

GL03604

FC
298

The adsorption of aqueous heavy metals on inorganic minerals

R. O. JAMES

Department of Applied Earth Sciences, Stanford University,
Stanford, CA 94305, U.S.A.

and

M. G. MACNAUGHTON

Environmental Chemistry Division, Environics Directorate, Tyndall AFB,
FL 32403, U.S.A.

(Received 13 January 1976; accepted in revised form 27 May 1977)

Abstract—Two models have been used to explain the *in-situ* control of heavy metals: (1) solubility controls, where precipitation of a solid phase occurs under varying metal and ligand concentrations, and (2) surface chemical controls, where adsorption or exchange occurs at the solid/solution interface. Based on experiments presented in this paper, surface chemical controls can account for the removal of heavy metals, particularly Zn(II), from metal solutions which are undersaturated with respect to the hydroxide, oxide, or other controlling solid phases. Adsorption isotherms are presented for varying solution pHs, total metal ion concentrations, ionic strengths, and mineral substrates. The minerals chosen for illustration are SiO₂, TiO₂, FeOOH, Al₂O₃, MnO_x and HgS which range widely in surface acidity, electrical double layer properties, specific surface areas, and surface functional groups.

INTRODUCTION

THE DISTRIBUTION of heavy metals between natural waters and mineral and other colloid surfaces has been extensively investigated in recent years because of the need for information about levels and controls of heavy metal concentrations in water and the association of heavy metals with suspended matter and sediments. Incentive for these studies has developed for diverse reasons, e.g. from investigations of trace metal deficiencies in animal diets and of heavy metal pollution and accumulation in natural water and marine organisms. Other applications range from the use of stream sediments as indicators in geochemical prospecting to the effect of corrosion-product oxides on the movement of radioisotopes and radiation fields in nuclear reactors.

There are two principal concepts which have been used as reference guides in discussing the control of heavy metals. These are: (1) solubility controls, where the precipitation and dissolution of solid phases of the metal ion dominate the variation of metal concentration as a function of solution parameters and time; (2) colloid and surface chemical controls, where the presence of insoluble phases, often with high surface areas, provide sites where adsorption or interfacial reactions can occur.

The interpretation of heavy metal control by both solubility and adsorption models for equilibrium processes has already reached a relatively high level of sophistication. For example, once it would have been necessary to investigate the solubility of the whole range of various solid precipitate phases that could occur for given metal, ligand, and pH conditions, and

then test whether one or more of the phases could be controlling the solubility by comparing computed with measured data.

Presently, computer programs such as HALT-FALL (INGRI *et al.*, 1967), REDEQL (MOREL and MORGAN, 1972), MINEQL (WESTALL *et al.*, 1976) and SOLMENEQ (KHARAKA and BARNES, 1973) can simultaneously handle homogeneous and heterogeneous equilibria in oceans and other natural waters with varying degrees of success, provided sufficient and accurate thermodynamic data are available. Computer programs are also available which account for the importance of adsorption in natural waters. The REDEQL heterogeneous equilibrium program of MOREL and MORGAN (1972) has been modified to include the JAMES and HEALY model (1972) for hydrolysable metal adsorption; however, this is generally an area that requires further development. To meet this need, the MINEQL program has been modified to include a rather more comprehensive adsorption model developed by YATES *et al.* (1974). Further study is still required to develop this model for complex solutes at low concentrations.

As adsorption control mechanisms may be important in many natural waters, we shall discuss some of the interfacial models that best explain the uptake of heavy metals onto inorganic surfaces. We will also show that pH, ligand concentration and metal concentrations are important to both solubility and adsorption mechanisms and that clear distinction between these models is not always possible.

The observed uptake of hydrolysable metal ions on oxide and other mineral surfaces may be summarized

as follows (JAMES and HEALY, 1972; MACNAUGHTON and JAMES, 1974):

(1) Uptake is strongly dependent on pH and usually occurs over a narrow pH range.

(2) The dependence of the fractional adsorption on pH is similar to the dependence of the fractional formation of soluble and insoluble hydrolysis products on pH; however, often the measured adsorption occurs at lower pH values than hydrolysis and usually the fractional adsorption decreases with increasing total concentration of metal. This suggests that polymerization and/or precipitation are not the controlling mechanisms.

(3) The shape of the fractional adsorption-pH curve shows that OH^- is consumed or H^+ is released as adsorption increases.

(4) The location of the adsorption region on the pH scale is characteristic of the metal ion and its complexes, and relatively insensitive to the adsorbent.

In experiments described in this paper we have used sorption theories to account for the controls on hydrolysable metal ion concentrations because the solutions are undersaturated with respect to even the most stable hydroxide phases.

The interpretation of the measured adsorption of heavy metal ions is complicated by the presence of hydrolysis products. If these are monomeric complexes, they are easily accounted for, provided their formation constants are known. However, in the more concentrated systems where polymeric species form at near saturation with respect to hydroxides or oxides, there are difficulties in allowing for the formation of kinetic intermediates to colloidal or microcrystalline solid phases.

