

# Sorption mechanisms and models. Their influence on transport calculation

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**Abstract.** Approaches for the prediction of transport of radioactive species in underground and surface water based on experimentally determined distribution coefficients ( $K_d$ ) and sorption isotherms have a limited predictive capability, due to their sensitivity to many parameters. Models based on thermodynamic equilibrium can account for the influence of multiple parameters, but show important theoretical and experimental limitations, which restrict their predictive character for transport calculation.

## Introduction

Sorption and desorption at the solid-liquid interfaces play a major role in many phenomena and technologies: catalysis, chemical separations, decontamination of liquid wastes, transport of toxic and radioactive species in surface and underground waters, prediction of the future evolution of waste depositories. Use of sorption data and modeling to transport prediction must be based on a very good knowledge of sorption mechanisms, otherwise the prediction, especially at long term, may be hazardous. In accordance with the length of this short review, we shall examine the main approaches and models used to quantify sorption processes. We shall emphasize the main theoretical and experimental problems connected to the acquisition and modeling of sorption data. We shall compare sorption models and examine their adequacy with sorption mechanisms. The cited references are only a few examples of numerous articles.

## Distribution coefficients

In transport models, the contribution of sorption is generally represented by the "distribution coefficient", noted  $K_d$  or  $R_d$ , which is the ratio of the concentration of the element in the solid phase to its concentration in the aqueous phase.  $K_d$  is generally used in the calculation of the migration of an element through the retardation factor  $R$ , which is the ratio of the velocity of water to the velocity of the element through the same volume. As an example, the most simple relation between the retardation factor  $R$  and  $K_d$  is (Serne 1987):

$$R = 1 + K_d \rho (1 - \varepsilon) / \varepsilon$$

where,  $\rho$  and  $\varepsilon$  are the volumic mass (in kg/L) and the porosity of the solid phase respectively, and  $K_d$  is expressed in L/kg. This expression is valid for a monodirectional flow in a homogeneous porous medium, with a constant  $K_d$ . Several models and computer codes have been developed (Jauzein 1989, Van der Lee 2002) for more complicated situations, close to natural systems.

$K_d$  values come either from experiments which are often gathered in data banks (Stenhouse 1994), or are calculated from models. Experimental  $K_d$  values depend on the experimental conditions and often do not represent an equilibrium value. They depend on many factors: temperature, concentration of the element, pH, influence of complexing agents and competing elements, kinetics. Therefore, extrapolation of  $K_d$  values to scales larger than those of laboratory experiments, especially to natural systems, is hazardous.

Empirical linear or non linear expressions of the concentration of competing elements have been proposed for the calculation of  $K_d$  (Holstetler 1980). However, these expressions are valid only for certain experimental conditions and are generally not based on real physico-chemical processes.

## Sorption isotherms

An isotherm represents the variation of the concentration of the element in the solid phase, or the variation of  $K_d$ , versus the equilibrium concentration of the element in the aqueous solution, at a constant temperature. An equilibrium of sorption is supposed to be achieved, but apparent isotherms are often used. Isotherms are fitted by several mathematical models, which have some theoretical bases, but are often used as empirical ones. We shall not detail them, but just indicate the more often used: the Langmuir (1918), derived from the sorption of gas molecules on a solid, whose sites have equal sorption energy, but often applied to a solid in aqueous solution, the Dubinin-Radushkevitch (1947) isotherm and the Freundlich (1926) isotherm, with non homogeneous sorption sites

Although sorption isotherms include the influence of the element concentration, they depend on many other parameters and are generally used as empirical models in transport calculation.

## Sorption models

Sorption models assume a certain number of sorption equilibria able to calculate the concentrations of all species of an element in the solution and on the surface of the solid. They suppose that equilibrium is achieved. Theoretically, they are able to calculate the  $K_d$  values of an element, taking in account all factors such as pH, competing elements, complexing agents. Two main models of that kind have been developed.

