

Sorption of Cs and Rb on purified and crude MX-80 bentonite in various electrolytes

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The adsorption of Cs on clayey materials such as bentonite and Na-montmorillonite was studied in various electrolytic conditions (concentration and composition), various solid to liquid ratios and various pH conditions. The results obtained for these different conditions were modeled considering an exchange model associated to the surface complexation concept. Then, the same approach was considered to model the sorption of Rb, which have the same chemical behavior than Cs. Experiments were carried out for various electrolyte, pH, and Rb concentrations. The stoichiometries corresponding to the sorption of Rb on bentonite and montmorillonite were then deduced from the experimental results.

Introduction

The development of technologies for avoiding pollution and its confinement has become a crucial social and industrial concern in Europe. In France, 75% of the electrical energy is produced by nuclear route. The French program for long-life and low to high activity nuclear waste management is still under investigations. One possible way of management for these waste consist in the storage in a deep geological repository (Jurassic argillite host rock in Eastern France). Cesium, a fission product, is present in radioactive waste. It has been widely studied because its unlimited solubility and chemical similarity to potassium make it possibly harmful for human beings.^{1,2} Many studies on the Cs sorption on the smectite clay group have been carried out. Among the smectite family, bentonites offer manifold possibilities to protect the environment because of their exceptional physical, structural and chemical properties.³ Spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) have revealed that Cs sorption on montmorillonite occurs as an inner- and outer- sphere complex, on two distinct surface sites.^{4–7} Several thermodynamical models have been proposed to describe the sorption process and elucidate the surface mechanisms at play.^{8,9} Nevertheless, these models involve empirical parameters regarding the edge sites, as for instance the so-called “strong and weak” surface sites together with their total concentration and amphoteric properties, all being characteristic of the considered mineral. This constitutes a limitation to their application to the whole of a mineral family.

In order to overcome this limitation, this work proposes an approach based on non-empirical edge sites parameters. The latter are related to the surface

properties of each elementary phase of montmorillonite: they characterize silica sites, alumina and exchange sites, for which chemical parameters (acid-base reactivity, total site concentration, sorption equilibriums and associated constants) were determined experimentally by assuming that the edge site reactivity of montmorillonite could be identified to that of pure silica and pure alumina. By this approach, the number of adjustable parameters is significantly reduced and the remaining ones can be applied to a crude material without any additional fit.

Our model has already been tested for Cs sorption on a MX-80 bentonite in synthetic groundwaters (SGWs) conditions.¹⁰ It is here applied to Cs in contact with Na-montmorillonite for a simple background electrolyte (NaNO_3) with various mass to volume ratios, pH values and atmospheric conditions. The model predictions for Cs sorption are first presented. Then, the model is checked against experimental results obtained for rubidium (Rb) sorption on a MX-80 bentonite in a SGWs medium. Since Rb is chemically similar to Cs, it allowed us to estimate its sorption equilibrium constant.

Experimental

Solid phase

The Na-montmorillonite used for the determination of the model parameters is stemming from a purifying treatment of the MX-80 bentonite.¹¹ The purification aims at eliminating mineral impurities from the material. The homoionic form (Na) of montmorillonite was obtained by saturation of the surface sites with sodium.

One kilogram of bentonite was dispersed in HCl ($0.1 \text{ mol}\cdot\text{L}^{-1}$) solution for 24 hours. The suspension was neutralized to pH 7 with NaOH ($1 \text{ mol}\cdot\text{L}^{-1}$).

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This treatment allowed the dissolution of impurities such as feldspaths, mica and quartz, but the main reactive phases (SiO_2 and Al_2O_3) and CEC were unchanged.¹² The saturation of the surface sites with sodium was performed using a NaCl ($0.5 \text{ mol}\cdot\text{L}^{-1}$) solution in contact with the solid for 72 hours. Finally, the montmorillonite sample was rinsed for two weeks by a dialysis process. During this dialysis, the ratio mass of solid to mass of ultrapure water was equal to $0.5 \text{ g}\cdot\text{g}^{-1}$, and the ultrapure water was replaced twice a day. At the end of this treatment, 500 g of dry “cleaned” material (Na-montmorillonite) was obtained.

