

SORPTION, DESORPTION, AND ISOTOPE EXCHANGE OF CESIUM (10^{-9} - 10^{-3} M) ON CHLORITE

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Abstract—Batch cation-exchange experiments were performed on chlorite, using synthetic ground water containing cesium in the concentration range 10^{-9} - 10^{-3} M. The sorption behavior was complex; with increasing Cs concentration, the distribution ratio of Cs decreased at first, but passed through a pronounced maximum at high Cs loadings. The desorption data differed from the sorption data only by a shift towards larger distribution ratios in the region of the maximum. The distribution ratios for isotope exchange were even larger, but varied less with Cs loadings. Similar results were obtained for KCl-treated chlorite; however, grinding or acid-treatment of the chlorite considerably altered its behavior, the absence of the maximum being the most striking change. Most of the effects at higher Cs loadings can be explained by postulating structural changes induced by the sorption of Cs.

Key Words—Acid treatment, Cation exchange, Cesium, Chlorite, Isotope exchange, Sorption.

INTRODUCTION

The plans of many countries to store nuclear wastes in geologic formations have led to a recent revival of sorption studies for radionuclides on a variety of rocks and minerals. Radionuclide sorption in geologic media may retard migration to the biosphere and the food chain. The understanding of sorption and desorption of long-lived fission products and actinide elements is, therefore, essential. Due to long half-lives ($\sim 10^6$ yr for ^{135}Cs , 30 yr for ^{137}Cs) and high solubilities, isotopes of Cs are among the most hazardous nuclides. The chemistry of Cs is simple and suitable for an investigation of complex sorption processes in nature. Thus, the environmental behavior of Cs has been studied extensively.

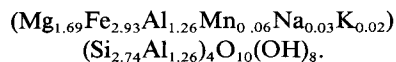
Glacio-fluvial sediments that cover large areas of the alpine countries contain shallow ground-water resources that are extensively used. These formations represent the final barrier to radionuclide migration from potential disposal sites before they reach the biosphere. The content of illite and chlorite in these formations governs the sorption of Cs. Whereas the sorption of Cs by illite has been studied by various authors (e.g., Jacobs and Tamura, 1961; Gaudette *et al.*, 1966; Brouwer *et al.*, 1983), a thorough investigation of Cs sorption on chlorite is, to our knowledge, presented here for the first time. Chlorite is also common in cracks and fractures of granite formations, which in many areas may be selected for the final storage of radioactive wastes.

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EXPERIMENTAL

Chlorite

Chlorite was collected from a fracture in a granite at Grimsel, Switzerland. Passing the raw material through a 40- μm sieve yielded almost pure chlorite ($< 40 \mu\text{m}$), as was judged from the X-ray powder diffraction pattern in Figure 1. Its chemical formula was calculated from chemical and microprobe analysis to be:



Synthetic ground water

Synthetic ground water of the following composition (in meq/liter) was used in this work: Ca^{2+} , 4.50; Mg^{2+} , 1.69; Na^+ , 0.67; K^+ , 0.08; SO_4^{2-} , 0.57; Cl^- , 0.74; NO_3^- , 5.21; alkalinity, 0.42. This composition is typical of shallow ground waters in calcite-rich aquifers; however, bicarbonate was largely replaced by nitrate in order to be able to work at the atmospheric pressure of CO_2 . The synthetic ground water was slightly undersaturated with respect to calcite. The pH was 7.8.

Procedure

The chlorite (50-200 mg) was weighed into thoroughly washed, 40-ml, closed polyallomer centrifuge tubes. The solid material remained within the centrifuge tube throughout the sequence of: (1) pretreatment, (2) sorption, and (3) desorption or isotope exchange. At the beginning of each step, 20 ml of synthetic ground water was added to the sample. The relatively coarse, $< 40\text{-}\mu\text{m}$ chlorite was rotated end-over-end at 1 rpm to avoid abrasion, whereas the powdered chlorite ($< 2 \mu\text{m}$) was shaken on a mechanical shaker. At the end

