

INTERACTION OF RADIUM WITH FRESHWATER SEDIMENTS AND THEIR MINERAL COMPONENTS. I.

FERRIC HYDROXIDE AND QUARTZ

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(Received June 20, 1983)

The radiotracer method has been used for investigation of the adsorption and desorption of traces of radium on ferric hydroxide and quartz under conditions similar to those prevailing in waste and surface waters. The effects of pH, liquid to solid ratio, ionic strength and presence of Ca^{2+} or SO_4^{2-} ions have been studied. It has been concluded that at pH less than 7 and at concentration of suspended sediments (of common composition) less than $100 \text{ mg} \cdot \text{l}^{-1}$ ferric hydroxide and quartz have negligible effect on the state and migration of radium in surface waters. Radium adsorbed on quartz can be easily desorbed with dilute solutions of hydrochloric acid or sodium chloride.

Introduction

Radium belongs among the most dangerous contaminants released to the environment from the nuclear fuel cycle. Most of the released radium is carried, dispersed or concentrated in surface waters.¹ It is well established^{1–4} that suspended and bottom sediments play an important role in the migration of radium in surface waters. Radium released into the waters in particulate forms undergoes sedimentation and is deposited in sediments. Dissolved forms of radium can interact with solid particles suspended in waters and particulate forms of radium thus formed again deposit on bottom. Radium concentrated in this way in bottom sediments can be released into the water phase, particularly if environmental conditions are changed, for instance in periods of high water flow.

The deposition of radium in sediments and its release have been well documented by field data¹ but the analysis of the data does not allow quantitative characterization of the processes involved. Therefore, a number of laboratory experiments were undertaken to obtain data characterizing the interaction of radium with sediments in simplified conditions, enabling better interpretation of the mechanisms and laws of

the interaction. Two general approaches were adopted: (1) investigation of radium distribution between natural water or aqueous solutions and natural sediments; (2) study of radium distribution between water phase and model solids representing components of natural sediments.

Because the laboratory experiments carried out so far failed to elucidate radium interaction with sediments in sufficient detail,¹ it seemed interesting to continue such studies. The aim of our work has been to combine both of the above approaches to get a better insight into the processes governing radium migration in surface waters and in this way to supplement our earlier investigations.^{5,6} However, our primary aim is not to produce quantitative data directly usable in migration models, but rather to find out which components of freshwater sediments are mainly responsible for radium uptake and how this uptake changes with changing composition of sediments or with changing ambient conditions.

In this paper data on radium interaction with ferric hydroxide and quartz are presented. Quartz represents a basic component of many freshwater sediments. Ferric hydroxides or oxides often occur in sediments as surface coatings of mineral particles⁷ and therefore can play an important role even if present at low concentrations. The content and the effect of ferric hydroxide can be particularly high in surface waters receiving mine effluents, which usually contain high concentrations of dissolved iron. The formation of flocks of amorphous ferric hydroxide in waste waters of a uranium mine was also found in an earlier study.⁵

Interaction of radium with the selected solids was studied by radiotracer method, when radium was represented by its short-lived isotope ^{224}Ra , whose behaviour is identical with that of ^{226}Ra . This greatly facilitated the study because of the higher sensitivity and precision of direct radioactivity measurement.

Experimental

Adsorbents and solution preparation

Ferric hydroxide was precipitated by mixing (1:3) stock aqueous solutions of 0.1M FeCl_3 and 0.1M NaOH at room temperature. The resulting suspension was either directly used for experiments or centrifuged and suitably diluted with distilled water. Both freshly prepared and aged precipitates were used. In the latter case the precipitate with mother liquor (pH 6.5–7.8) were left standing in closed polythene bottles at room temperature for the desired period of time.