### Ion exchange model

This model is based on the mass-action law, quantifying the exchange of ions between the solid and the solution, through a thermodynamic equilibrium constant  $K$ . No hypotheses have to be done on the real mechanisms at the atomic scale. However, calculation of the thermodynamic constant from concentrations needs activity coefficients. Generally, the activity coefficients in the liquid phase can be calculated, especially in dilute solutions. On the other hand, the activity coefficients in the solid phase cannot be calculated a priori. Therefore,  $K$  is replaced by a "corrected selectivity coefficient"  $K_c$ , from which the activity coefficients in the solid are excluded.

$K_c$  is generally not constant as the concentration of the element sorbed in the solid increases, but it may be almost constant, when the sorbed element is at trace level or when the interactions between adjacent sorption sites are negligible. However, the thermodynamic constant can be calculated from the Gaines-Thomas (1952) equation:

$$\ln(K) = (Z_A - Z_B) + \int_{X_B=0}^{X_B=1} \ln(K_c) dX_B \quad \text{and} \quad \Delta G^0 = -\frac{RT}{Z_A Z_B} \ln(K)$$

where  $X_B$  is the ionic fraction of the element B in the solid after exchange with the element A,  $Z_A$  and  $Z_B$ , the ionic charges and  $\Delta G^0$  the Gibbs free energy.

It is possible to interpret the variation of  $K_c$  with the concentration in the solid, by considering the partition function  $Q$  (Barrer 1956):

$$Q = \sum_j \exp\left(\frac{-E_j}{kT}\right) \quad \text{connected to } K \text{ and } K_c \text{ by } \Delta G^0 = -RT \ln Q$$

where  $E_j$  is the energy of each level in the solid. Often, the calculation can be simplified by limiting to the additional energy change in the solid when two adjacent sorption sites are occupied.

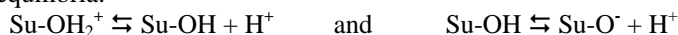
The ion exchange model is particularly useful for solids in which the sorption process is not superficial, but results from a penetration of the sorbed element into the bulk of the solid. As an example, the variation of  $\ln(K_c)$  with the  $\text{Sr}^{2+}$  concentration in poly-antimonic acid  $\text{H}_2\text{Sb}_2\text{O}_6$ , confirmed by X-ray diffraction, showed

that sorption proceeds through the successive substitution of two sites of the crystal framework (Zouad 1992).

## Surface complexation models

These models were developed for oxyhydroxides. They are based on the acid-base properties of superficial hydroxide groups of these solids. Several types of such models were developed: the monosite 2-pK and 1-pM models, the multisite 1-pK model, the pK-distribution model.

The "**monosite 2-pK model**" (Stumm 1992) assumes that the surface is covered by one type of hydroxide groups with amphoteric properties, leading to the following equilibria:



where Su represents the surface. The corresponding thermodynamic constants are:

$$K^+ = \frac{(\text{SuOH})(\text{H}^+)}{(\text{SuOH}_2^+)} \quad \text{and} \quad K^- = \frac{(\text{SuO}^-)(\text{H}^+)}{(\text{SuOH})}$$

Without other sorbed species leading to charged complexes, the "surface charge" is defined as:

$$Q = [\text{Su-OH}_2^+] - [\text{Su-O}^-]$$

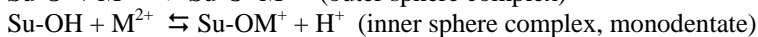
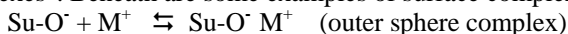
Another important parameter is the superficial density of sites  $Q_{\text{max}}$ , which is the maximum concentration of -OH surface sites able to react with protons.

The point of zero charge (pzc) is the pH value for which the surface charge is equal to zero. The variation of surface charge with pH is generally determined by acid or base titration of a suspension of the solid. The surface charge can also be measured by electro-kinetic methods.