To demonstrate the adsorption behavior of hydrolysable metals in colloidal dispersions, we have used aqueous zinc in trace amounts. It is conveniently analyzed as the Zn^{65} isotope or by atomic absorption spectrometry. The aqueous chemistry of zinc is fairly well known, Zn^{2+} being the predominant solution species in dilute solutions up to pH 8. Above this pH and for more concentrated solutions, polymerization and precipitation of hydroxides may occur. As examples of the various oxide and sulphide minerals that exist in contact with water, we have chosen α -quartz, SiO_2 ; anatase, TiO_2 ; goethite, $\alpha\text{-FeOOH}$; corundum, $\alpha\text{-Al}_2\text{O}_3$; manganese oxide, and cinnabar, HgS , as adsorbents for aqueous $\text{Zn}(\text{II})$. While these materials do not represent all, or the most commonly observed, materials in sediments, they do range widely in their surface acidities, their electric double layer properties—e.g. point-of-zero-charge (PZC) and isoelectric point (IEP)—and their specific surface areas.

EXPERIMENTAL

Reagents

All reagents used in this study were of analytical reagent (AR) grade quality and all water used was deionized, double distilled from an all-Pyrex still and stored in a

Pyrex container. This water had a conductivity of 1.1 megohm cm^{-1} or better at 25°C.

The stock solutions of zinc were generated from zinc oxide, pH and ionic strength were controlled using HNO_3 , KNO_3 and carbonate free KOH .

Preparation of solids

A. α -quartz, SiO_2 . α -Quartz was prepared by extensive cleaning of min-u-sil 5 (Pennsylvania Glass Sand Corp.). X-ray diffraction identified the silica as α -quartz. The B.E.T. N_2 adsorption surface area is $5 \pm 1.0 \text{ m}^2 \text{ g}^{-1}$, and the isoelectric point, as determined by microelectrophoresis, is at $\text{pH } 2.0 \pm 0.2$.

B. α -alumina, corundum, Al_2O_3 . α -Alumina was prepared by the repeated washing of 0.3 micron Linde A alumina abrasive (Union Carbide) with distilled water. X-ray diffraction identified the alumina as α -alumina. The B.E.T. N_2 adsorption surface area is $17 \pm 2.0 \text{ m}^2 \text{ g}^{-1}$ and the isoelectric point is at $\text{pH } 9.1 \pm 0.2$.

C. Anatase, TiO_2 . Titanium dioxide was obtained as the AR powder from the J. T. Baker Co. and was used after repeated washing with distilled water. X-ray diffraction identified the titania as anatase. The B.E.T. N_2 adsorption surface area is $7 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ and the isoelectric point is at $\text{pH } 7.2 \pm 0.2$.

D. Goethite, $\alpha\text{-FeOOH}$. Goethite was prepared by slowly adding 2.5 M KOH to a vigorously stirred $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution, then allowing the solution to age at 60°C for 24 hr. The resulting freeze-dried solid was identified by X-ray diffraction as goethite. The N_2 adsorption B.E.T. surface area was $49 \pm 1 \text{ m}^2 \text{ g}^{-1}$. The isoelectric point was at $\text{pH } 9.1$.

E. Manganese oxide, MnO_x . Manganese oxide was prepared by the room temperature oxidation of manganous sulphate. B.E.T. N_2 adsorption surface area was $95 \pm 5 \text{ m}^2 \text{ g}^{-1}$. Analysis by X-ray diffraction showed the resulting solid to be weakly crystalline and indicative of a mixture of MnOOH and Mn_2O_3 . The I.E.P. was 2.0 ± 0.5 .

F. Cinnabar, HgS . HgS was prepared from a mercury ore obtained from the Harry Tunnel Mine, New Almaden, California. The HgS was washed carefully in dilute acid followed by dilute KOH , then distilled water, and reground in a pebble mill; the -400 mesh fraction was retained for adsorption experiments. The red HgS powder gave an X-ray diffraction pattern identical to cinnabar. Its specific surface area determined by B.E.T. Kr adsorption was $0.6 \text{ m}^2 \text{ g}^{-1}$. The PZC by titration was approximately 3.5 ± 0.5 .

Adsorption analysis

The adsorption experiments were carried out in sealed Pyrex centrifuge tubes with Teflon seals and involved equilibration of a quantity of the solid substrate in a HNO_3 - KOH electrolyte solution containing $\text{Zn}(\text{II})$ at the desired initial concentration. The tubes were gently rotated end over end for 24 hr and then centrifuged to achieve solid-liquid separation prior to analysis.

Analysis for residual $\text{Zn}(\text{II})$ in those experiments concerned with the uptake by oxides was accomplished by atomic absorption spectroscopy (AAS). For those experiments involving HgS , labelled $\text{Zn}^{65}(\text{II})$ was utilized as a tracer and the Zn activity of the centrifuged solutions was measured using a Baird Atomic 2-inch NaI crystal well scintillation counter. Losses due to adsorption to the centrifuge tubes were not found to be significant.

RESULTS

The solution chemistry and solubility of zinc materials in natural water systems has been reviewed by HEM (1972). Using his selection of data, listed below,

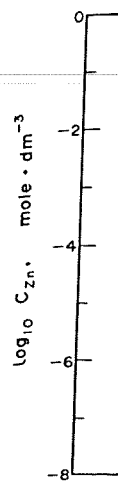
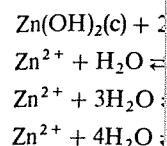


Fig. 1. Compar experiments with of pH in dilute

we have drawn for zinc hydro dm^{-3} ionic str some of the m experiments pr ship of the ads zinc hydroxide



Clearly, those saturated with $\text{Zn}(\text{OH})_2$. The solubility of zinc for the $\text{Zn} \cdot \text{SiO}_2$, SiO_2 should dis willemite, hemir PICKERING, 1974 to affect the sol is excessively hi

The fractiona and PARKS, 1972 KOH) is shown two orders of m shown as a dot $\text{Zn}(\text{OH})_2/\text{Zn}_{\text{tot}}$ (solid is unstable HEM's (1972) calc a useful compar tion and hydroly

When oxide s tively small char adsorption-pH d ted line in Fig.

