Selective Sorption of Trace Amounts of Calcium and
Strontium by Hydrous Oxides of Iron and Aluminum

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Soil Sci. Soc. Amer. Proc. 37:000-000. 1973.

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SOIL BRIEF

Selective Sorption of Trace Amounts of Calcium and Strontium by Hydrous Oxides of Iron and Aluminum

Heated gibbsite, and Fe and Al gels, are able to selectively sorb traces of Ca and Sr from NaNO_3 solutions even when the solids possess a net positive charge. This specific adsorption is highly pH-dependent since for each Ca^{2+} or Sr^{2+} sorbed, approximately one H^+ is released from the weakly acidic surface-OH groups.

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SOIL SCI. SOC. AMER. PROC. 37:000-000. 1973.

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by Hydrous Oxides of Iron and Aluminum¹

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ABSTRACT

Heated gibbsite, and freshly prepared Fe and Al gels selectively sorbed traces of Ca and Sr from solutions containing a large excess of NaNO_3 . The fraction of the total Ca(Sr) sorbed depended principally on the suspension pH, the amount of solid present, and only to a lesser extent on the NaNO_3 and Ca concentrations. Significant Ca and Sr sorption occurred on the heated gibbsite, Fe and Al gels, at pH's below their points of zero charge (8.25, 8.05 and 9.40, respectively), indicating specific adsorption. For the heated gibbsite and Fe gel, an empirical model based on the law of mass action fitted the data

1. Supported in part by the College of Agricultural and Life Sciences, University of Wisconsin, Madison, under project 1336; and in part by the Ecological Sciences Branch, Division of Biomedical and Environmental Research, United States Atomic Energy Commission Contract AT (11-1)-1515-Jackson (Paper C00-1515-38) through an International Consortium for Interinstitutional Cooperation in the Advancement of Learning (ICICAL). Presented in part before Div. S-9, Soil Science Society of America, New York City, NY, August 20, 1971. Received , 1973. Approved , 1973.

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reasonably well and suggested that for each Ca^{2+} or Sr^{2+} sorbed, about one H^+ was released, thereby leading to an increase in the net positive charge of the surface. Failure of the Al gel to fit the model is probably due to its rapid aging which leads to hysteresis in the sorption-pH curve.

Additional Key Words for Indexing: Fe gel, Al gel, point of zero charge, specific adsorption.

The high reactivity of the hydrous metal oxides has long led to their study and application in such diverse fields as analytical chemistry, radiochemistry, soil chemistry, geochemistry, water treatment, catalysis, medicine, mineral flotation, nuclear engineering and electrochemistry. As a result, there is a fairly extensive, but widely dispersed, literature on the chemistry and mineralogy of these materials. Various aspects of this literature have been dealt with in reviews (9, 22, 24, 26, 35, 36), but many of the details of the chemistry of the hydrous metal oxides remain uncertain.

It has long been known that the hydrous metal oxides are amphoteric, and in recent years there has been renewed interest in their charge properties (2, 3, 5, 20, 25, 27, 28). H^+/OH^- have invariably been found to be potential-determining ions and much of the research has been concerned with the relationship between pH and surface charge. It is now also clear that many anions show 'specific' adsorption on hydrous metal oxides (11), but it is not so generally appreciated that cations, especially multivalent cations, can also show quite marked specificity for these materials. Therefore to illustrate some of the principles governing the adsorption of divalent cations, we have chosen to study the adsorption of trace amounts of Ca and Sr by three synthetic hydrous oxides. Ca and Sr were chosen for this study since these cations have only a weak tendency to hydrolyze or to precipitate as hydroxides. Furthermore since sorption was carried out at low concentrations, these two cations provide the necessary radioactive isotopes.

MATERIALS AND METHODS

Preparation of Materials

Fe Gel--A stock suspension was prepared by the rapid (15 min) neutralization of A.R. $\text{Fe}(\text{NO}_3)_3$ with NaOH to pH 7 in a plastic beaker. After the suspension had been maintained at pH 7.00 for 1 hour, the suspension was made up to the appropriate volume so that the final suspension concentration was 0.33M with respect to Fe. 7.00 ml of this stock suspension were generally used per 25 ml sample, giving a final concentration of 0.093M Fe. The gel was completely soluble in both oxalate and 1M HCl indicating that there had been little crystallization, and this was confirmed by differential analysis (DTA) and X-ray diffraction (XRD). A batch of fresh gel was prepared for each experiment, but it was found that storage in the mother liquor at 5C for several days did not affect the sorption curves.