The main theoretical difficulty results from electrostatic interactions in the vicinity of the surface. The activity ( $\text{H}^+$ ) measured in the bulk of the solution is different from the activity in the vicinity of the surface and the apparent constants vary with the surface charge. For ions present in the electrical field of surface charge, it is necessary to consider an electrostatic free energy:  $\Delta G_{\text{elec}} = z F \Psi(x)$ , where  $z$  is the charge of the ion,  $F$  the Faraday constant and  $\Psi(x)$  the electric potential at a distance  $x$  to the surface. This potential cannot be calculated a priori. Several models, based on the distribution of ions near to the surface have been proposed in order to connect the potential to the surface charge (constant capacitance model, diffuse layer model, basic Stern model, triple layer model,...). These models use a certain number of parameters, which are fitted from experimental sorption data together with sorption constants. Through these models, it is theoretically possible to calculate the "intrinsic" thermodynamic constants  $K^+$  and  $K^-$ .

The sorption of ions depends on the nature and sign of the ion, together with the sign and charge of the surface, and, hence on pH. Two types of interactions are considered. Pure electrostatic interactions lead to "outer sphere" surface com-

plexes. Formation of covalent bindings with surface groups leads to "inner sphere complexes". Beneath are some examples of surface complexes:



As an example, the surface charge for the monodentate is:

$$Q = [\text{Su-OH}_2^+] - [\text{Su-O}^-] + [\text{Su-OM}^+]$$

Thermodynamic sorption constants can be calculated from these models together with  $K_d$  values, and their variation with pH and concentrations of other species in solution.

Another surface complexation model is the **1-pK "Multisite complexation model"** or "Music" (Hiemstra 1989). It considers that the surface presents several families of oxide and hydroxide sites, each one with a specific acidity constant pK. However, each type of sites **cannot** be amphoteric (1-pK model), but the occurrence of several families of sites may confer an amphoteric property to the surface. Another feature of this model is the fact that the charge of a site may be fractional, this charge depending on the coordinance of the surface site. An example is:



Contrary to the 2-pK model, the acidity constants are calculated here a priori, from atomic geometrical and electrostatic considerations and by comparison to the monomers of the same oxides. This model is more realistic than the monosite 2-pK model, but it requires a good knowledge of the crystal structure and surface orientations of the solid.

## Evaluation of sorption models

### Sorption mechanisms

The question is: do models represent the true sorption mechanisms? If not, what is the validity of such models when using them far from laboratory conditions, especially for radioactive waste, where prediction must be valid for more than thousands of years and applied to natural systems? To insure a safe extrapolation of models, it is necessary to know as better as possible the real sorption mechanisms. We must use methods able to localize the sorbed elements, determine the nature of their species and types of bindings. This goal can only be achieved by using a multidisciplinary approach, with several different methods (microscopic methods, bulk and surface spectroscopic methods) which bring complementary results.

As an example, we indicate in Table 1 the main sorption mechanisms for some elements on hydroxyapatites (Fedoroff 1999, Monteil-Rivera 2000). The main feature is that the sorption mechanisms depend strongly on the element and that tradi-

**Table 1.** Main sorption mechanisms of some elements on hydroxyapatites.

Element	Sorption mechanisms
$\text{Cd}^{2+}$	Exchange with $\text{Ca}^{2+}$ in the crystal framework in 2 sites, with diffusion in $\approx 3$ superficial unit cells. Equilibrium not achieved within 10 d at $75^\circ\text{C}$
$\text{Pb}^{2+}$	Formation of new solid phases + slight incorporation into apatite framework
$\text{UO}_2^{2+}$	Formation of new amorphous solid phase
$\text{Eu}^{3+}$	Superficial sorption (site 1) + Incorporation in the apatite framework (site 2)
$\text{SeO}_3^{2-}$	Exchange with $\text{PO}_4$ groups of 1 superficial unit cell

tional models, described above, cannot be applied. Equilibrium is not achieved in many cases.

In the case of oxy-hydroxides, the general principles of surface complexation can be applied, but the determination of the real sorption sites and complexes, and of the true thermodynamic constants present many theoretical and experimental difficulties. We shall examine only several of these problems.

