A Desorption–Dissolution Model for Metal Release from Polluted Soil under Reductive Conditions

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ABSTRACT

Various natural or provoked situations can cause significant variations in redox conditions that can induce reductive dissolution of soil components. When this happens, heavy metals that may be bound to solid phases are released. A surface desorption–dissolution model, which takes into account the effect of reductive conditions on surface site density, was established. This model is based on conventional reactions of surface hydroxyl groups, surface complexation reactions with cations and double-layer theory. The solid dissolution rate was taken into account, by following changes in total surface site number (i.e., cation exchange capacity [CEC]) under reductive conditions. This term was introduced in an electrostatic desorption model. Curves obtained by this calculation provided a good fit of experimental data as shown by statistical parameters. Experimental data corresponded to Pb and Cd released from a cultivated soil under reductive conditions induced by sodium ascorbate.

REDUCTIVE conditions play an important role on metal mobility in soils and sediments. They act by a mechanism of reductive dissolution by changing the oxidation degree of Fe(III) and Mn(IV) on Mn and Fe oxyhydroxides of soils (Deng, 1997; Stumm, 1992; Stumm and Sulzberger, 1992; Suter et al., 1991; Banerjee and Nesbitt, 1999). Manganese and Fe oxyhydroxides are well known to be strong adsorbents of heavy metals. When they are dissolved under reductive conditions, metals are released in the aqueous medium.

The effect of variations in redox potential on trace element mobility has been illustrated in rice fields (Reddy and Patrick, 1977; Asami, 1984), bay sediments (Gambrell et al., 1980), and freshwater estuary soils (Van den Berg et al., 1998). More recently, Clark et al. (1998) linked the metal partitioning in mangrove sediments to the geochemically distinct horizons and notably to their redox state. Moreover, several authors, such as Jensen et al. (1998) with phosphate and Chuan et al. (1996) with metalloids, showed an increase of these species bound to Fe and Mn oxides subjected to moderately reductive conditions. Our previous studies (Davranche and Bollinger, 2000a,b) evidenced this release with various natural or synthetic sorbents; in the present paper we want to model this metal mobilization under reductive conditions.

Many adsorption equilibrium models based on surface complexation equations are now widely used to describe surface–solution interactions, but none take into account solution redox variations. The surface complexation model was originally proposed by Stumm et al. (1970) to describe H^+ and metal adsorption at the pure oxide–water interface in terms of ion complexation with specific surface sites. Since then, modifications involving different descriptions of the electrical double layer have been introduced. Three main electrostatic models have been suggested, the double-layer model (DL), the constant capacitance model (CC), and the triple-layer model (TL). Many authors have tried successfully to apply these models to natural solids (sediments and soils) (Wen et al., 1998; Wang et al., 1997b; Goldberg and Sposito, 1984a,b; Schindler, 1984; Schindler et al., 1976). However, these models describe only cation or anion adsorption under oxidizing conditions.

The purpose of this study was to establish a physico–chemical model to describe metal release from soil under *reductive* conditions. This *desorption–dissolution* model is an application of the traditional surface complexation model with an adjustment in surface site density resulting from exposure of the solid to a reducing agent: (i) the surface complexation equation was written for *desorption* phenomena in order to obtain the free metal concentration; (ii) solid surface *dissolution* appearing under reductive conditions was introduced into the system of equations by considering the evolution of the total surface site number. Solids present sites at their surface, reacting with metal to form surface entities (Stumm and Morgan, 1996). Under reductive conditions some particles are solubilized, thus changing the number of these reacted surface sites. Consequently, in the case of heterogeneous solids such as a soil, total surface site number is modified. Changes in number of surface sites could be followed by determining the CEC of each sample under reductive conditions.

MATERIALS AND METHODS

Soil Sample

A soil sample was collected (upper 30 cm) in northern France (Nord Pas de Calais region). The site has been contaminated for several years through atmospheric transport from the nearby steel industry. This soil sample was air-dried and passed through a 2-mm sieve.

