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Sorption and desorption of radiostrontium on powdered bentonite: Effect of pH and fulvic acid

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The effect of pH and fulvic acid on the sorption of Sr on bentonite was investigated by using batch experiments. The sorption and desorption isotherms of Sr on bentonite were determined at room temperature, at pH 6.0±0.2 and in presence of 0.1M NaCl. It was found that the sorption of Sr is independent at pH<8, and then increases slightly with increasing pH. Fulvic acid increases the sorption of Sr significantly on bentonite at low pH, but decreases the sorption of Sr at pH>8. The sorption of Sr on bentonite can be described by a reversible sorption process and the sorption mechanism consists mainly of ion exchange.

Introduction

This paper is an extension of previous papers,[1-4] where we have studied the sorption of radiostrontium and its components on calcareous soil, the effect of fulvic acid on the sorption of radioeuropium on bentonite and kaolinite, and the diffusion of Eu(III) in compacted bentonite. In these studies, the distribution coefficients (K_d) of the sorption of radionuclides on bentonite and soil from aqueous solution were determined by using batch technique. The sorption behavior is often represented by the distribution coefficient, which is characteristic to the sorption ability of radionuclides in the solid phase.

For long-term performance assessment of nuclear waste repositories, the interaction between metal ions, humic substances and backfill materials is the main subject of various investigations.[5,6] Bentonite has been considered as backfill material for nuclear waste disposal sites due to the low hydraulic conductivity of compacted bentonite and its large sorption capacity.[7] The retardation capability for radionuclides is primarily controlled by their sorption potential. Safety analysis requires the understanding of sorption and migration processes of radionuclides on bentonite.

Radiostrontium is the characteristic radionuclide present in fallout of nuclear reactor accidents, nuclear weapon tests and in leakage of cooling water from nuclear power plants. The understanding of the sorption and desorption processes of Sr from aqueous solutions on bentonite is of great importance with regard to the potential contamination of groundwater, because sorption presents a principle control for the mobility of Sr. It was demonstrated that radiostrontium is a very mobile nuclide in comparison with lanthanide and actinide ions.

The concentration of surface species (≡SOH uncharged surface group, $\equiv SOH_2^+$ positively charged surface group, $\equiv SO^-$ negatively charged group) can be obtained as a function of pH. Various mechanisms have been developed to describe the metal ion sorption on an adsorbent. Approximatively, they are, including the ion exchange reaction:[9]

$$m(\equiv S\text{-}OH)+M^{z+} = (\equiv S\text{-}O)_m M^{z-m}+mH^+ \quad (1)$$

the sorption and hydrolysis at the surface of the adsorbent:

$$(\equiv S\text{-}OH)+mH_2O+M^{z+} = (\equiv S\text{-})M(OH)_{m+1}^{z-m}+mH^+ \quad (2)$$

and the hydrolysis followed by a sorption reaction:

$$M^{z+} + mH_2O = M(OH)_m^{z-m} + mH^+ \quad (3)$$

$$(\equiv S\text{-}OH)+M(OH)_m^{z-m} = (\equiv S\text{-})M(OH)_{m+1}^{z-m} \quad (4)$$

It is also well known that humic substances (HS) may influence the sorption of metal cations onto the mineral surface by their ability to complex metal cations. The presence of humic substances increases the sorption of metal ions at the mineral surface at low pH values, and normally decreases the sorption of metal ions at higher pH values. The increase of sorption can be explained by the sorption of HS onto the mineral surface followed by the complexation of metal ions with the sorbed HS, whereas the reduction of sorption can be explained by the formation of HS-metal ion complexes which stabilize the metal ion in aqueous solution because at higher pH the sorption of HS onto the surface of the mineral decreases.[8,9]

The aim of this work was to determine the sorption and desorption isotherms of Sr on bentonite by using batch method. Effect of pH and fulvic acid on the sorption were also investigated.

