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Incorporation of a Cation Exchange Model into Geochemical Computer Codes

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

ABSTRACT

A procedure for introducing cation exchange into geochemical/surface complexation codes is described. Beginning with selectivity coefficients, K_C, defined in terms of equivalent fractional ion occupancies, a general expression for the molar based exchange code input parameter, K_{ex}, is derived. In natural systems the uptake of nuclides onto complex sorbents often occurs by more than one mechanism. The incorporation of cation exchange and surface complexation into a geochemical code therefore enables sorption by both mechanisms to be calculated simultaneously. The code and model concepts are tested against sets of experimental data from widely different sorption studies. A proposal is made to set up a data base of selectivity coefficients. Such a data base would form part of a more general one consisting of sorption mechanism specific parameters to be used in conjunction with geochemical/ sorption codes to model and predict sorption.

ZUSAMMENFASSUNG

Es wird eine Methode aufgezeigt, die es ermöglicht, in geochemischen Computer-programmen, welche Oberflächenkomplexierung beinhalten, Ionenaustausch mitzu-berücksichtigen. Ausgehend von Selektivitätskoeffizienten K_c, welche über die äqui-valente fraktionelle Ionenbelegung definiert sind, wird eine allgemeine Gleichung für den molaren Austauschparameter K_{ex} hergeleitet. Die Sorption von Radionukliden an komplexen Festphasen wird in natürlichen Systemen durch mehrere Mechanismen beschrieben. Der Einbau von Ionenaustausch und Oberflächenkomplexierung in geo-chemische Computerprogramme erlaubt eine simultane Modellierung dieser Mecha-nismen. Das Programm und das Modellkonzept werden mit mehreren Sätzen experi-menteller Daten getestet, die unterschiedlichen Sorptionsstudien entnommen sind. Es wird vorgeschlagen, ergänzend eine Datenbank zu erstellen, die Selektivitätskoeffi-zienten enthält. Solch eine umfassende, mehr generelle Datenbank mit spezifischen, sorptionsmechanistischen Parametern dient als Basis für Sorptionsmodellrechnun-gen.

RÉSUMÉ

On décrit un procédé pour l'introduction de l'échange cationique dans des codes géochimiques de spéciation en solution et de complexation à la surface. Une expression générale pour le paramètre d'échange, K_{ex}, défini pour des concentrations exprimées en moles par litre, est dérivée d'un coefficient de sélectivité, K_c, défini en termes de fractions d'occupation cationique. Dans les systèmes naturels, la sorption des radionucléides sur des sorbents complexes est souvent décrite par la mise en jeu de plusieurs mécanismes. L'incorporation de l'échange cationique et de la complexation à la surface dans un code géochimique, permet ainsi, de simuler simultanément la sorption par ces deux mécanismes. Les concepts du modèle et du code sont testés pour des séries de données expérimentales issues de différentes études de sorption. Une proposition est faite pour mettre en place une base de données de coefficients de sélectivité. Une telle base de données ferait partie d'une base de données plus générale qui consisterait à utiliser conjointement les paramètres spécifiques des mécanismes de sorption avec les codes géochimiques pour prédire et modéliser la sorption.

Table of Contents

List of Figures

List of Tables

1   INTRODUCTION

In any natural rock water system, particularly those containing clay minerals, the ion exchange properties and exchange reactions of the minerals present are of fundamental and practical importance in understanding the water chemistry and sorption behaviour. In laboratory experiments interactions between the liquid and solid phases will almost invariably occur. Ion exchange reactions, depending on the conditions, can have a significant influence on the evolution of the water chemistry. For example, BAEYENS & BRADBURY (1991) have shown that cation exchange reactions must be taken into account in the interpretation of data from laboratory experiments designed to provide "in situ" pore water compositions for sedimentary rocks. Generally it is rather difficult, particularly for complex natural systems, to know a priori whether and to what extent cation exchange processes are contributing to rock-water interactions or radionuclide sorption.

In sorption studies there is an increasing trend towards trying to understand data in terms of mechanisms described by appropriate models. Although many geochemical codes contain a cation exchange sub-routine as an option, such options only allow sorption due to cation exchange to be calculated. A similar situation exists with most surface complexation codes in that only radionuclide uptake by this mechanism is calculated. However, a major requirement in modelling is to be able to calculate the contribution of multiple sorption mechanisms simultaneously. In many cases surface complexation and cation exchange are both contributing to the uptake of radio-nuclides, and, depending on the specific experimental conditions, either mechanism may be dominant. Obviously, serious errors will occur if a model based on one mechanism is used to interpret and/or fit sorption data where two (or more) different processes are taking place.

Because we considered what was available to be somewhat unsuitable for our purposes, we incorporated exchange reactions into a geochemical/surface complexation code, MINSURF*, which, with its multi-site type/multi-surface options, proved to be ideal in this respect. Also, rather than starting by directly defining an exchange parameter, K_{ex}, (section 3.1), which is usual in many cases e.g. WANNER (1986), CURTI (1993), we began with a selectivity coefficient, K_c, and derived from this an exchange parameter K_{ex}, in the form required by the code (section 3.2). This procedure produced some useful and interesting insights into the properties of the K_{ex} parameter.

Finally, checks on the code were carried out using our own and literature sorption data. The main purpose here was to confirm that we had incorporated the cation exchange model correctly into the geochemical computer code and that the code, together with the derived exchange parameters, calculated properly.

For each of the examples given in section 4, an analytical solution was available which fitted the experimental data for a given parameter set. We took the same parameters and experimental conditions and compared the results calculated using the code with the analytical solution/experimental data. Such a verification type exercise is essential before the code can be used for predictive modelling.

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*   MINSURF is the geochemical equilibrium code MINEQL (WESTALL et al. 1976) containing a diffuse layer surface complexation model

2   ION EXCHANGE AND THE SELECTIVITY CONCEPT

The surfaces of clay minerals carry a permanent negative charge arising from isomorphic substitution of lattice cations by cations of a lower valence. Charge neutrality is maintained by the presence of an excess of cations in solution in close proximity to the surface. These cations, held around the outside of the Si-Al clay mineral structural units, "belong" to the surface and cannot be separated away from it but are exchangeable and can undergo exchange reactions with ions in the aqueous phase. The cation exchange capacity (CEC) of a solid is defined as the total quantity of cations sorbed exchangeable per unit mass. The CEC is usually expressed on an equivalent scale e.g. equivalents g^{-1}. The CEC of a material is not a unique value, but varies, to a greater or lesser extent, with pH, particle size and the method of measurement (GRIM 1953).

If we consider the general case of a cation B, valence Z_B, in the aqueous phase exchanging with cation A, valence Z_A, bound to the clay mineral surface, the exchange reaction can be written as follows:

$$z_B . A - Clay + z_A . B \Leftrightarrow z_A . B - Clay + z_B . A \qquad [1]$$
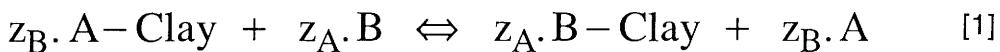
Cation exchange reactions are reversible, fast and stoichiometric. In the case of heterovalent exchange, the latter characteristic arises from the electroneutrality condition. A mass action relation is normally used to describe the reaction in terms of a so-called selectivity coefficient. Depending on the way in which the sorbed and aqueous quantities are treated, different values for selectivity coefficients for the same data sets can be obtained. These differently defined selectivity coefficients are all related to one another (see BRUGGENWERT & KAMPHORST 1982).

We have chosen to follow the definition of GAINES & THOMAS (1953) and accordingly define the selectivity coefficient, ${}_A^B K_C$, for equation [1] as:

$$
{}_A^B K_C = \frac{N_B^{Z_A}}{N_A^{Z_B}} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \qquad [2]
$$

a_A and a_B are the solution activities of cations A and B respectively. N_A and N_B are equivalent fractional occupancies defined as the equivalents of A (or B) sorbed per unit mass divided by the cation exchange capacity, in equivalents per unit mass.

For cation exchange models in general there is an implicit assumption regarding the surface activity coefficients of exchanged cations. At the present time it is not clear how to calculate such terms and they are normally set equal to unity. To some extent the validity of this assumption can be checked since a surface activity coefficient of unity implies that the selectivity coefficient should be constant as a function of fractional ion occupancies and ionic strength.