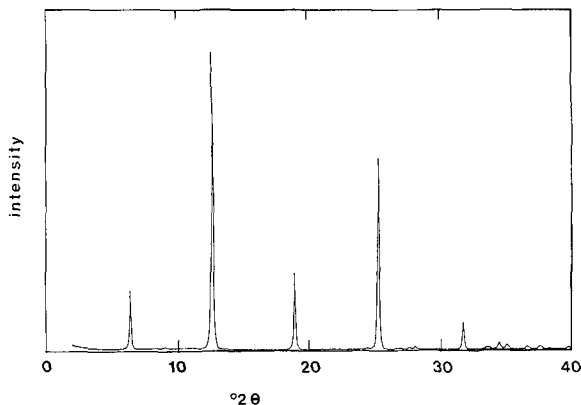


Figure 1. X-ray powder diffractogram of the untreated chlorite (CuK α radiation).

of each step the samples were centrifuged at 12,000 rpm in a swing-out head of a cooling centrifuge. After removal of the solution, a small amount (0.1–0.5 ml) remained in the centrifuge tube and was determined accurately by weighing. ^{137}Cs used as tracer, was measured by means of a Ge(Li) gamma-spectrometer, using 5-ml aliquots of the solutions. For low distribution ratios, the accuracy was increased by counting the radioactivity remaining in the centrifuge tubes.

In the pretreatment step the chlorite was equilibrated with the synthetic ground water. Five half-day treatments were followed by three treatments of 2–5 days each. After each treatment the phases were separated and 20 ml of new solution added. The concentrations of the major cations and the pH changed only slightly during pretreatment.

At the beginning of the sorption step, synthetic ground water containing Cs labeled with ^{137}Cs was added to the samples. Cs concentrations between 4×10^{-9} and 1×10^{-3} M were used. The sorption time was 7 or 28 days. In the desorption steps, which were of 7 or 14 days duration, Cs-free synthetic ground water was used. The results for the sorption or desorption experiments of different duration agreed, indicating that equilibrium was reached. The data presented in this work are mean values of 3–4 samples.

For the investigation of the isotope exchange, 21, 150-mg samples of the pretreated chlorite were exposed for 7 days to synthetic ground water containing 1.6×10^{-8} M CsCl labeled with ^{137}Cs . After this step, the solid phase was exposed for 7 days to synthetic ground water containing unlabeled CsCl in the concentration range of 10^{-9} to 10^{-3} M. The experiments were conducted in triplicate. The distribution ratio for the Cs that had been sorbed during the sorption step was obtained from radioactivity measurements. The Cs loadings of the chlorite at the end of the isotope exchange step were estimated from the total Cs inventory using the sorption curve of Figure 2.

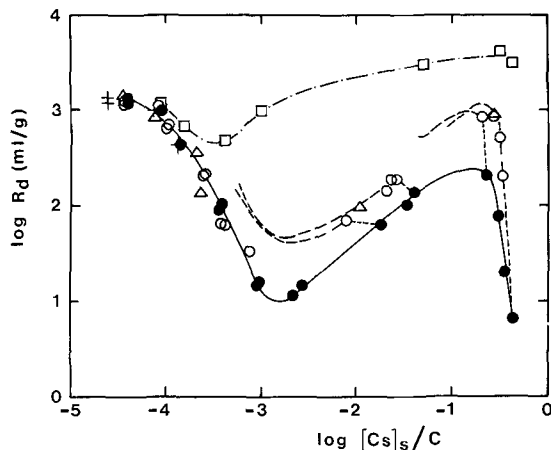


Figure 2. Sorption, desorption, and isotope exchange of Cs on a natural (<40 μm) chlorite. Solid circles = sorption; open circles = 1st desorption; triangles = 2nd desorption; dashed lines = multiple desorption (as many as 14 steps); squares = isotope exchange; crosses = sorptions, $[\text{Cs}]_s^0$ not taken into account. Standard deviation of $R_d < 10\%$.

