On the Surface Precipitation Model for Cation Sorption at the (Hydr)oxide Water Interface

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Abstract. The surface precipitation model has been developed to describe sorption data over a wide range of free sorbate concentration. It provides a smooth transition from adsorption to surface precipitation. The applicability of the model has been shown in several publications. In most of the previous applications of the surface precipitation model all sorbent present was supposed to take part in the formation of an ideal solid solution. We show that if only the sorbent present as surface sites contributes to the 'solid solution', the isotherm of the surface precipitation model reduces to the well-known BET isotherm. Between these limiting cases it is difficult to find a unique description of the macroscopic data. Some further problems involved in parameter estimation are discussed: especially for weakly adsorbing metal cations or those with low solubilities the choice of modelling parameters may be difficult. We describe how the observed difficulties may be used to estimate if adsorption constants, determined by modelling adsorption data, are reasonable and discuss the limitations of the proposed approach. Finally, it is concluded that apparent interfacial solubility products may be expected to change with pH and sorption density.

Key words: sorption isotherms, sorption, surface complexation model, surface precipitation model, solid solution, parameter estimation

1. Introduction

Sorption of metal cations onto (hydr)oxide surfaces from aqueous solution and description of metal/solid partitioning have been focussed on in aqueous chemistry, aqueous geochemistry and are of interest in environmental studies and for industrial applications, e.g. catalysts. The term (hydr)oxide is used to describe all potential sorbents occurring as oxides, hydroxides, and oxyhydroxides. A global suvey of sorption mechanisms is given in Table I. Following the nomenclature by Sposito (1984), the term sorption means overall deposition of inorganics on (hydr)oxide surfaces. The different mechanisms comprise adsorption, which is generally fast and prevails at low sorption densities with the formation of no more than one sorption layer, as well as surface precipitation and absorption. Distinguishing between the two latter may be difficult since both may result in the formation of a solid solution. The term surface precipitation is here used to describe the formation of a three-dimensional (hydr)oxide phase either consisting of several sorption layers of

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Table I. General survey of sorption mechanisms.

Sorption mechanism	Sorption density	Number of sorption layers	Dimension of sorbate	Sorption kinetics
Adsorption	low	≤ 1	2D	fast
Surface precipitation[a]	high	> 1	3D	slow
Absorption[b]	high or low	1 or > 1	2D or 3D	slow

[a]Via heterogeneous nucleation or solid-solution formation.
[b]Possibly resulting in solid-solution formation.

the sorbing cation formed via heterogeneous nucleation or a mixture of the solid formed by the sorbing cation with the sorbent via solid solution formation, i.e. due to dissolution/precipitation processes. Both of these pathways are expected to be slow. Absorption describes the diffusion process, which allows the sorbing cation to sorb into the bulk of the sorbent. It will generally occur through mass transport in pores of different sizes (pore diffusion) or through defects (solid state diffusion). Absorption must in general be considered to be accompanied by adsorption onto the actual particle aqueous solution interface as well as onto pore walls (van Riemsdijk and van der Zee, 1991).

The surface precipitation model (SPM) developed by Farley *et al.* (1985) is capable of describing sorption data over a wide range of metal concentration. It has proved to be a useful tool for interpretations which have to deal with both adsorption (at low free metal concentrations, adsorption densities) and precipitation (at high free metal concentrations, sorption densities). Sorbents to which this model has been successfully applied so far are hydroxides (Farley *et al.*, 1985; Dzombak and Morel, 1986, 1990; Charlet and Manceau, 1992) and carbonates (Comans and Middelburg, 1987; Wersin *et al.*, 1988). The model has been successfully applied to coprecipitation processes as well (Charlet and Manceau, 1992).

In the surface precipitation model the transition from adsorption to precipitation is achieved by considering precipitation reactions of both the sorbate and the sorbent. The precipitating species are assumed to form an ideal solid solution. As a rule of thumb, Dzombak and Morel (1990, p. 274) recommand to consider surface precipitation, if (i) dissolved sorbate concentration exceeds one-tenth of its solubility or (ii) 50% of the total surface site concentration is occupied. Van Riemsdijk and van der Zee (1991) conclude that the framework developed by Farley *et al.* (1985) cannot be distinguished from ion exchange.

The use of the model has so far been largely restricted to systems, where the respective investigators considered all the sorbent present to participate in the formation of the solid solution. Dzombak and Morel (1990, p. 243), however, also state that in applying the model to cristalline solids 'only a fraction of the mass of the sorbent may effectively participate in solid solution reactions'. More recently, Katz (1993) presented some calculations, for which she assumed a lower amount of

sorbent taking part in solid solution formation. Compared to the case, where all the sorbent takes part in solid solution formation, the resulting pH adsorption edge was less steep. From her results it is also apparent, that the formation of polynuclear surface complexes is at least equally successful in describing the difficult region close to site saturation. We will not consider polynuclear surface complexes. They may easily be incorporated using the general procedure in writing the required reaction stoichiometries (e.g. Gunneriusson, 1993).

Katz (1993) argues that if only part of the sorbent participates in solid solution formation the solid solution is no longer homogeneous. Bohn and Bohn (1986) summarizing work by others conclude that total equilibrium is impossible, because 'any dissolution or precipitation will change the composition of the surface from that of the bulk'. Only if all solid solution components are equally soluble and if kinetics is not a controlling factor for the dissolution or precipitation of any of the components, the composition of the surface will not be different from the bulk. From this point of view it may be concluded that in aqueous medium (i) all the components of the solid solution must be equally soluble, (ii) equal solubility is impossible, and (iii) thus total equilibrium is impossible, and completely homogeneous solid solutions do not exist (Bohn and Bohn, 1986). Considering that solid solution formation is extremely slow (van Riemsdijk and van der Zee, 1991), on the time scale of laboratory experiments we would not expect such an equilibrium, even if a total equilibrium could be reached. In view of these conclusions, it might be argued that in many cases only the superficial part of the sorbent mixes with the sorbate, corresponding to a pseudo-equilibrium state. Parameters determined for those cases do not correspond to true thermodynamic equilibrium, and it should be kept in mind that the parameters obtained from those cases correspond to pseudo-equilibrium. This is similar to an approach for transient surface complexation constants (Marmier et al., 1994). We would like to recall that the applied theories of solid solution and adsorption are equilibrium theories, whereas most probably a large part of experimental observations used for the application of these theories do not correspond to thermodynamic equilibrium. The definition of equilibrium criteria is a major problem when coherent data bases for surface complexation reactions are to be established (Dzombak and Morel, 1990). The end of the true fast adsorption process is difficult to estimate due to the onset of the slow absorption and/or surface precipitation steps. For the case of amorphous hydrous ferric oxides (HFO), it seems that the aging time of the sorbent and the equilibration time are equally important. For HFO, aging times should be preferably at least four hours in order to obtain a stable sorbent (Dzombak and Morel, 1990). Short aging times may be supposed to result in smaller and/or more reactive particles, which by means of increased surface site concentration and/or increased affinity causes an underestimation of adsorption when the data base is used to predict sorption. Prolonged aging may result in partial formation of crystalline iron oxide. It should be kept in mind that a data base such as the one established by Dzombak and Morel (1990) must be expected to have a maximum of predictive capacity when

applied to data obtained in agreement with the data selection criteria used for the establishment of the data base. The present authors presume that for hydrous ferric oxide short aging times (less than four hours) along with short equilibration times (less than four hours) at low sorbate to sorbent ratios, the HFO data base is no longer predictive. The coherent use of the data base is also associated to solution complexation reactions, e.g. the MINTEQA2 code (Allison et al., 1991) contains a thermodynamic data base for surface complexation reactions with HFO, but the thermodynamic data base for solution reactions is far more elaborate than the one used by Dzombak and Morel (1990).