Adsorption experiments

Adsorption as a function of pH and adsorption as a function of concentration were carried out for Cs and Rb using polycarbonate batches (Table 1). For all experiments, spikes of Cs or Rb were added after an equilibration time between the solid and the electrolyte (7 days). After spikes of Cs or Rb a reaction time of 3 days was respected to reach adsorption equilibrium. The pH of each suspension was then measured, the batches were centrifuged. Finally, the supernatants were filtered through a $0.45 \mu\text{m}$ membrane and acidified with HNO_3 before ICP-MS analyses.

In order to evaluate the carbonate dissolution effect, an adsorption of Cs on montmorillonite as a function of pH was carried out in a glove box, under argon atmosphere.

Blank experiments were performed to check how adsorption on filter is important. According to the concentrations used, the experimental errors and the results of the blank experiments, the adsorption on filters might be neglected.

The SGWs compositions (Table 2) correspond to equilibration between ground water and the Callovo-Oxfordian argilite geological formation found in Eastern France.¹³ The argilite contains clay, calcium carbonate

chlorite and sulphate phases (celestite and barytine). The SGW2 corresponds to water in equilibrium with the mineral phases of argilite. In the SGW1, sulphates were removed from the water composition to check the specific effect of sulphates. These SGWs were prepared in the laboratory using metallic salts from Table 2. Both SGWs were buffered at pH 7.4 and 8.2, using a carbonate buffer. Since the presence of sulphates ions in groundwater can reduce significantly the adsorption process of cations, one of the SGWs was prepared with $8.2 \text{ mmol}\cdot\text{L}^{-1}$ of SO_4^{2-} ion.

Model development

Ion adsorption on montmorillonite consist of two types: a pH-independent adsorption attributed to ionic exchange in the interlayer and a pH-dependent adsorption resulting of surface complexation reactions. On montmorillonite, the surface complexation groups are considered to be confined on the edges, in accordance with spectroscopic evidences.¹⁴ Most of the computer codes processed to describe adsorption on a clayey material are based on the surface complexation theory, which has been extensively applied to predict the adsorption behavior of metallic compounds in contact with hydrous ferric oxides. It was many times described and a number of variations in this model were developed (double and three layer theory, constant capacitance theory). The remaining assumptions are: the mineral surface is composed of specific functional groups that react with dissolved solutes to form surface species; the surface acidity and surface complexation reactions follow mass action laws; the electrical charge at the surface can be positive, negative or neutral, depending on the nature of the solid and the properties of the solution (especially pH); the apparent binding constants determined for the mass action equations are empirical parameters related to thermodynamic constants by the rational activity coefficients of the surface species.

Table 1. Description of the adsorption experiments

	$m/v, \text{g}\cdot\text{L}^{-1}$	pH*	Total concentration, $\text{mol}\cdot\text{L}^{-1}$	Electrolyte	Ionic strength, $\text{mol}\cdot\text{L}^{-1}$	Figure
Cs	4	4 to 10	$4\cdot 10^{-5}$	NaNO_3	10^{-2} $5\cdot 10^{-3}$ 10^{-2}	Figure 1
	2					
Rb	4	2 to 10	$5\cdot 10^{-7}$	SGW**	$5.3\cdot 10^{-2}$	Figure 2
		7.4	10^{-9} to 10^{-2}	NaNO_3 SGW**	$5\cdot 10^{-2}$ $5.3\cdot 10^{-2}$ $6.8\cdot 10^{-2}$	Figure 3
		8.2	10^{-9} to 10^{-2}	SGW**	$5.3\cdot 10^{-2}$ $6.8\cdot 10^{-2}$	Figure 4

* For experiments at varying pH values, the pH was adjusted by addition of micro-volumes of HNO_3 ($1 \text{ mol}\cdot\text{L}^{-1}$) for acidic pH or NaOH ($1 \text{ mol}\cdot\text{L}^{-1}$) for basic pH.

** See composition in Table 2.

Table 2. Composition of the synthetic ground waters

Ion	SGW 1	SGW 2
	Concentration, mmol·L ⁻¹	Concentration, mmol·L ⁻¹
K ⁺	0.3	0.3
Na ⁺	34.4	34.8
Ca ²⁺	5.8	5.8
Mg ²⁺	1.9	1.9
Cl ⁻	50.1	34.1
SO ₄ ²⁻	0	8.2
HCO ₃ ⁻ pH 7.4	0.16	0.16
HCO ₃ ⁻ pH 8.2	1.6	1.6

A practical difficulty with this model (in comparison with empirical models) is the large number of data required in terms of constants and parameters. This situation has led to a number of extrapolations from available data that have not been adequately justified.

