COMMISSARIAT A L'ENERGIE ATOMIQUE

INSTITUT DE PROTECTION ET DE SURETE NUCLEAIRE

DEPARTEMENT D'ANALYSE DE SURETE

D A S

RAPPORT DAS/667

GEOCHEMICAL MODELLING : WHAT PHENOMENA ARE
MISSING ?

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*2ND INTERNATIONAL CONFERENCE ON CHEMISTRY AND
MIGRATION BEHAVIOR OF ACTIVITIES AND FISSION
PRODUCTS IN THE GEOSPHERE ,MIGRATION 1989
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GEOCHEMICAL MODELLING : WHAT PHENOMENA ARE MISSING ?

P. JACQUIER*

Adsorption / modelling / geochemistry / colloids / organics / radionuclides.

ABSTRACT

In the framework of safety assessment of radioactive waste disposal, retention phenomena are usually taken into account by the Kd concept. It is well recognized that this concept is not enough for safety assessment models, because of the several and strong assumptions which are involved in this kind of representation.

One way to have a better representation of the retention phenomena, is to substitute for this Kd concept an explicit description of geochemical phenomena and then couple transport codes with geochemical codes in a fully or a two-step procedure. We use currently such codes, but the scope of this paper is to display the limits today of the geochemical modelling in connection with sites analysis for deep disposal.

In this paper, we intend to give an overview of phenomena which are missing in the geochemical models, or which are not completely introduced in the models.

We can distinguish, on one hand phenomena for which modelling concepts exist such as adsorption/desorption and, on the other hand, phenomena for which modelling concepts do not exist for the moment such as colloids, and complexation by polyelectrolyte solutions (organics).

Moreover we have to take care of very low concentrations of radionuclides, which can be expected from the leaching processes in the repository. Under those conditions, some reactions may not occur.

After a critical review of the involved phenomena, we intend to stress the main directions of the wishful evolution of the geochemical modelling. This evolution should improve substantially the quality of the above-mentionned site assessments.

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1. INTRODUCTION

One of the problems faced today by the nuclear industry is the disposal of radioactive wastes which are being generated. Uncertainties still exist regarding the environmental and geochemical behavior.

One of the major challenges in understanding the environmental behavior of the long-lived radionuclides associated with radioactive wastes is the obtention of a more adequate knowledge of the mechanisms by which these radionuclides are mobilized and transported in groundwaters. Predictions of the rate of movement of radionuclides in groundwaters, based on laboratory-derived Kd values, can lead in some cases to conclusions either erroneous or affected by large uncertainties concerning the groundwater mobility of various radionuclides. This happens because laboratory-derived Kd values have been obtained using ideal soluble tracers which probably were not in the same physicochemical form(s) as the mobile radionuclide species known to be present in some groundwaters. In addition, the Kd experiments have not considered the long-term leaching of soil- or rock-adsorbed radionuclides by ligands and complexing substances contained in groundwaters.

The aim of this paper is dual :

- first display the basic physicochemical phenomena which lead, for a given radionuclide, either to the retention in the geosphere or to the mobilization and transport in groundwater, propose a ranking of the main processes involved,

- secondly, for each sensitive phenomenon, appreciate the feasibility of its modelling.

2. STATE OF THE PRESENT MODELLING : THE DISTRIBUTION COEFFICIENT, KD, WHEN CAN WE USE IT ?

The Kd coefficient represents the ratio of the concentration in the solid $(\bar{C}_i)$ over the concentration in the fluid (C_i) for a given element i :

$$Kd, i = \frac{\bar{C}_i}{C_i}$$

$\bar{C}_i$ (g/g of solid) ; C_i (g/ml of solution) ; Kd, i (ml/g).