Al Gel--A stock suspension was prepared in a similar manner to the Fe gel described above using $\text{Al}(\text{NO}_3)_3$ instead of $\text{Fe}(\text{NO}_3)_3$. The freshly prepared gel was X-ray amorphous (by XRD), but on aging in the mother liquor ($\sim 0.95\text{M NaNO}_3$) for several months, broad gibbsite lines became detectable by XRD. This aging is accompanied by a drop in pH from 7.0 to about 5, which is indicative of the slow structural transformations that occur in freshly precipitated Al gels (30, 34).

Heated Gibbsite--Prepared by heating Mallinckrodt purified powder $\text{Al}(\text{OH})_3$ at 400C for 5 hours in a muffle furnace. The original material was identified by X-ray diffraction, scanning electron microscopy (SEM) and DTA as predominantly gibbsite with a small amount of bayerite. SEM of the heated material showed that it consisted of microporous particles, and the micrographs indicated that some sintering had already occurred. The empirical formula for the powder, deduced by its weight loss, was $\text{Al}_2\text{O}_3 \cdot 0.46\text{H}_2\text{O}$ and it showed a pronounced endotherm at 550C on the DTA pattern, suggesting that some boehmite had been formed hydrothermally during heating. Heating aluminum trihydrates at 400C (24) is known to produce highly reactive materials of high specific surface area ($\sim 300 \text{ m}^2/\text{g}$), and direct observation of a similar material has revealed cylindrical micropores of $27\text{\AA}$ diameter (8).

Experimental Procedures

Point of Zero Charge Determinations--The point of zero charge (pzc) of a hydrous oxide (Parks, 1965) is the pH at which the surface has zero net charge in the absence of specifically adsorbed ions, and may be determined by the potentiometric titration of oxide suspensions at different concentrations of indifferent electrolyte (1, 3, 6, 27). If only the pzc is required, then this may be rapidly and simply found by determining the pH at which there is no change in the suspension pH on addition of an indifferent electrolyte. In the present case, the electrolyte concentration of the gels was reduced by centrifugation and dilution to about 10^{-3} M NaNO_3 . The heated gibbsite powder was suspended in 10^{-2} M NaNO_3 for 20 hours to allow partial rehydration of the surface. Aliquots of the suspensions were then adjusted to various

pH's with NaOH or HNO_3 and after 60 min for equilibration, the pH's were measured and 1.0 g NaNO_3 added to bring the final electrolyte concentration to about 0.45M. After a further 60 min, the final pH was measured. The results are plotted as ΔpH (final pH - initial pH) against final pH, and the pzc is identified as the pH where $\Delta\text{pH} = 0$. This ΔpH method is quite distinct from that used by Alwitt (1972) which only gives the correct pzc if the solid initially has zero net charge. This is, in general, not the case.

Sorption Experiments--A typical sorption experiment was carried out as follows: 7 ml of the freshly prepared stock gel (2.33 mmole Fe or Al) suspensions, or 0.250 g heated gibbsite (4.55 mmole Al), were put into weighed acid-rinsed 30 ml Oak Ridge screw-top polyethylene tubes. Each suspension was adjusted to the desired pH with 1M NaOH or HNO_3 using a plastic syringe until a reasonably stable pH (± 0.1) had been maintained for about one hour. 2 ml of the appropriate stock sorbing solution was then added. The Ca stock solution was prepared by labeling a 1M NaNO_3 (A.R.) solution with 0.5 $\mu\text{Ci/ml}$ ^{45}Ca . The Ca impurity in the NaNO_3 together with the Ca added as tracer made the total Ca concentration in the final sorbing solution 2.10^{-6}M Ca. When Reagent Grade NaClO_4 was used, the impurities were first removed from solution by sorption on Fe gel at $\sim\text{pH } 10.5$ and the appropriate amount of Ca then added. The Sr stock solution ($2.5 \cdot 10^{-5}\text{M}$ Sr/1M NaNO_3) was labeled with 0.5 $\mu\text{Ci/ml}$ carrier-free ^{90}Sr . Each tube was made up to 25 ml with 1M NaNO_3 using a top-loading balance (± 0.01 g). The suspensions were shaken at room temperature for about 3 hours (6 hours for heated gibbsite) and then the pH was measured (± 0.005 pH) using a