In this paper we intend to show the place of the SPM within the framework of simple (one site/one species) sorption isotherms. The limited applicability of a one site/one species model is obvious, but the discussion is useful. We further attempt an analysis of the parameters of the SPM. We will show that the isotherm equation of the SPM as derived by Farley et al. (1985) may be considered to be one limiting case in a generalized surface precipitation model. The other limiting case is shown to be the well-known BET isotherm. We will then discuss some of the problems, which may be encountered in estimating adjustable parameters like intrinsic surface complexation constants or apparent solubility products. The proposed procedures can be applied to more often encountered situations (multiple site/one species models or one site/multiple species models). In practice a distinction of these two extreme situations will not be possible from macroscopic sorption data and the most probably realistic intermediate situation must be considered to have the disadvantage of having a too large number of adjustable parameters.

2. Theory

2.1. SURFACE CHEMICAL REACTIONS

Adsorption of cations onto oxides may be described by surface complexation models (SCMs). The removal of the cation is assumed to be given by a surface coordination reaction such as Equation (1):
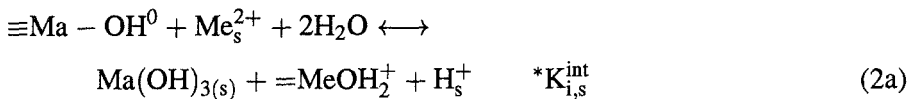
$$\equiv Ma - OH^0 + Me_s^{2+} \longleftrightarrow \equiv Ma - O - Me^+ + H_s^+ \qquad {}^*K_i^{int}, \qquad (1)$$
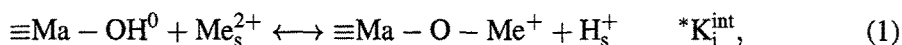
where Ma denotes the cation constituting the sorbent (hydr)oxide and Me is a divalent sorbing metal; $\equiv Ma - OH^0$ is a surface site; aqueous species with subscript 's' refer to their presence at the surface. Their concentrations are usually calculated from the bulk concentrations using an electrostatic term. ${}^*K_i^{int}$ is the so called intrinsic equilibrium constant, where the subscript 'i' denotes the type of site. There are several electrical double-layer (EDL) models available to calculate the contribution of electrostatics to the free energy of adsorption (Westall and Hohl, 1980; Davis and Kent, 1990). Other reaction stoichiometries than the one used in Equation (1) might be thought of and are especially required for modelling experimental results obtained from potentiometric titrations (e.g., Gunneriusson, 1993). Since establishing simple isotherms for more than one adsorbate species is
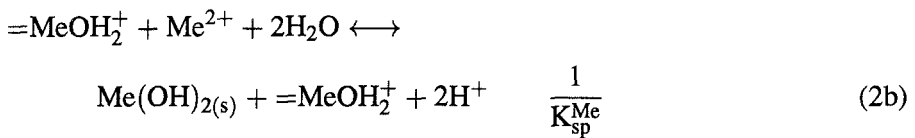
more difficult and less instructive, and as we will later refer to parameters published by Dzombak and Morel (1990), we restrict ourselves to the diffuse layer model as EDL and use the reaction given by Equation (1) only. The surface chemical reaction described by Equation (1) and the corresponding intrinsic equilibrium constant $^*K_i^{int}$ will be used as a reference in calculations presented later on. Since the use of more than one surface site will complicate the equations considerably, only one type of surface site is considered for the derivation of isotherm equations ($i = 1$). For calculations concerning the HFO data base two sites have to be considered for metal adsorption (Dzombak and Morel, 1990).

Apart from reactions in bulk solution and surface acid/base reactions, the surface precipitation model (Farley et al., 1985; Dzombak and Morel, 1990) may be characterized by the following set of chemical reactions:
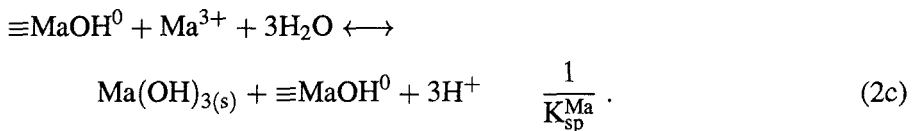
Adsorption of Me^{2+} on $Ma(OH)_{3(s)}$:

$$\equiv Ma - OH^0 + Me_s^{2+} + 2H_2O \longleftrightarrow$$
$$Ma(OH)_{3(s)} + =MeOH_2^+ + H_s^+ \qquad ^*K_{i,s}^{int} \qquad (2a)$$

Precipitation of Me^{2+}:

$$=MeOH_2^+ + Me^{2+} + 2H_2O \longleftrightarrow$$
$$Me(OH)_{2(s)} + =MeOH_2^+ + 2H^+ \qquad \frac{1}{K_{sp}^{Me}} \qquad (2b)$$

Precipitation of Ma^{3+}:

$$\equiv MaOH^0 + Ma^{3+} + 3H_2O \longleftrightarrow$$
$$Ma(OH)_{3(s)} + \equiv MaOH^0 + 3H^+ \qquad \frac{1}{K_{sp}^{Ma}} \cdot \qquad (2c)$$

The reactions are schematically displayed in Figure 1. Equation (2a) is not balanced with respect to the conservation of oxygen and hydrogen, since the schematic notation of the metal surface species does not show the full coordination structure. The activity of water at the interface is generally considered as unity and thus no different from bulk solution. So in all mass action laws the activity of water is not considered. However, activity of water at interfaces may actually be different from that of bulk solution conditions.

After having been adsorbed as described by Equation (2a), the adsorbed metal becomes a surface site itself, while the site on which it has been adsorbed is considered to be 'buried' (precipitated) in the solid phase. The precipitation reactions (2b) and (2c) might be considered as the adsorption of species j on a previously existing surface site formed by j. No electrostatic correction term is applied to these equations, although this might be more correct in general, since, e.g., pure $Co(OH)_{2(s)}$

surface complexation model

$$\equiv\text{Ma-O-H} + \text{Me}^{2+} + \text{H}_2\text{O} \quad \longleftrightarrow \quad \equiv\text{Ma-O-MeOH}_2^+ + \text{H}^+$$

$$\equiv\text{Ma-O-H} + \text{Me}^{2+} + 2\text{H}_2\text{O} \quad \longleftrightarrow \quad \overline{\text{Ma(OH)}_{3(s)}}=\text{MeOH}_2^+ + \text{H}^+$$

surface precipitation model

$$\overline{\text{Ma(OH)}_{3(s)}}=\text{Me-OH}_2^+ + \text{Me}^{2+} + 2\text{H}_2\text{O} \quad \longleftrightarrow \quad \frac{\overline{\text{Ma(OH)}_{3(s)}}}{\text{Me(OH)}_{2(s)}}=\text{Me-OH}_2^+ + 2\text{H}^+$$
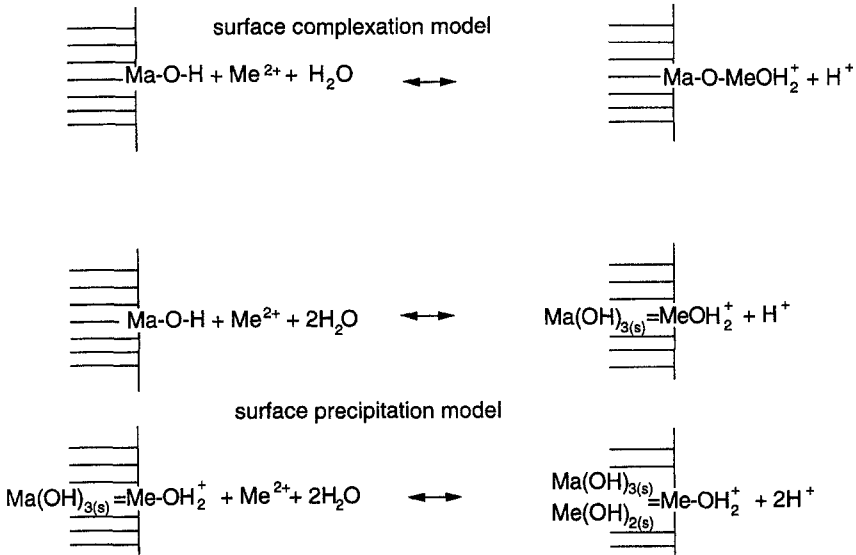
Figure 1. Scheme of surface complexation/precipitation reactions. Modified from Farley *et al.* (1985).

colloids are known to be variably charged as a function of pH (James and Healy, 1972). Adsorption of Ma^{3+} onto $\text{Me(OH)}_{2(s)}$ is possible and part of the model but only three of the four possible surface chemical reactions are independent (Dzombak and Morel, 1990).

