Calcium and Zinc Adsorption by Iron Hydrous Oxide Gel^{1/}

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ABSTRACT

MASTER

In the presence of 1M NaNO_3 , freshly precipitated iron hydrous oxide gel suspensions (0.093M Fe) selectively adsorbed Ca and Zn over a wide concentration range. Adsorption was highly pH dependent, especially for Zn. For Ca, the pH at which 50% adsorption occurred, pH_{50} , varied from pH 7.15 at $2 \times 10^{-6}\text{M}$ Ca (total) to pH 9.55 at 10^{-2}M Ca, whereas for Zn, the pH_{50} values varied from pH 5.00 at 10^{-7}M Zn to pH 6.25 at 10^{-2}M Zn. Adsorption isotherms for Ca (pH 8.0) and Zn (pH 5.5 and 6.5) showed no adsorption maxima. With high Zn concentrations at pH 6.5, Zn precipitated as a separate, visible zinc hydroxide (or hydroxycarbonate) phase. At

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1 an equilibrium concentration of 10^{-7} M Zn, Fe gel adsorbed approximately
2 5 µg Zn/g at pH 5.5 and an estimated 240 µg Zn/g at pH 6.5 indicating that
3 amorphous iron oxides retain small, but perhaps significant, quantities
4 of Zn at realistic soil solution concentrations.

5 Additional Index Words: specific adsorption, adsorption isotherm.

(Introduction)

1
2 In a previous paper (Kinniburgh, Jackson, and Syers, 1976), we showed
3 that freshly prepared iron and aluminum hydrous oxide gels are able to
4 adsorb a wide range of divalent cations in the presence of a 1M NaNO_3
5 solution. This adsorption occurred not only in the presence of a high
6 concentration of background electrolyte but occurred even though the
7 gels had a net positive surface charge. The "relative selectivity" of
8 adsorption (higher "relative selectivity" means adsorption at lower pH)
9 of the various cations correlated reasonably well with certain cation
10 properties, such as their first hydrolysis constants and tendency to
11 precipitate as metal hydroxides. However, these relationships were far
12 from perfect as evidenced by the differing cation selectivity sequences
13 found for the two gels. The relative selectivity of adsorption of a
14 particular divalent cation was characterized by the pH at which 50% of
15 the original amount of divalent cation was adsorbed, the pH_{50} , but this
16 parameter depends not only on the particular cation-solid combination
17 involved but also on the solid/solution ratio and the total divalent
18 cation concentration in the system. This concentration dependence is best
19 analyzed in terms of adsorption isotherms and it is this aspect that is
20 reported here. We have chosen Fe gel ('ferrihydrite') for study because
21 it has greater structural stability than Al gel, although the behaviour
22 of the adsorbed cations during aging is itself of interest. Two
23 divalent cations, Ca^{2+} and Zn^{2+} , were selected to contrast a cation showing
24 only a weak tendency to hydrolyze (Ca) with one showing a relatively strong
25 tendency to hydrolyze (Zn). Zn adsorption by Fe gel (Gadde and Laitinen,

1 1974; Shuman, 1977; Davis and Leckie, 1979) and goethite, α -FeOOH (Grimme,
2 1968; Bar-Yosef, Posner, and Quirk, 1975; Forbes, Posner and Quirk, 1976)
3 has previously been demonstrated but these studies have been over a
4 relatively narrow pH and concentration range. With the use of radiotracers,
5 we have extended our studies down to equilibrium concentrations of less
6 than 10^{-7} M.

7 MATERIALS AND METHODS

8 The method of preparation of the Fe gel and Al gel was that described
9 previously (Kinniburgh, Syers, and Jackson, 1975). The Fe gel had its
10 point of zero charge at $\text{pH } 8.1 \pm 0.1$, and when dried at 80°C , it had a
11 composition of 11.6 mmole Fe/g. Hematite was prepared by refluxing a
12 $\text{Fe}(\text{NO}_3)_3$ solution; goethite was prepared by aging a $\text{Fe}(\text{NO}_3)_3$ solution at
13 $\text{pH } 12$ and 60°C . After preparation, both oxide suspensions were desalted
14 by dialysis. Two experimental approaches were adopted depending on whether
15 adsorption was being determined at variable pH or constant pH.