Corning Model 12 expanded-scale pH meter. The suspensions were immediately centrifuged and 1 ml aliquots of the supernatant taken for counting the remaining ^{45}Ca or ^{90}Sr . A Triton-toluene scintillation cocktail (5 g PPO, 0.1 g dimethyl-POPOP, 1/3 l Triton X-100, 2/3 l toluene) was used since this was found superior to Bray's dioxane-based cocktail in terms of efficiency, quenching characteristics, and cost. In the case of the Sr samples, the samples were stored in their vials for 28 days before counting to allow ^{90}Sr to come to secular equilibrium with its daughter products. A Packard Tri-Carb liquid scintillation counter with external standardization was used for all counting.

RESULTS AND DISCUSSION

Point of Zero Charge Determination

Insert
Fig. 1

The pzc's for the Fe gel, Al gel, and heated gibbsite were found to be 8.05, 9.40 and 8.25, respectively (Fig. 1). Results in the literature (26) show a wide range of values for these materials due to such effects as impurities and degree of hydration, but recent results give the pzc for goethite as 7.6 (3), and for hematite, the range 8.3-9.2 (3, 25, 27). The present results show that the Al gel curve is peculiar in that there are two pH's where $\Delta pH = 0$. The first, at 9.40, is thought to be reasonably close to the true pzc, whereas the second, at pH 10.2, is probably due to the structural instability of Al gels at high pH. Above pH 9.5 or so, the Al gel tends to crystallize rapidly to bayerite, and this crystallization results in a reduction in the specific surface area of the gel. If, as is thought, the gel has a net negative charge at this pH, then this will lead to a net ejection of OH^- , which will counteract, and even exceed, the increase in OH^- adsorption brought about by the increased charge density. Electro-phoretic mobility measurements of surface charge do not suffer from this disadvantage, and such measurements indicate the pzc of Al gel and 'pseudoboehmite' to be in the range 9.0-9.2 (2, 10).

Effect of NaNO_3 Electrolyte Concentration on Sorption

Insert
Fig. 2

Differing results are found in the literature concerning the effect of the concentration of supporting electrolyte on the sorption of traces of divalent cations by hydrous metal oxides (4, 7, 33). We therefore studied the sorption of Ca by Fe gel at $\text{pH } 7.00 \pm 0.03$ as a function of NaNO_3 concentration. As can be seen from Fig. 2, there is a rather high scatter of points, but the data suggest that Na acts as a poor competitor for Ca on Fe gel. This is in marked contrast to similar experiments with montmorillonite and micaceous vermiculite which show a considerable decrease in the sorption of traces of Sr with increasing Na concentration (33). This difference in behavior is due to the specific interaction of divalent cations with hydrous metal oxides, as is evidenced in the present case by significant sorption even when the solids/ have a net positive charge. However, at high pH, the divalent cation may also compete for non-specifically adsorbed Na^+ , which may lead to a marked dependence of sorption on Na concentration. This has been observed for the coprecipitation of Sr by Fe gel at pH 11 (29). The influence of the indifferent electrolyte concentration may therefore depend on pH.

While working with gel systems, the use of a high concentration of background electrolyte has a number of advantages, both practical and theoretical. These are: (1) the gels remain flocculated over a wide pH range. This makes separation of the solid and solution phases possible without use of a high speed centrifuge which is desirable since high speed centrifugation may disturb the equilibrium due to the

development of centrifugation potentials (21). Low speed centrifugation is also considerably more convenient than dialysis; (2) the 'suspension effect' is eliminated at high electrolyte concentrations (6); (3) activity coefficients of the ions in solution remain more or less constant; (4) only highly selective sorption is detected since Na^+ and NO_3^- will satisfy most of the non-specific charge; (5) the rate of aging of the gels is reduced at high electrolyte concentrations.

For these reasons, all further sorption experiments were done in a 1M salt system, usually NaNO_3 , since this is an indifferent electrolyte for most hydrous oxides (1). Unfortunately, by using 1M NaNO_3 as a background electrolyte, one also sacrifices the ability to measure any simultaneous adsorption or desorption of Na^+ or NO_3^- ions.