The SPM intrinsic adsorption constant (Equation (2a)), $^*K_{i,s}^{int}$, is related to the SCM intrinsic adsorption constant (Equation (1)), $^*K_i^{int}$ by Equation (3):

$$\log(^*K_{i,s}^{int}) = \log(^*K_i^{int}) + \log(K_{sp}^{Ma}). \tag{3}$$

2.2. MASS LAW EQUATIONS AND MATERIAL BALANCES

A conditional adsorption constant, K_{ads}^*, which describes the assumed equilibrium given by Equation (2a), may be defined:

$$K_{ads}^* = \frac{[\equiv\text{MeOH}_2^+] \cdot [\text{H}^+]}{[\equiv\text{MaOH}^0] \cdot [\text{Me}^{2+}]} \cdot \{\text{Ma(OH)}_{3(s)}\}. \tag{4}$$

Here $[j]$ and $\{j\}$ denote concentration and activity of j, respectively. For an ideal solid solution the activity of $\text{Ma(OH)}_{3(s)}$ is calculated as the mole fraction of the sorbent in the solid solution. Activities of the solid species are defined by Equations (5) and (6):

$$\{\text{Ma(OH)}_{3(s)}\} = \frac{[\text{Ma(OH)}_{3(s)}]}{[\text{Ma(OH)}_{3(s)}] + [\text{Me(OH)}_{2(s)}]} = \frac{[\text{Ma(OH)}_{3(s)}]}{T_s}, \tag{5}$$

$$\{Me(OH)_{2(s)}\} = \frac{[Me(OH)_{2(s)}]}{[Ma(OH)_{3(s)}] + [Me(OH)_{2(s)}]} = \frac{[Me(OH)_{2(s)}]}{T_s}, \tag{6}$$

where T_s in molar concentrations is the total quantity of solid taking part in the formation of solid solution.

As the sum of mole fractions must equal unity in all cases, it might be expected that as long as there is no precipitation of $Me(OH)_{2(s)}$ the activity of $Ma(OH)_{3(s)}$ can be considered unity. As soon as the precipitation reaction (2b) occurs, the activity of the sorbent is changed. If the formation of solid solution occurs via absorption of sorbate the activity of the sorbent is also changed.

It is possible to construct a Langmuir-type isotherm from Equation (4):

$$q = q_{max} \cdot \frac{\dfrac{K_{ads}}{[H^+] \cdot \{Ma(OH)_{3(s)}\}} \cdot [Me^{2+}]}{1 + \dfrac{K_{ads}}{[H^+] \cdot \{Ma(OH)_{3(s)}\}} \cdot [Me^{2+}]}. \tag{7}$$

The conditional constant K_{ads} is related to the constant in Equation (4) by

$$K_{ads} = K_{ads}^* \cdot \alpha_1, \tag{8a}$$

where α_1 is the degree of protolysis of surface sites as defined by Stumm and Morgan (1995) and q is defined as the amount of sorbate, whereas q_{max} corresponds to the total amount of surface sites (including neutral, protonated, deprotonated and complexed sites). A Langmuir-type adsorption constant, K_L, may be defined as:

$$K_L = \frac{K_{ads}}{[H^+] \cdot \{Ma(OH)_{3(s)}\}}. \tag{8b}$$

In the case of true adsorption the sorbent activity is expected to be unity. At constant values of pH and constant ligand concentration, K_L may be considered as a constant. However, the electrostatic interactions may cause slight changes in its value with changes in sorbate concentration.

The solubility products of both hydroxides are in the case of solid solution defined as:

$$K_{sp}^{Ma} = \frac{[Ma^{3+}]}{[H^+]^3 \cdot \{Ma(OH)_{3(s)}\}}, \tag{9a}$$

$$K_{sp}^{Me} = \frac{[Me^{2+}]}{[H^+]^2 \cdot \{Me(OH)_{2(s)}\}}. \tag{9b}$$

The value of free metal concentration in equilibrium with the pure precipitate at saturation is:

$$[Ma^{3+}]_{sat} = K_{sp}^{Ma} \cdot [H^+]^3, \tag{10a}$$

$$[Me^{2+}]_{sat} = K_{sp}^{Me} \cdot [H^+]^2 , \tag{10b}$$

where the subscript 'sat' means saturation with the respective pure solid phase. From Equations (9) and (10), and the constraint on mole fractions, we can derive the following relationship:

$$\{Ma(OH)_{3(s)}\} = \frac{[Ma^{3+}]}{K_{sp}^{Ma} \cdot [H^+]^3} = 1 - \{Me(OH)_{2(s)}\} = 1 - z, \tag{11}$$

where $z = [Me^{2+}]/[Me^{2+}]_{sat}$ is defined as the concentration of free sorbate related to the free sorbate concentration in equilibrium with the pure precipitate. It should be noted, that the solubility products used here are written in terms of concentrations, with respect to the solutes and in terms of activities with respect to the solids. It is of course possible to readjust the value of the solubility product by activity corrections.

From Equation (11) we infer that we need the condition of vanishing free sorbate concentration in order to consider the pure sorbent, which is of course never the case. Moreover, within the framework of the SPM the sorbent activity will be affected even at very low sorbate concentration. Consequences of this problem will be discussed later on.

For calculations of chemical equilibria using the common speciation codes, it is necessary to use mole balances for the components. We only give those equations that will be important later. In the case of the surface precipitation model the reader is referred to Dzombak and Morel (1990, p. 30) for the full set of equations.

The mole balance for Ma is:

$$TOTMa = \frac{[Ma^{3+}]}{\alpha_0'} + [Ma(OH)_{3(s)}] + q_{max} - [\equiv MeOH_2^+]. \tag{12}$$

Here $TOTj$ means total analytical concentration of component j in molar concentrations and α_0' is defined as $[Ma^{3+}]/TOTMa_{aq}$, where the subscript 'aq' denotes the aqueous solution species of Ma. It is useful to define the parameter $TOTMa_{max}^*$ given by Equation (13):

$$TOTMa_{max}^* = TOTMa - q_{max}. \tag{13}$$

In using the tableau method (Table II), we may summarize the essential part of the equations for cation surface precipitation. By setting up a separate matrix for mass law action and mole balance, we solve the chemical equilibrium problem by computer codes, which allow a distinction between these matrices (see Table II).

It can be shown that $TOTMa_{max}^*$ is the value to be entered as the result of the mole balance for Ma if all Ma is allowed to take part in solid solution formation. It is denoted $TOTMa^*$ in the table, since we will consider values smaller than $TOTMa_{max}^*$. In such a case $TOTMa^*$ is a more general and in principle an adjustable parameter, the magnitude of which indicates the amount of TOTMa participating

Table II. Tableau giving the essential equations for calculating chemical equilibria within the framework of the surface precipitation model.

