanism involves competition with water, presumably for a Lewis acid site. The outer-sphere complexation mechanism would be expected to be an anion-exchange mechanism as in eqn. 17. Therefore the kernel (used for hypothesis A) is only approximately correct. As a result we choose to assume only two mechanisms (hypothesis B) for carbonate adsorption, an inner-sphere complex represented by eqn. 13 and an outer-sphere complex represented by the exchange of bicarbonate ion with perchlorate ion, eqn. 17. The results from the fit achieved using eqns. 13 and 17 are given in Table I. The fit achieved with hypothesis B had half the residual error as the fit achieved with hypothesis A.

Table I. Selectivities for carbonate ion derived from adsorption isotherm at pH 7.0.

	Site 1	Site 2
Hypothesis A		
Selectivity, K	0.1	90
Maximum Q(molal)	0.035	0.062
C ₀ (Molar)	0.010	0.010
Hypothesis B		
Selectivity, K	10000	85
Maximum Q(molal)	0.015	0.058
C ₀ (Molar)	55 ¹	0.010

Conclusions

The sorption of bicarbonate on goethite was found to be moderately large for goethite having a specific surface area of 76 m²/g. The maximum solid phase concentration of carbonate observed was 55 micromoles/g at pH 2.8, 3.0 micromoles/g at the point of

¹The molarity of water was used because water is assumed to be competing for the Lewis acid site.

zero charge, pH 9.1, and zero at pH 11.1. The maximum concentrations we report are not capacities because no attempt was made to saturate the surface with carbonate. The distribution coefficients ranged from 120 ml/g to 1700 ml/g at pH 2.8 depending on the ionic strength. The distribution coefficients range from 8 ml/g to 30 ml/g at pH 9.1, for carbonate concentrations of 0.001M and 0.00001M, respectively. The selectivity for surface complexation of bicarbonate on goethite was less than phosphate. Phosphate was used to displace carbonate for the purpose of measuring the solid phase concentration. This allowed us to determine the mass balance even at low pH where isotopic exchange with the atmosphere becomes more significant.

The sorption of bicarbonate on goethite proceeds via two mechanisms. The evidence for two mechanisms, an inner-sphere and an outer-sphere mechanism, is the shape of the adsorption isotherm and the dependence of sorption on ionic strength. At pH values below the point of zero charge the mechanism is dominantly outer-sphere. Furthermore if the inner-sphere mechanism is assumed to be competing with water for Lewis acid sites then it follows that the number of tightly bound bicarbonate ions is less than the more weakly bound bicarbonate at pH 7.0. This interpretation can be further tested by measuring isotherms at higher pH values.

The results of these experiments suggest that hydrous iron oxides may provide an additional mechanism for the retardation of ^{14}C released as carbon dioxide or carbonate from the long term storage spent fuel. These results also offer an explanation for the apparent irreproducibility of the point of zero charge of goethite and are consistent with the reflectance IR measurements of CO_2 adsorption of Russell⁸ et al..

Acknowledgements

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