### Choice among surface complexation and electrostatic models

The problem is the choice between the monosite or multisite models and among the different electrostatic models of the double layer. The same experimental system can often be fitted with different models, sometimes with different types of surface complexes. An important point is that calculated sorption constants for sorbed ions other than protons depend on the  $\text{K}^+$  and  $\text{K}^-$  constants for protons, which in turn depend on the electrostatic model chosen.

In Table 2, we show some examples of parameters found by fitting one titration curve of goethite by different models using a least squares method. Considering the sum of squares is not of good help to choose the “best” model. The parameters obtained for the monosite 2-pK model depend on the electrostatic model and on the way how the least square fitting was run. It should be noted that, while one could consider that the variation on pK's is not so high, the variation of the fitted site density is very important. In the given example, we have considered only one site for the 1-pK model. The ion exchange model gives also a good fit, but the values of pK's are different since this model does not consider any electrostatic effect.

**Table 2.** Examples of comparison of models used to fit a set of titration data for goethite: calculated intrinsic constants  $pK^+$  and  $pK^-$ , surface site density, capacitance and pzc.

Models and methods	$pK^+$	$pK^-$	Sites at/nm <sup>2</sup>	Cap. C/m <sup>2</sup>	PZC
Ion exchange	9.1	11.8	1.8		
2-pK monosite					
CCM, NWLS on H <sup>+</sup>	6.9	9.2	3.9	1.2	8.1
CCM, WLS on pH	6.9	8.7	1.5	1.7	7.8
DLM, WLS on pH	7.4	8.1	0.3		7.8
1-pK multisite -OH <sup>1/2</sup> -/OH <sub>2</sub> <sup>1/2+</sup>					
CCM, WLS on H <sup>+</sup>	7.8		6.6	1.1	
CCM, NWLS on H <sup>+</sup>	7.8		13	1.1	

CCM: constant capacitance model, DLM: diffuse layer model

WLS: weighted least squares, NWLS: not weighted least squares

Finally, at present time, it is difficult to make a choice. The main problem is that the electrostatic parameters are presently fitted from titration data. To our point of view, we should avoid using models with a large number of free parameters. One of the simplest but rather complete model is BSM (basic Stern model), which considers a layer with a constant capacitance, followed by a diffuse layer.

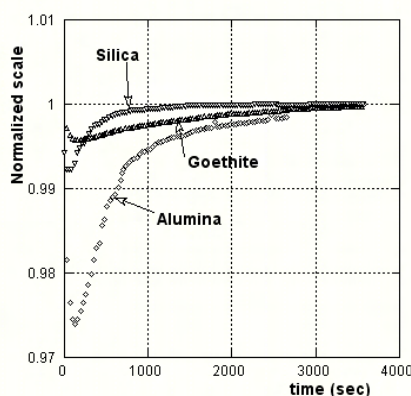
More and more examples show that the orientation of faces has an influence on the sorption properties. As an example, Rabung et al (2004) showed that Cm(III) is preferentially sorbed on (001) faces of sapphire by a factor of  $\approx 7$  compared to (110) planes and  $\approx 25$  compared to (018) planes at pH 4.5. So, for solids whose structure and crystal habits is known, it is likely to use the multisite model, rather than a monosite one.

For the sorption of ions other than protons and hydroxyls, the problem is the same, since it is also possible to fit the sorption isotherms with different types of surface complexes (monodentate, bidentates...). Spectroscopic methods have to be used to differentiate between complexes.

Another theoretical limitation is that, contrary to an equilibrium in a homogeneous liquid phase, there is no uniform definitions of standard and reference states for reactions at solid-liquid interfaces. The introduction of a reference site density has been proposed (Kulik 2002).

## Kinetics

Models shown above suppose that equilibrium is achieved. In fact, kinetic effects play an important role in sorption chemistry. Kinetics may be a critical factor which will limit the sorption process in column operation and for transport, even



**Fig. 1.** Kinetics of proton sorption during titration of alumina, silica and goethite.

when equilibrium  $K_d$  values are very high. It may be also a factor which disturbs the measurement of equilibrium thermodynamic constants.