The Kd distribution coefficient is a macroscopic expression of various processes involved simultaneously in the distribution of elements between solid and liquid phases ; these processes are the following : adsorption/desorption, precipitation (on the substrate surface or in the solution), co-precipitation with major or trace elements, inclusion in mineral lattices, adsorption on small particles and colloids (inorganic like silica, clay particles or organic like macro-molecules of humic or fulvic acids). Due to the complexity of the phenomena to be taken into account, the measured Kd value cannot be easily extrapolated to conditions other than those measured. It is well known that Kd varies with the history of the fluid-solid system and many chemical variables such as pH, Eh, ionic strength etc. Let us remark that, if we vary only one factor, the Kd value can be a reliable datum ; for instance, it is the case for the retention of cesium on clay minerals (illite) which is only controlled by ionic exchange.

In this case, the distribution coefficient means that the adsorption phenomenon is governed by an Henry law, which explains the linear shape of Langmuir isotherms at very low concentrations.

So the use of Kd values is questionnable and this raises two questions :

- what alternative concepts may be used ?

- for these concepts, what are the relevant parameters of the interaction processes and the appropriate methods to measure them ?

To have a better representation of the retention phenomena, we use currently geochemical models. These models relie upon thermodynamics (free energy of Gibbs) ; some of them take into account kinetics, using empiric laws. That allows speciation, precipitation/dissolution, adsorption/desorption computations. These geochemical models are coupled with transport models ; we use in France a program, called STELE, developped by the School of Mines of Paris /1/ (two-step procedure). The question is also, when we use such codes, to get a good knowledge of the physics or/and chemistry of the phenomena which lead, for example to adsorption, or precipitation.

3. ADSORPTION

3.1. Mechanisms - Origin of the nor al interaction adsorbate-adsorbent

Considering an adsorbent (the solid phase) and an adsorbate (a solute in the liquid phase, ionic or non-ionic form), an interaction may occur between them, leading to adsorption of the adsorbate molecules on the surface sites of the adsorbent.

The interaction energy φ_a can be expressed as follows :

$$\varphi_a = - z.\ e.\ \Psi + \Omega \tag{1}$$

where z is the valence of ion,

e is the charge of electron $(1,6 \times 10^{-19}C)$,

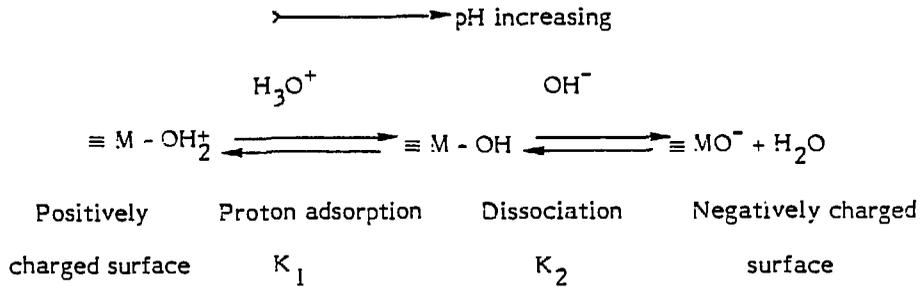Ψ is the potential at the plane of adsorption,

Ω is the energy of adsorption due to non electrostatic forces (physical or chemical bond).

φ_a also corresponds to the work required for breaking the adsorbate-adsorbent normal bond.

Generally speaking, most of the solids in water present a surface charge. It is the case for silicates, oxides, hydroxides, carbonates and phosphates.

The surface charge may originate, as follows :

- 1) isomorphous replacements within the lattice. For example, isomorphous replacement of an Si atom by an Al atom within the tetrahedral layer of a smectite creates a negative charge. Similarly, isomorphous replacements within the octahedral layer of a smectite may occur. The lack of charge, for instance, is balanced at the phase boundary by surface cations /2/. The surface charge magnitude is independent of the pH.

- 2) lack or excess of surface ions which come from the lattice. It is the case for sulphur and halogenide solids /3/.