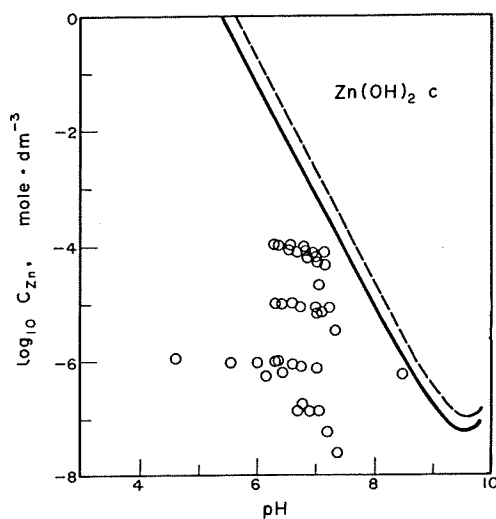
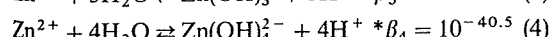
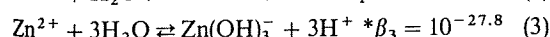
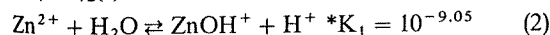
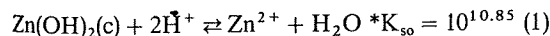


Fig. 1. Comparison of zinc concentration in adsorption experiments with the solubility of $Zn(OH)_2(c)$ as a function of pH in dilute—and 0.1 M ionic strength—(HEM, 1972).

we have drawn in Fig. 1 the solubility-pH diagram for zinc hydroxide in dilute solution and 0.1 mol dm⁻³ ionic strength. Also on this figure are indicated some of the measured concentrations of zinc in the experiments presented here to illustrate the relationship of the adsorption region to the precipitation of zinc hydroxide.



Clearly, those interfacial systems shown are undersaturated with respect to bulk precipitation of $Zn(OH)_2$. The only conditions which may exceed the solubility of zinc phases are those in the experiments for the Zn/SiO₂ system where, given sufficient time, SiO₂ should dissolve sufficiently to form zinc silicates, willemite, hemimorphite or other phases (TILLER and PICKERING, 1974). The solubility of ZnCO₃ is too high to affect the solution zinc concentrations unless there is excessively high alkalinity (HEM, 1972).

The fractional uptake of zinc on cinnabar (JAMES and PARKS, 1975) at 10⁻² M ionic strength (HNO₃-KOH) is shown in Fig. 2 for solutions ranging over two orders of magnitude on zinc concentration. Also shown as a dotted line is the fractional hydrolysis $Zn(OH)_x/Zn_{tot}$ for 10⁻⁴ mol dm⁻³ zinc. Thus, this solid is unstable relative to the solid phase used in HEM's (1972) calculations. However, the data provide a useful comparison between the fractional adsorption and hydrolysis over periods of a few hours.

When oxide substrates are used, only comparatively small changes are observed in the fractional adsorption-pH dependence relative to HgS. The dotted line in Fig. 3 shows the fractional hydrolysis of

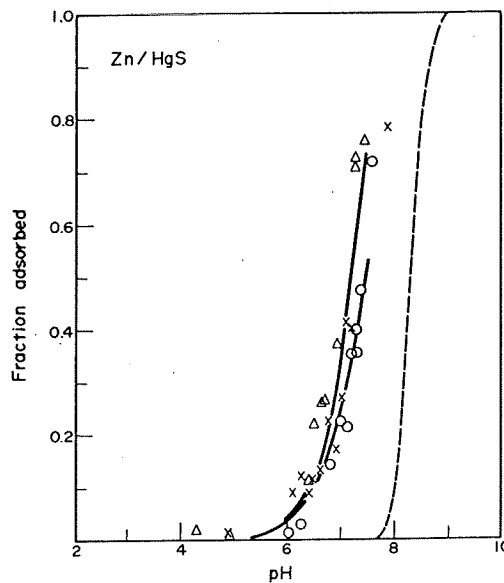


Fig. 2. Adsorption of Zn at the cinnabar/water interface as a function of pH and total zinc concentration. (Δ) 1.08×10^{-6} M, (\times) 1.08×10^{-5} M, (\circ) 1.08×10^{-4} M zinc, $24 \text{ m}^2 \text{ dm}^{-3}$ HgS and 10^{-2} M KNO₃. Dotted line shows fractional hydrolysis of 10^{-4} M zinc. The full lines show calculated adsorption using surface-hydrolysis model.