In the surface complexation model proposed by DZOMBACK and MOREL,¹⁵ the hydrous ferric oxide surface is schematized with two kinds of reactive surface sites: the strong sites (high affinity with metals but the site density is low), and the weak ones (high site density but low reactivity). This assumption was re-used and adapted for a montmorillonite surface by BRADBURY and BAEYENS¹⁶ and the adsorption process was efficiently modeled for various metallic compounds. The assumption of “strong” and “weak” sites still remains approximate and does not refer to a physical reality of the material. Indeed, in this model, the montmorillonite is compared to an alumino-silicated mineral (in reference with its mineralogical structure). The acid-

base behavior of montmorillonite could then result from hydrolysis of ≡AlOH and ≡SiOH groups on the edges.¹⁷ In that way, the definition of two distinct types of surface sites, ≡SiOH and ≡AlOH that coexist on the clay edge, is taken into account in our chemical model, in addition with the exchange sites in the interlayers. Hydrolysis constants of ≡SiOH and ≡AlOH surface sites were determined from acid-base titration of pure silica and pure alumina, respectively (Table 3),¹² fitting was obtained by using the calculation code FITEQL.¹⁸ According to previous studies on the choice of the model describing the solid/solution interface, the constant capacitance model is the most adapted to our study.¹⁹ This model is a simplification of the generalized two layer model in that the counter-ions are assumed to lie in a single plane adjacent to the sorbed ions. The repartition of charge in the diffuse layer is electrostatic and the relationship between surface charge and surface potential is linear. The capacitance value considered in the conditions of this study is 1.2 F·m⁻².²⁰

Results and discussion

Adsorption of Cs on Na-montmorillonite in NaNO₃ electrolyte

Cs adsorption experiments in contact with Na-montmorillonite in NaNO₃ electrolyte were carried out and modeled for different pH values, ionic strengths, mass/volume ratios and atmospheric conditions (Fig. 1).

Table 3. Model parameters

Surface reactions	Log ₁₀ K	Source
≡SiOH ↔ ≡SiO ⁻ + H ⁺	-7.6	Acid/base titration of pure silica ¹²
≡SiOH + Cs ⁺ ↔ ≡SiOCs + H ⁺	-5.5	Adsorption on pure silica ¹²
≡SiOH + Cs ⁺ ↔ ≡SiOHCs ⁺	2.05	Adsorption on pure silica ¹²
≡SiOH + Na ⁺ ↔ ≡SiOHNa ⁺	1.9	Adsorption on pure silica ¹²
≡AlOH ₂ ⁺ ↔ ≡AlOH + H ⁺	7.9	Acid/base titration of pure alumina ¹²
≡AlOH ↔ ≡AlO ⁻ + H ⁺	9.22	Acid/base titration of pure alumina ¹²
≡AlOH + Cs ⁺ ↔ ≡AlOHCs ⁺	3.6	Adsorption on pure alumina ¹²
≡AlOH + Cs ⁺ ↔ ≡AlOCs + H ⁺	-5.0	Adsorption on pure alumina ¹²
≡AlOH + Na ⁺ ↔ ≡AlOHNa ⁺	3.8	Adsorption on pure alumina ¹²
≡AlOH + Na ⁺ ↔ ≡AlONa + H ⁺	-5.0	Adsorption on pure alumina ¹²
≡XNa + H ⁺ ↔ ≡XH + Na ⁺	1.0	Adsorption on montmorillonite ¹⁰
≡XNa + Cs ⁺ ↔ ≡XCs + Na ⁺	1.2	Adsorption on montmorillonite ¹⁰
Concentration of ≡SiOH sites, mol/g	1.25·10 ⁻⁴	Saturation of montmorillonite surface ¹⁰
Concentration of ≡AlOH sites, mol/g	3.75·10 ⁻⁶	Saturation of montmorillonite surface ¹⁰
Concentration of ≡XNa sites, mol/g	6.25·10 ⁻⁴	Saturation of montmorillonite surface ¹⁰
Capacitance, F/m ²	1.2	
Solid/liquid ratio, g/L	4 or 2	