- 3) chemical reactions at the surface. Many solid surfaces contain ionizable functionnal groups : - OH, - COOH, - PO_4H_2. These groups exhibit an amphoteric behavior, after hydration and they behave like weak acids. The surface charge, in this case, depends on the pH, and its evolution can be summarized as follows (/4/, /5/) :

$$\text{\text-\textgreater pH increasing}$$

$$H_3O^+ \qquad\qquad OH^-$$

$$\equiv M - OH_2^{\pm} \; \underset{\longleftarrow}{\xrightarrow{\hspace{2cm}}} \; \equiv M - OH \; \underset{\longleftarrow}{\xrightarrow{\hspace{2cm}}} \; \equiv MO^- + H_2O$$

Positively   Proton adsorption   Dissociation   Negatively charged

charged surface K_1 K_2 surface

with M being a tetravalent ion.

The zero point of charge (Z.P.C) corresponds to the pH magnitude where the surface charge is null, in the absence of specific adsorption other than H^+ and OH^-. It depends on the surface chemical composition, i-e on the intrinsic values for the acidity constants, K_1 and K_2. This quantity, pH_{ZPC} is given by :

$$pH_{ZPC} = \tfrac{1}{2} \left[pK_{a,1} + pK_{a,2} \right] \qquad (2)$$

It is possible to measure the surface charge evolution versus pH, owing to electrokinetic methods, like the streaming potential or electrophoresis for small or colloidal particles, or to potentiometric titration methods.

The distribution of charges in the vicinity of a solid-solution interface is usually represented as an electrochemical double layer ; one layer of the double layer is envisaged as a fixed charge on surface charge attached to the solid, while the other layer is distributed more or less diffusely in the liquid in contact (figure 1). The first is known as the Stern layer and the second, the Gouy layer. The electrokinetic potential or zeta potential, ζ is the potential drop across the mobile part of the double layer. The isoelectric point (I.E.P) is the pH where a particle is electrokinetically uncharged (figure 2).

Now, when we consider specific adsorption of an electrolyte, for example, an anion R^-, to the solid surface, positively charged, the zeta potential changes and the I.E.P shifts towards a lower pH (figure 3).

We can roughly distinguish weak interactions from strong interactions :

Weak interactions :

- London - van der Waals forces (10 to 40 kJ mol^{-1}), the van der Waals attraction energy between two atoms is inversely proportionnal to the sixth power of the separating distance over small distance /6/,

- hydrogen bond, the same energy range (10 to 40 kJ mol^{-1}).
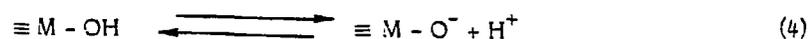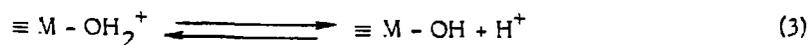
Strong interactions :

- electrostatic force of attraction or repulsion is inversely proportional to the second power of the distance between two point charges (a few hundred kJ mol^{-1}),

- chemical forces implie a covalent bond, i.e a merging of electron clouds ; they are not very common, because the activation energy required is quite high.

We have also to bear in mind the hydrophobic effect. Many organic molecules are of a dual nature ; they contain a hydrophobic part (aliphatic chain for example) and a hydrophilic polar or ionic group (e.g carboxyl or amino groups). They are called amphiphiles. They tend to adsorb on solid surface, owing to the hydrophilic group. They also can form micelles by self-association of the hydrophobic part which is sparingly soluble in water ; they make the surface hydrophobic due to the position of organic chains towards the solution /5/, /7/.

3.2. Adsorption - Modelling concept

After this brief review of mechanisms of interactions which occur at the solid (or particle) - solution interface, we have to consider the modelling concepts and their applicability to long term prediction models.