Effect of Ca Concentration on Ca Sorption

Insert
Fig. 3

An important aspect of adsorption is the relationship between adsorption and concentration. An example of this is shown in Fig. 3, plotted for convenience with rather unconventional coordinates. At low total Ca concentrations ($\text{Fe}/\text{Ca} > 10^5$) at $\text{pH } 8.00 \pm 0.02$, there is little change in the fraction of Ca sorbed with increasing Ca concentration, indicating a linear adsorption isotherm in this region (18). This is the limiting region where Henry's law is obeyed. As the Ca concentration is increased, the number of sites available for further sorption is reduced, and lateral interactions of the adsorbed ions increased. This leads to a decrease in the fraction sorbed, but even at the highest Ca concentration, saturation has not been achieved. In this paper, we are only concerned with the limiting concentration region at about 10^{-6} M total divalent cation concentration.

Effect of pH on Sorption

Insert

Fig. 4

The sorption of $2.10^{-6}M$ Ca(Sr) by heated gibbsite and Al and Fe gels as a function of pH is shown in Fig. 4(a). The sigmoid shape of the curves is evident, with a sharp increase in sorption occurring between pH 6.0 and 7.5 for the Fe gel and heated gibbsite, and between pH 7.5 and 9.0 for the Al gel. The Fe gel shows little selectivity between Ca and Sr, whereas the Al gel shows a preference for Ca over Sr. The heated gibbsite shows a small preference for Sr over Ca in agreement with the results of Belot et al. (1966) and Bonner et al. (1966) for similar materials.

The sigmoid shape of the sorption-pH curves suggests that the sorption process involves $M^{2+}-H^+$ exchange, the protons being derived from the weakly acidic surface-OH groups found on hydrated oxide surfaces. As a result, many workers have applied the law of mass action to the sorption and co-precipitation of divalent cations on hydrous oxides (see, for example, 7, 16, 17, 19). Kolařík (1962a) presents the most complete treatment of this approach, and his notation will be used here. Briefly, we can describe the sorption of divalent cations with the general equation

where H_qA represents the weakly acidic oxide exchanger and

$(M_b \langle H_{q-bn/a}A \rangle_a)^{b(2-n)+}$ represents the exchanger with some of the protons replaced by divalent cations, M^{2+} . At equilibrium, the reaction may be treated according to the law of mass action and an

overall equilibrium constant, K_{ab} , derived

$$K_{ab} = \frac{[(M_b \langle H_{q-bn/a} A \rangle_a)^{b(2-n)+}][H^+]^{bn}}{[H_q A]^a [M^{2+}]^b} \quad [1]$$

Expressing the reactants and products in terms of initial concentrations and the fraction of divalent cation sorbed, equation [1] leads to

$$K_{ab} = \frac{\frac{1}{b}(y m_{tot})^b (h)^{bn}}{(S_{tot} - \frac{a}{b} y m_{tot})^a (1-y)^b m_{tot}^b}, \quad [2]$$

where S_{tot} = concentration of solid before sorption

m_{tot} = initial concentration of divalent cation, M^{2+}

$h = [H^+]$

y = fraction of total M^{2+} sorbed

n = number of protons released for each M^{2+} sorbed.

At low concentrations of divalent cation, two assumptions are frequently used which enable the above equation to be considerably simplified (16). These assumptions are: (1) the activity of the solid is unaffected by sorption. This requires that only a small fraction of the total number of sorption sites is occupied, i.e. $S_{tot} \gg y m_{tot}$; and (2) $b = 1$. This is analogous to the concept of mononuclear complex formation in coordination chemistry, and although this concept cannot be rigorously defined in the present context, it is probably not an unreasonable assumption at low concentrations. With these assumptions, equation [2] gives

$$K_{al} = \frac{y h^n}{(S_{tot})^a (1-y)} \quad , \quad [3]$$

and putting [3] in logarithmic form and rearranging,

$$\log \left(\frac{y}{1-y} \right) = n \text{ pH} + \log K_{al} + a \log S_{tot} \quad , \quad [4]$$

where $y/(1-y)$ is a distribution coefficient representing the partitioning of the divalent cation between the solid and solution phases. Note from equation [3] that the fraction sorbed, y , is independent of m_{tot} . This is reasonably justified only at low concentrations (Fig. 3).

In Fig. 4(b), the sorption curves shown in Fig. 4(a) are plotted according to equation [4]. It should be noted that the distribution coefficient is particularly sensitive to the experimental errors when there is little sorption (i.e. at low pH) and to a lesser extent at very high sorption when background counting errors become significant. Therefore, in "eye-balling" the curves, the points at these extreme values were weighted somewhat less than the points in the intermediate sorption range. It can be seen that the data for the Fe gel and heated gibbsite conform reasonably well to single straight lines while the data for the Al gel seem to be divided into two approximately linear regions.

