Sorption mechanism of Sr(II) in natural bentonite

V. Garrido
M. Martinez
J. de Pablo
T. E. Eriksen
Royal Institute of Technology, Nuclear Chemistry Department, S-100 44 Stockholm 70, Sweden
L. Duro
QuantiSci S.L., Parc Tecnolòlgic del Vallès, 08290 Cerdanyola del J. Bruno
Vallès. Spain

Bentonite clay has been proposed as a buffer material in the final disposal concepts for spent nuclear fuel and other hazardous materials. As a consequence, a lot of work has been devoted to study the metal sorption capacity, particularly for sybthetic montmorillonites. In general, the sorption capacity has been studied in terms of K_d distribution coefficients, and interpreted as a cation-exchange process between the intterlayer cations metal ions such as Caesium(I) and Strontium(II) [1]. In the case of Strontium, K_d values reported in the literature vary from 0.006 to 2.14 m³ kg⁻¹. A more realistic picture of the overall process should include the interaction of the metal with OH-groups of the mineral surface [2], although the first hydrolisis reaction has a low equilibrium constant (log $\beta_1 = 0.86$).

In this work, we have studied the sorption of Strontium (II) on natural bentonite, data modelling has been carried out by considering ion-exchange and surface complexation processes.

Materials

The natural bentonite used in this work was the American Colloid Co. type MX-80 (Wyoming Nabentonite). Characterisation of this kind of mineral has been reported by Kruse (3), being montmorrillonite 67.2%, kaolinite 7.1%, illite 3.7%, feldspars 8.8%, quartz 10% and carbonate 2%. The whole clay content (2µm particle size) is approximately 85%.

All chemicals were of analytical grade. The ⁸⁵Sr isotope was purchased from DuPont Scandinavia as Strontium chloride. Tracer solutions were prepared by adding small aliquots of the active stock solution to the solutions used in the experiments. The Sr²⁺ concentration was 10⁻⁶ mol dm⁻³.

The ionic medium was prepared from sodium chloride stock solution in Millipore deionized, triple distilled water (10, 50, 100, 500 and 1000 mM of NaCl).

Procedure

The experiments were carried out at ambient temperature. Batch experiments were performed by shaking 110 mg of the solid and 20 cm³ of the aqueous phase. The pH measurements were made with a Metrohm 632 pH meter and a GK 2331 combined glass/reference electrode.

The bentonite was pre-treated at 110° C in order to remove the initial water content. Sr concentration was obtained by measuring the γ -activity of the solutions after at least one day shaking, to ensure equilibrium.

Results

Results are shown in Fig. 1. There are two striking features: 1) the pH dependence of the Sr(II) sorption and 2) the inverse relationship between dissolved Na(I) and Sr(II) concentrations.

From the distribution values obtained at pH<4, it is possible to estimate the stoichiometry of the Na/SrX exchange reaction.

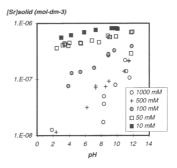


Fig. 1. Experimental results obtained from Sr sorption onto MX-80 bentonite.

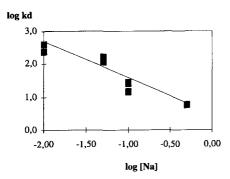


Fig. 2. Plot of log K_d vs log[Na] for the data obtained at acidic pH.

From the plot of $\log K_d$ versus $\log [Na]$ with a slope = 1.1 (see Fig. 2), considering the whole ionic strength the exchange reaction can be best described by the equilibrium:

$$NaX + Sr^{2+} = SrX^+ + Na^+$$

Data treatment

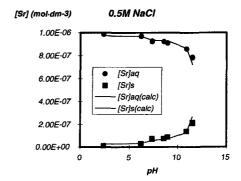
The data have been modelled by using an approach similar to the one used by Wieland *et al.* [4] and Wanner *et al.* [5]. The surface complexation constants have been determined by a trial and error procedure using the speciation code PHREEQC [6].

The best fitting has been obtained with the reactions and equilibrium constants collected in Table 1.

In Fig. 3a, as an example, modelling is compared to experimental data at ionic strength of 0.5. Good agreement between experimental results and modelling has been obtained for high ionic strength (0.1, 0.5 and 1). While, at low ionic strength (0.01 and 0.05) experimental Strontium sorption is larger than that predicted by the model (see Fig. 3b). Further work will be focused on analysing these discrepancies, which could be related to the contribution of bentonite accessory minerals to the overall sorption process.

TABLE 1. Reactions and equilibrium constants used in the modelling

$NaX + Sr^{2+} = SrX^+ + Na^+$	0.9
>SOH + Na ⁺ = $>$ SONa + H ⁺	-6.2
$>SOH + Sr^{2+} = >SOSr^{+} + H^{+}$	-3.6
>SOH + Sr ²⁺ + H ₂ O = $>$ SOSrOH + 2 H ⁺	-14.3



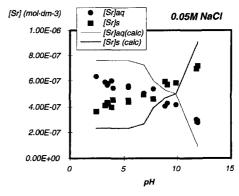


Fig. 3. Comparison between the data and the model for experiments performed (a) 0.5 and (b) 0.05 M NaCl as ionic media. Symbols stand for experimental data and solid lines for the model.

Acknowledgements

Thanks are due to European Commission (FI4W-CT95-0012) and CICYT (AMB96-1101-CO2-01) (Spain) for financial support.

References

Liang, T.J., Hsu, C.N. and Liou, D.C. (1993) Appl. Radiation Isotopes, 44, 1205-8.

Dzombak, D.A., Morel, F.M. (1990) Surface complexation modelling. Hydrous Ferric Oxide, John Wiley & Sons, 299–315.

Kruse, K. (1992) Die Adsorption von Schwermetallen an verschiedene Tone. Diss. ETH Nr.9737

Wieland, E., Wanner, H., Albinsson, Y., Wersin, P. and Karnland, O. (1995) Report SKB-95-26, 64 p.

Wanner, H., Wersin, P. and Sierro, N. (1992), Report SKB 92-37, 28 p.

Parkhust, C., (1995) USGS Water Resource Investigation, Report 95-4227, 143 p.