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doi:10.1016/j.gca.2005.01.022

Blind prediction of Cu(II) sorption onto goethite: Current capabilities of diffuse double layer model

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(Received July 9, 2004; accepted in revised form January 24, 2005)

Abstract—The paper presents examples illustrating the current blind predictive capabilities of the diffuse double layer model (DDL) as the model requiring the smallest set of parameters and thus being most suitable for substituting even more empiric sorption approaches such as distribution coefficients K_D . The general strategy for the selection of numerical data are discussed. Based on the information about the minerals compiled in the sorption database RES³T (Rossendorf Expert System for Surface and Sorption Thermodynamics), first a set of relevant surface species is generated. Then relevant surface complexation parameters are taken from RES³T: the binding site density for the minerals, the surface protolysis constants, and the stability constants for all relevant surface complexes. To be able to compare and average thermodynamic constants originating from different sources, a normalization concept is applied.

Our demonstration is based on a blind prediction exercise, i.e., the goal was not to provide optimal fits. The system considered is Cu(II) sorption onto goethite. The predictions are compared with raw data from three independent experimental investigations. The calculations were performed with the FITEQL 3.2 code. In most cases the model predictions represented the experimental sorption values for the sorbed amount of Cu(II), expressed as conventional distribution coefficients, within one order of magnitude or better.

We conclude that the application of DDL can indeed be used for estimating distribution coefficients for contaminants in well defined mineral systems. A stepwise strategy of species selection, data collection, normalization, and averaging is outlined. The SCM database so far assembled within the RES³T project is able to provide the parameter sets. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The partitioning of dissolved heavy metals between the solution and all relevant surfaces (including both engineered and natural systems) is usually characterized by equilibrium distribution coefficients – K_D values. These values are required by most modeling software for calculations regarding the remediation of contaminated sites, for environmental impact assessment in areas with elevated contaminant levels resulting from anthropogenic influences, or for the planning of waste disposal facilities. However, the K_D concept is a rather simplistic approach, because:

- Many very different basic physicochemical phenomena are contained in just one conditional parameter.
- The K_D values are sensitive to even slight changes in system parameters such as Eh or pH, the major cation content, or the presence of a new mineral phase.
- Any K_D value used in prognostic studies is generally just a snapshot for a specific parameter combination. It is impossible to measure the effect of all such combinations, which implies that extrapolating K_D values may involve very large uncertainties.

Thus, both from a scientific and from an application point of view, simple approaches such as the K_D concept are unsatisfactory. Empiric parameters are not able to portray complex processes on the surfaces. This complex behavior of natural systems can be better described by sorption isotherms (Lang-

muir, Freundlich). These models have found popular acceptance because they are mathematically simple and seem to fit experimental data (Benjamin, 2002). They take into account physisorption and chemisorption, but the determined coefficients are only applicable to the specific determination conditions. Moreover, they do not give any chemical mechanistic information. A scientifically founded description of the sorption processes at the mineral-fluid interface is possible with so-called surface complexation models (SCM). As the name implies, SCM accounts for adsorption of ions on surface sites as complexation reactions comparable to complexation in solution. The electrical charge at the surface is determined by the chemical reactions of the mineral functional groups, including acid-base reactions and formation of ion pairs and coordinative complexes. For a general discussion of the underlying SCM principles see, for example, Davis and Kent (1990) and Stumm (1992).

SCMs have evolved over time and are now available in various forms. The most important groups are the diffuse double layer model (DDL) (Stumm et al., 1970; Dzombak and Morel, 1990), constant capacitance model (CCM) (Schindler and Gamsjäger, 1972; Hohl and Stumm, 1976), triple layer model (TLM) (Yates et al., 1974; Davis, 1978; Hayes and Leckie, 1986), basic stern model (BSM) (Bowden et al., 1977; Westall and Hohl, 1980) and the (CD-)MUSIC model (Hiemstra et al., 1989a, b; Hiemstra and van Riemsdijk, 1996). The individual models differ from each other in the manner of describing the electrochemical double layer, i.e., the position and hydration status of the adsorbed ion and the mechanism of protonation. Finally, there are also models available not using any electrostatic contributions at all, named nonelectrostatic

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models (NEM) (Kurbatov et al., 1951; Bradbury and Baeyens, 1997).

The amount of published adsorption results where surface complexation models have been applied has increased drastically in the last decades. Now the time is appropriate for general applications. During the next decade SCM will probably replace the K_D approach only in some simple systems or systems dominated by just one mineral. But SCM can help to verify measured K_D values, to identify the most critical sensitive experimental parameters, to assign uncertainty limits, to fill gaps difficult to access in sorption experiments, and to help to gain a better process understanding.

The transition process to a chemically more realistic approach to sorption seems to be a rather slow one, hampered by several prejudices. SCM have drawbacks and limitations indeed. There are difficulties in separating intrinsic and electrostatic contributions to overall adsorption energies, describing heterogeneity, or estimating parameters (Lützenkirchen, 2002). Furthermore, the scope of the particular model concerning the ionic strength of the system is different, e.g., the CCM is not applicable to low ionic strength <0.01 M, and the DDLM cannot be used for high ionic strength >0.1 M (Hayes et al., 1991).

Though the experimental data may be equally well interpreted by different submodels (Westall and Hohl, 1980), the parameters derived from the particular models cannot be compared directly. Therefore, the high demands on the consistency of SCM data sets include using a uniform SCM submodel throughout a blind prediction task.

Another problem is that the models are not a proof for a correct mechanism. Often the proposed surface species are only the result of a best-fit of postulated structures. An independent proof by spectroscopy or other methods is essential.

Finally, the number of adjustable parameters ranges from three (the two protolysis constants and the surface site density) for the DDLM to seven (two protolysis constants, the surface site densities, two capacitance parameters, and two electrolyte binding constants) for the TLM. In any case this is of course more than just one K_D parameter.

2. GENERAL STRATEGY FOR THE NUMERICAL DATA COMPILATION

To overcome the above-described bias against SCM and the reluctance to use this approach in practical applications we think it is essential to develop a data supply strategy for modeling and to test whether SCM can already be applied successfully for predicting K_D values in environmental impact assessments. First we will consider the general strategy for the compilation of numerical data. The thermodynamic database RES³T (Rossendorf Expert System for Surface and Sorption Thermodynamics) (Brendler et al., 2003; Richter et al., 2003) represents a helpful foundation for this strategy. This Microsoft Access-implemented relational database RES³T is mineral-specific and based on the concept of SCM. The following stepwise approach describes our strategy for the parameterization of the mineral-specific part of the SCM concept:

1. As a first step, a data survey, mainly based on the RES³T database, helps to define the chemical system, i.e., the mineral properties (site density, protolysis constants as function of ionic

strength) and the set of surface species. The specific surface area is dependent on the sample preparation and cannot be generalized. It is thus part of the experimental conditions, and the experimentally determined value should be used also for the system definition in the blind predictions.