Geochemical characterization was carried out at the French Geological Survey (BRGM, Orléans) (Table 1). The total concentrations of heavy metals (Table 1) were determined after acidic digestion (Ritter and Bergman, 1978; Sung et al., 1984; Al-Shukry et al., 1991).

Grain size distribution was carried out using the ISO 11277 protocol (AFNOR, 1994). The sand, silt, and clay contents expressed as the percentage of dry weight (w/w) were 2, 78, and 20%, respectively.

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Abbreviations: CEC, cation exchange capacity; *S*, number of total surface sites.

Table 1. Geochemical composition and metal concentrations in the soil sample.

Components											
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	MnO	TiO	Organic C	CO_3^{2-}	Pb	Cd
% (w/w)										mg kg^{-1}	
77.8	7.40	2.50	1.30	<1.00	2.10	0.05	0.67	1.85	0.8	250	9

The soil was characterized by extractions with oxalate and pyrophosphate (Bigham et al., 1996). Oxalate extraction provides an estimate of noncrystalline iron oxide and organically complexed Fe. Pyrophosphate extraction gives an estimate of Fe complexed by organic matter. Oxalate-extractable Fe was measured by mixing 50 mg of dried soil with 20 mL of 0.2 *M* ammonium oxalate (pH 3). The solution was shaken for 2 h in the dark at 20°C and then filtered. Pyrophosphate-extractable Fe was measured by mixing 0.04 g of dried soil with 20 mL of 0.1 *M* sodium pyrophosphate solution at 20°C for 16 h. Iron in the oxalate and pyrophosphate extracts was analyzed by atomic absorption spectroscopy (FAAS). The amorphous iron oxyhydroxides content in the soil was 17% of total Fe.

Soil carbonate content was evaluated according to the Rauret protocol (Rauret et al., 1988). It was determined by back-titrating a 20-mL excess of 0.1 *M* HCl added to 6 g of dry soil sample with 0.1 *M* NaOH under a continuous stream of pure N_2(g). The carbonate content in soil was 0.8% (w/w).

Specific surface area (SSA) was measured by BET nitrogen adsorption on a Micromeritics (Atlanta, GA) ASAP 2000 apparatus.

Surface acidity constants of soil were determined from potentiometric titrations of 10 g L^{-1} of soil with NaOH (0.1 *M*) and HNO_3 (0.1 *M*) in a 0.1 *M* $NaNO_3$ medium as the supporting electrolyte (Kummert and Stumm, 1980; Sigg and Stumm, 1981). Titrations were carried out with a Metrohm (Herisau, Switzerland) 716 DMS Titrino apparatus equipped with a Metrohm combined (3 *M* KCl) glass electrode.

The CEC was determined by the cobalthexammine method ISO 11260 (AFNOR, 1994). Ions linked with the solid surface are exchanged with cobalthexammine ions; the CEC is the concentration of cobalthexammine ions eliminated from the solution. Fifty grams of soil were mixed with 50 mL of 0.017 *M* cobalthexammine solution for 3 h, the suspension was then centrifuged and the concentration of cobalthexammine ion remaining in the solution was measured by atomic absorption spectrometry, FAAS (Varian [Victoria, Australia] SpectrAA 220) (Table 2).

Desorption–Dissolution Experimental Data

Experiments were first conducted with a solid concentration of 10 g L^{-1} in a 0.1 *M* $NaNO_3$ medium with no reducing agent. The different pH values were regulated with concentrated solutions of HNO_3 or NaOH. The equilibration time was 48 h, determined by previous studies as a function of time under the same conditions for a pH fixed at 4.

The same protocol was used in a second series of experiments in the presence of the reducing agent: sodium ascorbate. The sodium ascorbate concentration was determined from an estimation of the soil oxidation capacity calculated using only the total iron concentration in soil (Barcelona and Holm, 1991; Heron et al., 1994). The equilibration time was determined by previous studies as a function of time under the same conditions for a pH fixed at 4. The redox potential obtained after the equilibrium time was −60 mV vs. Ag/AgCl, thus corresponding to a reductive soil following the ladder of Trolard et al. (1998). Speciation calculations were carried out beforehand using the SPE computer program (Martell and Motekaitis, 1992) in order to confirm that ascorbate did not complex Pb and Cd cations under our experimental conditions (results not shown).