The results show that under the present experimental conditions, we can describe the pH dependence of sorption on Fe gel and heated gibbsite by two parameters, namely the slope, n , and the pH intercept when $\log (y/1-y)$ equals zero. This is the pH at which there is 50% sorption and it is equal to $-\frac{1}{n} (\log K_{al} S_{tot}^a)$. Fig. 4(b) shows that the slopes of the plots for heated gibbsite and Fe gel are all between

0.8 and 1.0, as are the slopes of the lines for the Al gel curves at high pH. This range of values for n has been found for the sorption of a number of divalent cations on various hydrous oxides (7, 16, 17, 19). The significance of this value will be discussed later. The second parameter, the pH intercept at 50% sorption, gives a measure of the overall affinity of the system for the divalent cation. It includes both the equilibrium constant, K_{al} , which is related to the free energy of adsorption, and also the term S_{tot} which is related to the amount of surface available for sorption. Unfortunately no direct or indirect estimate of this is available.

The reason for the break in the slopes of the sorption curves for the Al gel is not certain, but is thought to be due to the greater instability of the Al gel. It was difficult to maintain the pH of the Al gel suspensions at the desired pH for any length of time, and this was particularly true in the pH 8-9.5 region. The pH continually drifted to lower values and this drift also occurred during the three hour equilibration with ^{45}Ca . Many of the data points in the steeper region of both curves had therefore drifted down from a higher pH.

In order to minimize the effect of aging of the Al gel, the Ca sorption curve obtained was compared with that obtained with the freshest possible gel - that obtained by coprecipitation of Ca with Al. All quantities were similar and one hour was allowed for equilibration. The resulting sorption curve (Fig. 5) is similar to the original curve, except at low pH where the sorption by coprecipitation is greater. Furthermore, the $\log(y/(1-y))$ -pH plot for coprecipitation (not shown) is linear over the entire pH range and has a slope of

Insert
Fig. 5

1.02, which is close to the value obtained for the Fe gel (0.95).

In view of the considerable change in pH of the Al gel during equilibration, we tested the reversibility of Ca sorption on Al gel by following Ca sorption over a 16 hour period as the pH drifted down. The Al gel suspension had just been adjusted from pH 7.0 to pH 9.5 and, in order not to change the solid/solution ratio, samples of the bulk suspension were taken for analysis. The results (Fig. 5) show that although for about the first hour the pH decreased, Ca sorption increased slightly. Subsequently, Ca was desorbed as the pH decreased, but the slope of the desorption curve is less steep than either the coprecipitation curve or the initial sorption curve, indicating some hysteresis.

Effect of Solid/Solution Ratio on Sorption

Naturally, as the amount of sorbent increases, so will the amount of sorption and equation [4] predicts the form of this dependence. The coefficient 'a' may be determined by measuring sorption as a function of solid/solution ratio at constant pH. S_{tot} is conveniently, but arbitrarily, defined in terms of μmoles of Fe or Al per 25 ml sample. Fig. 6 shows the results for Ca sorption on Fe gel and heated gibbsite at pH 8.00 ± 0.02 and 7.00 ± 0.03 , respectively. Reasonably good straight lines are obtained over a wide concentration range of solid, and the slopes of the lines, a, are 1.01 and 1.16 for the Fe gel and heated gibbsite, respectively. This compares with 'a' values of 1.2 for Sr sorption on Fe gel (16), and 1.0 for Co sorption on Fe gel (19) and for Sr sorption on MnO_2 (17). An implication of these results is that although the amount of sorption increases with increasing solid/solution ratio, the adsorption density (moles/cm^2) will normally decrease. This is evident since at low concentrations, the adsorption density is related to y/S_{tot} and for 'a' close to or less than one, rearrangement of equation [3] shows that y/S_{tot} decreases as S_{tot} increases. This is consistent with the observation that in the presence of adsorbed Co, the electrophoretic mobility of SiO_2 particles depends on the solid/solution ratio (14).