2. The first data item to be fixed is the surface site density, a parameter specific for each mineral. Here, a literature survey must take into account that some experimental methods are known to usually yield values higher than the site density really accessible to the sorbing ligand. If the available data are very uncertain or even missing, one could also use a site density of 2.31 sites nm^{-2} . Dzombak and Morel (1990) suggested this value for hydrous ferric hydroxide, while Davis and Kent (1990) proposed it as sort of a “universally” recommended site density for all minerals. The value has often been used since then by many groups.

3. The next step is the selection of reliable reaction data. The consistency of the data with respect to model, mineral, and aquatic speciation is an important quality criteria. But when there are too few data available, a pragmatic way should be chosen. It is better to consider questionable values than none at all. For example, sorption parameters from chemical analogs of either the adsorbate or the adsorbent can be used to derive sensible chemical models. A detailed example concerning the effects of missing important surface reactions was presented for the case of Np(V) sorption onto hematite (Brendler et al., 2004). Other systems covered therein are U(VI) sorption onto quartz and Se sorption onto goethite, broadening the basis of our conclusions.

4. Usually, the reported constants (protolysis constants, surface complexation constants) are related to different site densities Γ and refer to a nonequivalent standard state and therefore cannot be directly compared. It is necessary to convert them to a reference state to enable comparison and averaging (normalization). Kulik (2002) defined the standard state of a surface species when 1 mole of it occupies all sites of the reference total density $\Gamma_0 = 20 \mu\text{mol m}^{-2}$ (12.05 sites nm^{-2}) on a surface of one mole of a sorbent suspended in 1 kg of the solution at a reference pressure of 1 bar and a reference temperature of 25°C , in absence of external fields and at zero surface potential $\Psi = 0$. The outcome of this is the conversion of the conventional reaction constants K_C formulated for the unreacted surface site being on the left-hand side:

$$\log K_0 = \log K_C + \log \frac{\Gamma_C}{\Gamma_0} \quad (1)$$

After normalization and averaging the resulting protolysis constants can easily be converted to a surface site density relevant for the respective mineral, applying the same equation.

5. All reaction constants must be extrapolated to infinite dilution. Currently, there is no generally accepted convention for treating activity coefficients of surface species. For dissolved species, the Davies equation (Davies, 1962) can be used for the calculation of activity coefficients in a range up to an ionic strength of 0.5 M:

$$\log f = -A \cdot z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (2)$$

Table 1. Experimental conditions for blind prediction of Cu(II) sorption onto goethite.

	Ali and Dzombak (1996b)	Balistreri and Murray (1982)	Kooner (1992)
Solid concentration [gL ⁻¹]	1.6	0.55	0.6
Surface area [m ² g ⁻¹]	79.4 ^a	51.8 ^a	50.0 ^b
Total site concentration [mmolL ⁻¹]	2.54	0.57	0.6
Ionic strength of NaNO ₃ [molL ⁻¹]	0.01/0.1	0.1	0.1
pH range	3.7 to 6.5	3.2 to 6.7	3.9 to 6.6
Total Cu(II) concentration [μmolL ⁻¹]	2.3/23/98	0.32/1.8/31	7.8/78/157

^a N₂-BET method.

^b Derived from literature values in which the with same goethite synthesis method was used (N₂-BET method).

where I denotes the ionic strength, z the ion charge of the species, and A is the Debye-Hückel parameter ($0.5093 (I \text{ mol}^{-1})^{-1/2}$ for water at 25°C).

6. When key parameters are not available, various approximations can be utilized to derive them for SCM. These include the estimation of protolysis constants based on crystallography and thermodynamics (Sverjensky and Sahai, 1996) and extrapolation from chemically similar systems (with regard to both mineral and sorbent) by applying the linear free energy relationships (LFER) (Dzombak and Morel, 1990). If such approaches fail, a simple transfer of data from chemically similar systems (with identical charge) is acceptable. There, as a last resort and abandoning the internal data consistency, parameters based on electrostatic terms different from the chosen SCM may also be taken into account. Preliminary uncertainty analysis showed that in most cases the sorption modeling error caused by omitting a surface reaction totally is much larger than that introduced by using a surface complex formation constant with large uncertainties.

7. After normalization, all data records related to the same reaction (mineral surface protolysis and surface complex formation) must be compared and judged to identify and exclude outliers and doubtful data points. The remaining selected thermodynamic data records are then averaged (simple mean, because often there are no uncertainties published, making a weighting impossible) to obtain the respective model parameters. The averaging process also delivers the standard error of the mean.

This general strategy can be applied to every SCM. For pragmatic reasons we prefer the DDLM as SCM variant, because this choice minimizes the number of parameters. TLM may often come closer to the physical reality but needs more parameters and, probably even more important, delivers parameters valid only for a distinct background electrolyte. Thus it is very difficult to combine parameters from different background electrolytes to tackle practical challenges with mixed complex background electrolytes. Moreover, many published data sets are based on the DDLM, and the parameter sets are valid not

Table 2. Protolysis constants of goethite derived from RES³T for the DDLM (original values and normalized to SSD = 12.05 sites nm⁻² and extrapolated to zero ionic strength I).

Reference	I [mol L ⁻¹]	Γ ^a [sites nm ⁻²]	pK ₁	pK ₂	pK ₁ (norm, I = 0) ^b	pK ₂ (norm, I = 0) ^b
Atkinson et al. (1967)	0.1	0.56	6.99	8.40	5.76	9.84
Sigg (1979)	0.1	4.15	5.90	8.65	5.54	9.22
Sigg (1979)	0.1	4.30	6.40	9.25	6.06	9.81
Hayes et al. (1991)	0	10.00	7.10 ^d	10.24 ^c	7.02	10.32
Mesuere and Fish (1992)	0	1.50	7.90	10.70	7.00	11.60
Stone et al. (1993)	0	6.50	6.00	9.80	5.73	10.07
Van Geen et al. (1994)	0	2.31	7.91	10.02	7.19	10.74
Lumsdon and Evans (1994)	0.01	2.74	7.39	11.04	6.79	11.73
Turner and Sassmann (1996)	0	2.31	7.35 ^f	9.17 ^g	6.63	9.89
Ali and Dzombak (1996b)	0	1.40	7.68	8.32	6.75	9.25
Robertson and Leckie (1997)	0	7.00	6.91	10.80	6.67	11.04
Robertson and Leckie (1997)	0	2.31	7.72	10.09	7.00	10.81
Missana et al. (2003)	0 ^c	2.20	7.20	10.00	6.46	10.74
Buerge-Weirich et al. (2003)	0.01	1.3	5.6	8.9	4.68	9.91
Peacock and Sherman (2004)	0 ^c	6.02	6.78	10.10	6.48	10.40
Mean ± 2σ ^b			6.99 ± 0.38	9.70 ± 0.45	6.38 ± 0.36	10.36 ± 0.39
Mean ± 2σ (restricted) ^{hh}			6.94 ± 0.39	9.80 ± 0.44	6.36 ± 0.38	10.44 ± 0.38

^a Γ original surface site density.

^b Mean ± standard error (significance level 95%), rounded to two decimal places.

^c Extrapolation to zero ionic strength assumed, not explicitly cited.

^d σ = ±0.013.