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Experimental

All chemicals of analytical purity and the bentonite MX-80 were used without any purification. The clay fraction has a dry weight of (82±3)% and consists of montmorillonite with the stoechiometric formula $(Si_{3.96}Al_{0.04})(Al_{1.52}Mg_{0.26}Fe^{III}_{0.17})Na_{0.18}Ca_{0.11}O_{10}(OH)_2$.[10] The main mineral content are composed of quartz, felspar, calcite ($CaCO_3$), $(Ca,Fe)CO_3$), siderite and pyrite. The cation exchange capacity was 0.75 meq/g.[11]

Radiostrontium ($^{85+89}SrCO_3$) was dissolved and converted to $^{85+89}SrCl_2$ solution. The activities of Sr in the solution and in the supernatant was determined with a Geiger-Müller counter.

Fulvic acid was obtained from weathered coal from the area of Gongxian (Henan Province). The humic substance had been characterized in great detail[12] and used in many investigations.[4,9]

The Sr sorption and desorption isotherms were determined in the range of 10^{-7} to 10^{-5} mol/l $SrCl_2$ at pH 6.0±0.2 in the presence of 0.1M NaCl. All experiments were carried out at room temperature. The solutions were prepared using Milli-Q water. Polyethylene tubes were used in the batch experiments. The sorption of Sr on polyethylene tube wall can be neglected. Before the experiments, the bentonite was equilibrated with 0.1M NaCl by four washings. The suspension thus prepared with a bentonite concentration of 10 g/l was used as a stock suspension. The Sr/bentonite suspension solutions were prepared by mixing aliquots of NaCl solution, Milli-Q water, $^{85+89}SrCl_2$ solution and bentonite suspension. The volume of the solution in each tube was 10 ml. They were shaken for 2 days to reach equilibrium. Using kinetic experiments, this time was found to be sufficient. The solid phase was separated from the aqueous phase by centrifugation for 20 minutes at 18000 rpm. Aliquots of the supernatant were finally analyzed to derive the distribution coefficients and the amount of sorbed Sr on bentonite according to:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \frac{V}{m} \tag{5}$$

$$q = \frac{C_0 - C_{eq}}{1000} \frac{V}{m} \tag{6}$$

where C_0 is the initial aqueous concentration (mol/l), C_{eq} is the equilibrium concentration (mol/l), V is the volume of the solution (ml), m is the mass of the solid phase (g), q is the solid concentration (mol/g).

For desorption experiments, the suspensions of bentonite were centrifuged. After the sorption experiments, to 5 ml of the supernatant 5 ml of 0.1M NaCl solution was added, then the mixture was shaken and centrifuged under the same conditions as in the sorption experiments. Finally, the amount of Sr remained sorbed after desorption and the values of K_d and q were calculated.

Results and discussion

Time-dependence of sorption

Using the batch technique the dependence of the q value on the contact time was investigated at an initial Sr concentration of $1.4 \cdot 10^{-6}$ mol/l at pH 6.0±0.2 in the presence of 0.1M NaCl. The results are shown in Fig. 1. The sorption is rather quick, the major part of sorption takes place in the first hour of contact time and the steady state value of q is obtained in about several hours. According to these results, it is suggested that for sorption isotherm determination a contact time of 2 days will be enough to reach equilibrium.

Effect of pH on the sorption isotherm

The pH dependence of Sr sorption on bentonite at an initial Sr concentration of $1.4 \cdot 10^{-6}$ mol/l in absence and presence of 10 mg/l FA are shown by a $\log K_d$ versus pH plot in Fig. 2. In absence of FA, the K_d values of Sr sorption are pH independent in the range of 3 to 8, then they increases slightly at pH>8. The dominant sorption process for Sr is ion exchange,[2,11,13] although the small increase in K_d values for pH>8 is ascribed to surface complexation. MOLERA and ERIKSEN[11] also investigated the sorption and diffusion of Sr^{2+} in bentonite in 0.1M $NaClO_4$. Their results are quite close and similar to those of our work.