Several electrostatic models /8/, /9/, have been successfully used to describe the relationship between surface charge, σ_0, and pH. These models consider the amphoteric sites ($\equiv M$ -OH) which can ionize as follows :

$$\equiv M - OH_2^+ \rightleftharpoons \equiv M - OH + H^+ \qquad (3)$$

$$\equiv M - OH \rightleftharpoons \equiv M - O^- + H^+ \qquad (4)$$

The charged sites $\equiv M - OH_2^+$ and $\equiv M - O^-$ and uncharged sites $\equiv M - OH$ can

interact with the counter ions (complexation surface site theory), e.g. :

$$\equiv M - OH_2 \, Cl \rightleftharpoons \equiv M - OH_2^+ + Cl^- \qquad (5)$$

$$\equiv M - ONa \rightleftharpoons \equiv M - O^- + Na^+ \qquad (6)$$
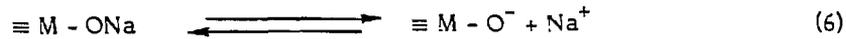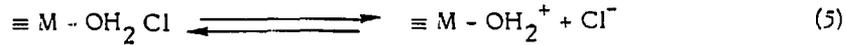
These reactions are responsible for the development of on electrical double layer at the

interface :

- an internal layer (Stern layer),

- an external diffuse layer made of solution ions (H^+, OH^-, Na^+, Cl^-).

The electrokinetic potential ζ is the slipping plane potential. ζ is measured, versus pH,

electrolyte concentration...

The model parameters are :

a) the active site density NS at the solid surface,

b) the superficial reaction constants Kj corresponding to amphoteric dissociation of

$\equiv M - OH$ and adsorption of counter ions like Na^+ and Cl^-.

Then adsorption isotherms for an element C^+ can be obtained experimentally. These

isotherms are plots of concentration of adsorbed element per unit mass of solid as a

function of concentration of dissolved element per unit volume of liquid.

This element, C^+, can interact for instance with the charged sites $\equiv M - O^-$, provided

pH is sufficiently high :

$$\equiv M - O^- + C^+ \rightleftharpoons \equiv M - OC \qquad (7)$$
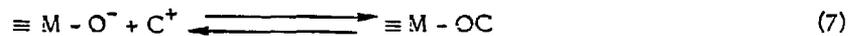
A good knowledge of the electrochemical properties of the surface, as a function of pH,

allows to explain the mechanism of the interaction, especially, whether it is entirely

electrostatic or not.

The theoretical Langmuir equation allows to link the adsorbed amount of C^+, Q, with its

equilibrium concentration in solution, (C^+) i.e :

$$Q = \frac{k \, (C^+)}{1 + k \, (C^+)} \qquad (8)$$

k is a function of the available sites number and of the surface binding constant (reaction (7)).

There are however two main assumptions :

- no lateral attraction between the adsorbate molecules in the adsorption layer,

- the surface has to be homogeneous.

The first condition is often fulfilled for inorganic adsorbate and mainly with dilute solution.

The second condition is practically never fulfilled, because natural solids always present some degree of surface heterogeneity due to the presence of different crystal faces and imperfections on the surface.

However, the surface may be treated as an assembly of different groups of sites, each group being characterized by its peculiar affinity constant of the relevant adsorption isotherm, /5/, /10/.

The overall isotherm is then obtained by a summation over the adsorption on each group of equal energy sites, weighted according to their relative prevalence.

If it is assumed that the distribution of adsorption free energies is continuous, the summation may be replaced by an integration according to :

$$\theta_t (c) \quad = \int_\Delta \quad \theta (q, c) \, f(q) \, dq \qquad (9)$$

Here $f(q)$ is the normalized free energy distribution function, $\theta(q, c)$ is the "local" (or actually, site peculiar) isotherm equation expressed as a fractional site -coverage, $\theta_t (c)$ is the overall isotherm, Δ is the range of possible variations in the adsorption free energy q, and c is the concentration (activity) of the adsorbate.