10⁻⁴ mol dm⁻³ zinc solutions in the absence of silica or manganese oxide. If, however, sufficient SiO₂ is dissolved from the silica over the 24-hr adsorption time, it is possible these points would lie near the limit of solubility of zinc silicates. Unfortunately, soluble silica was not measured, so this experiment may

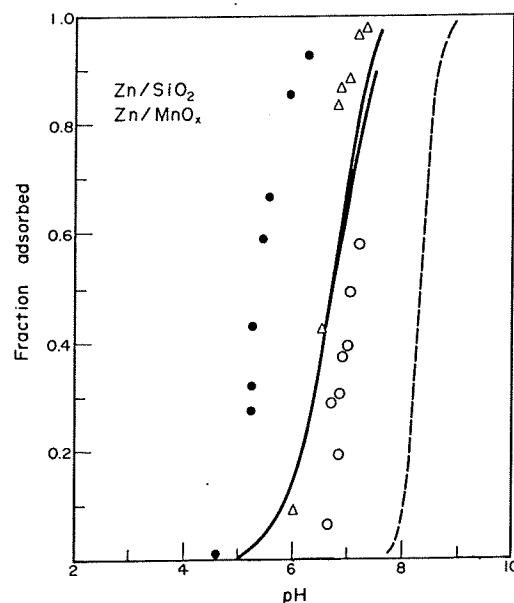


Fig. 3. Adsorption of zinc at the silica and manganese oxide/water interface as a function of pH and total zinc concentration. (\circ) 10^{-4} M, (Δ) 10^{-6} M zinc, $100 \text{ m}^2 \text{ dm}^{-3}$ SiO₂, (\bullet) 10^{-4} M zinc, $200 \text{ m}^2 \text{ dm}^{-3}$ manganese oxide. Dotted line shows fractional hydrolysis of 10^{-4} mol dm⁻³ zinc in the absence of SiO₂ or MnO_x. The full lines show computer calculated adsorption using surface-hydrolysis model for 10^{-4} M and 10^{-6} M zinc and silica.

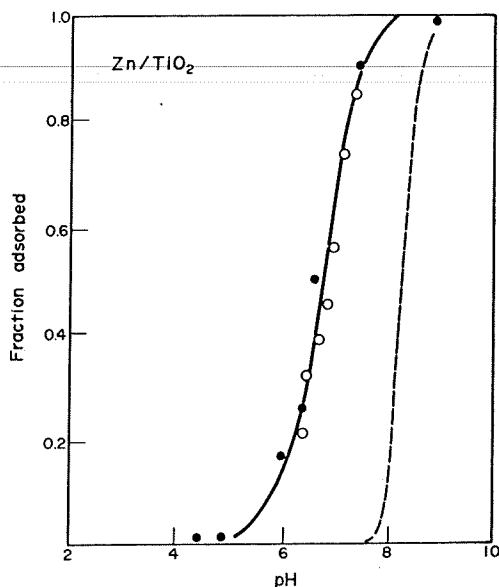


Fig. 4. Adsorption of zinc at the anatase/water interface as a function of pH and ionic strength. (○) 4 × 10⁻⁴ M, (●) 1 M KOH-HNO₃, 110 m² dm⁻³ TiO₂. Dotted line shows fractional hydrolysis of 10⁻⁴ mol dm⁻³ zinc in the absence of SiO₂ or MnO₂. Full line shows calculated uptake.

be ambiguous. The uptake of zinc onto anatase, TiO₂ (Fig. 4) shows a similar pH dependence. Figure 4 also shows there is little effect resulting from an increase in the ionic strength from approx 10⁻⁴ to 1 mol dm⁻³.

The pH dependence of zinc adsorption onto alu-

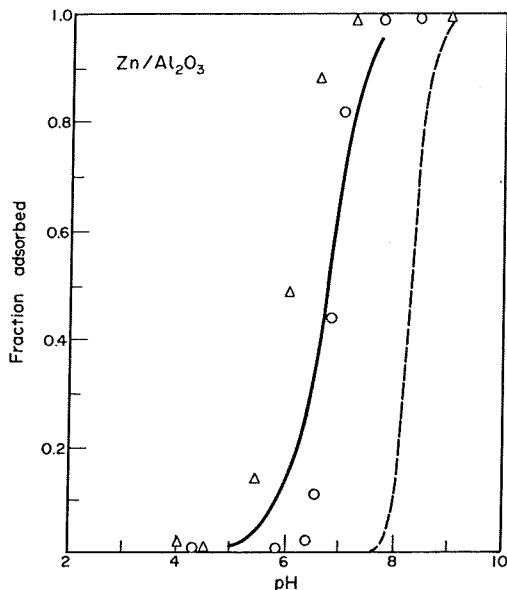


Fig. 5. Adsorption of zinc at the alumina/water interface as a function of pH and total zinc concentration. (Δ) 10⁻⁶ M, (○) 10⁻⁴ M zinc, 100 m² dm⁻³ Al₂O₃. Full line shows calculated uptake while broken line shows hydrolysis of 10⁻⁴ M zinc.

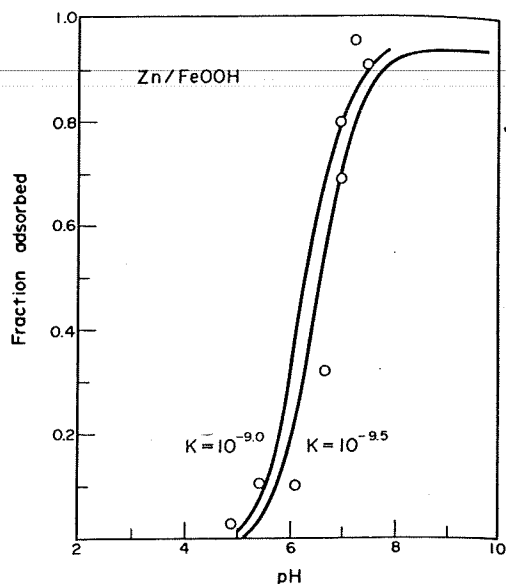


Fig. 6. Adsorption of zinc at the goethite/water interface as a function of pH. 5 × 10⁻⁴ M zinc, 98 m² dm⁻³ FeOOH. Full lines were calculated using the ion exchange model (DUGGER *et al.*, 1964) with k = 10^{-9.5} to show effect of uncertainty in exchange constant.

mina in Fig. 5 is similar. The concentration dependence may be somewhat more important here than for HgS or SiO₂. The shift of the adsorption edge to a lower pH with decreasing total zinc indirectly indicates that Zn removal from solution is not due to precipitation.