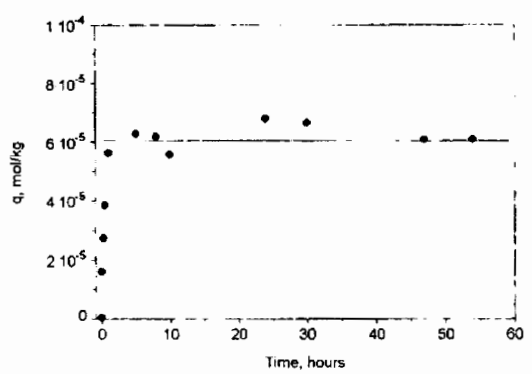

Fig. 1. Variation of radiostrontium concentration in bentonite with contact time; $C_{Sr} = 1.4 \cdot 10^{-6}$ mol/l, pH 6.0±0.2, $C_{NaCl} = 0.1$M, $C_{bentonite} = 4.4$ g/l

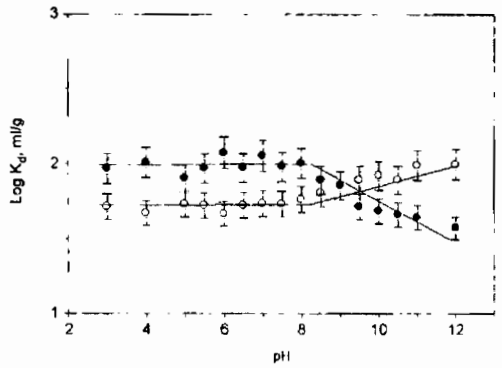

Fig. 2. Effect of pH on radiostrontium sorption on bentonite; $C_{Sr} = 1.4 \cdot 10^{-6}$ mol/l, $C_{NaCl} = 0.1$M, $C_{bentonite} = 4.4$ g/l, (●) $C_{FA} = 10$ mg/l; (○) $C_{FA} = 0$ mg/l

In the presence of 10 mg/l FA, the K_d values are obviously higher than those in absence of FA. At pH 3~8, $\bar{K}_d$ is 99±11 ml/g in presence of 10 mg/l FA and in absence of FA it is 52±4 ml/g. The presence of FA increases the sorption of Sr on bentonite significantly, however, at pH>8, the presence of FA decreases the sorption of Sr with increasing pH values. The reduction of sorption can be explained by the formation of FA-Sr complexes which stabilize Sr^{2+} in aqueous solution because at higher pH values the sorption of FA onto the surface of bentonite decreases as both the negatively charged FA and bentonite surface decrease.

Sorption and desorption isotherms

The sorption and desorption isotherms of radiostrontium for bentonite, at room temperature, pH 6.0±0.2 and in the presence of 0.1M NaCl are shown in Fig. 3. As can be seen, the two isotherms are linear in the range of Sr concentration used. The slopes of both lines are 51±2 and 53±2 ml/g, respectively, representing constant distribution coefficients. According to the standard deviation of ±2, the two isotherms should be considered as a single straight line, corresponding to a distribution coefficient of 53 ml/g.

The low K_d value yields a low retention which implies that the transport of radiostrontium is only slightly retarded with respect to the water velocity. The mergence of sorption and desorption isotherms implies that the sorption-desorption hysteresis is negligible and the transport of radiostrontium in bentonite can be described by a reversible sorption process.

Effect of FA on the sorption of Sr

The sorption isotherms of Sr in bentonite in presence and absence of FA are shown in Fig. 4. As can be seen, the two isotherms are linear, and are fitted by:

$$q = A + B \cdot C_{eq}$$

and the parameters are listed in Table 1. The fitting line goes through the origin, therefore, the sorption of Sr on bentonite can be considered as an ion exchange process. FA has a positive contribution to the sorption of Sr on bentonite. DU et al.[2] investigated the sorption of Sr on calcareous soils using batch experiments and a selective extraction method, and found that organic matters in calcareous soil contributes to the sorption of Sr significantly. Organic matter represents 1.7% of the mass of the whole soil, but contributes with 7% to the sorption of Sr on the whole soil. This suggest that organic matter has a relative large affinity for Sr. In our study, the average distribution coefficients of Sr sorption is 96±6 ml/g in presence of FA, which is much higher than that of Sr sorption in absence of FA. The high K_d values on bentonite suggest a very high relative affinity of Sr to FA sorbed on bentonite. Whether HS-M complexes are formed in solution or M-HS-bentonite/HS-M-bentonite sorption takes place on the surface of bentonite, it is difficult for the large molecules of humic substance-metal ion complexes to be transported in the pore volume of compacted bentonite,[14] thus HS inhibits the transport of metal ions in this phase.