One method of determining K_C values is via sorption measurements. If we define a sorption coefficient, $^B R_{CE}$, for the sorption by cation exchange of cation B as

$$^B R_{CE} = \frac{\text{Moles of B sorbed by cation exchange per unit mass}}{\text{Moles of B in aqueous solution per unit volume}} \quad [3]$$

or,

$$^B R_{CE} = N_B \cdot \frac{CEC}{Z_B} \cdot (B)^{-1} \quad [4]$$

where (B) is the concentration of B in moles per unit volume.
Hence,

$$N_B = {}^B R_{CE} \cdot \frac{Z_B}{CEC} \cdot (B) \quad [5]$$

For a bi-ionic system where one of the cations, B, is present at trace levels, we can take $N_A \sim 1$, and equation [2] simplifies to :

$$^B_A K_C = N_B^{Z_A} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \quad [6]$$

Substituting the expression for N_B from equation [5] into equation [6] yields a general expression relating the selectivity coefficient, $^B_A K_C$, to the sorption of cation B, $^B R_{CE}$, i.e.,

$$^B_A K_C = Z_B^{Z_A} \cdot \left(^B R_{CE} \right)^{Z_A} \cdot \frac{1}{(CEC)^{Z_A}} \cdot \frac{(\gamma_A)^{Z_B}}{(\gamma_B)^{Z_A}} \cdot (A)^{Z_B} \quad [7]$$

γ_A and γ_B are the solution activity coefficients of A and B respectively.

If the values of all parameters on the RHS of equation [7] are known, $^B_A K_C$ can be readily calculated.

Approaches to modelling cation exchange based on the Vanslow selectivity coefficient, K_V, (VANSLOW 1932) have been adopted for example by SHAVIV & MATTIGOD (1985), SCHINDLER et al. (1987), FLETCHER & SPOSITO (1989) and CHARLET et al. (1993). Here the fractional ion occupancies are defined on a molar scale in the mass action equation describing cation exchange. K_V is taken by the above authors to be a constant and this leads to the exchange parameter being dependent on the cation loadings on the exchanger. An iterative procedure in the code described by FLETCHER & SPOSITO (1989) is required to calculate new exchange parameters for each case being modelled.

It may be appropriate at this point to briefly discuss why we have chosen the Gaines and Thomas definition for the selectivity coefficient rather then the Vanslow definition. The question as to whether K_C or K_V is the most appropriate coefficient to use has been the subject of some discussion in the open literature, see particularly SPOSITO & MATTIGOD (1979).

At trace levels of adsorbing cations it can easily be shown that the two coefficients are directly proportional to one another e.g. for bivalent-monovalent exchange we have $K_C = 2K_V (1+M_B)$ where M_B is the molar fractional occupancy of the sorbing cation. For $M_B \rightarrow 0$ we have $K_C = 2K_V$. Therefore for sorption at trace levels the choice is arbitrary.

In other situations, for example studies on rock-water interactions, where the fractional cation occupancies can change drastically, the choice between K_C and K_V may be more critical. At higher fractional occupancies the direct proportionality between the two coefficients disappears. SPOSITO & MATTIGOD (1979) favour the Vanslow selectivity coefficient since they conclude that K_V is constant over a wider range of fractional occupancies for Na^+-Ni^{2+}, Na^+-Co^{2+}, Na^+-Cu^{2+}, Na^+-Zn^{2+} and Na^+-Cd^{2+} exchange on montmorillonite. However, this analysis is based on the experimental data of MAES et al. (1976) who interpreted their own data in terms of K_C values. It appears to us that with an anticipated error range of ±15% for each individual data set both coefficients can be regarded to a first approximation as being constant up to fractional ion occupancies of ~ 0.5, and higher in some cases. A similar picture to the one above also emerges when data from other sources are analysed e.g. Na^+-Ca^{2+} exchange on montmorillonite; VAN BLADEL et al. (1972); MAES & CREMERS (1977); SPOSITO et al. (1983). In our view, the evidence in favour of one or the other of these selectivity coefficients is inconclusive.

We see the main application of the work described here in modelling trace metal ion sorption by cation exchange. For this purpose, as will be shown in the next section, beginning with selectivity coefficients defined by equation [2] results in simple and transparent definitions of the exchange parameter values required in geochemical computer codes. The calculation of these parameters from K_C values is accomplished using a single equation which incorporates their dependency on the nature of the exchange (homovalent/heterovalent), the properties of the exchange medium and the sorbent concentration. The application to practical situations is generally straightforward.

3   INTRODUCTION OF CATION EXCHANGE INTO GEOCHEMICAL CODES

3.1   Basic Equations

The procedure for introducing cation exchange into geochemical/surface complexation codes is relatively straightforward. There are a number of possibilities available which differ mainly in the definition chosen for the master surface exchange species e.g. X^- or XNa or XH. Depending on the particular system being modelled, one or the other may be more convenient to handle in the code, but the results, whatever the choice, should be the same.

One method, which we have chosen to follow, has been fully described by WANNER (1986), and will only be briefly summarised here using the exchange of a bivalent cation, RN^{2+}, with Na^+ as an example. Cation exchange is represented by stoichiometric exchange reactions between aqueous cations and a negatively charged master surface species, X^-, which is also treated in the code as though it were dissolved, i.e.

$$X^- + Na^+ \Leftrightarrow X-Na \qquad {}^{Na}K_{ex} \qquad [8]$$

$$2X^- + RN^{2+} \Leftrightarrow X_2-RN \qquad {}^{RN}K_{ex} \qquad [9]$$

In order to ensure that clay surfaces associated with the fixed charge are neutral in aqueous solution, the logarithm of the reaction constant for equation [8] is arbitrarily set to a high value e.g. log $^{Na}K_{ex}$= 15. All exchange sites are then initially of the X-Na type.

All species in equations of the sort given in [8] and [9] are treated in geochemical codes as though they are occurring in the aqueous phase. Hence, all quantities, including those associated with the solid phase, must be given in terms of activities. The mass action equations corresponding to reactions [8] and [9] are, respectively,

$$^{Na}K_{ex} = \frac{Q_{Na}}{Q_X \cdot a_{Na}} \qquad [10]$$

$$^{RN}K_{ex} = \frac{Q_{RN}}{Q_X^2 \cdot a_{RN}} \qquad [11]$$

where "a" terms are solution activities and "Q" terms are sorbed quantities expressed in moles litre^{-1}. Activities should be used for "Q", but since little is known about surface activity coefficients these are set equal to unity by convention.

Exchange constants for the reactions given in equation [8] and [9] are required as input parameters for the code. Such data are not directly available, rather, measurements are usually carried out for exchange reactions of the type :

$$2X-Na \ + \ RN^{2+} \ \Leftrightarrow \ X_2 - RN \ + \ 2Na^+ \qquad {}^{RN}_{Na}K_{ex} \quad [12]$$
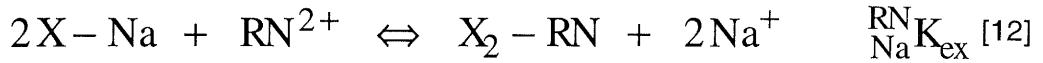
for which,

$${}^{RN}_{Na}K_{ex} \ = \ \frac{Q_{RN}}{Q_{Na}^2} \ . \ \frac{a_{Na}^2}{a_{RN}} \qquad\qquad [13]$$

In the above approach the "reference state" for the exchange medium is defined to be the Na form, (equation [8]), and hence data with respect to Na exchange are required. From equations [10], [11] and [13] it can easily be shown that :

$$\log {}^{RN}_{Na}K_{ex} \ = \ \log {}^{RN}K_{ex} \ - \ 2\log {}^{Na}K_{ex} \qquad [14]$$

or,

$$\log {}^{RN}K_{ex} \ = \ \log {}^{RN}_{Na}K_{ex} \ + \ 2\log {}^{Na}K_{ex} \qquad [15]$$

Recalling that $\log {}^{Na}K_{ex}$ was set equal to 15, then equation [15] becomes:

$$\log {}^{RN}K_{ex} \ = \ \log {}^{RN}_{Na}K_{ex} \ + \ 30 \qquad\qquad [16]$$

In the vast majority of cases, pore water chemistries, rather than sorption, have been calculated using geochemical/cation exchange codes. Normally, results from laboratory rock-water interaction experiments are taken to obtain K_{ex} values which are then used in modelling studies. The results are seldom checkable since the predictions often fall into regions inaccessible to laboratory tests. We are not aware of any such studies in which predictions made using one set of laboratory data have been checked against other measured data. There appears to be an a priori assumption that K_{ex}, defined in equation [13], is constant and can be treated the same as an aqueous stability constant. We will show that this assumption is not generally valid.