Adsorption of zinc from 5 × 10⁻⁴ mol dm⁻³ solutions by goethite is shown in Fig. 6, where the pH dependence of adsorption and the uptake are very similar to the other oxides, TiO₂, Al₂O₃, SiO₂ and the sulphide HgS.

Of the oxides used in adsorption studies, manganese oxides have shown at least two general behaviors: (1) they are difficult to characterize; and (2) they sometimes appear to show an exceptionally high affinity for metal ions (GADDE, 1974; MURRAY, 1975). Our brief results for zinc adsorption on manganese oxide in Fig. 3 illustrate this point. The pH dependence is similar; however, the adsorption occurs at about 2 pH units lower than for the other solid substrates.

DISCUSSION

Models of sorption

As an introduction to the discussion of the results, we will review some of the methods and models that can describe the sorption phenomena in colloidal systems of geochemical interest. There are at least two conceptual approaches to the problem:

(1) The estimation of the free energies of adsorption for each hydrolytic species of a metal and calculation of adsorption isotherms using the electrical double

layer the 1973).

(2) The the deriva these rea 1964; SCF GAMSJAGI These g general te concepts 1 FeOOH.

DUGGER ion is adsc released. T mercury a JAMES, 197 and PARKS the conce (M^{m+}) is us

The sorp tons can al induced hy

S +

S +

S +

where S is t

Here we d the ratio of of free and l

D = M

= Σ

Using the re (5)-(7),

D = M

=

where the *β the formation the stepwise s the formation ucts and S is the activity or is available fro ion-selective e coefficient, D,

D' = M

Thus the value the variation o of (H⁺).

These ion assume that ad dependent of t

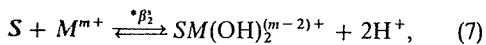
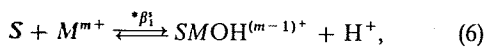
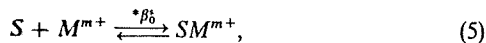
layer theory (JAMES and HEALY, 1972; BOWDEN *et al.*, 1973).

(2) The postulation of ion exchange reactions and the derivation of exchange constants or quotients for these reactions (JAMES *et al.*, 1975; DUGGER *et al.*, 1964; SCHINDLER and KAMBER, 1968; SCHINDLER and GAMSJAGER, 1972).

These general approaches have been discussed in general terms by JAMES *et al.* (1975) who applied the concepts to the adsorption of Cd(II) on TiO₂ and FeOOH.

DUGGER *et al.* (1964) consider that when a metal ion is adsorbed, an equivalent number of protons are released. This formulation has been used to describe mercury adsorption on quartz (MACNAUGHTON and JAMES, 1974) and zinc adsorption on cinnabar (JAMES and PARKS, 1975) with reasonable success, provided the concentration of the uncomplexed metal ion (M^{m+}) is used in this isotherm.

The sorption of metal ions and the release of protons can also be written as an adsorption and surface induced hydrolysis reaction, e.g.



where S is the concentration of surface sites.

Here we can define a distribution coefficient, D , as the ratio of the moles adsorbed and the total moles of free and hydrolysed metal ions.

$$D = \frac{M_{\text{surface}}}{M_{\text{solution}}} = \frac{\sum SM(OH)_i^{(m-i)+}}{\sum M(OH)_i^{(m-i)+}} \quad (8)$$

Using the reaction constants defined by equations (5)–(7),

$$D = M^{m+} \frac{\sum_{i=0}^j S * \beta_i^s / (H^+)^i}{\sum_{i=0}^j S * \beta_i / (H^+)^i} = S * \beta_0^s \frac{\sum * K_i^s / (H^+)^i}{\sum * \beta_i / (H^+)^i}, \quad (9)$$

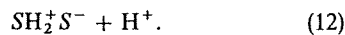
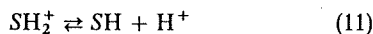
where the $* \beta_i^s$ are the overall stability constants for the formation of surface complex species, the $* K_i^s$ are the stepwise surface hydrolysis constants, the $* \beta_i$ are the formation constants of soluble hydrolysis products and S is the concentration of surface sites. If the activity or concentration of the free metal species is available from e.m.f. measurements by, for instance, ion-selective electrodes, we can define a distribution coefficient, D , in terms of the free metal species:

$$D' = \frac{M_{\text{surface}}}{M^{m+}} = S * \beta_0^s \frac{\sum * K_i^s / (H^+)^i}{\sum * \beta_i / (H^+)^i}. \quad (10)$$

Thus the values of $* \beta_i^s$ or $* K_i^s$ may be obtained from the variation of D or D' with the reciprocal power of (H^+) .