At the end of these experiments, one part of the solid suspension was filtered through a 0.2-μm cellulose nitrate filter (Sartorius, Goettingen, Germany). The filtrate was collected in a polypropylene tube to which 100 μL of 69% HNO_3 had been added to keep all metals in solution. Samples were stored at 4°C before analysis. The other part of the suspension was centrifuged at 3200 × *g* for 10 min (the centrifugal was rinsed several times with Milli-Q water (Millipore, Bedford, MA) in order to eliminate the ascorbate residual) and dried at 50°C in an oven. For each treated soil sample, CEC was determined following the ISO 11260 protocol (AFNOR, 1994).

The solutions of Cd and Pb were analyzed by voltammetry (DPASV) on a Metrohm VA746 Trace Analyzer and a VA747 stand with a triple electrode system: A calomel reference electrode (3 *M* KCl/1 *M* KNO_3), a graphite counter–electrode, and a mercury drop electrode. Dissolved oxygen was removed from the sample by prepurging N_2(g) through the solution for 10 min. The deposition step was carried out at −1.2 V for 60 s followed by metal stripping.

MODELS DESCRIPTION

Simple *Desorption* Model

A desorption model was first written without taking into account redox modifications in order to determine the Pb and Cd surface complexation constants K_{SOMe} necessary for establishing hereafter the desorption–dissolution model under reductive conditions. In a previous paper (Davranche and Bollinger, 2000a), a non-electrostatic desorption model was developed; the simple desorption model used in the present paper is based on the same hypothesis to which is added an electrostatic term (described hereafter) to access the double-layer model equations (Table 3).

Desorption–Dissolution Model under *Reductive* Conditions

Soils are considered as a whole of functional surface groups expressed as a generic binding site SOH (Schindler, 1981; Stumm, 1992; Sigg et al., 1997). The model was based on: (i) conventional reactions of surface hydroxyl groups formulated

Table 2. Models parameters.

m	*T*	*I*	SSA	Pb_T	Cd_T	CEC = S_T	pK_{a2}	pK_{a1}	pK^{int}_{SOPb}	pK^{int}_{SOCd}
g L^{-1}	K	*M*	m^2 g^{-1}	*M*						
10	293	0.1	110	1.22×10^{-3}	8×10^{-5}	1.32×10^{-3}	5.3	8.7	10.4	9.0

Table 3. Equations of the simple desorption model and the desorption–dissolution model under reductive conditions.†

	Simple desorption model	Desorption–dissolution under reductive conditions model
Surface	$\mathrm{SOH_2^+ \rightleftharpoons SOH + H_s^+}$	$K_{a2}^{\mathrm{int}} = \dfrac{[\mathrm{H^+}]\exp(-\Psi F/RT)\cdot[\mathrm{SOH}]}{[\mathrm{SOH_2^+}]}$
	$\mathrm{SOH \rightleftharpoons SO^- + H_s^+}$	$K_{a1}^{\mathrm{int}} = \dfrac{[\mathrm{H^+}]\exp(-\Psi F/RT)\cdot[\mathrm{SO^-}]}{[\mathrm{SOH}]}$
Surface complexation	$\mathrm{SOH + Me_s^{2+} \rightleftharpoons SOMe^+ + H_s^+}$	$K_{\mathrm{SOMe}}^{\mathrm{int}} = \dfrac{[\mathrm{H^+}][\mathrm{SOMe^+}]}{[\mathrm{SOH}][\mathrm{Me^{2+}}]\exp(-\Psi F/RT)}$
Total surface sites	$S_\mathrm{T} = [\mathrm{SOH_2^+}] + [\mathrm{SOH}] + [\mathrm{SO^-}] + \Sigma[\mathrm{SOMe^+}] = \mathrm{constant}$	$S = \dfrac{1.4\ \mathrm{pH}^{1.25}}{2.5 + \mathrm{pH}^{1.25}} = [\mathrm{SOH_2^+}] + [\mathrm{SOH}] + [\mathrm{SO^-}] + \Sigma[\mathrm{SOMe^+}]$
Free metal in solution	$[\mathrm{Me^{2+}}] = \mathrm{Me_T}/(1 + K_{\mathrm{SOMe}}^{\mathrm{int}}\cdot\exp(\Psi F/RT)\,[\mathrm{SOH}]\cdot[\mathrm{H^+}]^{-1} + \Sigma\beta_X^{\mathrm{OH}}\,[\mathrm{OH^-}]^x + \Sigma\beta_y^{\mathrm{CO_3}}\,[\mathrm{CO_3^{2-}}]^y + \Sigma\beta_z^{\mathrm{HCO_3}}\,[\mathrm{HCO_3^-}]^z)$	