Component	Ma^{3+}	Me^{2+}	H^+	P^b	$\equiv MaOH^0$	T_s	γ_{Ma}	γ_{Me}	log K
Species
$[Ma(OH)_{3(s)}]$	1	0	-3	0	0	1, 0	1	0	$-\log(K_{sp}^{Ma})$
$\{Ma(OH)_{3(s)}\}$	$1, 0^a$	0	$-3, 0$	0	0	0, 1	1	0	$-\log(K_{sp}^{Ma})$
$[Me(OH)_{2(s)}]$	0	1	-2	0	0	1, 0	0	1	$-\log(K_{sp}^{Me})$
$\{Me(OH)_{2(s)}\}$	0	1, 0	$-2, 0$	0	0	0, 1	0	1	$-\log(K_{sp}^{Me})$
$\equiv MeOH_2^+$	-1	1	2	1	1	0	-1	0	$\log(^*K_{1,s}^{int})$
Ma^{3+}	1	0	0	0	0	0	0	0	0
Me^{2+}	0	1	0	0	0	0	0	0	0
H^+	0	0	1	0	0	0	0	0	0
$\equiv MaOH^{0c}$	0	0	0	0	1	0	0	0	0
	TOTMa*	TOTMe	TOTH$^+$	q_{max}		1			

[a]Where two numbers are given, the first one is valid for mass law equations and the second one for mole balance.
[b]Electrostatic factor (see Dzombak and Morel (1990) for details).
[c]Surface species arising from acid/base reactions have been omitted.

in solid solution formation. The meaning of the parameters γ_{Ma} and γ_{Me}, which appear in Table II will be explained below.

Restricting themselves to a fixed value of pH and ionic strength, and assuming an ideal solid solution, Farley *et al.* (1985) derived from the above framework of chemical reactions, mass action and mole balance, a 'BET'-like equation hereafter referred to as FDM (Farley–Dzombak–Morel) isotherm. The relationship is given by the following equation:

$$q = (B - 1) \cdot z \cdot \frac{q_{max} \cdot (1 - z) + TOTMa \cdot (\frac{1}{B-1} + z)}{(1 - z) \cdot (1 + (B - 1) \cdot z)} - \frac{[Ma^{3+}]_{sat}}{\alpha'_0} \cdot z, \quad (14a)$$

$$q_{TOTMa} = \frac{(B - 1) \cdot z \cdot TOTMa \cdot (\frac{1}{B-1} + z)}{(1 - z) \cdot (1 + (B - 1) \cdot z)} = \frac{TOTMa \cdot z}{(1 - z)} \quad (14b)$$

$$q_{sp} = -\frac{[Ma^{3+}]_{sat}}{\alpha'_0} \cdot z, \quad (14c)$$

where B is a conditional constant. The terms q_{TOTMa} (Equation (14b)) and q_{sp} (Equation (14c)) are contributions to q, the importance of which will be discussed in some detail below. Equation (14) does not exactly correspond to Equation (18) given by Farley *et al.* (1985), because we considered a more exact mass balance for the sorbent by incorporating the hydrolysis products. The relationship between B and K_{ads} (Equation (15a)) is different from what Farley *et al.* (1985) report. In
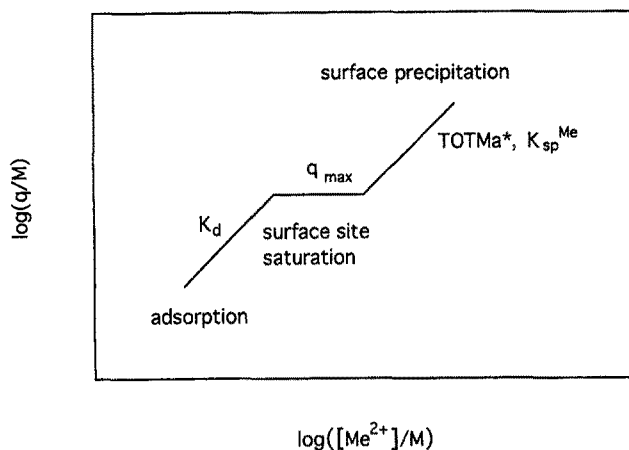
Figure 2. Scheme of the isotherm regions within the framework of the surface precipitation model. Modified from Farley *et al.* (1985).

the form as it is presented here, it can be rearranged to Equation (15b) by taking into account Equation (8):

$$B = K_{ads} \cdot K_{sp}^{Me} \cdot [H^+] \tag{15a}$$

$$B = K_L \cdot K_{sp}^{Me} \cdot [H^+]^2 \cdot \{Ma(OH)_{3(s)}\}$$

$$= K_L \cdot [Me^{2+}]_{sat} \cdot \{Ma(OH)_{3(s)}\}. \tag{15b}$$

By allowing the adsorption of Me^{2+} onto $Ma(OH)_{3(s)}$ as well as the adsorption of Ma^{3+} onto $Me(OH)_{2(s)}$, the available concentration of surface sites remains constant (Wersin *et al.*, 1988; Charlet and Manceau, 1992).

Figure 2 schematically displays the sorption isotherm given by Equation (14a) and gives the controlling parameters describing the respective concentration ranges. The symbol K_d represents the distribution coefficient, which is the product of the Langmuir constant and the site concentration. In our notation K_d is a parameter without dimension. It is a conditional parameter, which has a unique value for each value of pH at low metal concentrations. For multiple site/one species models or one site/multiple species models, the distribution coefficient is expected to vary even at constant pH and low metal concentrations.

3. Methods

Calculations were carried out using a slightly modified version of FITEQL (Westall, 1982). For the quality test of the parameters of the HFO data base, the generalized two-layer model (Dzombak and Morel, 1990) was applied. For the other examples only one site was involved (site density was estimated to be 0.2 TOTMa, specific

surface area and sorbent weight was used as specified for HFO by Dzombak and Morel (1990).

Corrections for ionic strength, which was fixed at 0.1 M for all the calculations, were done using the activiy coefficients given by Dzombak and Morel (1990). The DLM was used as the electric double layer model.

Stability constants for aqueous speciation and intrinsic surface complexation constants as well as the solubility product for HFO were taken from the data base for cation sorption on HFO (Dzombak and Morel, 1990). Values for the solubility products other than $Ma(OH)_{3(s)}$ have been taken from Smith and Martell (1976) and Lindsay (1979).

4. Results and Discussion

4.1. EXTENSION OF THE SURFACE PRECIPITATION MODEL TO THE LIMITING CASE OF HETEROGENEOUS NUCLEATION

Equation (14a) may be difficult to use in systems, where the amount of solid suspended in solution is considerable. This may be the case for instance with low surface area material. Essentially q_{TOTMa} (Equation (14b)) becomes too large yielding unreasonably high values for q. Therefore, TOTMa (or TOTMa*) must be adjusted to account for the part of the solid effectively taking part in solid solution.

For the following two conditions:

(i) $[Ma^{3+}]_{sat} = 0$ and $TOTMa^* = 0$
   or
(ii) $[Ma^{3+}]_{sat} = [Ma^{3+}]/(1 - z)$ and $TOTMa^* = [Ma^{3+}]_{sat}/\alpha'_0$

the FDM relationship reduces to the BET equation:

$$q = \frac{q_{max} \cdot K_{BET} \cdot z}{(1 - z) \cdot (1 + (K_{BET} - 1) \cdot z)} , \qquad (16)$$

where K_{BET} equals B, which has been defined previously.

In case (i) since the term q_{sp} (Equation (14c)) is neglected in Equation (14a), a completely insoluble sorbent is assumed, which is a more or less hypothetical case, whereas in case (ii) q_{sp} (Equation (14c)) is not neglected. Thus if only the original surface sites participate in the 'formation of an ideal solid solution' we obtain the well-known BET isotherm. The activity of the sorbent in this case should be considered to be unity, since there is no mixing between the precipitates and a phase boundary occurs at the location of the original surface sites. A coating is formed on the sorbent matrix. It seems more useful to think of heterogeneous nucleation as the mechanism involved than speaking of solid solution formation.