3.2   Selectivity Approach to Defining K_{ex}

There are a number of distinct advantages in choosing selectivity coefficients as a basis for deriving an expression for the computer code input parameter K_{ex}. First and foremost, the majority of studies on cation exchange reported in the open literature present results in terms of selectivity coefficients. These data are extensive and compilations of values are available for a wide variety of cation - clay mineral combinations (see for example BRUGGENWERT & KAMPHORST 1982). Since we are ultimately interested in model descriptions of sorption leading to a predictive capability, such compilations are an important source of data. Also, the selectivity concept is one which has stood the test of time and enabled cation exchange processes to be described and quantified over a wide range of experimental conditions. Further, having a widely based data source available as a reference, allows us to compare and check the consistency of our experimental data and modelling results with previous work.

Our premise is that the selectivity coefficient, K_C, is constant. For most (natural) systems the fractional ion occupancies on the exchanger are fixed by the major cation composition of the aqueous phase, and sorption takes place against this constant background. In most cases of practical interest sorbates are only present at trace levels ($<10^{-6}$ M), which generally means that their sorption by cation exchange results in (very) low fractional occupancies. Taking the selectivity coefficient to be constant under such conditions is a good approximation.

Further, experimental data are available in the literature defining fractional ion occupancy ranges in different cation/clay mineral systems for which K_C values are constant, e.g., Cs^+-Na^+ exchange on montmorillonite, N_B range: trace - 0.95 (CREMERS 1968); Na^+ exchange with Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} on montmorillonite, N_B range: 0.1-0.5 (MAES et al. 1976); and Ca^{2+}-Eu^{3+} exchange on kaolinite, N_B range: 0.1-0.9; illite, N_B range: 0.1-0.7; montmorillonite, N_B range: 0.1-0.6 and vermiculite, N_B range: 0.1-0.9 (BAEYENS 1982). Consequently, the problem reduces to the relatively simple task of converting sorbed quantities in equation [2] from a fractional ion occupancy scale to a molar concentration scale.

Let the cation exchange capacity of the solid be "CEC" equivalents g^{-1} and the sorbent concentration in the experiment "S" g litre^{-1}. In the most general case cation exchange reactions can be written as in equation [1], and the exchange parameter, K_{ex}, is then given by:

$$\begin{smallmatrix} B \\ A \end{smallmatrix} K_{ex} = \frac{Q_B^{Z_A}}{Q_A^{Z_B}} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \qquad [17]$$

The effective concentration of cation A sorbed on the solid, Q_A, expressed in mol litre^{-1}, is then:

$$Q_A = N_A \cdot \frac{CEC}{Z_A} \cdot S \qquad [18]$$

from which:

$$N_A = \frac{Z_A}{CEC} \cdot Q_A \cdot \frac{1}{S} \qquad [19]$$

Similarly:

$$N_B = \frac{Z_B}{CEC} \cdot Q_B \cdot \frac{1}{S} \qquad [20]$$

Substituting the above expressions for N_A and N_B into equation [2] yields:

$$_A^B K_C = \frac{\left\{\frac{Z_B}{CEC} \cdot Q_B \cdot \frac{1}{S}\right\}^{Z_A}}{\left\{\frac{Z_A}{CEC} \cdot Q_A \cdot \frac{1}{S}\right\}^{Z_B}} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \qquad [21]$$

or,

$$_A^B K_C = \frac{Q_B^{Z_A}}{Q_A^{Z_B}} \cdot \frac{a_A^{Z_B}}{a_B^{Z_A}} \left\{ \left(\frac{1}{CEC}\right)^{Z_A - Z_B} \cdot \frac{Z_B^{Z_A}}{Z_A^{Z_B}} \cdot \left(\frac{1}{S}\right)^{Z_A - Z_B} \right\} \qquad [22]$$

Substituting K_{ex} from equation [17] into equation [22] and re-arranging we obtain,

$$_A^B K_{ex} = {}_A^B K_C \cdot (CEC)^{Z_A - Z_B} \cdot \frac{Z_A^{Z_B}}{Z_B^{Z_A}} \cdot (S)^{Z_A - Z_B} \qquad [23]$$

Equation [23] shows that K_{ex} is related to K_C via the CEC of the solid phase, the valences of the exchanging cations and the sorbent concentration i.e. K_{ex} cannot generally be taken to be a constant.

The form of equation [23] changes dramatically depending on whether homovalent or heterovalent exchange is being considered. If the valences of the exchanging cations are the same i.e. homovalent exchange where $Z_A = Z_B$, then equation [23] simplifies to

$$\begin{array}{c}B\\A\end{array}K_{ex} = \begin{array}{c}B\\A\end{array}K_C \qquad\qquad [24]$$

Thus, for exchange between ions of like charge, K_{ex} is equal to K_C and can be regarded as a constant.

For heterovalent exchange the three expressions for K_{ex} given below are for bivalent - monovalent, trivalent - monovalent and trivalent - bivalent exchange respectively:

$$\begin{array}{c}2+\\1+\end{array}K_{ex} = \begin{array}{c}2+\\1+\end{array}K_C \cdot (CEC)^{-1} \cdot \frac{1}{2} \cdot (S)^{-1} \qquad\qquad [25]$$

$$\begin{array}{c}3+\\1+\end{array}K_{ex} = \begin{array}{c}3+\\1+\end{array}K_C \cdot (CEC)^{-2} \cdot \frac{1}{3} \cdot (S)^{-2} \qquad\qquad [26]$$

$$\begin{array}{c}3+\\2+\end{array}K_{ex} = \begin{array}{c}3+\\2+\end{array}K_C \cdot (CEC)^{-1} \cdot \frac{8}{9} \cdot (S)^{-1} \qquad\qquad [27]$$

At first sight these results may seem somewhat surprising. However, they are a logical consequence of the stoichiometric nature of cation exchange processes and the requirement that K_{ex} is defined on an activity scale (equation [17]) for inclusion as an input parameter in geochemical codes.

3.3   Use of K_{ex} in Practice

Before proceeding to describe various sorption test cases for cation exchange calculations, we would like to briefly discuss and summarise the practical implications inherently contained in the expression for K_{ex} derived in the previous section.

First and foremost, for heterovalent exchange, K_{ex} is not a constant. Its value depends not only on what we might term system parameters: the CEC of the sorbent, the valences of the exchanging cations and their selectivity coefficient, K_C, but also on an experimentally variable parameter, the sorbent concentration, S. In using a code containing cation exchange it is important to bear in mind that whereas CEC, cation valences and K_C values are generally fixed in a certain system from experiment to experiment, the sorbent concentration may not be, and the K_{ex} input values to the code depend on all these factors. The implication is that for any particular experimental system, the calculated K_{ex} value is associated with a particular S value. The two values are linked to one another and cannot be separated. In other words, if a pair of K_{ex}, S values have been used to describe one set of cation exchange data, the same K_{ex} value cannot be used to model another set of experimental data measured at a different sorbent concentration if heterovalent exchange processes are taking place i.e. K_{ex} values are not normally transferable. This is obvious when K_{ex} is defined via a K_C value, but is not so evident when directly defined as in equation [17].

Particular examples of this often occur in pore water chemistry modelling studies in which cation exchange plays a significant role. Typically, the exchange parameters are determined from laboratory rock water interaction experiments and then used together with mineralogical and solubility data to calculate the equilibrium pore water composition for a "real case" where the sorbent concentration is often orders of magnitude larger. Potentially serious errors may therefore result if the K_{ex} values used in the calculations are not changed to correspond to the "real" S value.