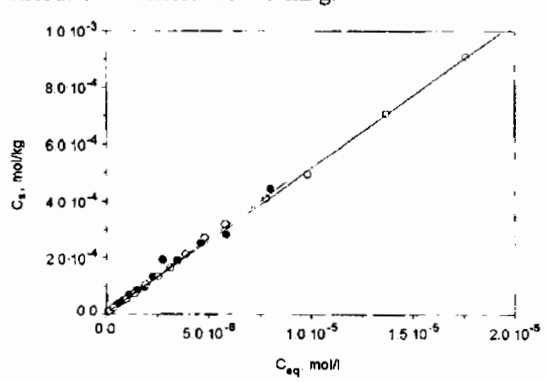

Fig. 3. Sorption (○) and desorption isotherms (●) of radiostrontium on bentonite; pH 6.0±0.2, $C_{NaCl} = 0.1$M, $C_{bentonite} = 4.4$ g/l

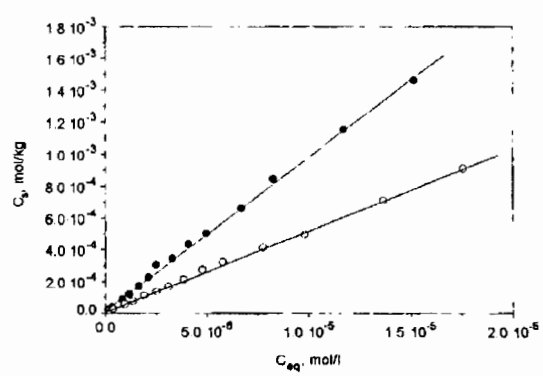

Fig. 4. Sorption isotherms of radiostrontium on bentonite; pH 6.0±0.2, $C_{NaCl} = 0.1$M, $C_{bentonite} = 4.4$ g/l; (●) $C_{FA} = 10$ mg/l; (○) $C_{FA} = 0$ mg/l

Table 1. Parameters of the equation $q = A+B \cdot C_{eq}$ and the average distribution coefficient of radiostrontium sorption on bentonite at pH 6.0±0.2

	A	B	Correlation coefficient	K_d, ml/g
Sorption	$(5.5 \cdot 10^{-6}) \pm (3.5 \cdot 10^{-6})$	51.2±0.5	0.999	51±2
Desorption	$(5.2 \cdot 10^{-6}) \pm (7.0 \cdot 10^{-6})$	53.1±2.1	0.999	53±2
Sorption in presence of FA	$(1.5 \cdot 10^{-5}) \pm (7.3 \cdot 10^{-6})$	96.5±1.1	0.999	96±6

Conclusions

The sorption of $^{85+89}Sr^{2+}$ in bentonite was studied by using batch techniques. The effect of pH and fulvic acid on the sorption of Sr was also investigated. The dominant sorption process for Sr in bentonite is ion exchange although a small increases in K_d values for pH>8 is ascribed to surface complexation. Fulvic acid increases the sorption of Sr at low pH values, but decreases the sorption at high pH because the sorption of fulvic acid on bentonite decreases at high pH values. The sorption and desorption isotherms are linear and the sorption of Sr on bentonite can be considered as a reversible sorption process. On the other hand, the results are important when applied to environmental conditions. After the migration, the metal ions are incorporated into the organic layer of the host phase. This results show that the complexation behavior of organic-inorganic hybrids with respect to metal ions is completely distinct of the corresponding binary systems. The importance of humic substances in the sorption/transport of metal ions indicate that it is necessary to clarify the environmental behavior of humic substances to understand the role of metal ions in natural aquifers.

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