† β_i^L is the formation constant for the $\mathrm{MeL_i}$ complex with the ligand L, $\mathrm{H_s^+}$ is the proton from the surface, and $\mathrm{Me_s^{2+}}$ is the cation from the surface.

by analogy with reactions already known to occur in a simple amphoteric compound and (ii) the electrostatic double-layer model.

However, equations were written not in order to obtain complexed cation forms but to describe free metal concentration in solution (Table 3). In this model, only the monodentate surface complex was considered, as it was previously shown that this type of complex could reasonably well describe the cation sorption edge (Van Benschoten et al., 1998). The metal species included in the model were free metal, hydroxide, carbonate, and hydrogenocarbonate complexes of metal cation.

The electrostatic term used in the double-layer model was determined as follows. A solid surface charge σ_0 is written as:

$$\sigma_0 = \frac{F}{\mathrm{SSA}\ m}[(\mathrm{SOH_2^+}) + (\mathrm{SOMe}^{(n-1)+}) - (\mathrm{SO^-})] \qquad [1]$$

where σ_0 is the surface charge (C $\mathrm{m^{-2}}$), F is the Faraday constant, SSA is the specific area ($\mathrm{m^2\ g^{-1}}$), m is the solid concentration (g $\mathrm{L^{-1}}$), and $\mathrm{SOH_2^+}$, $\mathrm{SOMe}^{(n-1)+}$, and $\mathrm{SO^-}$ are the charged surface entities for $\mathrm{Me^{n+}}$ surface adsorption, whose concentrations are given in mol $\mathrm{g^{-1}}$.

σ_0 could be determined by potentiometric titration. The surface charge Q in mol $\mathrm{g^{-1}}$ is defined as:

$$Q = (\mathrm{SOH_2^+}) + (\mathrm{SOMe}^{(n-1)+}) - (\mathrm{SO^-}) \qquad [2]$$

For each point of the titration:

$$Q = (\mathrm{Ca} - \mathrm{Cb} + [\mathrm{OH^-}] - [\mathrm{H^+}])/m \qquad [3]$$

where Ca and Cb are the molarity concentrations of $\mathrm{HNO_3}$ and NaOH added during titration.

As:

$$\sigma_0 = \frac{F}{\mathrm{SSA}}Q \qquad [4]$$

the following relation is obtained (Wang et al., 1997a):

$$\sigma_0 = (\mathrm{Ca} - \mathrm{Cb} + [\mathrm{OH^-}] - [\mathrm{H^+}])\frac{F}{\mathrm{SSA}\ m} \qquad [5]$$

The electrical potential ψ (V) is deduced from the Gouy–Chapman double-layer theory:

$$\sigma_0 = (8RT\varepsilon\varepsilon_0 I)^{1/2}\sinh\left(\frac{z\psi}{2RT}\right) \qquad [6]$$

where I is the ionic strength (M), R is the gas constant (8.314 J $\mathrm{K^{-1}\ mol^{-1}}$), ε_0 is the permittivity of free space (8.854×10^{-12} $\mathrm{C^2\ N^{-1}\ m^{-2}}$), ε is the dielectric constant of water (80.1 at 20°C), z is the ion charge absolute value, and T is temperature (K).

