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Reply to some comments

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1. Introduction

We would like to express our thanks to the three colleagues who examined our manuscripts and tried to help us with their suggestions. The views expressed by Prof. W. Stumm are very similar to our own. Although the approach taken was to try and set up a mechanistic model for describing sorption processes, we do appreciate that such a model is only a 'near-mechanistic model', as stated by Prof. Stumm.

The points raised by Prof. J. Cases were also useful, particularly those concerning the possibility of calculating surface site capacities. This would be even more interesting when the contributions of the different amphoteric site types could be estimated. We would like to reply to two comments made by Prof. Cases.

First, the potentiometric titrations were not primarily carried out to determine site capacities, but rather to obtain the protolysis constants essential for the sorption model. It is interesting to note that the measured distribution of site type capacities (structural and amphoteric) for the conditioned Na–montmorillonite used in our studies are in full agreement with the numbers given by Prof. Cases.

Secondly, we fully take the point made with respect to surface area measurements, and recognize the general problem concerning such determinations and what they actually mean. Because we ultimately abandoned the electrostatic term in the modelling, the surface area parameter was not required, so had no relevance to the modelling described from Section 3.3, Part II, onwards.

The comments made by Prof. F. Morel require somewhat more detailed replies. To make the discussion easier to follow, we have numbered specific comments and replied under the same numbers below.

2. Point One

The position of the maximum in the sorption edge data is not of concern to us per se, but it is one of the main measured characteristics of Ni, Zn and Mn sorption on

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Na–montmorillonite. Therefore, it is important that a model can reproduce the peak values in the correct pH ranges.

The reason for the decrease in sorption predicted by the model for Ni (pH of about 9.5), Zn (pH of about 8.5) and Mn (pH of about 11) (see Figs. 8, 11 and 12, Part II) is, in each case, the formation of hydroxy species. The assumed surface complexation reactions involve M^{2+} cations, so that hydrolysis will automatically result in decreased sorption.

We believe that our modelling efforts are valid up to pH values of between 10 and 11, depending on the metal. At higher pH values, other processes could be occurring, and it might be speculated that one of the possibilities could be surface precipitation—but we do not know yet. (In the case of Ni, we do have some experimental data that suggest additional processes occurring at pH values greater than 10.5.) However, in highly alkaline solutions, the question of the clay mineral stability arises, and it is debatable whether it makes sense to talk of metal uptake processes in terms of sorption—and the sort of model described in Part II—when the surface state of the solid phase is unstable and changing as a function of time.

3. Point Two

We agree, and have included the solid-to-liquid ratios (S:L values) in the figure captions for completeness. However, when sorption is expressed in terms of distribution ratios, the sorption edges and isotherms are independent of this parameter (see also Point 3 (a)).

In Section 4.1.1 (Part I), we have stated clearly that, for all sorption edge measurements, the concentrations of Ni and Zn added were always less than 3×10^{-7} M and 10^{-9} M respectively. No background Ni was detectable, and the natural Zn background present in the system was taken into account in the calculation of all R_d (Zn) values (Section 4.1.2, Part I).

In the papers, we took care to reference the thermodynamic database used in the calculations (Pearson and Berner, 1991; Pearson et al., 1992), because the sorption modelling results do depend on the thermodynamic data. Although the 'numbers' are not given in the papers, they are defined and accessible to anybody who would like to repeat our calculations.

4. Point Three

In the presentation of our experimental results, we deliberately chose to express sorption in terms of distribution ratios rather than as 'per cent sorbed' values, i.e. $(C_{init} - C_{eq})/C_{init} \times 100$. This 'percentage sorbed' approach is more common in the environmental sciences literature, where the percentage sorbed versus pH sorption edges provide the main data sets used in modelling. The reasons that we preferred the R_d representation are listed below.

(a) Sorption edges are independent of the S:L ratios chosen. (The proviso is that the initial concentrations are low enough to ensure that sorption is only occurring on the high affinity sites and that there are no site saturation effects. We were always careful to choose experimental conditions that fulfilled these requirements.)