^e σ = ±0.033.

^f σ = ±0.11 (95% confidence interval).

^g σ = ±0.08 (95% confidence interval).

^h Without Ali and Dzombak (1996b)

Table 3. Surface complexation constants for the Cu(II) sorption onto goethite taken from RES³T for the DDLM (original values and normalized to 12.05 sites nm⁻² and extrapolated to zero ionic strength).

Reference	Surface species	I [mol L ⁻¹]	Orig. Γ [sites nm ⁻²]	Log K ^c	Log K (norm., I = 0) ^c
Ali and Dzombak (1996b)		0	1.4	2.21	1.28
Robertson and Leckie (1998) ^a		0 ^b	2.65	1.32	0.66
Buerge-Weirich et al. (2002)		0.01	2.3	2.93	2.35
Buerge-Weirich et al. (2003)		0.01	1.3	0.71	-0.12
Mean $\pm 2\sigma^c$	=FeO-Cu ⁺			1.79 \pm 0.98	1.04 \pm 1.04
Mean $\pm 2\sigma$ (restricted) ^{cd}	=FeO-Cu ⁺			1.65 \pm 1.32	0.96 \pm 1.46
Robertson and Leckie (1998) ^a	=FeO-CuOH	0 ^b	2.65	-6.49	-7.15

^a Weak sites.

^b Extrapolation to zero ionic strength assumed, not explicitly cited.

^c Mean \pm standard error (significance level 95%), rounded to two decimal places.

^d Without Ali and Dzombak (1996b)

just for a specific background electrolyte. To keep the system as simple as possible, we did not distinguish between strong and weak binding sites on goethite, taking into consideration that so far there is no clear spectroscopic evidence for such a distinction. If complexation constants are published only for the sorption on weak and strong binding sites we took the values for the sorption on weak sites, because of their greater abundance, especially if the experimental concentrations are not in the tracer region.

3. APPLICATION EXAMPLE: CU(II) SORPTION ONTO GOETHITE

Iron (hydr)oxides are important scavengers of contaminants in the environment because of their common presence in soils and sediments, their generally high surface area and strong affinity for many elements. The sorption of trace metals, heavy metals, and radionuclides on iron (hydr)oxides has been the object of a multitude of experimental and theoretical studies, e.g., by Davis (1978), Sigg (1979), Dzombak and Morel (1990), Smith and Jenne (1991), Turner and Sassmann (1996), and Kosmulski (2001).

A metal ion often investigated is Cu(II), since it is ubiquitous in soils and aquatic systems. It is a trace essential for the well-being of people and most other animals as well as plants. Nevertheless it can be damaging at high concentrations, which may occur as a result of contaminants from ore smelting or other industrial processes. The degree of Cu bioavailability and mobility, and therefore also toxicity, is determined and affected by aqueous (especially organic) complexation and by adsorption to soil components. In particular, the system Cu(II)/goethite (α -FeOOH) has been the subject of many experimental investigations, e.g., Forbes et al. (1976), Balistrieri and Murray (1982), Padmanabham (1983), Kooner (1992), Rodda et al. (1993), Ali and Dzombak (1996a, b), Robertson and Leckie (1998), Palmqvist et al. (1999), Christophi and Axe (2000), Buerge-Weirich et al. (2002, 2003), and Peacock and Sherman (2004). The extent of metal uptake by soils is strongly influenced by several parameters: pH, ionic strength, metal concentration, mineral/sorbent ratio (i.e., solid concentration), reaction temperature, and time. Organic matter is also important in many natural systems. Substances such as humics, owing to their widely varying structure, size, and conformation, are difficult to assess in experiments. So far the parameters re-

quired in SCM are only available for rather simple organic sorbents (e.g., Ali and Dzombak, 1996a; Buerge-Weirich et al., 2002).

The following three publications contain a broad coverage of parameter combinations (with exclusion of organics) and a high level of experimental quality and documentation:

- Ali and Dzombak (1996b): 64 batch sorption data points with an experimental error of 4%; variation of pH and total Cu(II) concentration (CO₂ free).
- Balistrieri and Murray (1982): 34 batch sorption data points, variation of pH and total Cu(II) concentration (at air P_{CO2}).
- Kooner (1992): 46 batch sorption data points with an experimental error of 2%; variation of pH and Cu(II) concentration (at air P_{CO2}).

These experiments therefore qualified as test candidates for our predictive modeling. In this work, "blind prediction" means that each prognosis is based solely on the specific experimental conditions, such as total Cu(II) concentration, ionic strength, surface area of goethite, solid concentration, and pH range. Table 4 provides details of the selected experiments. We did not use the experimentally measured sorption data in any way, so it is not a fitting procedure.

All thermodynamic parameters (surface site density, protolysis constants, surface complexation constants, aqueous complex formation, mineral solubilities) are taken from appropriate databases (Brendler et al., 2003; Smith and Martell, 1997). The model is set up as follows.

We used a value for the surface site density of 2.31 sites nm⁻² (Dzombak and Morel, 1990; Davis and Kent, 1990). The literature data for goethite vary from 0.56 (Atkinson et al., 1967) to 18 (Hsi and Langmuir, 1985) sites nm⁻², with the mean at 4.63 and the median at 2.56 sites nm⁻², taking into account that the site density should not depend on a special electrostatic model. If we restrict our data comparison to only those values listed in Table 1 and originating from experiments, we obtain a mean of 3.24 and a median of 2.74 sites nm⁻². Both views thus justify the use of a value of 2.31 sites nm⁻² for our study.

The values of pK₁ and pK₂ for the two successive protolysis steps always refer to the following deprotonation reactions:

Table 4. Surface complexation constants for the H₂CO₃ sorption onto goethite taken from RES³T for the DDLM (original values based on H₂CO₃ adsorption, normalized to 12.05 sites nm⁻² and extrapolated to zero ionic strength).

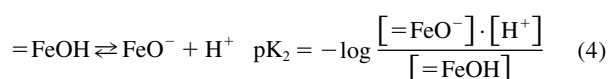
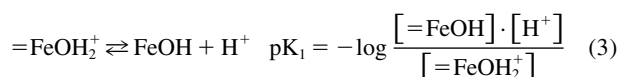
Reference	Surface species	Ionic strength [mol L ⁻¹]	SSD [sites nm ⁻²]	Log K	Log K (norm., I = 0) ^a
Van Geen et al. (1994)		0	2.31	4.1	3.38
Appelo et al. (2002)		0.1	0.72	3.62 ^c	2.61
Mean ± 2σ ^a	=FeO-CO ₂ H			3.86 ± 0.68	3.00 ± 0.77
Van Geen et al. (1994)		0	2.31	-3.97	-4.69
Sigg (1979)		0.005	4.3	-3.85	-4.33
Mean ± 2σ ^a	=FeO-CO ₂ ⁻			3.91 ± 0.17	-4.51 ± 0.36
Appelo et al. (2002) ^b	=FeOH-CO ₃ ²⁻	0.1	0.72	-11.90 ^d	-13.55

^a Mean ± standard error (significance level 95%), rounded to two decimal places.