Taking $\theta (q, c)$ as the Langmuir equation, with $\exp(q)$ defining the factor K appearing in the standard Langmuir equation according to $K = K_o \exp(-q/RT)$ the integral of Eq. (9) can be solved analytically for three types of distribution functions, $f(q)$, leading to Freundlich-type adsorption equations of the form :

$$\theta_t (c) \quad = \quad \frac{(Kc)^m}{1 + (Kc)^m}$$

$$t^{(c)} = \left(\frac{Kc}{1 + Kc} \right)^m$$

$$t^{(c)} = \frac{Kc}{\left(1 + (Kc)^m\right)^{1/m}}$$

The parameter m is a measure of the heterogeneity of the surface ; a homogeneous surface would correspond to m = 1.

In conclusion, the understanding of adsorption phenomena relies upon the electrochemical double layer theory. The adsorption isotherms of ionic components are essentially extended versions of the basic Langmuir equation, and that equation has to be used in adsorption models.

4. MODELLING ADSORPTION PHENOMENA RELEVANT TO NUCLEAR WASTE
   DISPOSAL

   Generally speaking, most of the components of geological formations present ionizable functional groups like hydrous oxides, carbonates, silicates, phosphates, except in the case of clay minerals (mainly montmorillonite). The adsorption of trace elements, like radionuclides, could be modelled owing to a surface complexation model, derived from Langmuir equation as we saw above.

The surface complexation model requires mainly two parameters :

1) the surface binding constant or pK_s,

2) the available sites number (or density).

The heterogeneity of the surface is included in pK_s, which is a mean value.

The success of the surface complexation model comes from its accountability of the strong pH dependence of adsorption and of surface charge /11/.

Measuring the surface binding constants for all types of surfaces and all radionuclides

would be fastidious. Fortunately, as A. Bourg has noticed /12/ for trace elements in aquatic systems, correlations exist for :

(a) trace metals, between surface constants and solution hydrolysis constants (fig. 4),

(b) ligands, between surface complexes and solution complexes of the metal or metalloid involved in a given surface (e.g Al, Si, Fe or Mn) (fig. 5).

So, provided we get these surface binding constants by a good characterization of the electrochemical properties of the surface with electrokinetic and potentiometric titration methods, we can reach a reliable modelling of the adsorption phenomena. Such calculations for goethite e.g. still exist, /12/, (table 1). In this way, one can extend the calculated description of the speciation of the aqueous phase to the solid - solution interface and introduce such a modelling in the geochemical codes for safety assessment of radioactive waste disposal :

However, two main problems remain, considering geochemical modelling of radioactive waste disposal :

1 - adsorption on small particles or colloids,

2 - adsorption/complexation, on/by natural organic material (solid and dissolved).

For the first point, in the frame of K.B.S-3 report analysis, an attempt to estimate the respective role of colloids and solute in the migration through the geosphere has been made /19/. The authors show that the colloids can have a very strong influence on the transport of radionuclides to the biosphere. The figure 6 shows that if we suppose that the colloids move in fractures, at the water velocity, they arrive at the outlet only after 300 years which can lead to quite high dose rates. For the second point, organic complexant-enhanced mobility of radionuclides in low-level wastes has been widely studied, especially in U.S.A /20/, but only in laboratory experiments ; the authors show also a potentially strong influence of organics (desorption of radionuclides from solids).

4.1. Adsorption on colloids

Considering only natural colloids in groundwater, these are small solid particles of oxides, hydroxides etc and they present the same adsorbent behavior as minerals from geological formations. Basically, the mechanisms of adsorption relie also upon the electrochemical double layer theory.

The problem is :

1) to characterize the dispersion state of that suspension ; methods like photon correlation spectroscopy allow to obtain the size distribution of the particles,

2) to couple their adsorption capacities (pK_s determination) with their transport in groundwater.

Today it seems difficult to correctly model these two points. However, for the first one, the D.L.V.O theory (Derjaguin. Landau. Vervey. Overbeck) /21/ allows an evaluation of the rate of flocculation, derived from potential energy interaction between the particles. For the second one, the pK_s determination is possible, it has been done for TiO_2 dispersions /22/, by potentiometric and titration methods. But we may ask if we are able to assess the colloids - rocky medium interaction. Today, that question seems quite difficult to solve. However several attempts have been made /23/ and we can hope that they will succeed.