Insert

Fig. 6

Mechanism of Sorption

The slopes of the $\log (y/(1-y))$ -pH curves (Fig. 4(b)) suggest that approximately one proton is released for each divalent cation sorbed. This has prompted several authors to believe that the mechanism involves the sorption of monovalent ion pairs or complexes from solution (4). For example, the most abundant ion pair in a Ca system is CaNO_3^+ and using the ion pair dissociation constant of 0.167 (23), CaNO_3^+ accounts for more than 80% of the total Ca in a 1M NaNO_3 system. To see what effect this ion pair formation has on sorption, we studied Ca sorption by Fe gel in a 1M NaClO_4 system in which the degree of ion pairing is generally believed to be low. The results showed that there was very little difference between the two systems, and that the slope of the $\log (y/(1-y))$ -pH plot was still close to one, indicating that CaNO_3^+ ion pair formation in solution does not appreciably affect sorption. This is presumably because the overall strength of the Ca^{2+} -Fe gel interaction is considerably greater than that of the Ca^{2+} - NO_3^- ion pair.

Taking into account the stoichiometry of the reaction, a possible mechanism for the specific adsorption of a divalent cation on Fe gel, for example, at the point of zero charge, may be represented as

A consequence of this mechanism is that the positive charge of the surface is increased, since the specifically adsorbed divalent cation is assigned to the solid side of the solid-solution interface (Stern layer). This increase in positive charge is counterbalanced by a simultaneous adsorption of NO_3^- or desorption of non-specifically adsorbed Na^+ . Electrokinetic measurements provide direct evidence for an increase in the net positive charge of the surface, and in some cases specific adsorption of divalent cations is even sufficient to reverse the surface charge (12, 14). Similarly, it is well known that divalent cation sorption can lead to the flocculation of dispersed hydrous oxide suspensions as a result of the reduction of the negative surface charge (31).

From an experimental point of view, the release of one H^+ is equivalent to the co-adsorption of one OH^- , and so the sorption reaction may alternatively involve the specific adsorption of hydrolyzed species, such as MOH^+ . Indeed, it has often been observed (13) that in general, the greater the tendency for a cation to hydrolyze, the more readily it is adsorbed. Recently, James and Healy (1972c) have described a quantitative model for the adsorption of hydrolyzable metal ions on metal oxides. They postulate that hydrolysis, by lowering the average ionic charge of the metal ion, leads to a large decrease in the secondary solvation energy of the ion, which opposes adsorption. This more than compensates for the decrease in the coulombic interaction energy of the lower charged species and hence results in greater adsorption of the hydrolyzed species. This model is an interesting attempt to rationalize the 'adsorption-hydrolysis'

phenomenon, but many problems still remain. For example, if it is merely the lowering of ionic charge that is important, then ion pair and complex formation should also lead to increased adsorption. There is no evidence for this. Furthermore, under our experimental conditions, at pH 7 approximately 50% of the Ca is sorbed on Fe gel and heated gibbsite and yet the fraction of the total Ca that is CaOH^+ ion pairs ($-\log K_1 = 12.6$) is exceedingly small. One would therefore have to postulate a very marked specificity for CaOH^+ compared with Ca^{2+} .

The hysteresis found in the pH-sorption curve for the Al gel, although not nearly as great as generally observed for anions such as phosphate, does suggest that some of the sorbed ions become sterically inaccessible. Significantly, Tadros and Lyklema (1969) found hysteresis for the specific adsorption of alkaline earth cations on SiO_2 , although non-specifically adsorbed counterions were reversibly sorbed. Hysteresis therefore seems to be commonly associated with specific adsorption. It is interesting to note that when comparable quantities of certain di- and tri-valent cations are coprecipitated as hydroxides, they can form more or less discrete compounds, the so-called 'double hydroxides'. Perhaps the adsorption found here merely represents a limiting example of this more general phenomenon, since, for cations at least, sorption and coprecipitation are remarkably similar.

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Titles of Figures

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- Fig. 2. Effect of Na concentration on Ca sorption by Fe gel at pH 7.00 ± 0.03 .
- Fig. 3. Effect of Ca concentration on Ca sorption by Fe gel at pH 8.00 ± 0.02 .
- Fig. 4. Ca and Sr sorption by Fe gel, Al gel, and heated gibbsite as a function of pH. (a) Sorption expressed in terms of fraction sorbed; (b) sorption expressed in terms of a distribution coefficient. Numbers indicate the slope of the lines.
- Fig. 5. Ca sorption by Al gel as a function of pH determined by adsorption, coprecipitation, and desorption while aging.
- Fig. 6. Ca sorption by Fe gel and heated gibbsite as a function of solid/solution ratio. Numbers indicate the slope of the lines.

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