Calculation of concentrations and distribution ratios

Assuming a constant specific activity for Cs during sorption and desorption, the following formulae apply:

$$R_{d,n} = \frac{[\text{Cs}]_{s,n}}{[\text{Cs}]_{\text{aq},n}} = \frac{A_{s,n}}{A_{\text{aq},n}} \quad (1)$$

$$[\text{Cs}]_{s,n} = A_{s,n} \cdot \frac{[\text{Cs}]_{\text{aq}}^0}{A^0} \quad (2)$$

$R_{d,n}$ is the distribution ratio for Cs at the end of step n ; $[\text{Cs}]_{s,n}$, the Cs concentration in the chlorite (meq/g); $[\text{Cs}]_{\text{aq},n}$, the Cs concentration in the solution (M); $A_{s,n}$, the radioactivity per gram of chlorite; and $A_{\text{aq},n}$, the radioactivity per milliliter of solution. A^0 is the radioactivity per milliliter and $[\text{Cs}]^0$ the concentration of cesium in the solution added at the beginning of the sorption step. $A_{s,n}$ is given by

$$A_{s,n} = A_{s,n-1} + \frac{1}{w} (A_{\text{aq},n-1} \cdot \Delta V_{n-1} - A_{\text{aq},n} \cdot (V_n + \Delta V_{n-1})), \quad (3)$$

where w is the weight of solid material present in the sample, V_n is the amount of solution added at the beginning of step n , ΔV_n is the amount of solution remaining in the centrifuge tube at the end of step n , and n denotes the position in the sequence sorption, 1st desorption, 2nd desorption, etc. $A_{s,n}$ at the end of the sorption step was obtained by inserting $A_{s,n-1} = V_n \cdot A^0/w$ and $A_{\text{aq},n-1} = 0$ into Eq. (3), or from measuring the radioactivity of the chlorite.

For the multiple desorption experiments the calcu-

lations were performed in the reverse sequence using the following equation:

$$A_{s,n} = A_{s,n+1} + \frac{1}{w} (A_{aq,n+1} \cdot (V_{n+1} + \Delta V_n) - A_{aq,n} \cdot \Delta V_n). \quad (4)$$

At the end of the experiment the radioactivity in the chlorite was determined directly.

If the concentration of exchangeable Cs present in the chlorite at the beginning of the sorption step ($[Cs]_s^0$) was not negligible, the Cs concentrations in the liquid and solid phases had to be multiplied by the following correction factor:

$$f = \frac{[Cs]_s^0 \cdot w}{[Cs]_s^0 \cdot V} + 1,$$

where V is the volume of solution added at the beginning of the sorption step. $[Cs]_s^0$ was estimated by neutron activation analysis from the Cs concentrations in the solutions of the last pretreatment. The values for $[Cs]_s^0$ were $\sim 3 \times 10^{-7}$ meq/g for both the $<40\text{-}\mu\text{m}$, and the ground ($<2\text{-}\mu\text{m}$) chlorites, and 3×10^{-8} meq/g for the HCl-treated, $<40\text{-}\mu\text{m}$ chlorite. The results of this investigation (Figures 2–4) include the contribution of $[Cs]_s^0$, unless otherwise stated. Furthermore, the fractional loading of the clay minerals $[Cs]_s/C$ instead of the Cs concentrations $[Cs]_s$ has been used throughout this paper. C is the cation-exchange capacity (meq/g) of the chlorites. It was measured by the Na-saturation procedure of Chapman (1965) which was modified for small samples using ^{22}Na . The following values were obtained for C : chlorite ($<40\text{ }\mu\text{m}$) = 0.0145; chlorite (ground, $<2\text{ }\mu\text{m}$) = 0.38; chlorite (HCl-treated, $<40\text{ }\mu\text{m}$) = 0.009 meq/g.