In our experimental conditions (Table 2), this relation becomes:

$$\sigma_0 = 2.5 \times 10^{-7}\sinh(\psi) \qquad [7]$$

For each point of the titration, namely for each pH value, surface charge and electrical potential of the soil sample could be determined. Both σ_0 and ψ evolutions were determined in our experimental pH range (2.5 to 6).

Under reductive conditions, soil particles are dissolved in part. Dissolution induces the release of metals bound to the surface of these particles. If this dissolution phenomena could be introduced into a desorption model, the process of metal release under reductive conditions as a function of pH could be modeled. From the evolution of the solid total surface site number S as a function of the pH, it was possible to take into account the dissolution of particles under reductive conditions. For each pH value, the CEC of the solid treated under reductive conditions was measured and considered to be equivalent to S. With the nonlinear regression computer program WinReg (Debord, 1997), an empirical equation expressing the CEC under reductive conditions as a function of pH was determined. This equation, expressing the total surface site number changes under reductive conditions as a function of pH, was the essential term influencing the calculation of metal release:

$$\mathrm{CEC} = \frac{Y\cdot\mathrm{pH}^a}{K^a + \mathrm{pH}^a} \qquad [8]$$

where $Y = 1.4 \pm 0.6$, $K = 2.1 \pm 0.1$, and $a = 1.25 \pm 0.12$ (number of data points = 17, residual standard deviation = 0.06, and adjusted determination coefficient = 0.78).

$\mathrm{Me_T}$ was measured, $[\mathrm{OH^-}]$ was calculated from pH, and $[\mathrm{CO_3^{2-}}]$ and $[\mathrm{HCO_3^-}]$ were determined from knowing the pH value and the total carbonate concentration in the sample. Literature thermodynamic constants (Smith and Martell, 1975, 1976, 1977, 1982, 1989; Lacour et al., 1999) were recalculated for an ionic strength of 10^{-1} M according to the Davies equation. Metals included in the system were Pb and Cd simultaneously (Table 2). The pK_a and CEC determined for our soil sample represent values often found in the environment: $\mathrm{pH_{zpc}} = \mathrm{p}K_{\mathrm{a1}} + \mathrm{p}K_{\mathrm{a2}}/2$ of 7 and CEC around 1.3×10^{-4} mol $\mathrm{g^{-1}}$ (Stumm and Morgan, 1996). The surface complexation constants K_{SOPb} and K_{SOCd} were determined by fitting with experimental data under nonreductive conditions with the first simple desorption model.

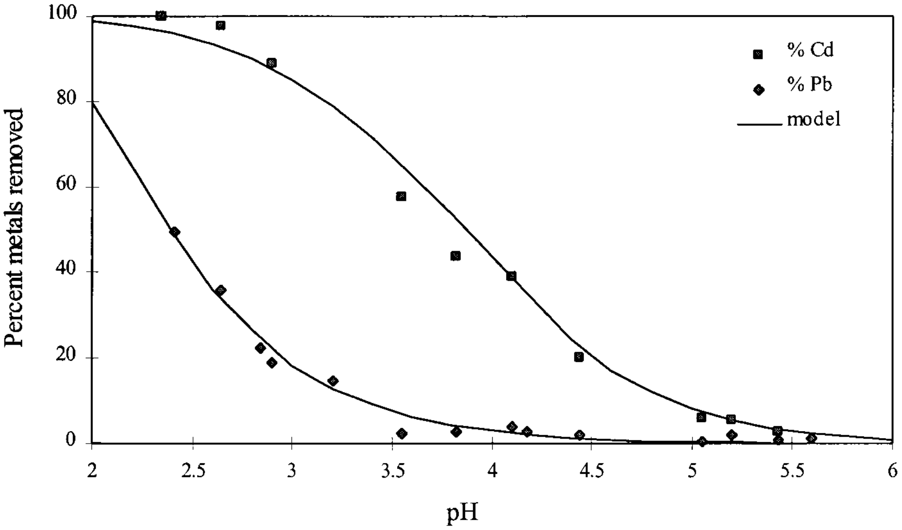

Fig. 1. Metal release from soil sample under nonreductive conditions, comparison between experimental data for Pb and Cd and desorption model results.