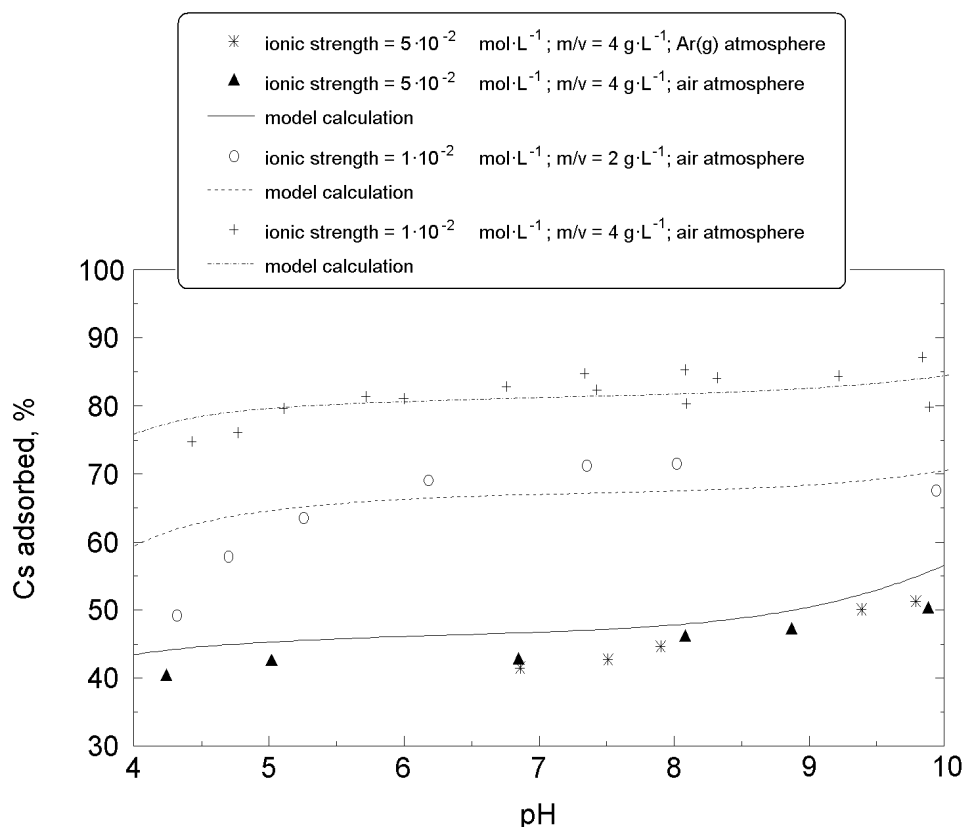


Fig. 1. Adsorption of Cs ($4 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) as a function of pH and model calculations

For the pH-range considered during experiments (from 4 to 10), the adsorption of Cs on montmorillonite surface sites is not strongly affected by the pH value, while it is correlated with the ionic strength of the media. Indeed, when the ionic strength increases, the amount of Cs adsorbed on the exchange sites decreases. This is explained by the competitive effect of sodium with cesium on the surface. These two trends in the behavior of Cs confirm that Cs is adsorbed on exchange sites (pH independent sites). The choice of controlled atmospheric conditions for adsorption experiments is not crucial since Cs behavior is unchanged whether the latter are carried out in argon atmosphere or not. The amount of Cs adsorbed on the surface depends on the total site density. Indeed, when the m/v ratio decreases, the adsorption of Cs decreases. For each experiment, the present model is able to account for changes in Cs behaviour without any fit.

The model robustness is checked since a good description of adsorption of Cs on the Na-montmorillonite for various experimental conditions is obtained, without any changes in the physical and chemical model parameters.

Adsorption of Rb on bentonite in SGWs electrolytes, as a function of pH

Adsorption experiments as a function of pH on bentonite were carried out, with rubidium, a chemical analogue of Cs. The model parameters from Table 3 were applied to the experimental results, without any changes regarding the competitive cations reactivity, total sites concentrations, and hydrolysis constants.