RESULTS AND DISCUSSION

The results of the sorption, desorption, and isotope exchange studies of Cs on chlorite ($<40\text{ }\mu\text{m}$) are shown in Figure 2. The distribution ratio for sorption decreased from 1000 to 10 ml/g up to a fractional loading ($[Cs]_s/C$) of $<10^{-3}$, meaning that energetically less favorable sites became involved with increasing Cs concentration. At Cs loadings $>10^{-3}$, the distribution ratio increased to a maximum and decreased very sharply at loadings $>10^{-1}$. This sorption behavior can be explained by structural changes. Jacobs and Tamura (1961), Jacobs (1963), and Tamura (1964) found similar maxima for the sorption of Cs on hydrobiotite, an interstratified mica vermiculite consisting of $\sim 50\%$ of each component. They explained this sorption maximum by the collapse of the $14\text{-}\text{\AA}$ vermiculite layers to $10\text{ }\text{\AA}$. The sorption behavior of chlorite at Cs loadings $>10^{-3}$ suggests that a small fraction of the interlayers in this mineral has a vermiculite-like character. An amount of $<2\%$ for this fraction can be estimated from the cation-exchange capacities of the chlorite (0.014

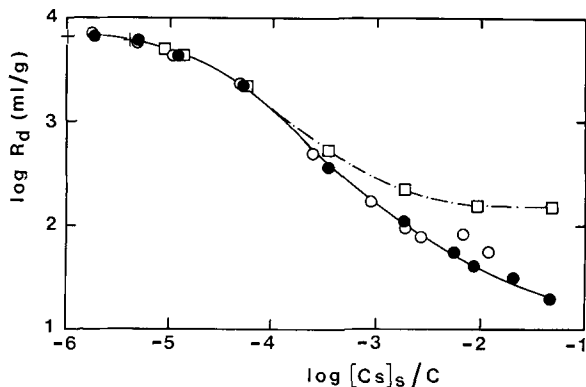


Figure 3. Sorption, desorption, and isotope exchange of Cs on chlorite after grinding to $<2\text{ }\mu\text{m}$. Solid circles = sorption; open circles = desorption; squares = isotope exchange; crosses = sorption, $[Cs]_s^0$ not taken into account. Standard deviation of $R_d < 10\%$.

meq/g) and of vermiculite (>0.7 meq/g; Jacobs, 1963; Grim, 1968). XRD did not reveal $10\text{-}\text{\AA}$ structures in the chlorite after Cs sorption, probably due to too low a content. If such vermiculite-like interlayers collapsed, sites having higher sorption energies were probably created, thereby increasing the distribution ratio until a maximum was reached at the end of this process. Towards saturation of the chlorite with Cs the distribution ratio decreased steeply.

The desorption data agree with those for sorption at the lower fractional Cs loadings ($<10^{-3}$), suggesting equilibrium conditions. At the higher Cs loadings the desorption was displaced to higher distribution ratios; however, the shape of the sorption curve was preserved in desorption, as demonstrated by the data of multiple desorption experiments (Figure 2). Thus, the desorption in the region of the sorption maximum was retarded. This observation is in agreement with the proposed collapse that would bury Cs within the structure and hinder its desorption.

The isotope-exchange behavior of Cs on chlorite (Figure 2) can also be explained by layer collapse. For complete isotope exchange, sorption and isotope exchange curves should coincide. Indeed, sorption and isotope exchange data nearly agreed at fractional Cs loadings $<10^{-4}$. At higher fractional loadings, however, the isotope-exchange curve deviated drastically from the sorption curve, demonstrating that only a small fraction of the labeled Cs had exchanged. The labeled Cs was only moderately accessible because it was apparently buried within interlayers that collapsed at the beginning of the isotope-exchange step due to sorption of unlabeled Cs. Cesium concentrations in the exchange solutions as low as 10^{-7} M apparently initiated the collapse. Such exchange experiments are, thus, sensitive tools for the detection of structural changes.