These ion exchange models, as written above, assume that adsorption interaction is specific and independent of the surface charge substrate and ignore

the dissociation of the mineral surface:



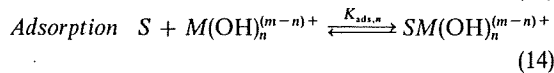
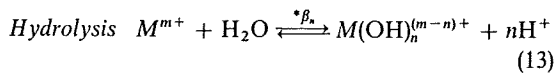
One reason that this is possible may be that usually SH^0 sites are dominant and they do not change significantly until the solution pH is far from the point of zero charge. If we adopt the idea of estimating the concentration of surface sites SH_2^+ , SH^0 and S^- in terms of moles of sites per dm³, then the surface dissociation and ion exchange equilibria can be conveniently handled by "solution equilibria" computer programs such as COMICS (PERRIN and SAYCE, 1967), MINICOMICS and SPECON (PERRIN, personal communication, 1975).

In fact, the values of surface reaction "constants" usually vary with the surface charge and potential (SCHINDLER and GAMSJAGER, 1972) in a similar manner to the dissociation of polyacrylic acids (STUMM *et al.*, 1970) and proteins due to the electrostatic interaction of already charged groups with the leaving protons.

The above models can always be used to describe metal ion uptake, provided the data used in calculating the D and D' vs $(H^+)^{-1}$ are of high accuracy and reproducibility. However, these models are not predictive since the experiment must be performed to evaluate the constants which may later be used for similar systems.

An adsorption model that reduces to a form similar to the above model was proposed by JAMES and HEALY (1972). In this model the adsorption of metal species from the entire suite of soluble hydrolysis products is estimated by *a priori* calculation of the free energy of adsorption of each species. This can then be inserted into an adsorption isotherm and an appropriate model of the electrical double layer at the mineral/water interface.

The model is developed thus:



$$\text{Isotherm } \Gamma = \frac{\Gamma_{\text{max}} M^{m+} \sum K_{\text{ads},n} * \beta_n / H^{n+}}{1 + M^{m+} \sum K_{\text{ads},n} * \beta_n / H^{n+}} \quad (15)$$

where $K_{\text{ads},n}$ for each adsorption step was estimated from

$$K_{\text{ads},n} = \exp(-\Delta G_{\text{ads},n} / RT)$$

and

$$\Delta G_{\text{ads},n} = \Delta G_{\text{coul},n} + \Delta G_{\text{solv},n} + RT \Delta G_{\text{chem},n};$$

i.e.

$$\Delta G_{\text{ads},n} = Z_n e \psi + f \left(\left(\frac{Z^2 e^2}{r} \right) \left(\frac{1}{\epsilon_{\text{interface}}} - \frac{1}{\epsilon_{\text{solution}}} \right) \right) + \Delta G_{\text{chem}}. \quad (16)$$

Where z_n is the charge of the adsorbing species, $e\psi$ is the energy required to move an ion across the interface, and r is the hydrated radius of the adsorbing species. The terms $\Delta G_{\text{coul},n}$ and $\Delta G_{\text{solv},n}$ are the changes in electrostatic free energy and secondary solution energy as the adsorbing ion moves from bulk solution with a dielectric constant ($\epsilon_{\text{solution}}$) to its equilibrium position in the interface ($\epsilon_{\text{interface}}$). The estimation of these contributions depends on the model assumed for the charge and potential distribution in the interface region (LEVINE, 1971; YATES *et al.*, 1974). James and Healy assumed that in dilute concentrations the adsorption of metal species would not greatly perturb the potential distribution due to excess background electrolyte, and hence they used the simple Gouy-Chapman potential decay. A model using the same isotherm for the uptake of metal ions but using the more complete Gouy-Chapman-Stern model has recently been proposed by BOWDEN *et al.* (1973), to describe the calculation of adsorption of zinc on goethite. In the James and Healy model, ΔG_{chem} is used to improve the fit of the data and to allow for errors in ΔG_{coul} and ΔG_{solv} . The ΔG_{chem} term has the same value for each of the species in a suite of hydrolysis products.

In the future, progress will hopefully be made in predictive models by a combination of the above descriptions. For example, the *a priori* approach of James and Healy should be applied to the latest developments in the Gouy-Chapman-Stern models for oxide/electrolyte interfaces (YATES *et al.*, 1974); PERAM *et al.*, 1974; BOWDEN *et al.*, 1973).

Because the data for zinc adsorption on cinnabar have been measured over quite a wide concentration range, we have used these results for application of the surface hydrolysis-ion exchange model.

Previously, JAMES *et al.* (1975) calculated the distribution coefficient D as the ratio of the moles of adsorbed ions per kilogram of solid to the moles per dm^3 of solution. In our case, where we have adsorption onto solids of different specific surface area, it is more rational to define a distribution coefficient in terms of the moles adsorbed per metre², the surface area per litre and the equilibrium concentration in moles per dm^3 .

$$D = (\text{mol m}^{-2})(\text{m}^2 \text{ dm}^{-3})/\text{mol dm}^{-3} \\ = \sum_{i=0}^j SM(\text{OH})_i^{(m-i)+} / \sum M(\text{OH})_i^{(m+i)+}, \quad (17)$$

$$D = S \sum * \beta_i^m / (\text{H}^+)^i \Big/ \sum_{i=0}^n * \beta_i / (\text{H}^+)^i, \quad (18)$$

$$\sum_i * \beta_i / \text{H}_i = 1; \text{ i.e. } \alpha_{\text{Zn}^{2+}} = 1, \quad (19)$$

since, for our systems, the free ion Zn^{2+} is at least 95% of the zinc in solution (HEM, 1972).