(b) At the S:L ratios that were experimentally convenient for sorption edge measurements on Na–montmorillonite (about 1 g L^{-1}), modelling the sorption data presented in terms of R_d values was more sensitive to the parameters values.

(c) In a 'percentage sorbed' representation, the fits are strongly biased towards a narrow pH range that covers the steeply rising portion of the sorption edge; the fits give much less weight to the pH region where high sorption is occurring (above 95% sorbed). If the sorption (R_d) values in higher pH regions are of interest, i.e. outside the steeply rising portion of the sorption edge, then it seems that good fits to the percentage sorbed versus pH edges did not necessarily provide a good representation of the measured R_d data (see example given under Point 7).

(d) Finally, in radioactive waste management and environmental sciences, where the migration of radionuclides and/or contaminants is of central interest, the quantity of critical importance is the concentration of radionuclides or contaminants in the groundwater along the flow path. Representing the sorption data in terms of distribution ratios rather than the percentage sorbed better reflects the sensitivity of the aqueous concentrations to changing conditions.

5. Point Four

We think that there is a slight misunderstanding here. The modelling referred to by Prof. Morel (Figs. 5 and 6, Part II) is meant to be illustrative of the sort of procedures (simplified in the paper) that we went through to reach the final proposal for the model. With an electrostatic term and one protolysis site type, we could fit the titration data but failed miserably with fitting the sorption edge data. An important point here is that, with the chosen surface complexation reaction (Eq. (8), Part II), the inclusion of electrostatics in the model predicted a slope in the rising edge of the log R_d versus pH sorption edge of about 1.6, whereas the experimental data indicated that the value should be nearer unity. The value of this slope is a major characteristic of the sorption edge, and any model must be able to reproduce it (as well as reproducing the titration and sorption isotherm measurements.) The point of Fig. 6, Part II, is to show that, with no electrostatics, we can account for a slope in the log R_d versus pH plot of near unity. However, this modelling attempt was poor at fitting the peak height, so required further refinement. (This is also clear from the fit to the titration data.) The further refinements chosen are documented.

The introduction of a second protolysis site type automatically implied that a better fit to the titration data could be found, simply because there were now more fit parameters available. However, we would like to re-emphasize that seeking 'best fits' to specific (limited) data sets was not the point of the exercise. Rather, the aim was to find the simplest chemically reasonable model capable of providing a good representation of all our measurements carried out over a wide range of conditions (titration, sorption edge and isotherm data), and one that we could use for making predictions. We tried to view the modelling in this wider context.

6. Point Five

We would like to point out that the protolysis constants fitted to the titration data in Figs. 5 and 7, Part II, are fits without the electrostatic term, and the same constants would not provide satisfactory fits with an electrostatic term included. However, the questions and proposals of Prof. Morel in this context are interesting but, most probably, can only be properly resolved by a new and different modelling approach to all the data sets available.

7. Point Six

The protolysis constants do have an effect on the sorption edge characteristics of Ni, Zn and Mn. The reason is simply that the same constants are taken for the high affinity sites (S^SOH sites) as for the weak $S^{w1}OH$-type sites. (The concentration of the S^SOH sites is so low that it is not possible to determine their acid–base behaviour separately.)

8. Point Seven

We find many of the comments and issues raised by Prof. Morel in this part of his letter very useful and relevant. We freely admit that our modelling approach (without electrostatics) may not be unique. It would be very useful to have other experts in this area look at our data from a different perspective, and try to reproduce the titration data, the sorption edges and the sorption isotherms with, for example, a model that contained an electrostatic term. In this context, we would be more than pleased to accept the 'double bet' proposed by Prof. Morel and, as an added incentive to the 'fine Swiss chocolate', we would also offer some equally fine 'Belgian pralines'. However, we would add that the requirement is to model all the data contained in the paper.

We would like to illustrate a further point in connection with data representation (Point 3) and modelling, using Fig. 1(i) and Fig. 1(ii) in this 'comments' paper. A reasonable fit to the percentage of Zn sorbed versus pH data (Fig. 1(i)) could seemingly be found by using the protolysis constants fitted to the titration data with electrostatics (Fig. 2, Part II). (The modelling of the edge was also carried out with an electrostatic term.) However, the apparently good fit to the data when expressed as the percentage sorbed became a totally unacceptable fit when the same data were plotted as log R_d versus pH (see Fig. 1(ii)).