16 An aliquot of freshly prepared Fe gel suspension containing 2.33
17 mmole Fe (0.20 g oxide) was adjusted to the desired pH with either 0.1M
18 NaOH or 0.1M HNO_3 made up in 1M NaNO_3 . The appropriate amount of Ca or Zn
19 was then added from a stock solution also made up in 1M NaNO_3 . This was
20 labelled with either ^{45}Ca or ^{65}Zn for the more dilute solutions. Radio-
21 tracers were used to measure the relative adsorption when the total Ca
22 concentration was 2×10^{-6} M and when the total Zn concentration was 10^{-4} M
23 or less. The total Ca concentration ranged from 2×10^{-6} M to 1×10^{-2} M,
24 and the total Zn concentration ranged from a nominal 3×10^{-8} M to
25 1×10^{-2} M. The Zn concentration in the most dilute solution was

1 actually probably closer to 10^{-7} M because of impurities in the NaNO_3
2 solution and in the NaOH and $\text{Fe}(\text{NO}_3)_3$ used to prepare the gel. The total
3 volume of suspension was made up to 25 ml with 1M NaNO_3 by weighing.
4 The suspensions were shaken in stoppered polypropylene centrifuge tubes
5 for about six hours. No attempt was made to exclude atmospheric CO_2 . The
6 pH of the suspensions were then measured (± 0.01 pH), the suspensions
7 centrifuged, and the supernatant analyzed for Ca or Zn either by atomic
8 absorption spectrophotometry (Perkin Elmer Model 306) or, if tracers had
9 been used, by measurement of the remaining radioactivity. ^{45}Ca was
10 counted on a Packard liquid scintillation beta spectrometer using a
11 scintillation cocktail based on toluene/Triton X-100, and ^{65}Zn was counted
12 directly on a Packard gamma spectrometer. Adsorption was calculated by
13 difference. Room temperature varied between 20 and 27°C, although vari-
14 ations during any one run were much less than this.

15 For measurements at constant pH, a similar procedure was used, except that
16 gel aliquots were taken from a large batch of gel which had been adjusted
17 to the desired equilibrium pH (pH 8.00 for Ca and pH 5.50 and 6.50 for Zn).
18 After addition of variable amounts of Ca or Zn solution to these
19 individual aliquots, the suspension volumes were made up to about 20 ml with
20 1M NaNO_3 . The suspension pH's were checked for each suspension and read-
21 justed as necessary until they had stabilized to within ± 0.01 of the
22 desired pH. The suspensions were centrifuged and the amount of Ca or
23 Zn adsorbed determined as before. The time required for reaching a
24 stable pH varied from a matter of minutes for the lowest concentrations
25 to about 30 hr for the highest Zn concentrations at pH 6.50. In all
preparations, the suspensions were allowed to equilibrate for six hr or more.

RESULTS AND DISCUSSION

Adsorption as a Function of Divalent Cation Concentration and pH

Curves of the percent adsorption of Ca and Zn by Fe gel as a function of total divalent cation concentration and pH (Fig. 1) show characteristic sigmoid shapes. As expected, Zn was adsorbed at a considerably lower pH than Ca, but it is also significant that the Zn curves are steeper than the corresponding Ca curves, especially at high divalent cation concentrations. The large separation of the Zn and Ca curves indicates that even high Ca concentrations will probably not interfere greatly with Zn adsorption. The % adsorption against pH curve at the lowest Zn concentration (10^{-7} M) is at, or very close to, the limiting curve for this solid/solution ratio since there is little difference between this curve and the 10^{-5} M curve. At higher total Zn concentrations, the curves show a shift to higher pH indicating a non-linear adsorption isotherm in this region. This shift in curves is the reverse of the trend expected if zinc hydroxide or hydroxycarbonate precipitation were controlling Zn concentrations in solution and indicates that adsorption rather than precipitation was the dominant mechanism of retention.