The situation is somewhat different in the case where, for example, a cation exchange based model is being used to generate a non-linear sorption isotherm, or to calculate the sorption value for a given equilibrium radionuclide concentration. Here the sorbent concentration can be arbitrarily chosen, i.e. the results from such calculations are independent of the sorbent concentration used provided that the K_{ex} value corresponds to the chosen S value according to equation [23]. The reason that systems can be modelled in this way is that there is no need to fix any inventory conditions in these calculations. The inventories are adjusted by the geochemical code to correspond to the S value chosen and any other boundary conditions defined.

An important consequence of this approach is that it allows in situ field sorption values or isotherms to be calculated provided that relevant cation exchange and water chemistry data are available.

4   MODEL TESTING AND CODE VERIFICATION

In this section we wish to test code calculations against experimentally measured sorption data. We are checking the "correctness" of the formulation of cation exchange in the geochemical code plus the concepts developed for parameter value determination.

The key to being able to calculate the component of sorption due to cation exchange with such codes is, in our view, an understanding of the meaning of K_{ex} and how to set its input values.

4.1   Ni and Ca Sorption on Na-Montmorillonite

We have measured the sorption of Ni^{2+} and Ca^{2+} on Crook County Na-montmoril-lonite as a function of pH over a range of $NaClO_4$ concentrations, nuclide inventories, and at different sorbent concentrations (BAEYENS & BRADBURY, unpublished results). The data presented here are taken from these sorption studies for pH ranges where cation exchange was the major cation uptake mechanism.

Trace Ni^{2+} sorption experiments were carried out for $NaClO_4$ concentrations ranging from 0.1 to 0.003 M and at sorbent concentrations varying between 0.5 and 1.5 g litre^{-1}. The cation exchange sorption values (R_{CE}), for combinations of these experimental conditions, varied over approximately three orders of magnitude from ~100 to ~70,000 ml g^{-1}. These data are summarised in Table 1 and plotted as log R_{CE} versus log $NaClO_4$ concentrations in Figure 1. In all cases the Ni^{2+} fractional occupancies were less than 0.01.

Table 1:   Nickel R_{CE} and K_C data for Na-montmorillonite (BAEYENS & BRADBURY, unpublished results). Errors represent the spread of data from multiple measurements

Data Sets	Number of Measurements	$NaClO_4$ [M]	S [g litre^{-1}]	$^{Ni}R_{CE}$ [ml g^{-1}]	K_C (I = 0)
Ni (1)	17	0.1	1.5	90±15	3.4±0.5
Ni(2)	6	0.03	1.1	1100±200	3.3±0.6
Ni (3)	10	0.01	1.1	10000±1500	3.1±0.4
Ni (4a)	8	0.003	1.1	67500±9000	1.6±0.2
Ni (4b)	4	0.003	0.5	56000±6500	1.4±0.2

The selectivity coefficients, K_C, given in Table 1, were calculated from the sorption data using the equations derived in section 2. For $NaClO_4$ concentrations between 0.1 and 0.01 M a constant K_C value of 3.2 ± 0.6 was calculated. This compares well with the (limited) available literature values of 3.2 (MAES 1973) and 3.7 (MAES et al.

1976) measured at similar Na concentrations and Ni fractional occupancies up to 0.5. At the lowest Na concentration of 0.003 M (data set Ni(4a)), the calculated K_C value was a factor of two lower. This result was confirmed in a second set of measurements, Ni(4b). At the present time we have no explanation for these lower selectivity values.

Similar data sets for trace Ca^{2+} sorption measurements on Na-montmorillonite over an almost equally wide range of $NaClO_4$ and sorbent concentrations are summarised in Table 2 and log R_{CE} versus log $NaClO_4$ concentrations are plotted in Figure 2. For the five independently measured data sets, the corresponding K_C values, calculated from equation [7], show little variability and have a mean value of 4.4 ± 0.3. This value is in agreement with the literature data from VAN BLADEL et al. (1972), MAES & CREMERS (1977) and SPOSITO et al. (1983) for fractional ion occupancies less than 0.3.
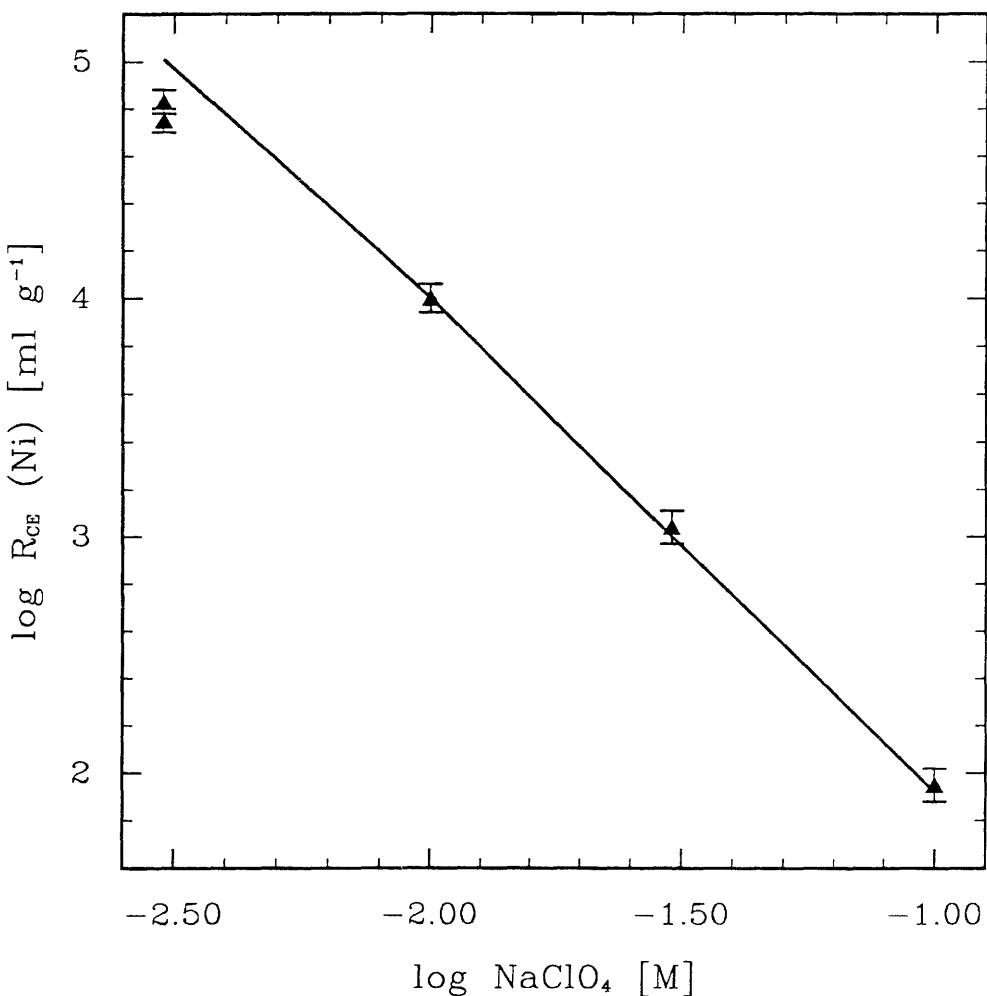

Figure 1:   Trace Ni^{2+} sorption on Na-montmorillonite as a function of $NaClO_4$ concentrations. The continuous line is calculated and the symbols are measured data.

The experimental data depicted in Figures 1 and 2 for the trace sorption of Ni^{2+} and Ca^{2+} respectively are independent of the sorbent concentration but very dependent on $NaClO_4$ concentrations. Such behaviour would be expected on the basis of a cation exchange mechanism and is described by equation 7 which can be reexpressed as:

$$\log {}^B R_{ce} = -2 \log Na + \log \left({}^B_{Na} K_c \cdot \frac{1}{2} \cdot CEC \cdot \frac{\gamma_B}{\gamma_{Na}^2} \right) \qquad [28]$$

where B is Ni^{2+} or Ca^{2+}.