The complete model (under reductive conditions) consists of a system of three algebraic equations with three unknown concentrations, [SOH], $[Pb^{2+}]$, and $[Cd^{2+}]$, which varied as a function of pH. They were solved by successive iterations with ProSolver Version 1.0. The maximum number of iterations was set at 200.

Goodness of Fit

The goodness of fit of the model was evaluated by statistical parameters, the adjusted determination coefficient r_a^2, and the standard error SE (Neter and Wasserman, 1974):

$$r_a^2 = 1 - \frac{(n-1)\mathrm{SSE}}{(n-p)\mathrm{SSTO}} \quad [9]$$

$$\mathrm{SE} = \sqrt{\frac{\mathrm{SSE}}{(n-p)}} \quad [10]$$

where n is the number of data points, p is the number of fitted parameters, SSE is the error sum of squares, and SSTO is the total sum of squares.

RESULTS AND DISCUSSION

Results of fitting this simple desorption model to the experimental data obtained for Pb and Cd desorption as a function of pH appear in Fig. 1. The model could reasonably well reproduce experimental data, as shown by the high values of r_a^2 (0.980 for Cd and 0.997 for Pb) and low values of SE (2.4% for Cd and 0.57% for Pb) (number of data points = 13). This modeling approach adequately described the soil *desorption* process. Moreover, surface complexation constants fitted by the desorption model were in good concordance with constants determined by Wang et al. (1997b) from 11 different natural sediments with the FITEQL program (Westall, 1985) (Table 4).

In order to model Pb and Cd release under reductive conditions, total surface site number was followed by the CEC values determined between pH 2.5 and 6 (Fig. 2). Indeed, values obtained for pH < 2.5 were out of the reliability field of the cobalthexammine method (Orsini et al., 1976). Reductive dissolution is a pH-dependent process. The reducing agent is adsorbed to form surface entities, and this adsorption is a function of the pH, which is the reason why the dissolution of the solid matrix and consequently CEC values were lower for acidic pH. Moreover, at pH 6, the nontreated soil CEC value (1.32×10^{-4} mol g^{-1}) was not reached; the evolution of the surface sites was due to the reducing agent and not to pH only.

In this second model type no parameters were fitted, all were known. The newly-evidenced *desorption–dissolution* model was tested with the experimental data for Pb and Cd release under reductive conditions as a function of the pH (Fig. 3). The model reproduced reasonably well Pb and Cd released under reductive conditions as confirmed by the r_a^2 values (0.996 for Cd and 0.999 for Pb) and SE values (2.4% for Cd and 0.13% for Pb) (number of data points = 11). The model calculation for Cd release reproduced perfectly the aspect of the experimental curve. However, a 6 to 8% divergence was observed between experimental data and the model at acidic pH values, which found expression in a higher SE value (2.4%).

CONCLUSION

Complexation equations written for desorption (and not adsorption, as they are currently used) described reasonably well metal release from a solid as a function

Table 4. Comparison of the fitted constants of the desorption model.

Solids	pK'_{SOPb} $SO^- + Pb^{2+} \rightleftharpoons SOPb^+$	pK'_{SOCd} $SO^- + Cd^{2+} \rightleftharpoons SOCd^+$
Soil sample	**1.7**	**0.3**
Surface sediments (Wang et al., 1997b)	**1.3 to 3.5**	**−0.83 to 1.85**