The adsorption of Rb on bentonite is pH independent and confirms that ion-exchange is the main mechanism occurring at the solid/liquid interface (Fig. 2). Cations from the SGW are competitive in the adsorption process because when the SGWs are used as electrolyte, a decrease in Rb adsorption is observed in comparison with similar experiments in NaNO_3 . An explanation is that Ca^{2+} and Mg^{2+} ions from the SGWs have a strongest affinity for exchange sites than sodium. Due to the similar behavior of Rb and Cs, the stoichiometries chosen for the surface reactions were similar to caesium ones. The equilibrium constants were fitted by using the results from Fig. 2, and the best fits of experimental results were obtained when the equilibrium constants from Table 4 were considered.

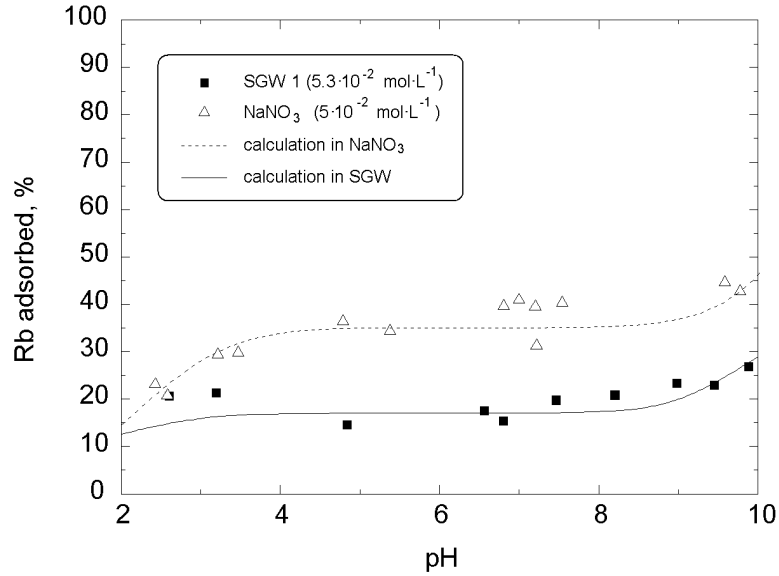


Fig. 2. Adsorption of Rb ($5 \cdot 10^{-7} \text{ mol}\cdot\text{L}^{-1}$) as a function of pH in NaNO_3 and SGW1

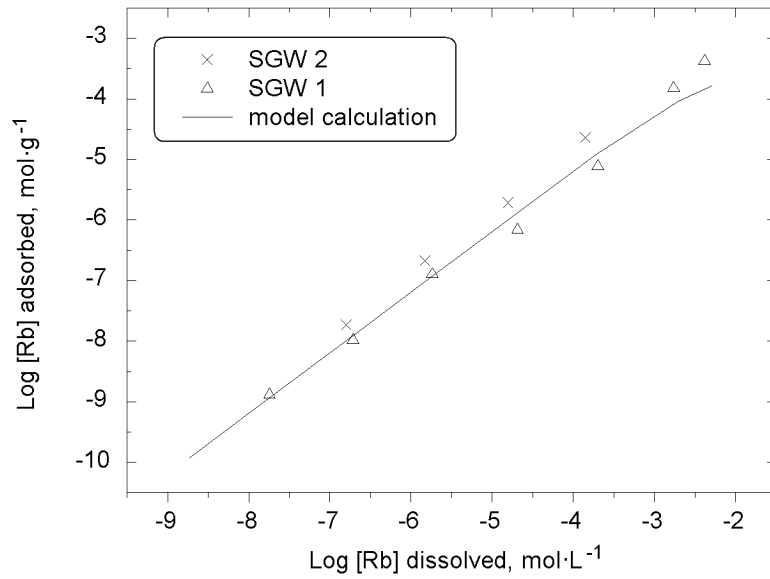


Fig. 3. Adsorption of Rb on bentonite as a function of concentration in SGW 1 and SGW2 at pH 7.4; solid line: model calculation

Table 4. Surface reactions and equilibrium constants corresponding to the best fit of the model with experimental results from Fig. 2