Table 2: Calcium R_{CE} and K_C data for Na-montmorillonite (BAEYENS & BRADBURY, unpublished results). Errors represent the spread of data from multiple measurements

Data Sets	Number of Measurements	$NaClO_4$ [M]	S [g litre^{-1}]	CaR_{CE} [ml g^{-1}]	K_C (I = 0)
Ca (1)	3	0.267	1.73	10±2	3.9±0.5
Ca (2)	3	0.1	1.73	115±5	4.3±.02
Ca (3)	12	0.1	1.14	120±10	4.6±0.4
Ca (4)	3	0.032	1.05	1270±130	4.2±0.4
Ca (5)	3	0.01	1.00	13600±850	3.9±0.2

Provided that K_C values (Tables 1 and 2) and CEC data ($8.5 \pm 0.5 \times 10^{-4}$ equivalents g^{-1}; BAEYENS & BRADBURY, unpublished results) are available, K_{ex} values can be evaluated from equation [25] and used in the code to calculate the sorption by cation exchange of Ni^{2+} and Ca^{2+} depicted by the continuous lines in Figures 1 and 2 respectively.

Clearly, for the simple bi-ionic system presented here, it is not necessary to use a geochemical code incorporating cation exchange to calculate sorption. As mentioned previously, the point here is to test the code calculations for a well defined system for which experimental data and an analytical expression describing the cation exchange (equation 28) are available.

In more realistic multi-ionic systems simple analytical solutions describing cation exchange are not available. For example, even with the relatively limited data given above, it is possible, using the procedures outlined in sections 2 and 3, to make a prediction for Ni^{2+} sorption by cation exchange on montmorillonite as a function of Na^+ concentration and pH in a calcite saturated solution.
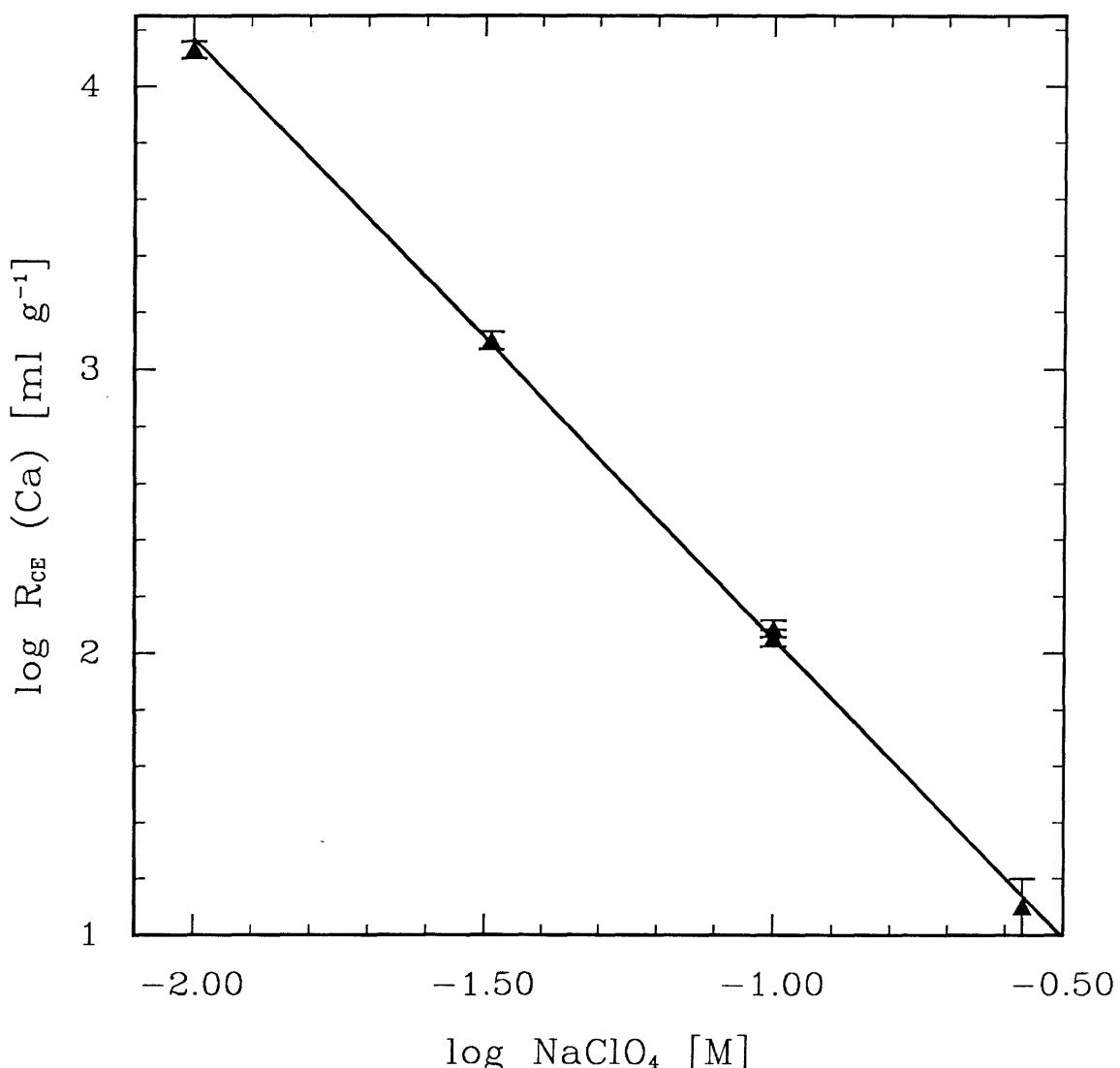
Figure 2:   Trace Ca^{2+} sorption on Na-montmorillonite as a function of $NaClO_4$ concentrations. The continuous line is calculated and the symbols are measured data

4.2   Sulphate and Ionic Strength Effects on Eu Sorption

In the second example a slightly more complicated test of the code was undertaken using data from MAES & CREMERS (1986). In this work the influence of ionic strength and sulphate concentration on the sorption of europium at trace concentrations on Na- and Mg-Camp Berteau montmorillonite was investigated. The measurements were carried out in nitrate/sulphate solutions at ionic strengths between 0.1 and 0.6 M at pH=3. In the presence of SO_4^{2-}, trivalent europium forms complexes which result in a decrease in sorption with increasing SO_4^{2-} concentrations. The experimental results of six different data sets are shown in Figures 3 and 4. Although each exchange system only involves two cations, as in the previous example,

trivalent-monovalent and trivalent-bivalent exchange, varying ionic strength and varying degrees of europium complexation need to be taken care of in the code in order to calculate the europium sorption.

The calculations were performed using a CEC of 10^{-3} equivalents g^{-1} (MAES & CREMERS 1986), a sorbent concentration of 1 g litre^{-1} and the aqueous stability constants given in Table 3.

Table 3: Stability constants for aqueous europium and magnesium species. (Data from SMITH & MARTELL 1976)

REACTION	log K
Eu^{3+} + SO_4^{2-} <=> $EuSO_4^+$	3.67
Eu^{3+} + $2SO_4^{2-}$ <=> $Eu(SO_4)_2^-$	5.41
Mg^{2+} + SO_4^{2-} <=> $MgSO_4$	2.37

A single K_{ex} value was fitted to each of the six individual data sets over the entire sulphate concentration range. K_c values were derived from K_{ex} values using equation [23]. These data are summarised in Table 4. An important point to make is that within each series of experiments the total normality was fixed. Because mixtures of 1-1, 1-2 and 2-2 background electrolytes were used, a fixed total normality leads to a variation in ionic strength. The range of these variations is also indicated in Table 4.