^b Weak sites.

^c σ = ±0.53 (95% confidence interval).

^d σ = ±0.14 (95% confidence interval).



A search using RES³T resulted in 15 independent DDLM data records for the goethite surface protolysis. Table 1 shows the originally published protolysis constants of goethite as contained in the database, together with the values after normalization to a reference site density of 12.05 sites nm⁻² and extrapolation to infinite dilution, as described in the previous section. In case of papers with different data records for different ionic strengths without an extrapolation to infinite dilution, we took the values for the lowest ionic strength and performed the extrapolation ourselves. If authors listed several different values but recommended only one data record, we took that data record.

After normalization, none of these pK values showed obvious inconsistencies or differed significantly enough from the other to become suspect. Thus, averaging seemed to be appropriate. The errors given correspond to two standard deviations of the mean:

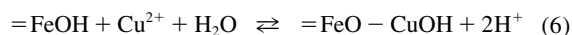
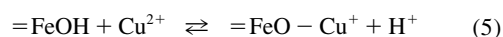
$$pK_1 = 6.38 \pm 0.36; pK_2 = 10.36 \pm 0.39.$$

For a blind prediction of the experimental data of Ali and Dzombak (1996b) the protolysis constants (and subsequently the complexation constants as well) derived by these authors were excluded—otherwise it would not have been a proper blind prediction. The derived average protolysis constants are then:

$$pK_1 = 6.36 \pm 0.38; pK_2 = 10.44 \pm 0.38.$$

After selecting appropriate protolysis constants we had to build a realistic set of surface species. Not all surface species proposed in the literature are actually supported by spectroscopic evidence; most of them result from best fits to sorption isotherms. The surface species =FeO-Cu⁺ and =FeO-CuOH have been reported for all iron (hydr)oxides and various SCM (e.g., Rodda et al. 1996; Jung et al. 1998; Robertson and Leckie, 1998; Buerge-Weirich, 2002; Subramaniam, 2003). These species have been shown to exist spectroscopically

(EXAFS) by Bochatay (1997), Parkman et al. (1999), Alcacio et al. (2001), Lin et al. (2004), and Flogéac et al. (2004).



Rodda et al. (1996) fitted their experimental data by a Langmuir model for describing the competitive sorption of monomeric CuOH⁺ and dimeric Cu₂(OH)₂²⁺ onto goethite. According to Subramaniam (2003) the last species appears only at high surface loadings. In a very recent publication, Peacock and Sherman (2004) proposed bidentate mononuclear (=FeOH)₂Cu(OH)₂ and tridentate binuclear (=Fe₃O(OH)₂Cu₂(OH)₃) surface complexes from interpretation of their EXAFS data. There was no evidence for monodentate surface complexes or surface precipitates (Cu(OH)₂(s)). They fitted their own experimental Cu(II) adsorption data and those of Ali and Dzombak (1996b) successfully.

Yet another species, =FeOH-Cu²⁺, reported by Palmqvist et al. (1999), was the result of a best fit (CCM). Also, Criscenti and Sverjenski (2002) recommended this species from refitting the raw data of Robertson (1996). This species is not proven spectroscopically yet.

The averaged log K ± 2σ for the selected species for the Cu(II) onto goethite, normalized and extrapolated to infinite dilution (see Table 2 for the original data), is

$$\log K_{=FeO-Cu^+} = 1.04 \pm 1.04$$

For a prediction of the sorption results of Ali and Dzombak (1996b) the log K for the surface species =FeO-Cu⁺ derived by the authors must be omitted, giving a new average of

$$\log K_{=FeO-Cu^+} = 0.96 \pm 1.46$$

Only one DDLM value was found in the literature (Robertson and Leckie, 1998) for the complexation constant of the surface species =FeO-CuOH:

$$\log K_{=FeO-CuOH} = -7.15$$

A search of RES³T gave the following surface reactions for carbonate sorption onto goethite:

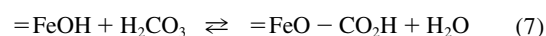
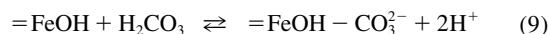
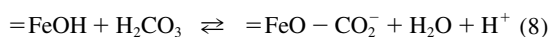


Table 5. Summary of log K for protolysis and surface complexation derived from RES³T and used for blind prediction of Cu(II) sorption onto goethite (SSD = 2.31 sites nm⁻²).

Protolysis and surface complexation reaction	Blind prediction for Ali and Dzombak (1996b)	Blind prediction for Balistrieri and Murray (1982) and Kooner (1992)
=FeOH + H ⁺ ↔ =FeOH ₂ ⁺	7.08	7.10
=FeOH ↔ =FeO ⁻ + H ⁺	-9.72	-9.64
=FeOH + Cu ²⁺ ↔ =FeO-Cu ⁺ + H ⁺	1.68	1.76
=FeOH + Cu ²⁺ + H ₂ O ↔ =FeO-CuOH + 2H ⁺	-6.43	-6.43
=FeOH + H ₂ CO ₃ ↔ =FeO-CO ₂ H + H ₂ O		3.72
=FeOH + H ₂ CO ₃ ↔ =FeO-CO ₂ ⁻ + H ₂ O + H ⁺		-3.79
=FeOH + H ₂ CO ₃ ↔ =FeOH-CO ₃ ²⁻ + H ₂ O + 2H ⁺		-12.83



The averaged log K ± 2σ for the selected reactions are given below, again normalized and corrected to infinite dilution (for literature values see Table 3):

$$\log K_{=FeO-CO_2H} = 3.00 \pm 0.77$$

$$\log K_{=FeOH-CO_2^-} = -4.51 \pm 0.36$$

$$\log K_{=FeOH-CO_3^{2-}} = -13.55$$

The modeling was performed with the FITEQL code, version 3.2 (Herbelin and Westall, 1996). In Table 5 the model setup used for the blind predictions of Cu²⁺ sorption onto goethite is summarized. Here, we have converted the averaged log K values from Tables 1–3 to the site density of 2.31 sites nm⁻² by applying Kulik's conversion:

$$\log K_{2.31} = \log K_{12.05} + \log \frac{12.05}{2.31} \quad (10)$$

The aqueous speciation of Cu(II) is rather complex and will therefore significantly influence the sorption. Thus it has to be considered properly in all modeling efforts. All data for aqueous speciation for Cu and auxiliary species (Table 6) are taken from the NIST database (Smith and Martell, 1997).

The log K values for Cu(OH)₃⁻ of -27.5 and for Cu(OH)₄²⁻ of -40.4 are only valid for an ionic strength of 1.0 M. Here, the values given by Stumm and Morgan (1981), -26.3

Table 6. Aqueous speciation reactions of aqueous Cu(II) and auxiliary species (Smith and Martell, 1997).