The concept of the formation of an ideal solid solution, however, may be used to allow for the description of heterogeneous nucleation on a nonconditional base. The BET isotherm was supposed to describe heterogeneous nucleation by several
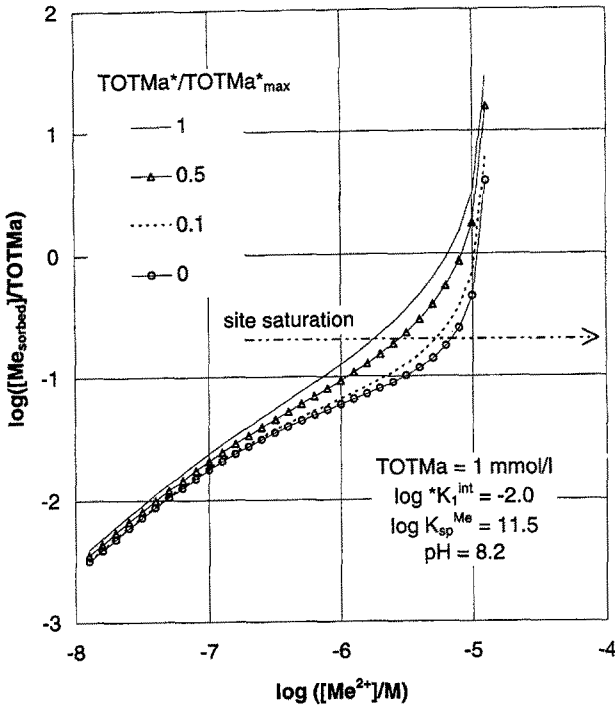
Figure 3. Effect of varying TOTMa* on the form of isotherms.

authors (Stumm, 1992; Benjamin and Leckie, 1981). Stumm (1992) takes into account the possibility that a metastable phase may nucleate before the formation of the least soluble phase occurs (Ostwald step rule).

Our results indicate that the form of the surface precipitation model that has been used so far, that is, all Ma is able to participate in solid solution, is only one limiting case. The assumption that only the part of Ma, which is present as surface sites, takes part in 'solid solution' formation yields the other limiting case.

Figure 3 gives an example of the effect of the variation of TOTMa* on sorption density with the two limiting cases. It is obvious that, in the concentration range where surface precipitation is the controlling mechanism, TOTMa* has a major importance. Usually, we have only access to few points which have to be described by the precipitation mechanism. Therefore, as shown in Figure 4, it is possible to find more than one description of the data by adjusting both TOTMa* and K_{sp}^{Me}. Using TOTMa*$_{max}$ will yield the largest possible value for K_{sp}^{Me}.
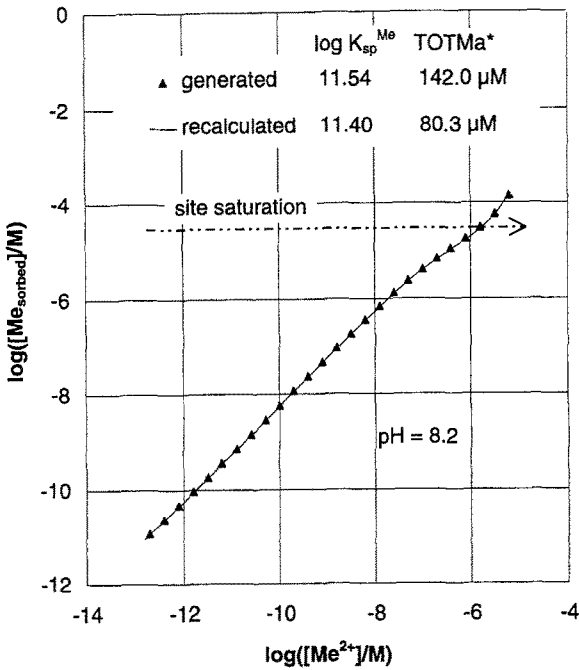
Figure 4. Adjustment of K_{sp}^{Me} and TOTMa* to model a generated isotherm.

4.2. EXTENSION OF THE SURFACE PRECIPITATION MODEL TO NONIDEAL SOLID SOLUTIONS

By incorporating activity coefficients for the solid species, it is possible to account for nonideality in the solid solution (Farley *et al.*, 1985; see Equations (17) and (18)).

$$\{Ma(OH)_{3(s)}\}_{nonideal} = \gamma_{Ma} \cdot \frac{[Ma(OH)_{3(s)}]}{T_s}, \tag{17}$$

$$\{Me(OH)_{2(s)}\}_{nonideal} = \gamma_{Me} \cdot \left(1 - \frac{[Ma(OH)_{3(s)}]}{T_s}\right), \tag{18}$$

where γ_{Ma} and γ_{Me} are activity coefficients for the solid species $Ma(OH)_{3(s)}$ and $Me(OH)_{2(s)}$, respectively. Tiffreau *et al.* (1995) have used such an approach for the Hg(II)/HFO system, concluding that the solid solution formed between $Hg(OH)_{2(s)}$ and HFO is nonideal, which is in agreement with the findings of Dzombak and Morel (1990). The degree of ideality will depend on how well the sorbing metal ion can be incorporated in the sorbent matrix. In other words the better the sorbing cation fits in the sorbent network, the closer to unity will be the value of γ_{Me}.

If Equations (17) and (18) are to be incorporated in a chemical speciation calculation, the relation between γ_{Ma} and γ_{Me} and the mole fraction of $Ma(OH)_{3(s)}$

in the solid solution must be known. While this would be possible using existing empirical relationships, we will not focus on this any further, but show how to use the activity coefficients of the solids for parameter extration. We will assume an ideal solid solution and use the activity coefficients as 'dummy' components similar to the treatment proposed by Westall and Herbelin (1992) for total concentrations.

When Dzombak and Morel (1990) evaluated the intrinsic adsorption constants for the HFO data base, they always fitted the data first for those concentration ranges, where no precipitation interferred. In the cases where precipitation was supposed to occur the values of the apparent solubility product were manually adjusted later. Indeed FITEQL (Westall, 1982) cannot handle fits for apparent solubility products as incorporated in the surface precipitation model, because the apparent solubility product appears for two species (see Table II). However, FITEQL is able to optimize values of free concentrations of components. Thus γ_{Ma} and/or γ_{Me} may be defined as components for which free concentrations are known and then be used as parameters to be optimized. As there are seldom experimental values for aqueous sorbent concentrations, in a first step γ_{Ma} may be omitted and γ_{Me} used as the only additional fitting parameter. For the Hg(II)/HFO case, the value of the solubility product estimated by numerical optimization is the same as the one obtained by Tiffreau $et\ al.$ (1995) manually.

The activity coefficients will not be constant in a nonideal solid solution even for the conditional case. Indeed, close examination of literature sorption data concerning Cd sorption on three sorbents (Lützenkirchen $et\ al.$, 1993) shows that apparent solubility products determined manually by best fits with Equation (14a) vary with pH. For low pH, low values of the apparent solubility product must be chosen, while with increasing pH the apparent solubility product appears to tend towards the thermodynamic value. The same trend may appear at constant pH when sorption density varies. Our remarks concerning the first point are in agreement with the modelling results reported by Farley $et\ al.$ (1985), who used one isotherm fit to obtain the value for the sorbate solubility product and used this to model pH sorption edges. This procedure resulted in an exact model at the pH of isotherm fit only, whereas at lower pH the model underpredicts sorption and at higher pH the model overpredicts sorption. If Farley $et\ al.$ (1985) had used different values of pH for the isotherm fit, they would have obtained a different value for the solubility product.