The term S is the equilibrium surface not covered by metal ions. It is again convenient to express S as moles of surface sites per litre for mass balance pur-

poses. This can be done by assuming that hydrated metal ions occupy about 50 \AA^2 per site; then for $24 \text{ m}^2 \text{ dm}^{-3}$ of HgS we have $24 \times 10^{20}/50/6 \times 10^{23}$ moles of sites; i.e. $S_0 = 8 \times 10^{-5}$ moles of sites/ dm^3 .

The equilibrium number of sites uncovered is given by

$$S = S_0 - C_{\text{Zn}_{\text{ads}}}, \text{ mol dm}^{-3}. \quad (20)$$

Graphs of D/S vs $1/\text{H}$ and DH/S vs $1/\text{H}$ for the Zn/HgS data were plotted to give the constants $*\beta_1$ and $*\beta_2$ as the coefficients of the equation

$$D/S = 5 \times 10^{-4}/\text{H}^+ + 2 \times 10^{-11}/(\text{H}^+)^2. \quad (21)$$

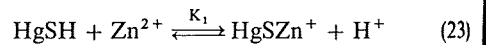
This expression may be used to calculate the fractional adsorption, F , from solution at various added concentrations C_T and surface areas, or surface site concentration, S_0 .

$$D = F/(1 - F) \text{ and } S = S_0 - FC_T. \quad (22)$$

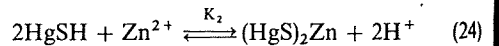
This gives a quadratic equation for F in terms of D/S , S_0 and C_T . These calculations were performed for the oxides as well as cinnabar using the above values of $*\beta_1$ and $*\beta_2$.

Results of the calculations are shown as full lines on Fig. 2-5. It becomes obvious that, whatever the solid, there must be similar interactions between the adsorbed ion and its environment, because the parameters for the "surface hydrolysis" and "ion exchange" hypotheses give reasonably good agreement among all the different experiments.

JAMES and PARKS (1975) applied the adsorption model for hydrolysed metal ions developed by JAMES and HEALY (1972) and the simple ion exchange model of DUGGER *et al.* (1964) to the Zn/HgS results with similar agreement to the above method. They found that for the James-Healy model, $\Delta G_{\text{chem}} = -6.5 \text{ kcal mol}^{-1}$ gave satisfactory results. The Dugger model for the two equilibria considered involved the exchange of either one or two protons for each metal ion adsorbed, thus:



and



where the exchange constants are $K_1 = 10^{-3}$ and $K_2 = 10^{-10.5}$, respectively. The present analysis is an improvement on the simple ion exchange of Dugger *et al.* because it allows for a two-step reaction. At low pH, approximately one proton is released per adsorbed zinc, and at the higher pH of the adsorption range about two protons are released. It should be noted that the H^+ exchanged per Zn(II) adsorbed usually varied with pH (JAMES *et al.*, 1975), and that one-step reactions that exchange equivalent amounts of H^+ and Zn^{2+} charge, like the reactions assumed by DUGGER *et al.* (1964), should only apply to the high pH region of adsorption isotherms.

For the adsorption of zinc onto goethite in Fig. 6, we have used the simple DUGGER *et al.* (1964) for-

mulation
exchange
adsorptic
two valu
surface c
per liter.

2FeO

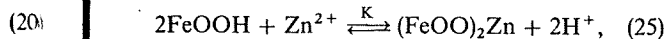
$K = 10^{-9}$
experimen
exchange

We have
to the upt
mineral su
conceived,
electrical d
models wit
chemical st
mental syst
certain oxid
action betw
are similar.

It should
approaches
potential be
Some work
for simple s
of a relation
surface poter
of the miner
SMITH, 1971;
by SCHINDL
(1976) have fe
metals as a su
tions. Howev
static perturb
largely ignor
recent modifi
to handle sur
potential rela
some of the v
comparison o

BOWDEN J. W.
QUIRK J. P.
cation adsor
Science) 245,
CHAN D., PERR
(1975) Regula
faces during
Faraday Tran
DUGGER D. L., S
CUMMINGS W
exchange of t
silanol group
GADDE R. R. and
metal adsorpt
oxides. Anal. C

mulation of the ion exchange model to obtain exchange constants and to calculate the fractional adsorption from solutions. This has been done for two values of the constant for the reaction where the surface concentration is expressed as moles of sites per liter.



$K = 10^{-9}$ and $10^{-9.5}$, to demonstrate the effect of experimental uncertainty in evaluation of ion exchange constants.

CONCLUSIONS

We have shown that various models can be applied to the uptake of aqueous metal ions onto colloidal mineral surfaces. In the form that these models were conceived, they fall naturally into two groups: (1) electrical double layer models; and (2) ion exchange models without real consideration of the physicochemical structuring of the interface. In the experimental system studied here it is apparent that for certain oxides and other minerals the chemical interaction between the adsorbed ion and its host surface are similar, the principal exception being manganese.

It should be possible in the future to combine these approaches by rigorous account of the charge and potential behavior as well as specific interactions. Some work has already been published in this area for simple systems. This is based on the derivation of a relationship between the surface charge, σ_0 , and surface potential ψ_0 via the acid-base self dissociation of the mineral surface (YATES *et al.*, 1973; LEVINE and SMITH, 1971; CHAN *et al.*, 1975). Very recently studies by SCHINDLER *et al.* (1976) and HOHL and STUMM (1976) have formulated the adsorption of hydrolysable metals as a surface complex with electrostatic interactions. However, in their analysis of results, the electrostatic perturbation of the adsorption constants is largely ignored due to computational difficulties. The recent modifications of such programs as MINEQL to handle surface reactions with charge and surface potential relationships may allow differentiation of some of the various ways adsorption may occur by comparison of experiment and theory.