The 2×10^{-6} M Ca curve is also at, or very close to, the limiting curve for Ca at this solid/solution ratio. Reasonably good linear plots (not shown) were obtained when these limiting curves were plotted in terms of the logarithm of the distribution coefficient, $\underline{D}$, against pH (Kinniburgh *et al.*, 1975; Kinniburgh, Sridhar, and Jackson, 1977), where $\underline{D}$ is given by $[\% \text{ adsorbed} / (100 - \% \text{ adsorbed})]$. The slopes, n , were 0.95 for Ca and 1.65 for Zn indicating a distinct difference in the H^+ / M^{2+} exchange stoichio-

metry. Davis and Leckie (1979) suggested that ZnOH^+ was the only zinc ion adsorbed by Fe gel, but it is difficult to see how this could give rise to the pH dependence observed here. Unfortunately direct measurement of H^+ released is not possible at these low concentrations since the overall drop in suspension pH is extremely small (always less than 0.005 pH for the 10^{-4} M curve, for example). At concentrations above about 10^{-5} M (total), the slope of the log D against pH plots no longer reflect the true H^+/M^{2+} stoichiometry although all the Ca plots remain linear. The slope of the 10^{-5} M Zn plot is 1.54 but above 10^{-4} M Zn, the Zn plots became distinctly non-linear with increasing slope at higher pH, perhaps indicating an increase in the H^+/M^{2+} stoichiometry with increasing pH under these circumstances.

The pH_{50} 's for the limiting Ca and Zn curves, pH_{50}^* , were 7.15 and 5.00, respectively. For the 10^{-2} M curves, the pH_{50} 's had increased to 9.55 for Ca and 6.25 for Zn - the greater increase in the case of Ca suggests that Ca was perhaps less prone to forming a surface hydroxide coating than Zn, as might have been expected. There were no signs of the direct precipitation of a separate solid Zn phase in any of the samples. We have measured the isotopic exchangeability of adsorbed Zn in a separate determination of the 10^{-2} M Zn curve and have found that after six hours equilibration, between 92 and 103% (mean = 96%) of the 'adsorbed' Zn was isotopically exchangeable in two hours whereas only 40% of the Zn in a freshly precipitated Zn gel was exchangeable under similar conditions. This provides additional evidence that in this case, most of the Zn was present as adsorbed ions or as a surface

coating of molecular dimensions rather than as a separate solid Zn phase.

Although we have not studied the adsorption isotherms at trace concentrations in detail here, Fig. 1 suggests that at equilibrium concentrations of less than about 10^{-6} M M^{2+} , the adsorption isotherms are linear since below this concentration, the % adsorbed is independent of the initial concentration. By making use of this, together with the parameters obtained from the linear log D versus pH plots (n and pH_{50}^*), it is possible to derive an empirical two-parameter adsorption equation which accounts for both the concentration and pH dependence of trace adsorption. The equation in its general form is

$$x/m = k_1 \times 10^n (\text{pH} - \text{pH}_{50}^*) \times c_e \quad (1),$$

where x/m is the amount of adsorption per unit weight of solid, k_1 is a constant related to the solid/solution ratio at which pH_{50}^* was obtained, and c_e is the equilibrium solution concentration. In the present case, $k_1 = (1/1000 \times 0.093) = 0.011 \text{ l/mmole Fe}$, and substitution of the appropriate constants into equation (1) gives for Ca adsorption,

$$x/m = 0.011 \times 10^{0.95 (\text{pH} - 7.15)} \times c_e \quad (2),$$

and Zn adsorption,

$$x/m = 0.011 \times 10^{1.65 (\text{pH} - 5.00)} \times c_e \quad (3),$$

where x/m is in $\mu\text{mole M}^{2+}/\text{mmole Fe}$ (multiply by 11.6 for $\mu\text{mole M}^{2+}/\text{g}$) and c_e is in $\mu\text{mole/l}$.