Reaction	log K
Cu ²⁺ + H ₂ O ↔ CuOH ⁺ + H ⁺	-7.5
Cu ²⁺ + 2H ₂ O ↔ Cu(OH) ₂ + 2H ⁺	-16.2
2Cu ²⁺ + 2H ₂ O ↔ Cu ₂ (OH) ₂ ²⁺ + 2H ⁺	-10.6
3Cu ²⁺ + 4H ₂ O ↔ Cu ₃ (OH) ₄ ²⁺ + 4H ⁺	-20.8
Cu ²⁺ + H ₂ CO ₃ ↔ CuHCO ₃ ⁺ + H ⁺	-4.55
Cu ²⁺ + H ₂ CO ₃ ↔ CuCO ₃ + 2H ⁺	-9.91
Cu ²⁺ + 2H ₂ CO ₃ ↔ Cu(CO ₃) ₂ ²⁻ + 4H ⁺	23.16
Cu ²⁺ + H ₂ CO ₃ + 2H ₂ O ↔ CuCO ₃ (OH) ₂ ²⁻ + 4H ⁺	-29.80
H ₂ CO ₃ + H ₂ O ↔ CO ₃ ²⁻ + 2H ⁺	-16.68
HCO ₃ ⁻ ↔ CO ₃ ²⁻ + H ⁺	-10.33
H ₂ O ↔ H ⁺ + OH ⁻	-14.00

and -39.4, respectively, for ionic strength of 0 are more appropriate. However, both species are irrelevant under the experimental conditions considered here (pH range 3–7), and therefore are not included in the modeling.

Formally, also the solid phases Cu(OH)₂(s) and CuO(s) with log K of -8.68 (Smith and Martell, 1997) and -7.8 (Baes and Mesmer, 1976), respectively, have to be considered. However, because there was no evidence for surface precipitation in any of the experiments, these reaction processes seemed to be kinetically inhibited in these experiments and were not considered in the modeling.

4. RESULTS AND DISCUSSION

4.1. Blind Prediction Compared to Raw Data of Ali and Dzombak (1996b)

Figure 1 illustrates the predictions of Cu(II) sorption onto goethite based on the relative amount of Cu(II) bound to the goethite surface for 2.3 μM, 23 μM, and 98 μM initial Cu(II) at an ionic strength of 0.01 M NaNO₃. In Figure 2 the graph is shown for 0.01 M and 0.1 M NaNO₃ at 98 μM Cu(II) total concentration. The quality of the predictions is, in general, very satisfactory. However, the dependence of the quantity sorbed on the initial Cu(II) concentration is not well reflected by the

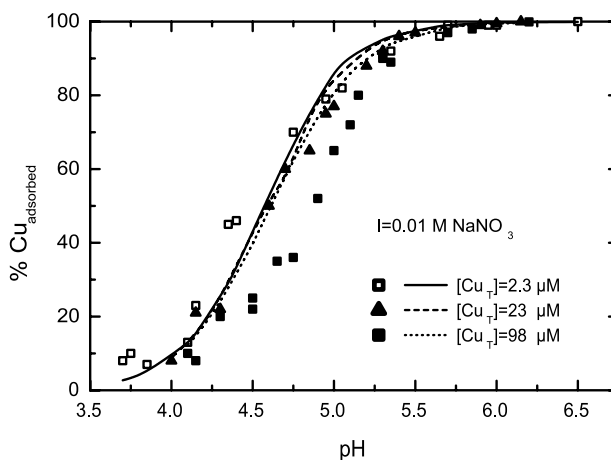


Fig. 1. Predicted percentages of Cu(II) sorbed onto goethite (lines) compared to the raw data of Ali and Dzombak (1996b) (symbols) at I = 0.01 M NaNO₃.

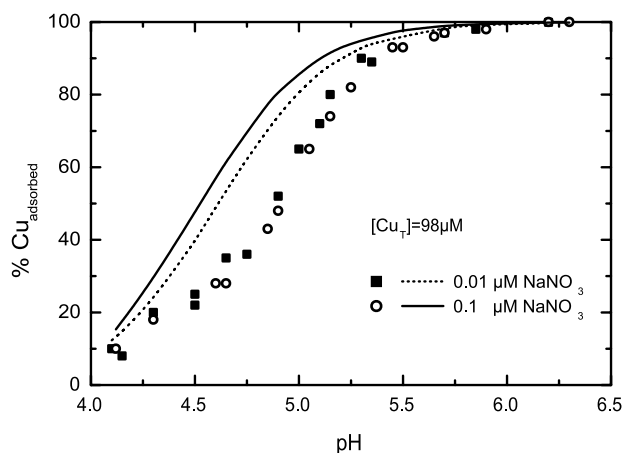


Fig. 2. Predicted percentages of Cu(II) sorbed onto goethite (lines) compared to the raw data of Ali and Dzombak (1996b) (symbols) at 98 μM initial Cu concentration.

model (Fig. 1). In addition the modeling indicates a dependence on the ionic strength, which is not found in the experiment (Fig. 2).

Figure 3 shows that the correspondence between predicted and measured sorption is always within one order of magnitude when the conventional distribution coefficient K_D representation is considered.

4.2. Blind Prediction Compared to Raw Data of Balistrieri and Murray (1982)

Balistrieri and Murray (1982) performed their experiments in air, and therefore carbonate equilibria were also considered. No effect of carbonate surface species are expected at these rather low pH values of 3 to 7, as was confirmed by the modeling.

As can be seen in Figures 4 and 5, the quality of the predictions is not as good as it was for the previous case, but still the number of experimental points deviating by more than one order of magnitude in K_D is small. The reason for the

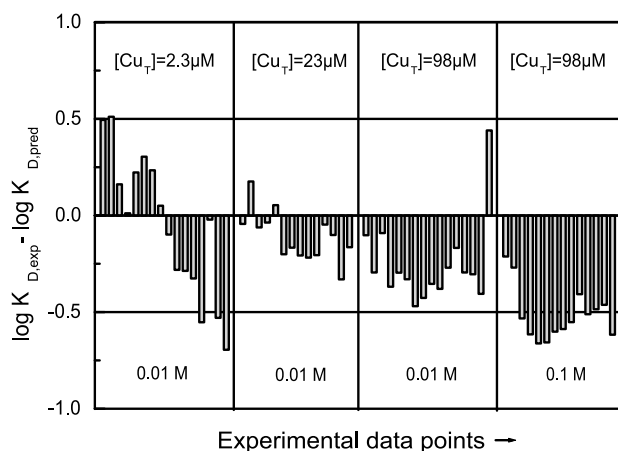


Fig. 3. Difference between experimental (Ali and Dzombak, 1996b) and predicted $\log K_D$.

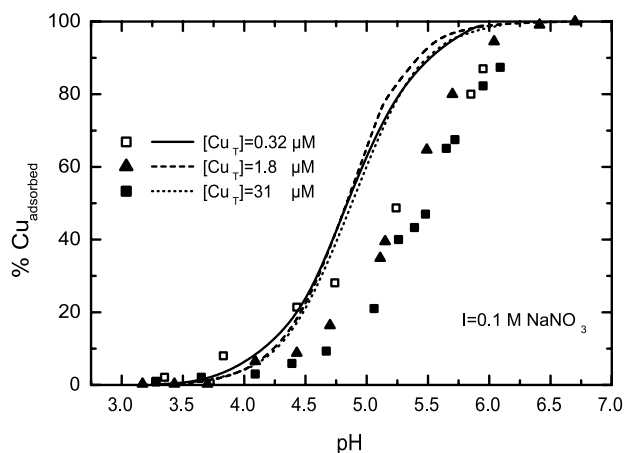


Fig. 4. Predicted percentages of Cu(II) sorbed onto goethite (lines) compared to the raw data of Balistrieri and Murray (1982) (symbols) at $I = 0.1 \text{ M NaNO}_3$.

overestimations of the Cu(II) sorption is as yet not clear. Some suggested explanations are discussed under Chapter 5.