The calculated europium sorption as function of sulphate concentrations for Na- and Mg-montmorillonite are represented by the continuous lines in Figures 3 and 4 respectively. The agreement between the calculations and the experimental data is good. The calculated sorption values reflect very nicely the weaker dependency of Eu^{3+} sorption on sulphate concentration in the Mg system compared with the Na system, as measured experimentally. The explanation is that Mg forms ion pairs with sulphate, whereas Na^+ does not. Consequently, for the same total sulphate the free sulphate concentration is less in the Mg system. This leads to the formation of fewer europium sulphate complexes and therefore to a correspondingly smaller decrease in sorption.
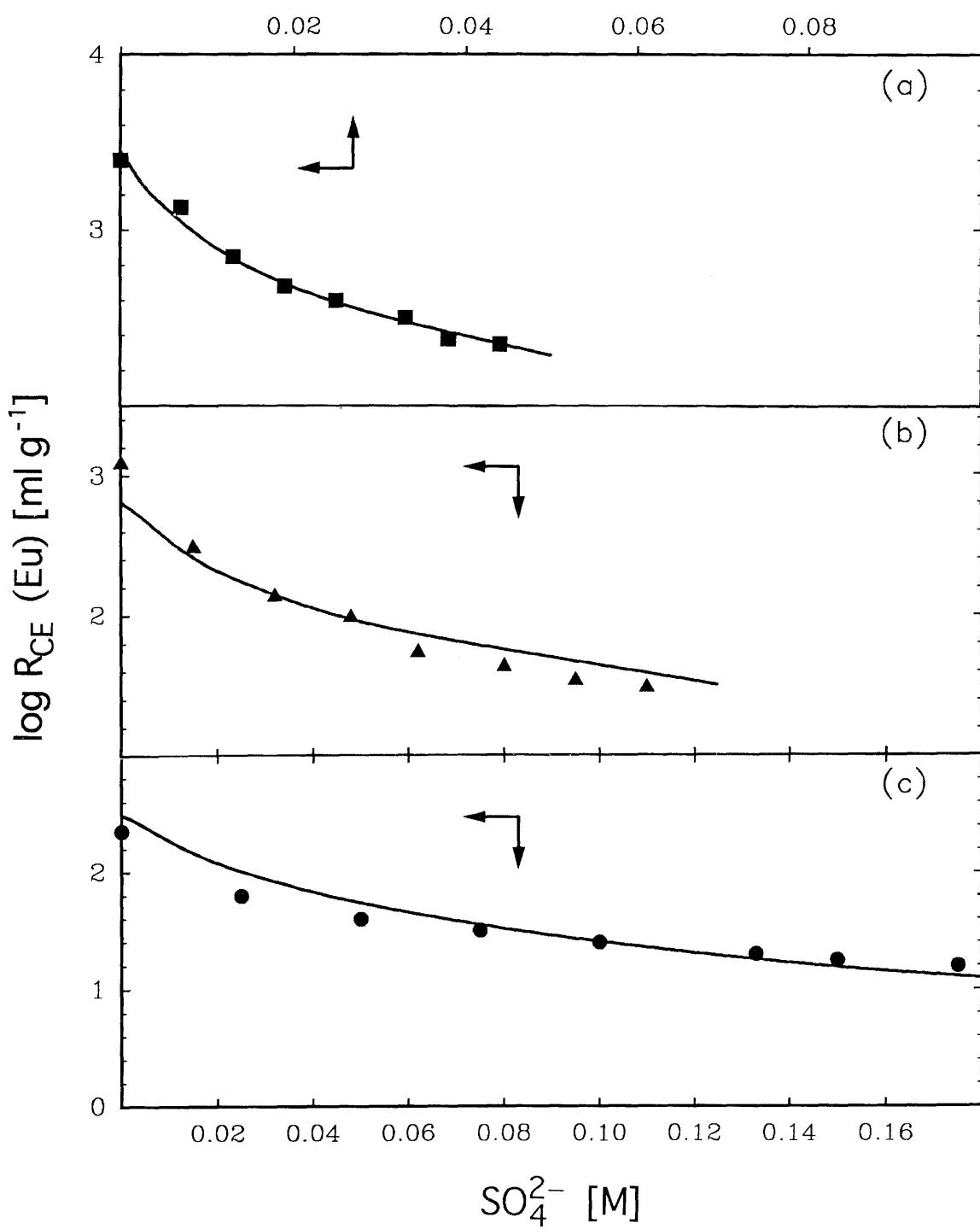
Figure 3:   Trace europium sorption on Na-montmorillonite as a function of sulphate
            concentration at total concentrations of: (a) 0.1 N (b) 0.25 N (c) 0.4 N
            (MAES & CREMERS 1986). Arrows indicate the appropriate scales.
   The continuous lines are calculated and the symbols are measured data.
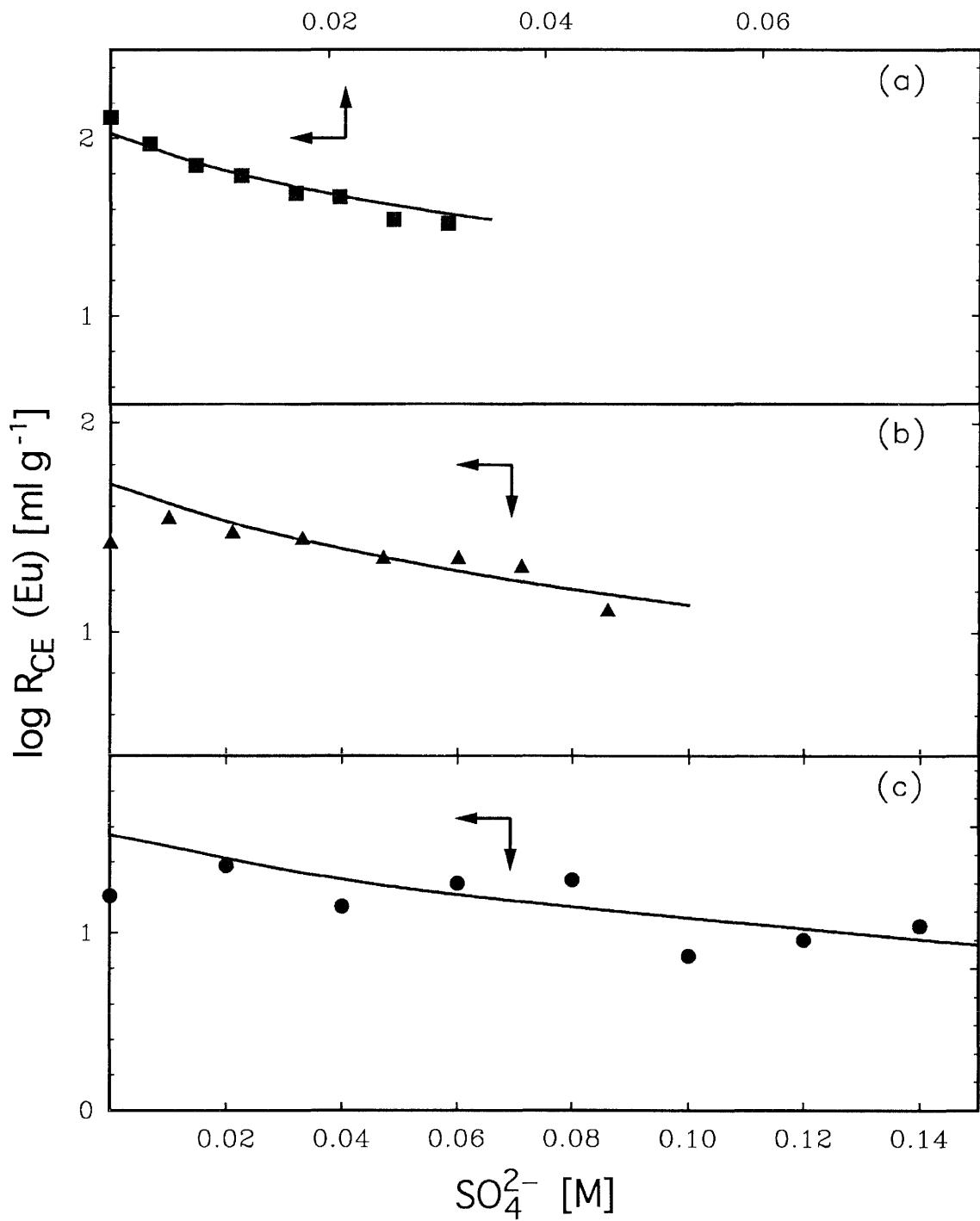
Figure 4: Trace europium sorption on Mg-montmorillonite as a function of sulphate concentration at total concentrations of: (a) 0.1 N (b) 0.25 N (c) 0.4 N (MAES & CREMERS 1986). Arrows indicate the appropriate scales.
The continuous lines are calculated and the symbols are measured data.