Previous data (Kinniburgh et al., 1975) for Ba gives,

$$x/m = 0.011 \times 10^{1.02 (\text{pH} - 6.45)} \times c_e \quad (4).$$

These equations indicate the importance of precise pH measurement

and control when studying trace adsorption on oxides. For example, a pH change of ± 0.01 would lead to a change of about 4% for Zn adsorption and 2% for Ca and Ba adsorption.

Adsorption as a Function of Equilibrium

Solution Concentration at Constant pH

The Ca (pH 8.0; Fig. 2) and Zn (pH 5.5 and 6.5; Fig. 3 and 4) adsorption isotherms show that in no case was a distinct adsorption maximum reached and none of the three isotherms fitted the Langmuir isotherm over a wide range of concentrations. There was a striking increase in Zn retention at high Zn concentration at pH 6.5 (Fig. 4). This was due to zinc hydroxide, or hydroxycarbonate (Baes and Mesmer, 1976) precipitation. Precipitation was visible in the samples denoted with an asterisk in Fig. 4 by the increase in bulk volume of the gel and by its lightening in color. The maximum zinc concentration found was $3.3 \times 10^{-2} \text{ M}$ but this would have probably decreased with aging as a more stable solid phase formed. There was some evidence for this in the back-turn shown by the sample that had the largest Zn addition (Fig. 4, I). This onset of visible precipitation corresponded with 'adsorption' of about 350 $\mu\text{mole Zn/nmole Fe}$ (4060 $\mu\text{mole Zn/g}$) (Fig. 4) which is of the same order as the maximum (250 $\mu\text{mole Zn/nmole Fe}$) found for Zn sorption on Fe gel at pH 6 (Gadde and Laitinen, 1974). This compares with a total site density of 9850 $\mu\text{mole OH/g}$ calculated by Davis and Leckie (1979). If it is assumed that the gel has a specific surface area of $320 \text{ m}^2/\text{g}$ (Gast, Landa and Meyer, 1974), then 350 $\mu\text{mole Zn/nmole Fe}$ is equivalent to a uniform surface density of about one Zn ion per 0.13 nm^2 or an average spacing of 0.36 nm. This density could have been accommodated as a monolayer but

1 another possibility is that at these very high adsorption densities some
2 of this Zn was in the form of discrete Zn hydroxide or hydroxycarbonate
3 particles, perhaps formed while adjusting the suspension pH. However,
4 there were no obvious breaks or inflections in the isotherm at lower
5 zinc concentrations indicative of a definite transition from a precipitation
6 region to an adsorption region. There appears to be a continuum ranging
7 from adsorption at discrete sites on the Fe gel at low concentrations to
8 bulk precipitation at high concentrations, perhaps with a region of
9 surface-induced hydroxide precipitation at intermediate concentrations.

10 Shuman (1977) has recently reported good linear Langmuir plots for
11 Zn adsorption by fresh and aged Fe and Al gels using a limited
12 amount of data, but we have found that the Zn isotherms showed systematic
13 non-linear Langmuir plots (not shown) which extended to well below 10 μ mole
14 Zn/ μ mole Fe. This corresponds to a mean separation of about 21 nm
15 between adsorbed ions and it seems unlikely that direct interaction of the
16 adsorbed ions would be significant at such large separations, although
17 Forbes et al. (1976) suggested that interactions of adsorbed ions on
18 goethite may have been significant at even greater separations. However,
19 at least part of the non-linear adsorption behaviour observed by Forbes
20 et al. can probably be interpreted in terms of the filling of a
21 significant fraction of the total number of adsorption sites (decrease
22 in SH activity in their terminology), a concept that is incorporated in
23 the Langmuir equation. Adsorbed ion interactions would be expected to be
24 greater for Ca than Zn because of the lower H^+ release (OH^- uptake) by
25 Ca compared with Zn. Another possible reason for the non-Langmuirian

1 behaviour of Fe gel is surface heterogeneity. This would not be
2 surprising since many of the physical properties of Fe gel, as character-
3 ized by its X-ray and DTA patterns are infrared and Mössbauer spectra,
4 are poorly defined (van der Giessen, 1968; Gast et al., 1974),
5 and therefore a variety of types of surface sites would be quite plausible.