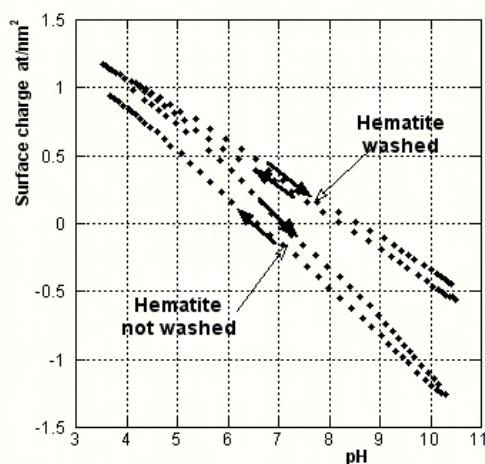
As an example, we show the variation of pH after an addition of acid during titration of a suspension of alumina, silica or goethite, in order to determine the surface charge versus pH curve (Fig. 1). The delay to obtain an equilibrium value depends on the solid and is connected to several factors such as its porosity. For this type of alumina, a delay of 1 hour is needed after each addition, otherwise the pH and calculated surface charge do not correspond to equilibrium values.

Apart from the sorption of protons, kinetics limits also more or less the sorption of many ions. Kinetics and reversibility should be measured systematically, since they may be the main factors controlling the transport of ions. They can also indicate the nature of the sorption process.

### Some factors affecting surface charge measurement, sorption and transport

It is evident that it is important to consider the different species of the elements present in the solution. Several computer codes and data banks such as the code developed by Van der Lee (2001) can be used to predict speciation. In certain cases, precipitation, either in the bulk of the solution, either on the surface of the solid may occur. Dissolution of the solid has also to be taken into account, since it has an effect on the pH during titration experiments and, hence, on the calculated surface charge. A correction for dissolution must be applied. In the case of the titration of  $\gamma$ -alumina (Lefevre 2004), the surface charge not corrected for dissolution seems to increase continuously with increasing  $H^+$  concentration in solution,





**Fig. 2.** Influence of washing treatment on forward and backward titration curves of hematite

in contradiction with a defined surface site density. After correction for dissolution, the real charge achieves a maximum, which corresponds to the surface density of active sites.

It is well known from geological processes, that mineral species are subject to alteration, dissolution, recrystallization. However, the quantitative impact of such processes on the long term is difficult to be estimated, although some information can be deduced from thermodynamic data on the stability of minerals and through exchange of knowledge between chemists and geologists. An example is the large decrease of the density of active sites when  $\gamma$ -alumina is kept in water (Lefevre 2002). Investigation by X-ray diffraction, scanning electron microscopy (SEM), TGA and DTA showed that this modification of surface reactivity is induced by a transformation of  $\gamma$ -alumina into bayerite ( $\text{Al}(\text{OH})_3$ ).

Impurities and, especially, surface contaminations, can hide the "intrinsic" surface reactivity of a solid. We show on Fig. 2 the influence of a washing procedure, including treatments by acid and basic solutions, on the titration curves of hematite. This procedure removes species such as carbonates and sulfates, shifts the titration curves and, hence, the calculated surface charge and the pzc.

The majority of laboratory sorption experiments are supposed to be done in clean and abiotic conditions. This is certainly not the case in many of them, but the problem is quite more important in natural media. Presence of colloids in underground water can drastically accelerate the mobility of elements, if these elements are preferentially sorbed on colloids and if the porosity of the media allows the motion of colloids. In other conditions, sorption on colloids can reduce the mobility of radionuclides. Bacteria, by the possibilities of specific interactions with dissolved elements, can also have an important effect on the transport.

## Conclusion

This short review could not describe all aspects of sorption processes and their impact on transport. We hope that we could, however, show the progress obtained in the knowledge and modeling of sorption processes and, in the same time, the new problems that this progress has induced. Among the next steps for future progress, we may quote: use of high-purity solids with known surface orientations, use of better electrostatic models with parameters determined independently from sorption measurements, models with realistic surface electron density taking into account surface reconstruction. Experimental and theoretical work has to be done to transpose knowledge on simple solid phases to complex systems, with choice of the pertinent major parameters for transport prediction.

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