4.2. Organic matter

First, from a safety assessment point of view, it is very difficult today to estimate the influence of organic matter.

Second, we have to bear in mind that organic matter presents a very high exchange cationic capacity with respect to minerals (several hundreds of milliequivalent per 100 g against several tens).

The most important problem with organic matter that we are tackling is the prediction of the configuration of polymeric molecules in solution (rods, helix, coil, ...) and the

physical state in solution (flexibility, impermeability to salts) /24/.

Most models today (site binding with "conditional" pK) are actually formulations to interpret measured data /25/. Only for simple molecules, the models are reliable. That is to say, that we can model radionuclide complexation with very simple carboxylic acids, i.e short chains, like citric or tartric acid. For more complex molecules, the modelling today is quite intractable, because the configuration of these molecules is very variable : the short and long distance interactions between molecular groups imply that the configuration depends upon ionic strength, pH etc.

However, there is an exception for one case : the long chain tensio-active adsorption. The two-dimensionnal condensation theory on heterogeneous surface takes into account the overall of potential energies (normal accountable for adsorption, and lateral accountable for condensation) and the overall of entropic terms (conformation due to the fluidity of the chains above the Krafft point and external vibration of the gravity center of the molecule in its site) and the surface energetic heterogeneity. Tensio-active are used as indicators of surface heterogeneity /5/.

5. CONCLUSION

The geochemical modelling of radioactive waste disposal, at the present time, can take into account :

- speciation in solution, precipitation/dissolution.

- adsorption or minerals, said otherwise, speciation of the surfaces owing to surface binding constants and available surface site density. A big effort has to be done to obtain the data, particularly for actinides, which are multivalent elements.

Adsorption of radionuclides on natural colloids can be modelled, in the same way as adsorption on minerals. However the colloids transport behavior should be better defined, and also their adsorption behavior.

Organic matter seems today very difficult to model because of the heterogeneity of binding sites which depends upon the configuration of the polymeric molecules.

Moreover we have to take care of very low concentrations of radionuclides, which can be expected in the geosphere.

The improvement of the safety assessment of radioactive waste disposal strongly depends in our sense upon the above - mentioned questions. The C.E.A / I.P.S.N with the School of Mines of Paris turn their attention particularly to these questions.

Acknowledgments

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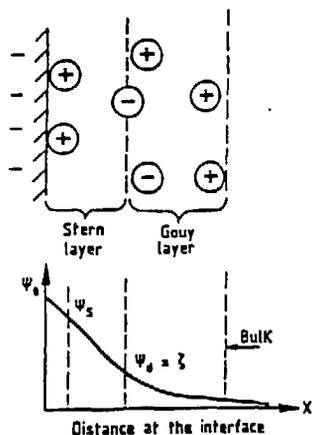
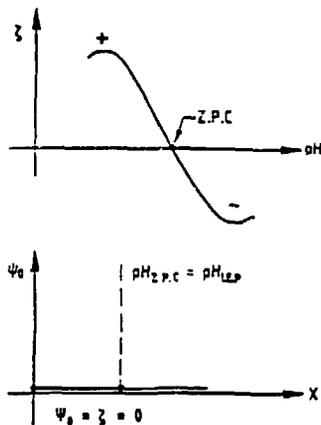Figure 1 : Distribution of charges and potential at a solid-solution interface.

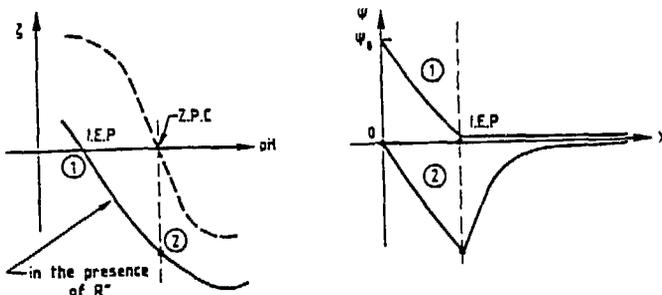Figure 2 : Potential evolution at pH = PC in the absence of specific adsorption.