4.3. Blind Prediction Compared to Raw Data of Kooner (1992)

The blind prediction of Cu(II) sorption onto goethite is illustrated in Figures 6 and 7. Again, the quality of the predictions is not as good as it was for Ali and Dzombak (1996b). The difference between the experimental and predicted $\log K_D$ is, in most of the cases, within one order of magnitude. Generally, the experimental sorption values are very low in comparison with the data of Ali and Dzombak (1996b) and Balistrieri and Murray (1982) despite the similarity in the experimental conditions. Maybe the separation of the supernatant from the solid was not sufficiently good, because Kooner (1992) did not filter after centrifugation. A potential fine dispersed goethite fraction with sorbed Cu(II) therefore would then have been erroneously assigned to the aqueous phase after dissolving with acid before analysis.

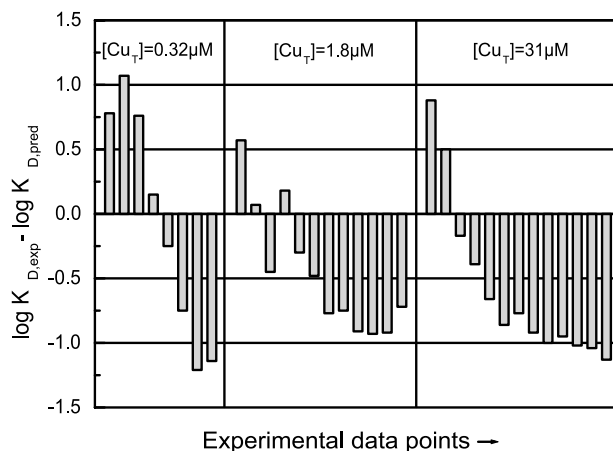


Fig. 5. Difference between experimental (Balistrieri and Murray, 1982) and predicted $\log K_D$ values at $I = 0.1 \text{ M NaNO}_3$.

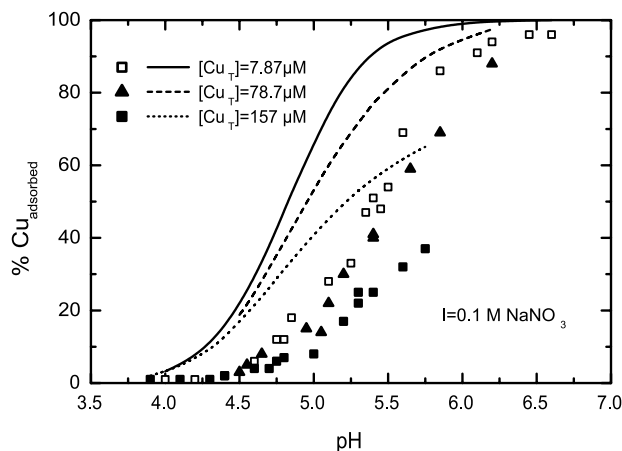


Fig. 6. Predicted percentages of Cu(II) sorbed onto goethite (lines) compared to the raw data of Kooner (1992) (symbols) at $I = 0.1 \text{ M NaNO}_3$.

4.4. Comparison and Generalization

In general the quality of the predictions of the Cu(II) sorption onto goethite is good. The following means of absolute $\Delta \log K_D$ were obtained for the three comparisons:

Ali and Dzombak (1996b)	0.31
Balistrieri and Murray (1982)	0.71
Kooner (1992)	0.80

One should also keep in mind that for the regions with very high surface loadings (above 99.5%) small deviations between analytical determinations and model predictions will translate into high K_D discrepancies. That the prediction quality is nevertheless satisfactory, even in these regions, can easily be seen in Figures 1, 2, and 4. Exactly for this reason, surface loadings above 99.9% have not been taken into consideration, even if by chance the modeling gave very good predictions.

If one compares more closely all three prediction cases, it becomes obvious that the deviation is not evenly distributed. There are much more overestimations than underestimations of the amount of adsorbed Cu(II) calculated in the sorption model.

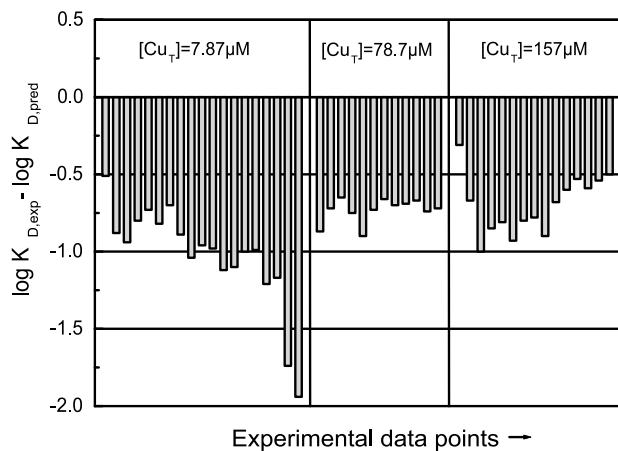


Fig. 7. Difference between experimental (Kooner, 1992) and predicted $\log K_D$ values at $I = 0.1 \text{ M NaNO}_3$.

We think that this indicates either that the formation constants of the Cu(II) sorption complexes derived in other studies are somewhat high or that some of the aqueous formation complexes are too weak. In addition, during the original parameter fitting the set of aqueous Cu(II) species differed among the authors. Another possible explanation would be that the number of surface binding sites used in our predictions was too high. A reason for this would be that the surface determined by N_2 -BET is higher than the effective surface really available for Cu(II) ions in aqueous medium.

5. CONCLUSIONS

It can be concluded that the application of DDLM can indeed be used for estimating distribution coefficients for contaminants in well defined mineral systems. The SCM database so far assembled within the RES³T project is able to provide the parameter sets, following the stepwise strategy of species selection, data collection, normalization, and averaging. We think that our strategy is robust enough that it can be a useful tool for engineers, researchers, and governmental authorities dealing with waste management in a general sense.