4.3. ANALYSIS OF PARAMETER EFFECTS ON THE SHAPE OF THE FDM ISOTHERM

Effect of q_{max}: The value of surface site concentration alters the niveau of transition between adsorption and precipitation. The effect of changing surface site concentration would essentially be the same as in the case of a surface complexation model. It should be noted, however, that this parameter is a very critical one in systems in which surface precipitation is supposed to occur. Besides the problems already examined for surface complexation models (Goldberg, 1991) in the surface
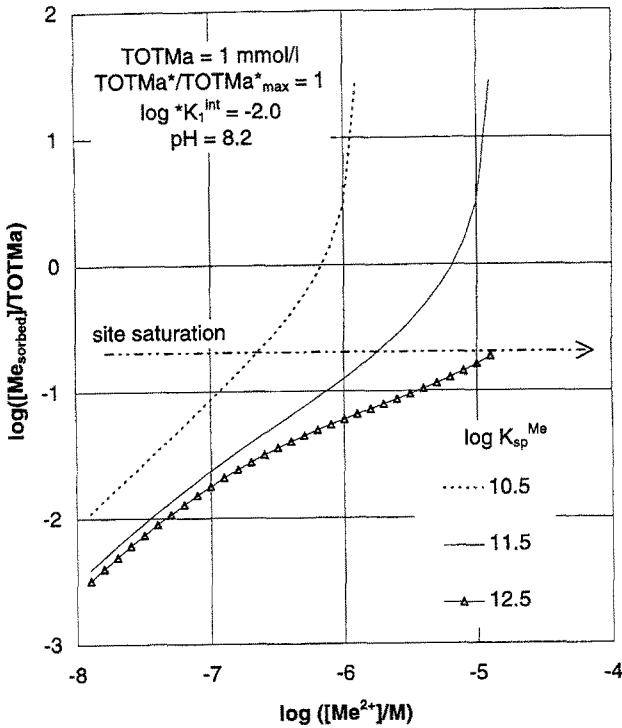
Figure 5. Effect of varying K_{sp}^{Me} on the form of isotherms.

precipitation model a fixed value for the surface site concentration means that all experimental data points above surface site concentration have to be accounted for by surface precipitation. This is valid for the case when we do not consider polynuclear surface complexes.

Effect of K_{sp}^{Ma}: Our calculations using the HFO case show, as has been reported by Farley *et al.* (1985), that there is practically no effect of this parameter on the isotherm shape. This is due to the extremely low solubility of HFO. With sorbents other than HFO, we may however expect that K_{sp}^{Ma} causes a decrease in sorption with increasing sorbent solubility via q_{sp} (Equation (14c)).

Effect of K_{sp}^{Me}: Figure 5 shows that there may be critical effects of this parameter on the isotherm shape. For low values of the apparent solubility product of the sorbing metal, precipitation may affect the sorption isotherm over the whole range of free sorbent concentration. This is not intended by the surface precipitation model, since Langmuir type adsorption is to control the sorption isotherm at low sorbate concentrations (see Figure 2). The effect becomes more pronounced with increasing pH, since the pH dependence of the precipitation reaction is stronger than that of the adsorption reaction considered here. Therefore, parameters determined at low pH may fail to describe adsorption at higher pH and should be tested at high pH conditions. Note that there is no such effect for the BET limiting case.
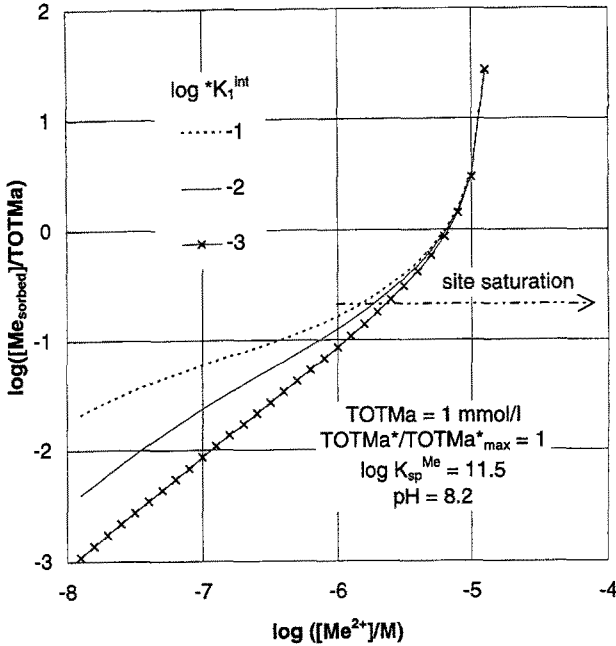
Figure 6. Effect of varying $*K_1^{int}$ on the form of isotherms.

The effect may be considered to be related to the activity of the sorbent. In cases, where this activity affects the apparent adsorption constant (Equation (8b)), the Langmuir constant increases as the sorbent activity will decrease. Following the arguments presented before that no mixing between sorbent and sorbate occurs and assuming consequently that in the BET limiting case the sorbent activity should be considered unity, it can be inferred that the Langmuir part of a BET isotherm like surface precipitation approach will always reduce to the surface complexation case.

Effect of $*K_1^{int}$: Similar to the effect of K_{sp}^{Me}, the intrinsic adsorption constant, $*K_1^{int}$, may seriously affect the shape of the isotherm (see Figure 6). For reasonable values of K_{sp}^{Me}, decreasing the intrinsic adsorption constant leads to the same deviation in the shape of the isotherm as in the preceding case. Therefore, the choice of the intrinsic adsorption constant is crucial. We recommend that the model should be tested at higher pH values using a surface precipitation approach with thermodynamic values of the solubility product to avoid too low values for $*K_1^{int}$.
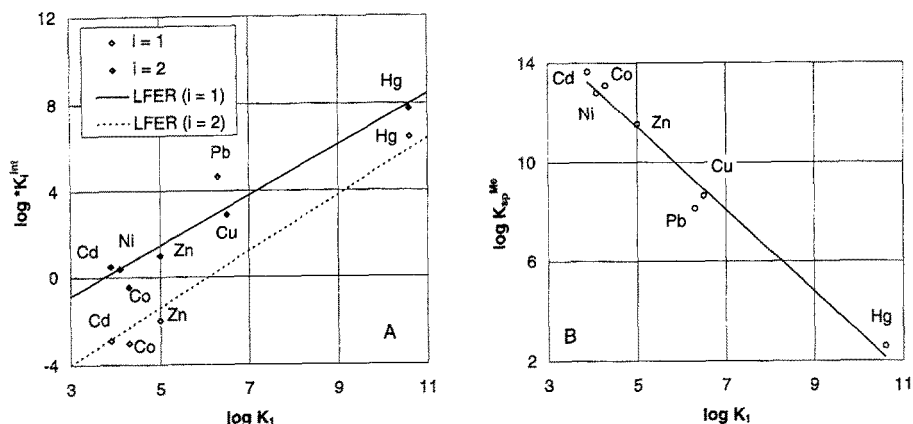
Figure 7. LFERs between the first hydrolysis constant (Equation (19)) and (A) the intrinsic surface complexation constants for the strong and weak site on HFO, or (B) the solubility products for divalent cations. The drawn line in B corresponds to a linear regression yielding a regression coefficient of 0.98, a y-intercept of 19.71 and a slope of -1.66. The values for the solubility products are for crystalline hydroxides and have been taken from Lindsay (1979) except those for Co and Ni which are not available from Lindsay and are from Smith and Martell (1976). The values for the other metals which are listed in both sources agree with each other. For amorphous hydroxides the values for all metals of interest in this study could not be found in a restricted number of compilations. The alkaline earth metals were omitted, because they exhibit partially different adsorption behaviour. Inclusion of solubility behaviour of alkaline earth metals in (b) results in a significant decrease of the regression coefficient.

4.4. A POSSIBILITY FOR QUALITY CONTROL OF INTRINSIC ADSORPTION CONSTANTS

For quality control in parameter estimation procedures, the possible difference between surface complexation and precipitation at low free metal concentrations can be used to estimate the goodness of obtained values for intrinsic adsorption constants. When surface precipitation is favoured, the value of the apparent solubility product should be tested in isotherms at high pH values in order to find out, if the choice is reasonable. This procedure would be a good test for the intrinsic adsorption constant, if another possibility is not available. This other way would be to use linear free energy relationships (LFERs) between stability constants of solution and surface complexes (see Figure 7A). In this respect it seems that there is more need for data bases such as the one for sorption on HFO. Implicitly, it is the same way of testing model constants. As is shown in Figure 7B, the logarithm of the solubility product is linearly related to the logarithm of the respective first hydrolysis constant, which is given by Equation (19):