Table 4:   Summary of K_{ex} and K_c data for Eu^{3+} exchange with Na- and Mg-Camp Berteau montmorillonite

	Total Normality (N)	Ionic Strength (M)	log K_{ex}	log K_c
Na-mont.+ Eu^{3+}				
(a)	0.1	0.1 - 0.13	7.1	1.6
(b)	0.25	0.25 - 0.3	7.8	2.3
(c)	0.4	0.4 - 0.46	8.1	2.6
Mg-mont.+ Eu^{3+}				
(a)	0.1	0.15 - 0.12	4.8	1.9
(b)	0.25	0.38 - 0.24	5.4	2.5
(c)	0.4	0.6 - 0.3	5.7	2.8

The trend in the K_{ex}/K_c values is that they appear to increase with increasing ionic strength, though within limited ionic strength ranges they may be taken to be constant, see Table 4. Constant selectivity coefficients are only expected in systems which behave more or less ideally. As mentioned in section 3.1, lack of knowledge concerning surface activity coefficients leads to the adoption of a convention whereby they are set equal to unity. At high ionic strengths such an assumption may be invalid.

Also, there are major uncertainties associated with activity coefficients in high ionic strength solutions. The activity coefficients of trivalent ions begin to become uncertain in solutions with ionic strengths above 0.1 M and there can be significant differences between the values calculated by different methods. (In MINSURF the Davies method is used.) Both of these factors could lead to large uncertainties in the calculation of K_c values.

4.3   Non-Linear Sorption of Cs on Mylonite and Cs/Rb on Illite

In a third set of examples we wish to consider the non-linear sorption behaviour of Cs/Rb.

In some previous work (BRADBURY & BAEYENS 1992), we developed a two site cation exchange model to describe the non-linear sorption behaviour of Cs on mylonite in Grimsel groundwater (AKSOYOGLU et al. 1990; FRICK et al. 1992) at different potassium concentrations. The main sorbents in the system were mica minerals and the major cations in the groundwater were Na^+, K^+, Mg^{2+}, Ca^{2+} and Sr^{2+}. Each of these cations will have a fractional ion occupancy on the solid phase in accord with its selectivity coefficient .

The bivalent cations Mg^{2+}, Ca^{2+}, Sr^{2+} are chemically very similar, and their selectivity coefficients with respect to other cations in a wide variety of clay systems have been shown to be approximately the same (BRUGGENWERT & KAMPHORST 1982; BROUWER et al. 1983). On this basis we assumed that we could treat "the bivalent

cations" together, and describe their exchange behaviour with respect to Cs^+ with a single selectivity coefficient, $^{Cs}_BK^{PS}_C$. Separate equations were used for the exchange of Cs^+ with monovalent Na^+ and K^+. An analytical solution was derived for this set of exchange reactions which, together with selectivity coefficients from the literature, enabled us to describe the non-linear sorption of Cs^+. A summary of the data used is given in Table 5, and the fit of the analytical solution to the laboratory data for Cs sorption is shown in Figure 5a at two different K concentrations.

Table 5:   Selectivity coefficient values for modelling Cs sorption on mylonite (BRADBURY& BAEYENS 1992)

Type of sites	Site concentration [equivalents g^{-1}]	Selectivity coefficients
Frayed-edge sites	$6.5 \ 10^{-8}$	$^{Cs}_KK^{FES}_C = 3000$
Planar Sites	$1.3 \ 10^{-5}$	$^{Cs}_{Na}K^{PS}_C = 40$ $^{Cs}_BK^{PS}_C = 500$ $^{K}_{Na}K^{PS}_C = 5$

B = Mg + Ca + Sr.
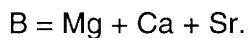
The code calculated values are shown in Figure 5b as individual points on the solid line representing the cesium isotherms produced from the analytical solution. The calculations were performed for three arbitrarily chosen sorbent concentrations, given in Table 6, together with the corresponding K_{ex} values.

Table 6:   Cation exchange equations and K_{ex} values (from equation [23]) used for the calculations shown in Figure 5b

REACTIONS	log K_{ex}		
	S = 1 g litre^{-1}	S = 20 g litre^{-1}	S = 500 g litre^{-1}
FES SITES			
K-MYL + Cs$^+$ = Cs-MYL + K$^+$	3.48	3.48	3.48
PLANAR SITES			
Na-MYL + Cs$^+$ = Cs-MYL + Na$^+$	1.6	1.6	1.6
B-MYL$_2$ + 2Cs$^+$ = 2Cs-MYL + B^{2+}	-1.89	-0.59	0.81
K-MYL + Cs$^+$ = Cs-MYL + K$^+$	0.7	0.7	0.7

MYL = mylonite; B^{2+} = Mg^{2+}+ Ca^{2+} + Sr^{2+}
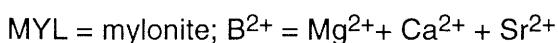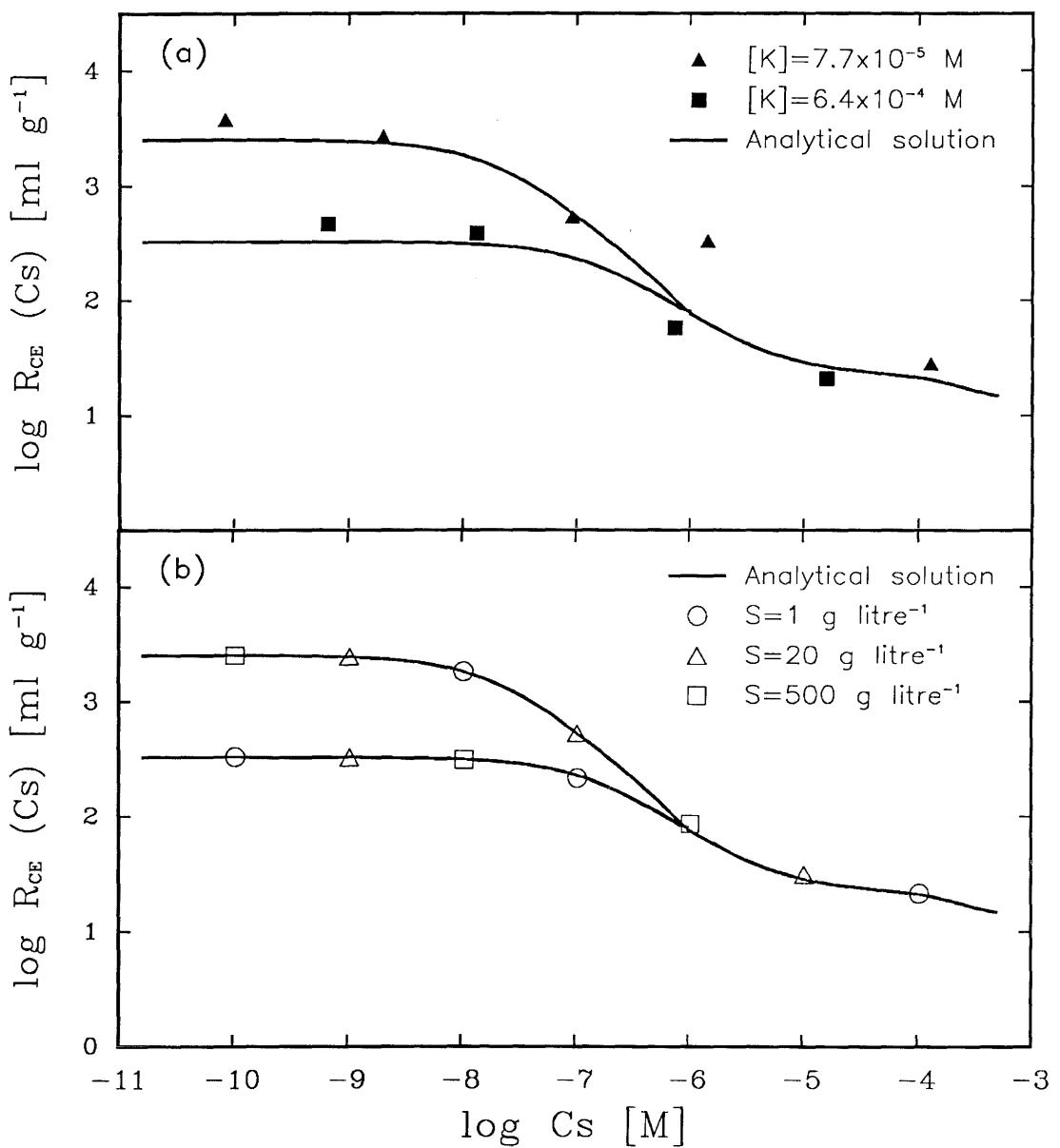
Figure 5:   (a) Experimental data (▲ , ■) for Cs sorption on mylonite in synthetic Grimsel groundwater at two potassium concentrations (AKSOYOGLU et al. 1990).