Concerning the decision of what SCM submodel should be used, it should be made clear that DDLM is only one possible choice. There is nothing wrong with NEM, TLM, BSM, or (CD-)MUSIC. The question is simply what specific needs these models suit best. Any model will necessarily reflect only certain aspects of reality, with different focus and different degrees of complexity. Often, a balance between scientific reason and pragmatic use must be kept—certainly a difficult task. Whereas TLM and (CD-)MUSIC are very complex models requiring extra parameters difficult to extrapolate to mixed-electrolyte systems, the situation for BSM is better. Unfortunately, the sheer number of published complex formation constants is rather small, so for many systems of practical relevance there is only one or even no parameter set available. At present (end of 2004) RES³T, e.g., contains totally 2,630 surface complexation constants, of which 1,147 (TLM), 636 (CCM), 478 (DDLM), and 170 (NEM) records respectively. The same holds for 1-pK models—an otherwise very attractive approach owing to a reduced number of reaction equations. If this situation will improve in the future, a move from 2-pK DDLM to a 1-pK BSM could be very promising. This was the outcome of the SOPRO 2004 Workshop (March 25–26, 2004, Karlsruhe, Germany), where the panel discussion encouraged the scientists to process their sorption experiments also with respect to a 1-pK BSM.

The goal of providing reliable SCM parameter sets will be striven for further, not only by a steady extension of the RES³T sorption database, but also by international efforts to derive commonly accepted guidelines for approaching sorption from data generation to data processing and modeling. Questions of consistent chemical models and the quality variance of different experimental methods also must be addressed. The usage of different models by the respective authors can be a source of inconsistency. Certainly a refitting of all the experimental data with a uniform aqueous speciation can improve the data. In addition, the composition and structure of relevant surface species is often not clear. When more data for other surface species (including any independent evidence of already pro-

posed species), particularly concerning bi- and tridentate surface sorption complexes of Cu(II) onto goethite, becomes available, further blind prediction approaches may be performed.

This should enable commonly accepted recommended data sets for surface complexation models to be established. Such efforts have to be accompanied by the development of better modeling tools to overcome the shortcomings of the FITEQL code.

Acknowledgments—The development of the mineral-specific sorption database RES³T was funded by the German Federal Ministry of Economics and Labor (BMWA) under contract No. PtWt+E 02E9471. We thank J. Rustad and two anonymous reviewers, whose comments and suggestions improved the final version of this manuscript.

Associate editor: J. R. Rustad

REFERENCES

- Alcacio T. E., Hesterberg D., Chou J., Martin J. D., Beauchemin S., and Sayers D. E. (2001) Molecular scale characteristics of Cu(II) bonding in goethite-humate complexes. *Geochim. Cosmochim. Acta* **65**, 1355–1366.
- Ali M. A. and Dzombak D. A. (1996a) Competitive sorption of simple organic acids and sulfate on goethite. *Environ. Sci. Technol.* **30**, 1061–1071.
- Ali M. A. and Dzombak D. A. (1996b) Effects of simple organic acids on sorption of Cu²⁺ and Ca²⁺ on goethite. *Geochim. Cosmochim. Acta* **60**, 291–304.
- Appelo C. A. J., van der Weiden M. J. J., Tournassat C., and Charlet L. (2002) Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* **36**, 3096–3103.
- Atkinson R. J., Posner A. M., and Quirk J. P. (1967) Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. *J. Phys. Chem.* **71**, 550–558.
- Baes C. F. and Mesmer R. E. (1976) *The Hydrolysis of Cations*. Wiley, New York.
- Benjamin M. M. (2002) *Water Chemistry*. McGraw-Hill, Boston.
- Balistreri L. S. and Murray J. W. (1982) The adsorption of Cu, Pb, Zn and Cd on goethite from major ion seawater. *Geochim. Cosmochim. Acta* **46**, 1253–1265.
- Bochatay L., Persson P., Lövgren L., and Brown G. E. (1997) XAFS study of Cu(II) at the water-goethite (α -FeOOH) interface. *J. Physique IV* **7**, C2-819–C2-820.
- Bowden J. W.; Posner A. M., and Quirk J. P. (1977) Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. *Aust. J. Soil Res.* **15**, 121–136.
- Bradbury M. H. and Baeyens B. (1997) A mechanistic description of Ni and Zn sorption on Na-Montmorillonite. Part II: Modeling. *J. Contam. Hydrol.* **27**, 223–248.
- Brendler V., Vahle A., Arnold T., Bernhard G., and Fanghänel Th. (2003) RES³T—Rossendorf expert system for surface and sorption thermodynamics. *J. Contam. Hydrol.* **61**, 281–291.
- Brendler V., Arnold T., Richter A., and Bernhard G. (2004) Capability of surface complexation models and databases for predicting radionuclide sorption. *Conf. Proc. Waste Man. 2004*, February 29–March 4, 2004, Tucson, AZ.
- Buerge-Weirich D., Hari R., Xue H., Behra P., and Sigg L. (2002) Adsorption of Cu, Cd and Ni on goethite in the presence of natural groundwater ligands. *Environ. Sci. Technol.* **36**, 328–336.
- Buerge-Weirich D., Behra P., and Sigg L. (2003) Adsorption of copper, nickel and cadmium on goethite in the presence of organic ligands. *Aquat. Geochem.* **9**, 65–85.
- Criscenti L. J. and Sverjensky D. A. (2002) A single-site model for divalent transition and heavy metal adsorption over a range of metal concentrations. *J. Colloid Interface Sci.* **253**, 329–352.
- Christophi C. A. and Axe L. (2000) Competition of Cd, Cu and Pb adsorption on goethite. *J. Environ. Eng.* **126**, 66–74.
- Davies C. W. (1962) *Ion Association*. Butterworths, Washington.
- Davis J. A. (1978) *Adsorption of Trace Metals and Complexing Ligands at the Oxide/Water Interface*. Ph. D. thesis, Stanford Univ., CA.
- Davis J. A. and Kent D. B. (1990) Surface complexation modeling in aqueous geochemistry. In *Reviews in Mineralogy, Vol. 23: Mineral-Water Interface Geochemistry*. (eds. M. F. Hochella and A. F. White), pp. 177–258. Mineralogical Society of America, Washington, DC.
- Dzombak D. A. and Morel F. M. M. (1990) *Surface Complexation Modeling. Hydrous Ferric Oxide*. Wiley & Sons, New York.
- Flogéac K., Guillon E., and Aplincourt M. (2004) Surface complexation of copper(II) on soil particles: EPR and XAFS studies. *Environ. Sci. Technol.* **38**, 3098–3103.
- Forbes E. A., Posner A. M., and Quirk J. P. (1976): The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite. *J. Soil Sci.* **27**, 154–166.
- Hayes K. F. and Leckie J. O. (1986): Mechanism of lead ion adsorption at the goethite-water interface. In: *ACS Symposium Series 323: Geochemical Processes at Mineral Surfaces*. (eds. J.A. Davis and K.F. Hayes), pp. 115–141. American Chemical Society, Washington, DC.
- Hayes K. F., Redden G., Ela W., and Leckie J. O. (1991) Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.* **142**, 448–469.
- Herbelin A. L. and Westall J. C. (1996) *FITEQL -Version 3.2*. Report 96-01, Department of Chemistry, Oregon State Univ.
- Hiemstra T. and van Riemsdijk W. H. (1996) A surface structural approach to ion adsorption: The charge distribution (CD) model. *J. Colloid Interface Sci.* **179**, 488–508.
- Hiemstra T., van Riemsdijk W. H., and Bolt G. H. (1989a) Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach. I. Model description and evaluation of intrinsic reaction constants. *J. Colloid Interface Sci.* **133**, 91–104.
- Hiemstra T., de Wit J. C. M., and van Riemsdijk W. H. (1989b) Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach. II. Application to various important (hydr)oxides. *J. Colloid Interface Sci.* **133**, 105–117.
- Hohl H. and Stumm W. (1976) Interaction of Pb²⁺ with hydrous γ -Al₂O₃. *J. Colloid Interface Sci.* **55**, 281–286.
- Hsi C. D. and Langmuir D. (1985) Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* **49**, 1931–1941.
- Jung J. H., Cho Y. H., and Hahn P. (1998) Comparative study of Cu²⁺ adsorption on goethite, hematite and kaolinite: Mechanistic modeling approach. *Bull. Korean Chem. Soc.* **19**, 324–327.
- Kooner Z. S. (1992) Adsorption of Cu(II) onto goethite in aqueous systems. *Environ. Geol. Water Sci.* **20**, 205–212.
- Kosmulski M. (2001) *Chemical Properties of Material Surfaces*. Marcel Dekker, New York. 753 pp.
- Kulik D. A. (2002) Gibbs energy minimization: approach to modeling sorption equilibria at the mineral-water interface: Thermodynamic relations for multi-site-surface complexation. *Am. J. Sci.* **302**, 227–279.
- Kurbatov M. H., Wood G. B., and Kurbatov J. D. (1951) Isothermal adsorption of cobalt from dilute solutions. *J. Phys. Chem.* **55**, 1170–1182.
- Lin S. H., Kao H. C., Cheng C. H., and Juang R. S. (2004) An EXAFS study of the structures of copper and phosphate sorbed onto goethite. *Colloid Surfaces A* **234**, 71–75.
- Lützenkirchen J. (2002): Surface complexation models of adsorption. In: *Encyclopedia of Surface and Colloid Science* (ed. A. Hubbard), pp. 5028–5046. Marcel Dekker; New York.
- Lumsdon D. G. and Evans L. J. (1994) Surface complexation model parameters for goethite (α -FeOOH). *J. Colloid Interface Sci.* **164**, 119–125.
- Mesuer K. and Fish W. (1992) Chromate and oxalate adsorption on goethite. I. Calibration of surface complexation models. *Environ. Sci. Technol.* **26**, 2357–2364.
- Missana T., García-Gutiérrez M., and Maffiotte C. (2003) Experimental and modeling study of the uranium(VI) sorption on goethite. *J. Colloid Interface Sci.* **260**, 291–301.