$$Me^{2+} + OH^- \longleftrightarrow MeOH^+ \qquad K_1. \tag{19}$$

For the HFO data base we tested the reliability of the cation adsorption constants using the above described procedure. Some typical results are given in Figures 8 and 9. The Zn example (Figure 8) corresponds to the expected pattern of the model.
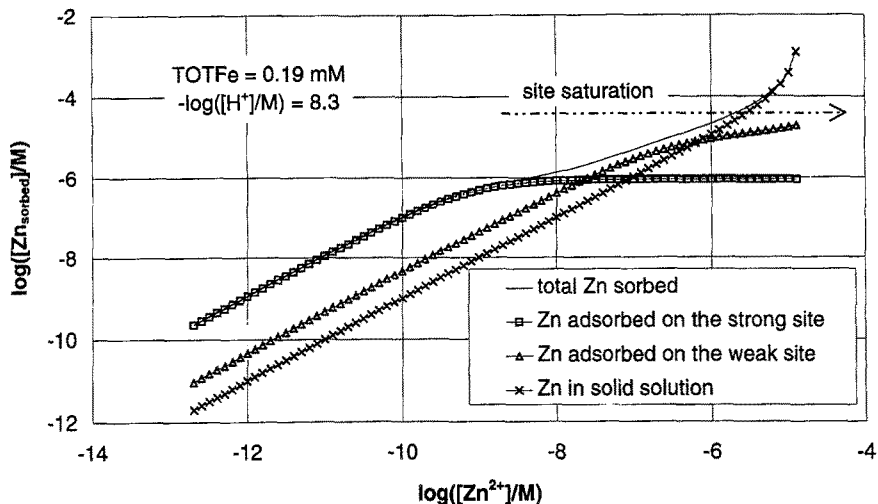
Figure 8. Typical surface precipitation isotherm as calculated for the Zn-HFO system using parameters from Dzombak and Morel (1990) and the solubility product from Figure 7b.
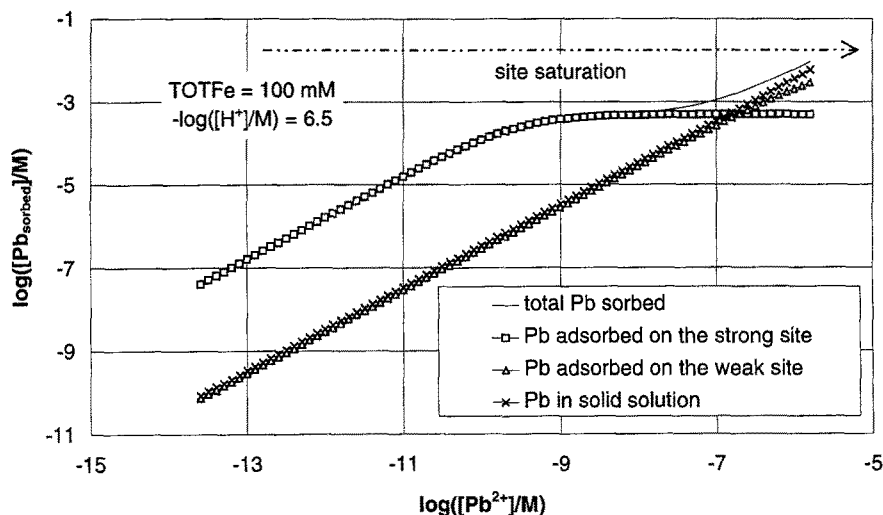
Figure 9. Typical surface precipitation isotherm as calculated for the Pb-HFO system using parameters from Dzombak and Morel (1990) and the solubility product from Figure 7b.

Adsorption onto the strong site at low surface coverage, prevailing adsorption onto the weak site at intermediate surface coverage and solid solution formation at high surface coverage. In the Pb example (Figure 9) solid solution formation is more important than adsorption to the weak site, indicating that the adsorption constant for this site may be too low. For Pb(II), Dzombak and Morel (1990) already state that the weak site adsorption constant calculated from a linear free energy relationship is most probably too low, because the strong site constant

was considerably higher than the value expected from the corresponding LFER (Figure 7A). For the seven cations considered, only for Pb(II) and Hg(II) we found that the calculations using literature values for the solubility products do not correspond to the expected pattern. For Hg(II), the model by Dzombak and Morel may be shown to be inconsistent with respect to the fact that adsorption is always stronger on the weak site than on the strong site (Tiffreau et al., 1995). Tiffreau et al. (1995) have therefore used only one site to model Hg(II) sorption onto HFO. It seems that for a sufficiently high sum of aging and equilibration times, adsorption of cations onto HFO is more successfully described by considering only one surface site but more than one surface species and surface precipitation if necessary (Lützenkirchen and Behra, 1994). The amount of surface sites and along with this the heterogeneity of surface sites seems to decrease with increasing sum of aging time and equilibration time. If the Hg(II) model by Dzombak and Morel (1990) is considered to be wrong, the LFERs for cations, which are mainly based on the Hg(II) constants, must be considered with caution. In this context it is also noteworthy that the LFER for the third anion adsorption constant for HFO is based on no more than eight data points for selenite adsorption.

In cases where nonideal solid solution occurs which increases sorbate solubility, the proposed approach is at a loss. It is clear that in such a case the literature value will overpredict sorption. This is one limitation of the test: literature values should only be taken as estimates and the proposed procedure only gives hints, where problems may occur.

A further apparent lack of our approach of testing adsorption constants is the fact that it is mathematically necessary for much of the sorbent to take part in solid solution formation for the effect to occur. With sorbents other than HFO or certain carbonates, little is known about surface precipitation modelling. Even in the former cases, TOTMa* is a parameter the value of which has been arbitrarily fixed at the maximum rather than evaluated. Parameter estimation will be much more difficult for those sorbents that are situated between the two limiting cases as can be concluded from results shown in Figure 4.

4.5. REMARKS ON INTERFACIAL SOLUBILITY PRODUCTS

As has been shown in the previous section, with low apparent solubility of the sorbing metal, the surface precipitation model may predict that the precipitation mechanism controls overall sorption over the whole range of sorbate concentration. Both in one-site adsorption models and a pure precipitation approach, the slopes in constant pH isotherm plots are unity on a log-log scale. Thus if both mechanisms were physically possible it would not be possible to distinguish between them (Sposito, 1984). While the mechanism at low sorption density has been identified as actual adsorption, the discussion of interfacial solubility products has been going on for some decades, with no general agreement being achieved. Though low interfacial solubility products might explain precipitation mechanisms at low

sorption densities, we will, in view of the recent achievements in *in-situ* surface spectroscopy (e.g. Brown, 1990; Charlet and Manceau, 1992), consider that the precipitation mechanism at very low sorption densities is no more than a mathematical artifact, which may be used as described above to some degree to test the reliability of adsorption constants. However, some remarks should be made on low interfacial solubility products. The latter have frequently been reported (e.g. James and Healy, 1972; Fendorf *et al.*, 1992) in the literature. Fendorf *et al.* (1992) conclude that there is an electrostatic effect on the value of interfacial solubility products. If this was the case, values of these apparent solubility products should vary with pH and sorption density. In fact this is what model calculations (Lützenkirchen *et al.*, 1993) show and what the rigorous application of the model by James and Healy (1972) predicts. It is not questionable, whether electrostatic effects and possible non-ideal mixing of precipitates might be distinguished. Both models may theoretically cause changes of apparent solubility products with pH and sorption density.

5. Summary

The surface precipitation model contains two limiting cases:

- the FDM isotherm, where all solid sorbent present takes part in solid solution formation;
- the BET isotherm, where only surface sites of the solid sorbent take part in the formation of an 'ideal solid solution'.

Between these two limiting cases if the value of the solubility product is fixed, TOTMa* is an adjustable parameter. For only a few experimental points above surface site saturation, it is possible to obtain similar fits for the FDM limiting case by adjusting both TOTMa* and K_{sp}^{Me}.