Potassium-treated chlorite showed a sorption be-

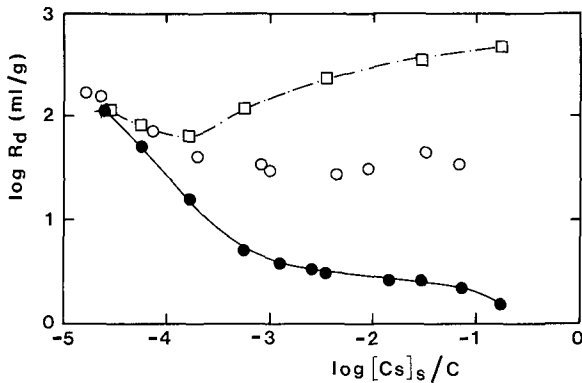


Figure 4. Sorption, desorption, and isotope exchange of Cs on chlorite after treatment with 1 M HCl. Solid circles = sorption; open circles = desorption; squares = isotope exchange; cross = sorption, $[Cs]_s$ not taken into account. Standard deviation of $R_d < 10\%$.

havior close to that of untreated chlorite. On the other hand, Jacobs and Tamura (1961), Jacobs (1963), and Tamura (1964) found no maximum at high Cs loadings for the K-treated hydrobiotite in contrast to the natural or Na-treated material. These authors explained this change in the sorption behavior by a collapse of the vermiculite layers, induced during the K-treatment. The different behaviors of hydrobiotite and chlorite after K-treatment indicate the absence of extended vermiculite layers in the chlorite. In this mineral the layer collapse may be limited to those parts of the interlayers adjacent to the surfaces.

The sorption, desorption, and isotope exchange behavior of the chlorite changed markedly if the original $<40\text{-}\mu\text{m}$ material was ground to $<2\ \mu\text{m}$ (Figure 3). Higher R_d -values resulted at low Cs loadings, and the maximum at higher Cs loadings disappeared. Evidently the sorption of Cs in the ground material was dominated by the freshly produced surfaces having a larger surface area but exposing interlayers which were not sensitive to structural changes in contrast to the (weathered) interlayers adjacent to the natural surfaces. This interpretation is supported by the fact that the distribution ratios for desorption in the ground material did not deviate greatly from the sorption curve, and the differences between sorption and isotope exchange were much smaller than for the original $<40\text{-}\mu\text{m}$ material. These results demonstrate that care should be taken in the preparation of samples for such studies.

Treating the $<40\text{-}\mu\text{m}$ chlorite with 1 M HCl for 1 hr produced pronounced changes in sorption, desorption, and isotope exchange (Figure 4). After the HCl-treatment the chlorite was thoroughly washed and treated with synthetic ground water. The distribution ratios for the HCl-treated chlorite were considerably lower than those for the untreated chlorite at all loadings. The maximum at Cs loadings $>10^{-3}$ in the latter curve was reduced to an extended plateau. This plateau

is probably due to remnants of the vermiculite-like structures, as shown by the differences in the desorption and exchange results compared with those for sorption.

CONCLUSIONS

The sorption and desorption behavior of Cs on chlorite is complex; the distribution ratios decreased with increasing Cs concentrations at fractional Cs loadings $<10^{-3}$. At higher Cs loadings the distribution ratios showed a maximum and desorption was retarded. The isotope exchange was drastically hindered at fractional Cs loadings of $>5 \times 10^{-4}$. The maximum in the sorption and desorption curve, the retarded desorption, and the hindered isotope exchange at fractional Cs loadings $>10^{-3}$ can be explained by the presence of interlayers that collapsed due to sorption of Cs at higher concentrations. A comparison of the behavior of ground ($<2\ \mu\text{m}$), KCl- or HCl-treated chlorite with that of the original material suggests that the collapse was restricted to those parts of the interlayers adjacent to the surfaces of the chlorite grains.

ACKNOWLEDGMENTS

The authors thank the following persons for discussions and/or experimental contributions: E. Höhn, R. Keil, U. Krähenbühl, L. Jacobs, Tj. Peters, and U. Zimmermann. They acknowledge B. L. Sawhney, L. L. Ames, F. A. Mumpton, and an anonymous reviewer for valuable comments and improvements. The work was supported by H. P. Alder, the Bundesamt für Energiewirtschaft, and the National Science Foundation.

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(Received 3 August 1985; accepted 29 August 1986; Ms. 1508)