

Cation diffusion in compacted bentonite

M. Molera
T. E. Eriksen

Royal Institute of Technology, Department of Chemistry, Nuclear
Chemistry, S-100 44 Stockholm 70, Norway

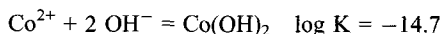
Metals that form strong complexes with OH^- in water generally bind strongly to hydroxyl groups on mineral surfaces.

The first hydrolysis reaction and equilibrium constants for Sr^{2+} and Co^{2+} are given by



Co^{2+} may therefore be expected to be more strongly sorbed than Sr^{2+} by reactions with OH^- groups on mineral surfaces (1).

At high pH there is a solubility constraint due to the formation of $\text{Co}(\text{OH})_2$.



The sorption of Co^{2+} on $\alpha\text{-SiO}_2$, kaolinite (2) and $\gamma\text{-Al}_2\text{O}_3$, TiO_2 (3) and fissure fillings from granitic rock (4) has been extensively studied. Typically cobalt is strongly sorbed on oxide minerals (5), increasing with increasing pH from almost zero to nearly complete (>90%) removal from water within a narrow pH range.

Sorption and diffusion experiments have been carried out with bentonite saturated with perchlorate solution and Allard, Nask and Äspö groundwater solutions.

Materials

The bentonite used in this investigation is the American Colloid Co. type MX-80 (Wyoming Na-bentonite). The bentonite (MX-80) has a clay content (< $2\mu\text{m}$) of approximately 85% and a montmorillonite content of 80-90 wt.% of this fraction. The remaining

silt fractions contains quartz, feldspar and some micas, sulphides and oxides. Perchlorate and three different synthetic groundwaters solutions (Allard, Nask and Äspö) were used in the diffusion experiments.

Diffusion experiments

The diffusion cell, made of PEEK, is shown schematically in Fig. 1. Bentonite was statistically compacted in the diffusion cylinder (internal diameter 10 mm and 5 mm long) to a dry density of $1,8 \text{ kg dm}^{-3}$. The diffusion cylinder and endplates, containing in and outlet channels fitted with metallic filters (0,81 mm thick), were assembled and the clay equilibrated with the aqueous solution for at least three weeks by pumping solution from reservoirs through the end plate channels, see Fig. 2. After water saturation a small volume of diffusant solution, containing the tracer and inactive carrier required to give the chosen diffusant concentration, was added to the reservoir at the inlet side of the diffusion cell. The activity of the solutions in inlet and outlet reservoirs were monitored by γ -spectrometry on small sample volumes using a germanium detector and multi-channel analyser. At the end of the experiments the diffusion cell was dismantled and the bentonite sliced into thin sections. Each section was weighed and the activity measured by γ -counting.

The diffusion properties of the filters were determined in separate diffusion experiments, using a package of five filters, and the filter porosity was measured by weighing dry and water saturated filters.

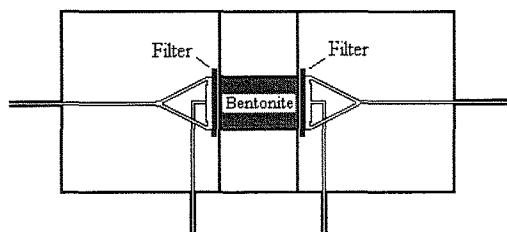


FIG. 1. Schematic drawing of diffusion cell.

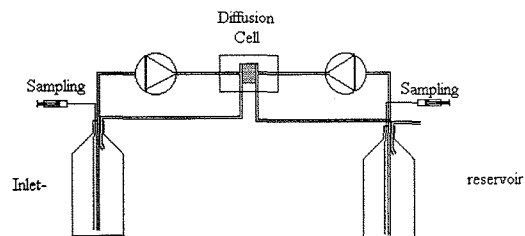


FIG. 2. Arrangement of through diffusion experiments.

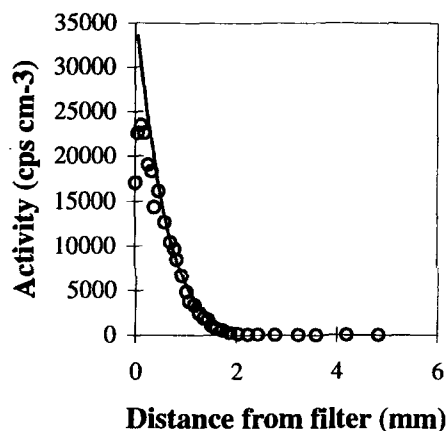


FIG. 3. Simulated diffusion profile and experimental data plotted as activity g^{-1} vs. distance (mm) from inlet filter. Äspö solution, $D_a=2E-9\text{cm}^2\text{s}^{-1}$, $K_d=2000\text{cm}^3\text{g}^{-1}$.

Sorption

Sorption was measured in batch experiments with 0.1 g bentonite and 20 cm^3 spiked solutions. The experiments were carried out at different pH and constant ClO_4^- concentration.

Data evaluation

The computer code ANADIFF (6) has been used to simulate the activity distribution in the compacted bentonite and the end of the diffusion experiments.

Experimental results

Diffusion profiles in compacted bentonite saturated with Allard, NASK, Äspö ($t=21.1$ days) and 0.1M perchlorate ($t=16.7$ days) solutions were obtained. Simulated activity distribution curves were fitted by varying the apparent diffusivity D_a , and the distribution coefficient K_d , see Fig. 3.

The diffusion and sorption coefficients obtained by simulation of the activity profiles are given in Table 1.

The pH dependence of cobalt sorption in the perchlorate/bentonite system and the sharp increase in sorption over a narrow pH range is to be expected for cations sorbed by surface complexation. The distribution coefficients obtained by simulation of the diffusion profiles are in good agreement with the batch sorption data.

Discussion

In earlier diffusion experiments with Sr^{2+} and Cs^+ the

TABLE 1. Diffusion and sorption coefficients from computer simulations (dry density 1.8gcm^{-3})

Solution	pH	D_a (cm^2s^{-1})	K_d (cm^3g^{-1})
Allard	8.6	n.e.	n.e.
NASK	7.7–7.8	1.5×10^{-9}	1500
Äsp	7.8–8	2.0×10^{-9}	2000
0.1 M ClO_4^-	5.6–6	8.0×10^{-10}	1000

pore water diffusivities were found to be 3×10^{-6} and $8 \times 10^{-6}\text{cm}^2\text{s}^{-1}$ respectively. Assuming the formation factor to be the same (i.e. the same diffusion path) for the three cations, the pore water diffusion coefficient for Co^{2+} (having nearly the same diffusivity as Sr^{2+} in water) should be approximately $3 \times 10^{-6}\text{cm}^2\text{s}^{-1}$.

The apparent diffusion coefficient for Co^{2+} should, using the simple porous media model with diffusion in the pore water only and K_d 2000–1000 cm^3g^{-1} , be $(0.8-1.7)10^{-9}\text{cm}^2\text{s}^{-1}$ in bentonite with dry density 1.8gcm^{-3} .

We have as yet not been able to properly fit the diffusion profile for the Allard solution/bentonite system. The experiment was carried out with 10^{-7} M cobalt solution and solubility should not, according to the solubility data, be a problem. The $\text{Co}^{2+}/\text{CoOH}^+$ hydrolysis equilibrium may, however, have an effect on the pore water diffusivity.

The results from experiments in progress will give more information on the effect of hydration and hydrolysis on the sorption by ion exchange and surface complexation processes.

References

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