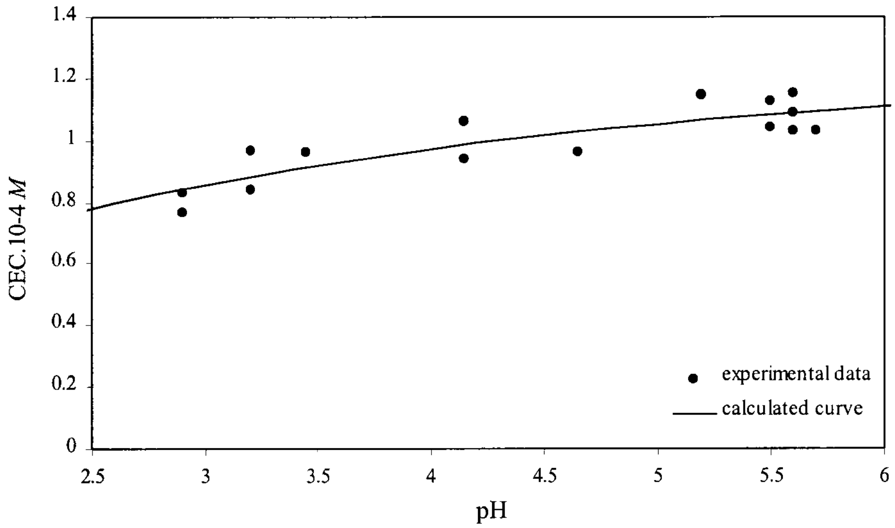

Fig. 2. Cation exchange capacity (CEC) evolution under reductive conditions, experimental data and calculated data.

of pH. Total metal concentration, total surface sites, ionic strength, and an electrostatic term were factors in sufficient numbers to simulate metal desorption behavior. Our models confirmed that classical electrostatic theory introduced first for simple solids and especially for oxides could be used for a natural heterogeneous solid, like a soil.

This effect of the reductive conditions was caused by dissolution of some constitutive particles of the solid or the solid itself. If the dissolution of the solid matrix was considered to decrease the surface site number, it was possible to quantify this surface dissolution. This solubilization phenomena depended on reducing agent strength or quantities and consequently on redox potential values (Davranche and Bollinger, 2000a). The introduction of this variation of solid total site number *S* in a simple desorption model could reasonably describe metal release from a polluted solid under reductive conditions. *S* variation as a function of the pH appeared to be the more influential parameter on the metal released under reductive conditions.

However, this model needs further work for potential application to soil remediation. It must be validated with other soil types and in natural environments. A study of the variation of total surface sites as a function of different redox potentials for a fixed pH should be performed on different types of solids. This will allow the variation to be modeled more precisely, and obtain a *desorption–dissolution* model depending on redox potential and not pH. This type of model will be more appropriate for predicting phenomena occurring in the environment or for applying it to soil remediation.

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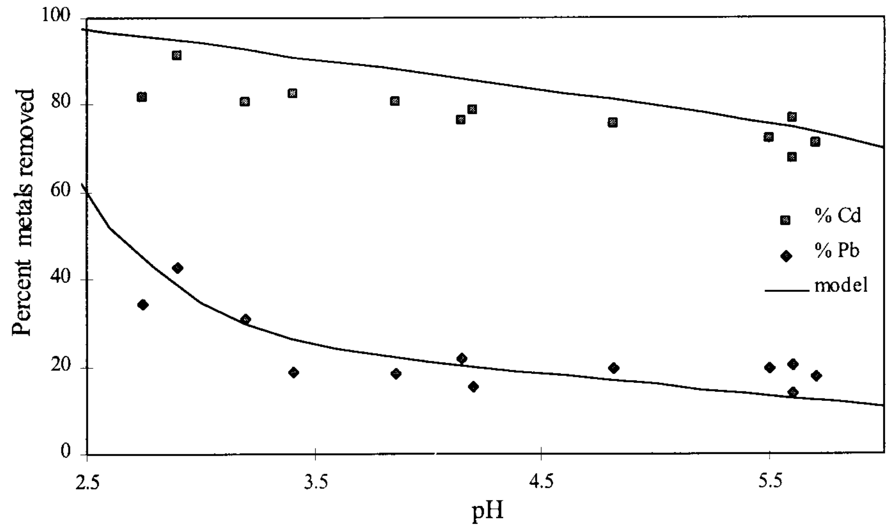

Fig. 3. Metal release from soil sample under reductive conditions, comparison of experimental data for Pb and Cd and desorption–dissolution model results.

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