Surface reactions	$\text{Log}_{10} K$
$\equiv\text{SiOH} + \text{Rb}^+ \leftrightarrow \equiv\text{SiORb} + \text{H}^+$	-5.5
$\equiv\text{SiOH} + \text{Rb}^+ \leftrightarrow \equiv\text{SiOHRb}^+$	2.05
$\equiv\text{AlOH} + \text{Rb}^+ \leftrightarrow \equiv\text{AlOHRb}^+$	3.6
$\equiv\text{AlOH} + \text{Rb}^+ \leftrightarrow \equiv\text{AlORb} + \text{H}^+$	-5.0
$\equiv\text{XNa} + \text{Rb}^+ \leftrightarrow \equiv\text{XRb} + \text{Na}^+$	1.0

Adsorption of Rb on bentonite in SGWs electrolytes, as a function of concentration

To check the model capabilities over a large range of experimental conditions, adsorption as a function of Rb concentration were performed.

The behavior of Rb at the bentonite surface is unchanged whatever the considered SGW. This shows that the presence of sulphates ions in SGW has no influence on the adsorption of Rb, because the affinity of Rb with sulphates ions is low.

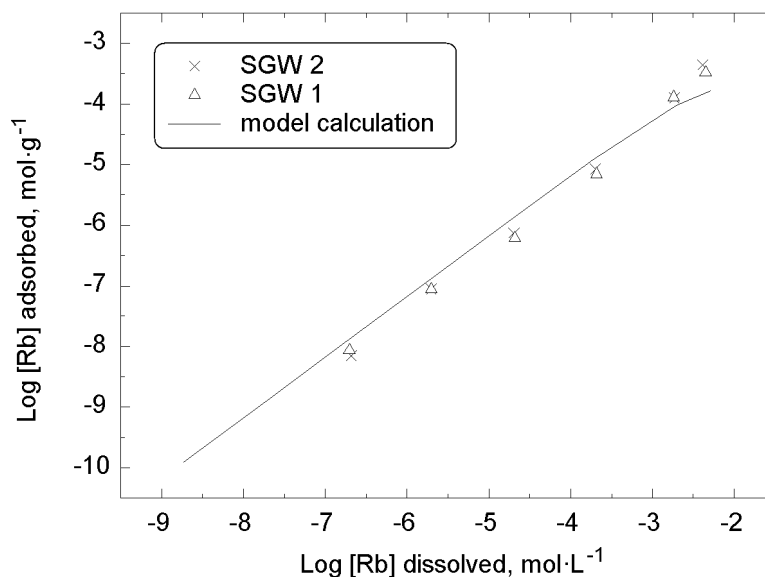


Fig. 4. Adsorption of Rb on bentonite as a function of concentration for SGW1 and SGW2 at pH 8.2

The variation in ionic strength between SGW 1 and SGW 2 has no influence on experimental results because the amount of competitive cations (Ca^{2+} , Mg^{2+}) is the same for both SGWs. Rb adsorption is linear with a slope circa 0.94 (versus 0.97 for Cs)¹⁰ regardless the initial concentration of Rb, and adsorption isotherms are Freundlich like. The empirical equation of such isotherms can be deduced from Figs 3 and 4: $[\text{Rb}]_{\text{sorbed}} = 0.1003 \times [\text{Rb}]_{\text{dissolved}}^{1.012}$ (regression coefficient >0.99) with $[\text{Rb}]_{\text{sorbed}}$ in $\text{mol}\cdot\text{g}^{-1}$ and $[\text{Rb}]_{\text{dissolved}}$ in $\text{mol}\cdot\text{L}^{-1}$. The coefficients of the Freundlich equation are very close to the Freundlich coefficients of Cs,¹⁰ thus confirming the similar behavior of Cs and Rb face to the bentonite surface.

Conclusions

The surface complexation model described in this study allows a good description of adsorption phenomena on a Na-montmorillonite sample and can be applied to a bentonite without any changes in the parameters. Adsorption was correctly described by the model for trace and high concentrations and for various pH conditions. For cesium and rubidium, the main adsorption mechanism is ion-exchange. Adsorption is strongly affected by the presence of competing cations such as Ca^{2+} and Mg^{2+} from the SGWs, whereas anionic species such as sulphates have no influence on the adsorption. The competing effect was successfully described by the model.

The simple model proposed in this study is only based on the surface complexation theory. The number of adjusted parameters is very limited because the surface properties of the material were determined by independent experiments.

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