It is possible to establish a framework of simple isotherm equations and relate the parameters of the well-known isotherm equations to those of the other more complicated ones. This has been done in Figure 10. For the reduction of the FDM isotherm to the BET isotherm, we may consider the two extreme cases noted above. In between the FDM and BET limiting cases, we may distinguish two basically different mechanisms for the mixture between sorbent and sorbate to form:

- The sorbent is completely insoluble. This would correspond to a diffusion mechanism of the sorbate into the sorbent. At equilibrium this would require all the sorbent to take part in the solid solution formation. In general the equilibration times used in laboratory experiments are too short for this equilibrium to be reached and the data collected should be considered as corresponding to a certain equilibration time (pseudo-equilibrium).
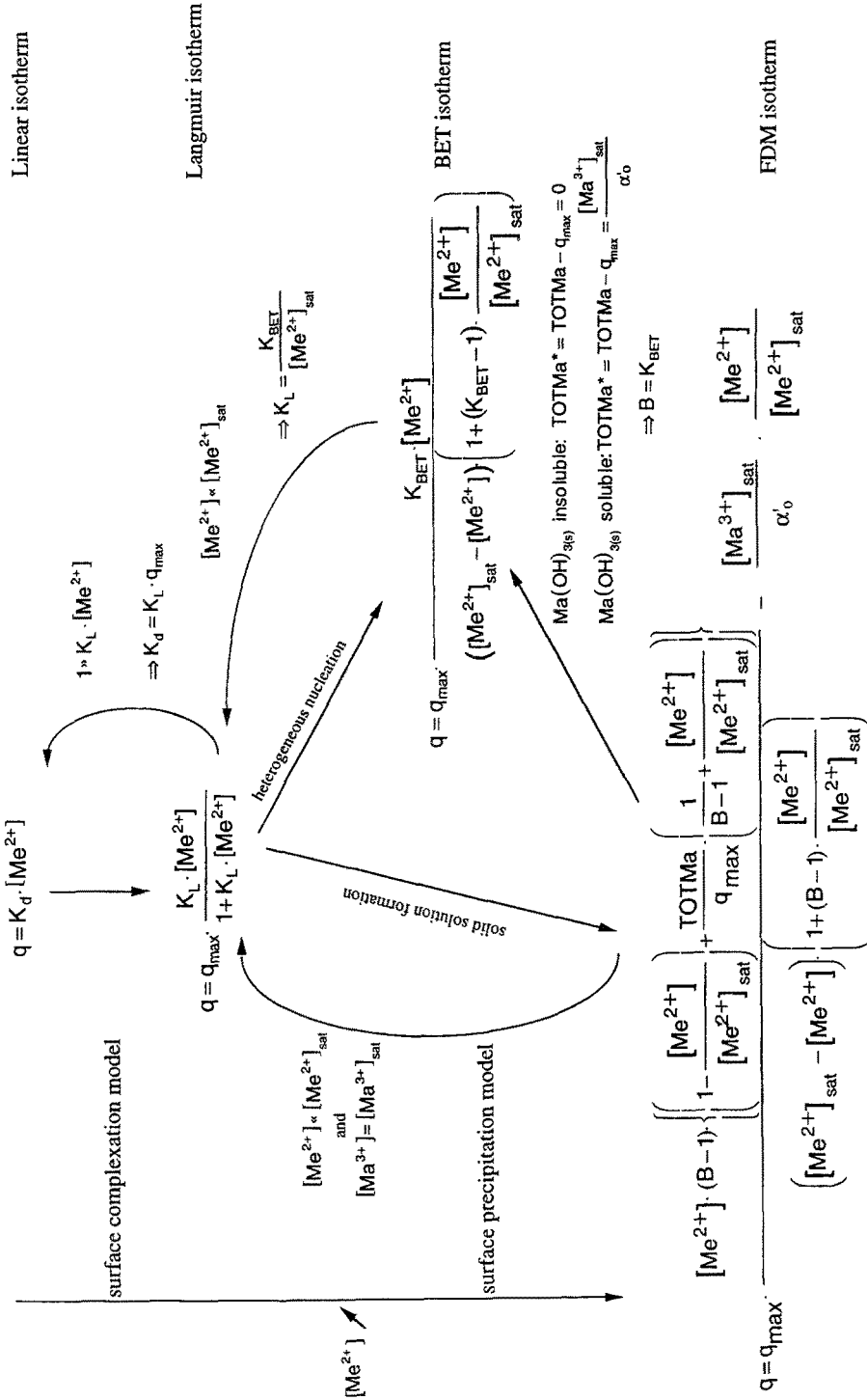
Linear isotherm

Langmuir isotherm

BET isotherm

FDM isotherm

surface complexation model

surface precipitation model

heterogeneous nucleation

solid solution formation

$$q = K_d \cdot [Me^{2+}]$$

$$1 \gg K_L \cdot [Me^{2+}]$$

$$\Rightarrow K_d = K_L \cdot q_{max}$$

$$q = q_{max} \cdot \frac{K_L \cdot [Me^{2+}]}{1 + K_L \cdot [Me^{2+}]}$$

$$[Me^{2+}] \ll [Me^{2+}]_{sat}$$

$$\Rightarrow K_L = \frac{K_{BET}}{[Me^{2+}]_{sat}}$$

$$q = q_{max} \cdot \frac{K_{BET} \cdot [Me^{2+}]}{([Me^{2+}]_{sat} - [Me^{2+}]) \left(1 + (K_{BET}-1) \cdot \frac{[Me^{2+}]}{[Me^{2+}]_{sat}}\right)}$$

$$\Rightarrow B = K_{BET}$$

$$[Me^{2+}] \ll [Me^{2+}]_{sat} \quad \text{and} \quad [Ma^{3+}] = [Ma^{3+}]_{sat}$$

Ma(OH)$_{3(s)}$ insoluble: TOTMa* = TOTMa $-$ q$_{max}$ = 0

Ma(OH)$_{3(s)}$ soluble: TOTMa* = TOTMa $-$ q$_{max}$ = $\dfrac{[Ma^{3+}]_{sat}}{\alpha'_o}$

$$q = q_{max} \cdot \frac{[Me^{2+}] \cdot (B-1) \cdot \left(1 - \frac{[Me^{2+}]}{[Me^{2+}]_{sat}}\right)}{\left([Me^{2+}]_{sat} - [Me^{2+}]\right) \cdot \left(1 + (B-1) \cdot \frac{[Me^{2+}]}{[Me^{2+}]_{sat}}\right)} + \frac{TOTMa}{q_{max}} \cdot \left[\frac{1}{B-1} + \frac{[Me^{2+}]}{[Me^{2+}]_{sat}}\right] - \frac{[Ma^{3+}]_{sat}}{\alpha'_o} \cdot \frac{[Me^{2+}]}{[Me^{2+}]_{sat}}$$

$$[Me^{2+}]$$

Figure 10. Summary of single site/one species isotherms and relationships between the isotherm parameters.

— The sorbent is easily soluble. Solid solution formation occurs by simultaneous adsorption and dissolution/(re)precipitation and/or co-precipitation reactions.

Note that there is no simple way to reduce the FDM isotherm to the Langmuir-type equation, since two conditions must be fulfilled: The sorbent activity must be unity *and* sorbate concentrations must be low. Only if both conditions are met, the surface complexation approach yields the same isotherm at low sorbate concentrations as the surface precipitation model.

Using as extreme cases weakly adsorbing and strongly precipitating cations, the SPM may show a considerable deviation from the respective SCM. Assuming that this deviation does not actually occur, which is reasonable in view of spectroscopic evidence (e.g. Charlet and Manceau, 1992), the mathematical artifact may be used as follows: By applying the surface precipitation model to adsorption data in the low concentration range, it is possible to verify if the fitted value of the intrinsic sorption constant is reasonable. If in an isotherm plot, sorption density *vs.* free metal concentration, a reasonable value for the solubility product of the sorbing metal hydroxide leads to a domination of the precipitate over the whole concentration range, it is probable that a too low value for the intrinsic adsorption constant has been chosen, assuming that site density does not interfere. If on the other hand a value of an apparent solubility product fitted at low pH causes the above mentioned deviation at higher pH values, the value should be critically analysed. Restrictions to this method of verifying adsorption constants have been discussed.

Finally we conclude that, if interfacial solubility products depend on electrostatics, (Fendorf *et al.*, 1992), apparent interfacial solubility products may be supposed to change with pH and sorption density.

Acknowledgements

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