REFERENCES

- BOWDEN J. W., BOLLAND M. D. A., POSNER A. M. and QUIRK J. P. (1973) Generalized model for anion and cation adsorption at oxide surfaces. *Nature (Physical Science)* **245**, 81-83.
- CHAN D., PERRAM J. W., WHITE L. R. and HEALY T. W. (1975) Regulation of surface potential at amphoteric surfaces during particle-particle interaction. *J. Chem. Soc., Faraday Trans. I*, **71**, 1046-1057.
- DUGGER D. L., STANTON J. H., IRBY B. N., MCCONNELL B. L., CUMMINGS W. W. and MAATMAN R. W. (1964) The exchange of twenty metal ions with the weakly acidic silanol group of silica gel. *J. Phys. Chem.* **68**, 757-760.
- GADDE R. R. and LAITINEN H. A. (1974) Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Anal. Chem.* **46**, 2022-2026.
- HEM J. D. (1972) Chemistry and occurrence of cadmium and zinc in surface water and ground water. *Water Resour. Res.* **8**, 661-679.
- HOHL H. and STUMM W. (1976) Interaction of Pb^{2+} with hydrous Al_2O_3 . *J. Colloid Interface Sci.* **55**, 281-288.
- INGRI N., KAKOTOWICZ W., SILLEN L. G. and WARNGVIST B. (1967) HALTAFALL, A general program for calculating the composition of equilibrium mixtures. *Talanta* **14**, 1261-1286.
- JAMES R. O. and HEALY T. W. (1972) Adsorption of hydrozable metal ions at the oxide-water interface III. A thermodynamic model of adsorption. *J. Colloid Interface Sci.* **40**, 65-81.
- JAMES R. O. and PARKS G. A. (1975) Adsorption of zinc (II) at the sulphide/water interface. *A.I.Ch.E. Symposium Series 150* **71**, 157-164.
- JAMES R. O., STIGLICH P. J. and HEALY T. W. (1975) Analysis of models of adsorption of metal ions at oxide/water interfaces. *Gen. Disc. Faraday Soc.* **59**, 142-156.
- KHARAKA Y. K. and BARNES I. (1973) SOLMENEQ: solution-mineral equilibria computations. *U.S. Geol. Surv. W.R.D.* 73-002.
- LEVINE S. and SMITH A. L. (1971) Theory of the differential capacity of the oxide/aqueous electrolyte interface. *Gen. Disc. Faraday Soc.* **52**, 290-301.
- LEVINE S. (1971) Discussion of the calculation of solvation energy charges. *General Disc. Faraday Soc.* **52**, 320-325.
- MACNAUGHTON M. G. and JAMES R. O. (1974) Adsorption of aqueous mercury complexes at the oxide/water interface. *J. Colloid Interface Sci.* **47**, 431-440.
- MOREL F. and MORGAN J. J. (1972) A numerical method for solution of chemical equilibria in aqueous systems. *Environ. Sci. Technol.* **6**, 58-67.
- MURRAY J. W. (1974) The surface chemistry of hydrous manganese dioxide. *J. Colloid Interface Sci.* **46**, 357-371.
- MURRAY J. W. (1975) The interaction of metal ions at the manganese dioxide-solution interface. *Geochim. Cosmochim. Acta* **39**, 505-519.
- MURRAY D. J., HEALY T. W. and FUERSTENAU D. W. (1968) Adsorption of aqueous metal on colloidal hydrous manganese oxide. In *Adsorption from Aqueous Solutions*, pp. 74-81. Amer. Chem. Soc. Adv. Chem. Series 79.
- PERRAM J. W., HUNTER R. J. and WRIGHT H. J. L. (1974) The oxide-solution interface. *Aust. J. Chem.* **27**, 461-475.
- PERRIN D. D. and SAYCE I. G. (1967) Computer calculation of equilibrium concentrations in mixtures of metal ions and complexing species. *Talanta* **14**, 833-842.
- SCHINDLER P., FURST B., DICK R. and WOLF P. V. (1976) Ligand properties of surface silanol groups I. Surface complex formation with Fe^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} . *J. Colloid Interface Sci.* **55**, 469-475.
- SCHINDLER P. and GAMSJAGER H. (1972) Acid/base reactions of the TiO_2 (anatase)-water interface and the point of zero charge of TiO_2 suspensions. *Colloid Polym. Sci.* **250**, 759-763.
- SCHINDLER P. and KAMBER H. K. (1968) The acidity of silanol groups. *Helv. Chem. Acta* **57**, 1781-1787.
- STUMM W., HAUNG C. P. and JENKINS S. R. (1970) Specific chemical interaction affecting the stability of dispersed systems. *Croat. Chem. Acta* **42**, 223-244.
- TILLER K. G. and PICKERING J. G. (1974) The synthesis of zinc silicates at 20°C and atmospheric pressure. *Clays Clay Minerals* **22**, 409-416.
- WESTALL J. C., ZACHARY J. L. and MOREL, F. M. M. (1976) MINEQL—A computer program for the calculation of chemical equilibrium composition of aqueous systems. Technical note 18 Ralph M Parsons Laboratory for Water Resources and Environmental Engineering Massachusetts Institute of Technology.
- YATES D. E., LEVINE S. and HEALY T. W. (1974). Site binding model of the electrical double layer at the oxide/water interface. *J. Chem. Soc., Faraday Trans. I*, **70**, 1807-1818.