9. Point Eight

Wanner et al., 1994 have presented some titration data on Na–montmorillonite, based on continuous rather than batch measurements, at ionic strengths down to 5×10^{-3} M. They do not see any clear evidence of strongly intersecting titration curves at different ionic strengths. Indeed, the data appear to be overlapping in the pH range from 5 to 8 for ionic strengths of 5×10^{-3} M and 5×10^{-2} M.

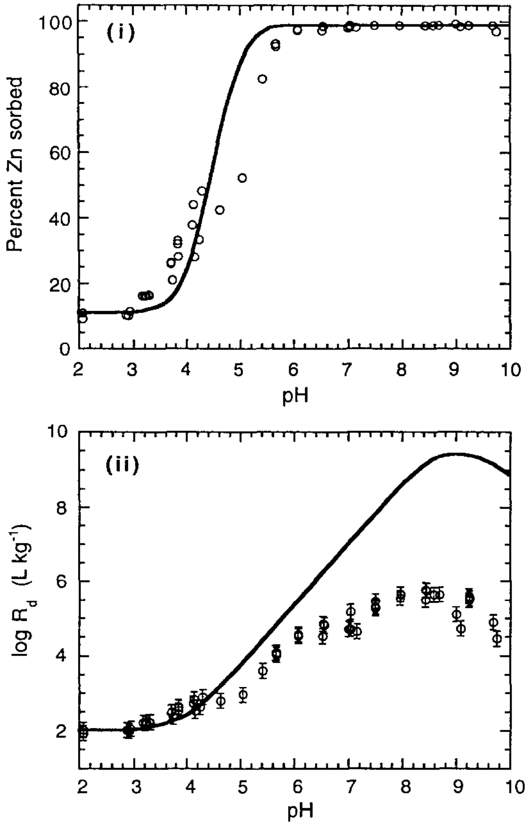

Fig. 1. Sorption edge data for Zn measured on Na-montmorillonite at 0.1 M $NaClO_4$: (i) data presented as the percentage sorbed versus pH; (ii) data presented as distribution coefficient (log R_d) versus pH. The curve is the best fit obtained with the DDL-model. Fixed parameters: see Table 1, Part II; Zn inventory, 10^{-3} mol kg^{-1}; surface area, 3.5×10^4 m^2 kg^{-1}; SOH site capacity, 8×10^{-2} mol kg^{-1}; S^SOH site capacity, 2×10^{-3} mol kg^{-1}; log $K_{int}(+)$ 6.2; log $K_{int}(-) = -8.3$. Fit parameter: log ${}^SK_{int}(Zn) = 3.7$ (Fitted to the sorption edge data represented as the percentage sorbed versus pH).

As mentioned by Prof. Morel, lower ionic strengths mean that H^+–Na^+ exchange becomes increasingly more important and the necessary corrections increasingly greater. The Na–montmorillonite titration measurements were difficult in any case, and moving to lower ionic strengths will increase this difficulty and the magnitude of the corrections required; although such experiments are certainly not impossible and probably need to be carried out.

10. Point Nine

Four pK values are required, rather than six. The same protolysis constants were taken for the high affinity sites (S^SOH sites) as for the weak $S^{w1}OH$-type sites (see Point 6).

11. Point Ten

The comment regarding the effect of the ionic strength on the sorption edges is well taken, but it is in the nature of the Na–montmorillonite system that changes in background electrolyte concentrations significantly affect the sorption on the cation exchange sites. (We are planning to carry out a similar programme of work for illite, which has a considerably lower cation exchange capacity. It will be interesting to compare the titration and sorption characteristics of the two clay minerals.)

We would like to express our thanks to Prof. F. Morel for his detailed and searching comments, and for raising a number of key questions that need to be resolved. We see this work on Na–montmorillonite as a beginning and not as an end. We are continuing our experimental and modelling work in the direction of Ca–montmorillonite and natural bentonite systems, as further and more severe tests of the predictive capability of the 2SPNE-Model.

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