- Padmanabham M. (1983) Adsorption-desorption behaviour of copper(II) at the goethite-solution interface. *Aust. J. Soil Res.* **21**, 309–320.
- Palmqvist U., Ahlberg E., Lövgren L., and Sjöberg S. (1999) Competitive metal ion adsorption in goethite systems using in situ voltammetric methods and potentiometry. *J. Colloid Interface Sci.* **218**, 388–396.
- Parkman R. H., Charnock J. M., Bryan N. D., Livens F. R., and Vaughan D. J. (1999) Reactions of copper and cadmium in aqueous solution with goethite, lepidocrocite, mackinawite and pyrite. *Am. Mineral.* **84**, 407–419.
- Peacock C. L. and Sherman D. M. (2004) Copper (II) sorption onto goethite, hematite and lepidocrocite: A surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* **68**, 2623–2637.
- Richter A., Brendler V., and Bernhard G. (2003) The mineral-specific sorption database RES³T: Concept description, implementation and application towards contaminated systems. *Geochim. Cosmochim. Acta* **67**, A397.
- Robertson A. P. (1996) *Goethite/Humic Acid Interactions and Their Effects on Copper(II) Binding*. Ph.D. thesis, Stanford Univ., CA.
- Robertson A. P. and Leckie J. O. (1997) Cation binding predictions of surface complexation models: Effect of pH, ionic strength, cation loading, surface complex and model fit. *J. Colloid Interface Sci.* **188**, 444–472.
- Robertson A. P. and Leckie J. O. (1998) Acid/base, copper binding and Cu²⁺/H⁺ exchange properties of goethite, an experimental and modeling study. *Environ. Sci. Technol.* **32**, 2519–2530.
- Rodda D. P., Johnson B. B., and Wells J. D. (1993) The effect of temperature and pH on the adsorption of copper(II), lead(II) and zinc(II) onto goethite. *J. Colloid Interface Sci.* **161**, 57–62.
- Rodda D. P., Wells J. D., and Johnson B. B. (1996) Anomalous adsorption of copper(II) on goethite. *J. Colloid Interface Sci.* **184**, 564–569.
- Schindler P. W. und Gamsjäger H. (1972) Acid-base reactions of the TiO₂ (Anatase) – water interface and the point of zero charge of TiO₂ suspensions. *Kolloid-Z. Z. Polym.* **250**, 759–763.
- Sigg L. M. (1979) *Die Wechselwirkung von Anionen und schwachen Säuren mit α -FeOOH (Goethit) in wässriger Lösung*. Ph.D. thesis, ETH Zürich.
- Smith R. W. and Jenne E. A. (1991) Recalculation, evaluation and prediction of surface complexation constants for metal adsorption on iron and manganese oxides. *Environ. Sci. Technol.* **25**, 525–531.
- Smith R. M. and Martell A. E. (1997) *NIST - Critically Selected Stability Constants Of Metal Complexes Database—Version 4.0*. Report, U.S. Department of Commerce.
- Stone A. T., Torrents A., Smolen J., Vasudevan D. and Hadley J. (1993) Adsorption of organic compounds possessing ligand donor groups at the oxide/water interface. *Environ. Sci. Technol.* **27**, 895–909.
- Stumm W. (1992) *Chemistry of the Solid-Water Interface*. Wiley, New York.
- Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley, New York.
- Stumm W., Huang C. P., and Jenkins S. R. (1970) Specific chemical interaction affecting the stability of dispersed systems. *Croat. Chem. Acta.* **42**, 223–245.
- Subramaniam K., Vithayaveroj V., Yiacomou S., and Tsouris C. (2003) Copper uptake by silica and iron oxide under high surface coverage conditions: Surface charge and sorption equilibrium modeling. *J. Colloid Interface Sci.* **268**, 12–22.
- Sverjenski D. A. and Sahai N. (1996) Theoretical prediction of single-site surface protonation equilibrium constants for oxides and silicates in water. *Geochim. Cosmochim. Acta* **60**, 3773–3797.
- Turner D. R. and Sassman S. A. (1996): Approaches to sorption modeling for high-level waste performance assessment. *J. Contam. Hydrol.* **21**, 311–332.
- van Geen A., Robertson A. P., and Leckie J. O. (1994) Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters. *Geochim. Cosmochim. Acta* **58**, 2073–2086.
- Westall J. C. and Hohl H. (1980) A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.* **12**, 265–294.
- Yates D. E., Levine S., and Healy T. W. (1974) Site-binding model of the electrical double layer at the oxide/water interface. *J. Chem. Soc. Faraday Trans. 1* **70**, 1807–1818.