Continuous lines: Calculated from the analytical solution to the Cs sorption model (BRADBURY & BAEYENS 1992).

(b) Continuous lines: Calculated from the analytical solution to the Cs sorption model (BRADBURY & BAEYENS 1992).

Symbols: Points calculated from MINSURF for Cs sorption at different sorbent concentrations, S.

As can be seen, the calculated points lie exactly on the curve and the isotherm is independent of the relative quantities of solid and liquid considered.

As a further example we have taken the results of BROUWER et al. (1983). These authors measured the sorption of Cs^+ and Rb^+ on Ca^{2+}, Sr^{2+} and Ba^{2+} saturated illites as a function of Cs^+ and Rb^+ concentration. For a total concentration of 0.04 N they were able to fit their data with a 3 site model for which they gave selectivity coefficients and site capacities (see Table 1 in BROUWER et al. 1983). Using these site capacities and K_C values we have calculated with the code the Cs^+ and Rb^+ exchange isotherms. These are given by the continuous lines in Figure 6 and again the calculated non-linear isotherms fit the experimental measured data well.
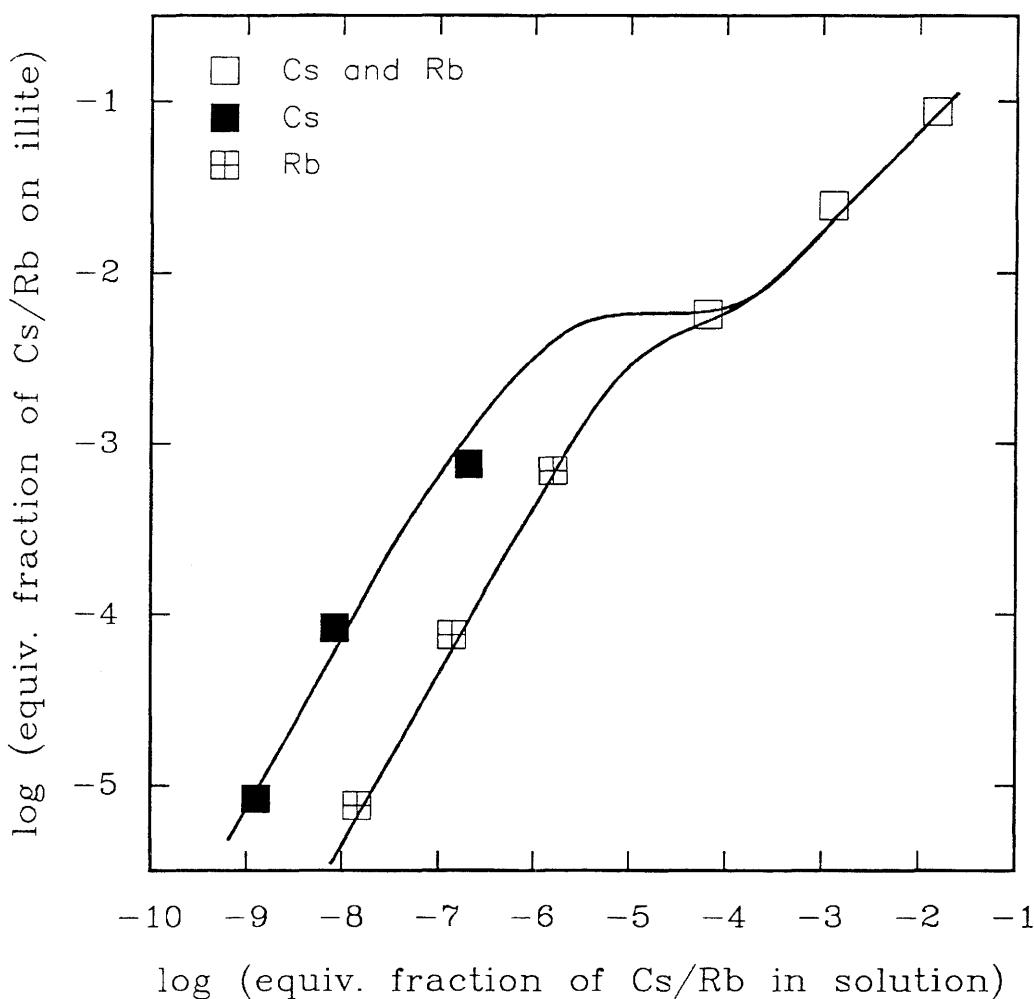

Figure 6:   Cesium and Rubidium exchange isotherms in Ca, Sr, and Ba saturated illites at a total concentration of 0.04 N (BROUWER et al. 1983). The solid lines are the calculated non-linear sorption isotherms.

5   SELECTIVITY COEFFICIENT DATA BASE FOR SORPTION

In the previous sections we have shown that it is relatively easy to introduce cation exchange reactions into geochemical/surface complexation codes such as MINSURF and to calculate sorption due to cation exchange. The relationship between the input exchange parameter required by the code, K_{ex}, and the corresponding constant K_C value, equation [23], was derived on the basis of the GAINES & THOMAS (1953) definition of selectivity coefficients.

A potential limitation to this approach is that selectivity coefficients are assumed to be constants. For radionuclides at trace levels in natural systems, where the fractional ion occupancies on the exchanger are fixed by a constant water composition of moderate ionic strength, such an assumption is justified. Under more severe conditions such as high ionic strengths and for fractional ion occupancies of the sorbing radionuclides exceeding ~0.3, the concept of a constant K_C may break down or only be valid over a narrow range of conditions.

With the above limitations in mind, we would propose that now would be an opportune time to set up a data base for cation exchange consisting of selectivity coefficients and cation exchange capacities for different minerals and mineral assemblages. Since equation [23] is so simple to use in practice (see sections 3 and 4) we would further suggest that the Gaines and Thomas definition be used for the selectivity coefficients in the data base and that they are calculated with Na as the reference cation.

A data base of this sort would be used in conjunction with codes of the type previously described, to calculate radionuclide sorption in geochemical systems, taking into account simultaneously aqueous phase speciation (inorganic and organic ligands) and competitive effects on sorption from other cations. Such an approach would not only be applicable to the interpretation of sorption experiments, but would also find a potentially important application in radioactive waste management performance assessment studies. The basic concept in this context would be to generate classical sorption data bases (individual R_d values/sorption isotherms) for use in transport codes from a source data base consisting of sorption mechanism specific parameters. The generated sorption data base would therefore be system specific. Instead of having to justify and defend individually selected sorption values, the quality and robustness of the calculated values would rest on concepts, models, codes and data which had already been experimentally tested.

6   SUMMARY

The ability to include exchange phenomena in modelling studies on sorption is important, particularly in natural systems. Here, sorption may often result from a combination of different mechanisms e.g. surface complexation and cation exchange, and it is clearly necessary to be able to model both simultaneously.

The key input parameters required by codes for calculating sorption by cation exchange are the exchange coefficients, K_{ex}, expressed on a molar scale. The approach chosen here to obtain values for these parameters was via selectivity coefficients, K_C, where exchanged quantities on the solid phase are expressed as equivalent fractional cation occupancies (GAINES & THOMAS 1953).

A simple, general relation between K_C and K_{ex} has been derived. This relationship clearly shows that the value of K_{ex} is dependent on the cation exchange capacity, the valences of the exchanging cations, and the sorbent concentration. The conclusion was that K_{ex} can only be regarded as being constant in the special case of homovalent exchange.

Cation exchange has been incorporated into the geochemical/surface complexation code MINSURF. The code, which calculates with the derived expression for K_{ex}, (equation [23]), has been successfully checked against a number of distinct sets of cation exchange sorption data where analytical solutions were available which fitted the experimental results. MINSURF is capable of calculating the total sorption due to both cation exchange and surface complexation.

Finally, a proposal was made to set up a data base of selectivity coefficients. Such a data base would form part of a more general one consisting of sorption mechanism specific parameters. These would be used in conjunction with geochemical/sorption codes of the sort mentioned here to model and predict sorption.

7   ACKNOWLEDGEMENTS

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