Insert

Fig. 5

6 Fig. 5 summarizes Zn adsorption data for several iron and aluminum
7 oxides at pH 5.5. Differences in background electrolyte (all in 1M NaNO₃
8 except G1 and G2) have been ignored. At high Zn concentrations the fresh
9 Fe gel is able to adsorb more Zn than a similar weight of goethite because
10 of its high specific surface (~320 m²/g for Fe gel against 75 m²/g for
11 synthetic goethite, G1). However, previous work (Kinniburgh et al., 1977)
12 has shown that at very low equilibrium Zn concentrations (~10⁻⁷ M), aged
13 Fe gel generally adsorbed more Zn than a similar weight of fresh Fe gel.
14 This suggested that the partial crystallization of the Fe gel had resulted
15 in the disappearance of a number of low energy sites and the appearance of
16 a smaller number of high energy sites. However, even at very low con-
17 centrations, completely crystalline goethite (G3) and hematite (H) adsorbed
18 less Zn than a similar weight of fresh Fe gel (Fig. 5). Adsorption by the
19 Al gel is similar to that of the Fe gel when expressed on a weight of gel
20 basis.

21 The concentration of free Zn²⁺ in the soil solution is probably of
22 the order of 10⁻⁷ M in non-calcareous soils (Hodgson, Geering, and Norvell,
23 1965) which would correspond to 0.0072 μmole Zn/mmmole Fe (5 μg Zn/g) at
24 pH 5.5 and 0.32 μmole Zn/mmmole Fe (240 μg Zn/g) at pH 6.5. These figures
25 refer to adsorbed Zn (isotopically exchangeable) and suggest that the

1 hydrous metal oxides are capable of adsorbing (and desorbing) small, but
2 perhaps significant, quantities of Zn at realistic soil solution concen-
3 trations. Probably the greatest uncertainty at present is the extent to
4 which naturally occurring soil organic materials can affect the surface
5 chemistry of these oxides. Zn adsorption by whole soils/^{and soil clays} is rarely as pH
6 dependent as found with the oxides (Shuman, 1975; Tiller, Nayyar, and Clayton, 1979)

7 It is well known that a considerable pH gradient can exist in the
8 soil close to plant roots, and that the direction of this gradient depends
9 on the relative rate of uptake of cations over anions (excluding H^+ , OH^-
10 and HCO_3^-) by the plant roots (Riley and Barber, 1969). If, as is
11 usually the case, the rate of uptake of anions is greater than that of
12 cations, then HCO_3^- will be released by the plant roots in order to maintain
13 electrical neutrality and the pH of the soil solution close to the root
14 will be increased. Consequently, Zn adsorption, both on soil oxides and
15 organic matter, will also tend to be increased and the soil solution
16 in this zone will become depleted in Zn. This will tend to make it more
17 difficult for the plant to absorb Zn, although as with plant uptake,
18 diffusion of Zn from regions of high Zn concentration to regions of low Zn
19 concentration will tend to counteract this. If different varieties of a
20 given crop have different effects on the soil solution pH near their roots,
21 then this might be usefully exploited when selecting varieties for growing
22 on low Zn soils. Also, varying the composition of fertilizer used (e.g.
23 NH_4^+ vs NO_3^- and NO_3^- vs Cl^-) might be used to advantage in increasing,
24 or decreasing, plant uptake of Zn and other heavy metals.

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Fig.4--Zn adsorption isotherm on Fe gel at pH 6.5 after 72 hr equilibration. Asterisks in I denote samples showing an increase in bulk volume and a lightening in color indicative of Zn hydroxide (or hydroxycarbonate) precipitation.

Fig.5--Zn adsorption on various iron and aluminum oxides as a function of equilibrium Zn concentration at pH 5.5. Unlabelled full circles are for fresh Fe gel; sample A is for an aged (35 months) Fe gel (Kinniburgh et al., 1977; sample C); G1 (Bar-Yosef et al., 1975), G2 (Grimme, 1968), and G3 are for synthetic goethites; H is for synthetic hematite; Al is for fresh aluminum gel (shown for comparison with results for Fe systems).

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