Figure 3 : Potential evolutions in the case of specific adsorption.
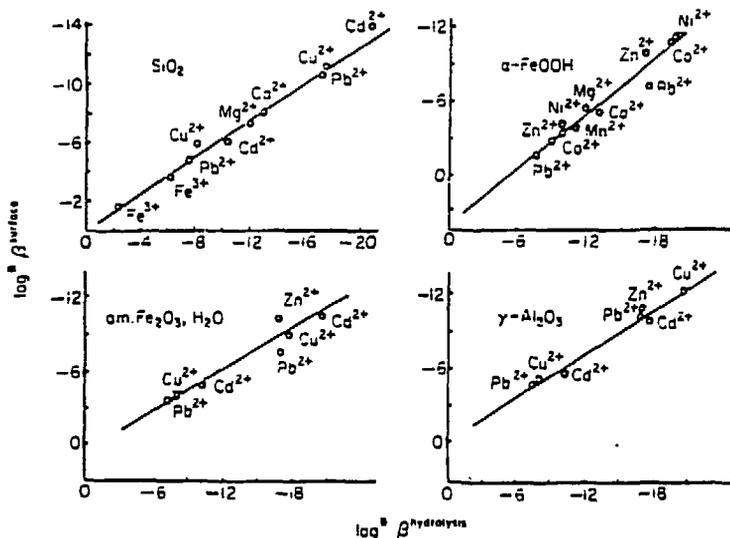

Figure 4 : Correlations between the surface stability constants and the hydrolysis constants of metals. SiO_2 from Schindler et al. /13/; and α-FeOOH from Balistrieri et al. /14/; Fe_2O_3 amorphous and γ-Al_2O_3 from Davis and Leckie /15/, /16/.
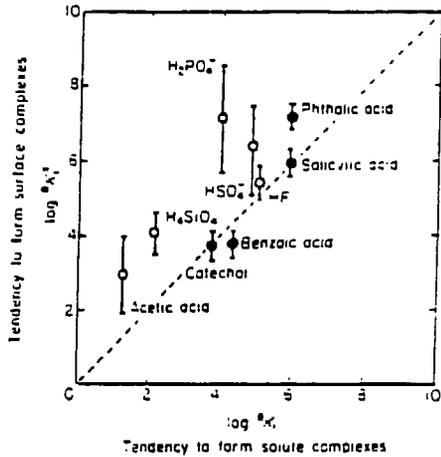
Figure 5: Correlation between the tendency to form surface complexes and that to form solute complexes (from Stumm et al. /17/). (o) with FeOOH and $FeOH^{2+}$, respectively ; (●) with Al_2O_3 and $AlOH^{2+}$, respectively.

Figure 6: MIGRATION SOLUTE + COLLOIDS CMAX=0.1 MG/L
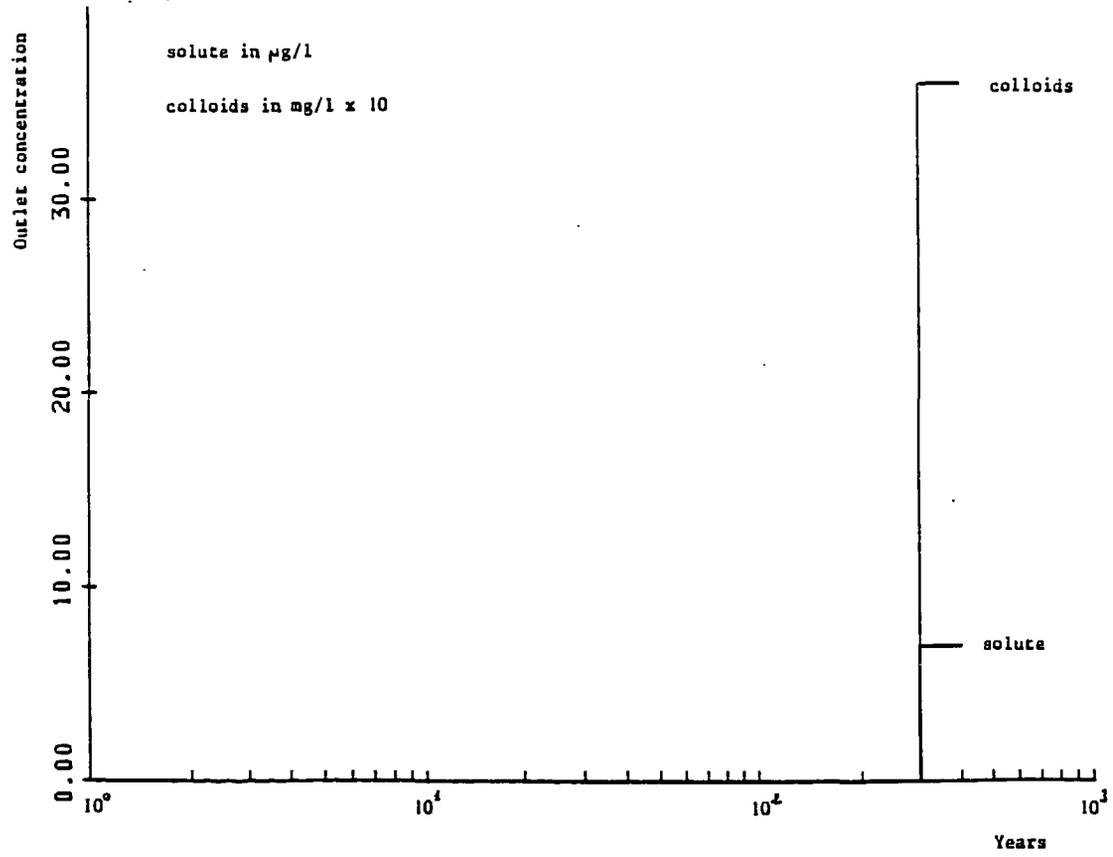

solute in μg/l

colloids in mg/l x 10

Table 1 : Speciation of the goethite surface in a natural lake water[*] (pH = 7.5 and = $FeOH_{total}$ = 1×10^{-6} mol dm^{-3} [**]).

Dissolved components	Total concentration in the aquatic system (dissolved and adsorbed) (mol kg^{-1})	Surface species	Log $K_{.nir}$	% of surface sites
—	—	=FeOH	—	25
H^-	3.2×10^{-4}	=FeOH$_2^+$	−6.4	16
OH^-	4.9×10^{-7}	=FeO$^-$	−9.25	0.05
SO_4^{2-}	1.0×10^{-4}	=FeSO$_4^-$	−5.3	0.001
$H_2PO_4^-$	1.0×10^{-6}	=FeHPO$_4^-$	7.2	35
H_4SiO_4	5.0×10^{-5}	=FeH$_3$SiO$_4$	4.1	15
		=FeH$_2$SiO$_4^-$	−3.3	2.4
HCO_3^-	5.0×10^{-3}	=FeCO$_3$	2.5[*]	49
Mg^{2+}	2.0×10^{-4}	=FeOMg$^+$	−6.2	0.8
Ca^{2+}	1.0×10^{-3}	=FeOCa$^+$	−8[*]	0.05
Pb^{2+}	1.0×10^{-8}	=FeOPb$^+$	−3[*]	0.05

[*] From Sigg and Stumm /18/; [**] = $FeOH_{total}$ = 1×10^{-3} g dm^{-3} with = $FeOH_{total}$ = 1×10^{-3} mol g^{-1}; [*] estimated.