Alfa quartz was represented by quartz sand supplied by Labora (Prague, Czechoslovakia) as a standard for analysis. The sand contained 99.35% SiO_2 , 0.249% Al_2O_3 .

and several other components (TiO_2 , Fe_2O_3 etc.) in amounts less than 0.1%. Its weight loss by ignition was 0.169%. Fraction containing grains in the range 0.05–0.08 mm was used for experiments without further pretreatment. The specific surface area of the fraction was $0.81 \text{ m}^2 \cdot \text{g}^{-1}$, as determined by the low temperature (liquid N_2) adsorption of nitrogen from the mixture of hydrogen and nitrogen at a ratio of 3:1.⁸

All the solutions used in this work were prepared from distilled water and p.a. reagents. Dilute solutions of sodium hydroxide were prepared from 50% solution of NaOH. Stock solution of radionuclide ^{224}Ra (carrier-free, $T = 3.64 \text{ d}$) was periodically obtained by milking of a generator⁹ with 0.01M HCl.

The experimental solutions were prepared by gradually mixing water and stock solutions of hydrochloric acid, sodium hydroxide, suitable reagents and ^{224}Ra (in this sequence) so as to obtain the desired pH, composition and ionic strength of the solution. In order to ensure constancy of pH in the systems with quartz as the adsorbent, the pH values in the region of 6.5–9.2 were mostly adjusted with 0.005 or 0.0005M solution of sodium tetraborate, which was used instead of sodium hydroxide. It was verified that the presence of tetraborate did not affect the results. Radium concentration in the experimental solutions varied between 8 and 40 $\text{pg} \cdot \text{l}^{-1}$, the variation exerted no influence on the results.

Procedures and apparatus

Ten milliliters of experimental solution were shaken with a known amount of adsorbent in a 30 ml polythene bottle at room temperature for 17 hrs. Adsorbent was either weighed dry into the bottle or was added in the form of a suspension. When the coprecipitation of radium with ferric hydroxide was studied, radium was added to the stock solution of 0.1M FeCl_3 and after suitable dilution ferric hydroxide was precipitated with 0.1M NaOH. After shaking, the bottle was centrifuged at 3000 r.p.m. for 10 min and 5 ml of supernatant was sampled for measurement of radioactivity of radium remaining in the solution (X). For each series of experiments a standard was prepared, representing the activity of the original experimental solution (S). The solution remaining in the bottle after sampling was used for the measurement of pH. Unless desorption from adsorbent was to be determined, the adsorbent was removed from the bottle which was then shortly rinsed with distilled water and shaken with 10 ml of 1M HCl for 3 hrs. It was proved that in this way all the radium adsorbed on the walls of the bottle was desorbed. 5 ml of the desorbing solution was used for measurement of the activity of the adsorbed radium (Y).

The adsorption or coprecipitation A (in %) was evaluated from the equation $A = 100 (S - X - Y) (S - Y)^{-1}$. Simultaneously the percentage of radium lost by adsorp-

tion on the walls of the polythene bottle was calculated as $100 Y \cdot S^{-1}$. It was found that the amount of radium so adsorbed seldom exceeded 5% of the total radium present.

Desorption of radium from the adsorbent was studied in the following way. The solution remaining in the polythene bottle after adsorption, centrifuging and sampling was almost quantitatively removed by pipette, great care being taken not to remove the adsorbent. Then 10 ml of desorption solution was added and the bottle was again shaken at room temperature for 17 hrs. Desorption generally started within 24 hrs of the beginning of adsorption. Desorption percentage D was calculated from the radioactivity of 5 ml of the desorption solution after the desorption (Z): $D = 100 Z \cdot (S-X)^{-1}$. It was determined that errors due to incomplete removal of adsorption solution before the desorption were lower than 2%. Desorption with the solution of the same composition (except for radium which was absent) and pH as that used for the preliminary adsorption was employed for determination of the reversibility of adsorption. The reversibility R (in %) was calculated using the formula $R = 100 D \cdot (100-A)^{-1}$.

pH measurements were done with glass electrode G 202 C and a digital pH-meter PHM-52 (Radiometer, Copenhagen). 5 ml samples of solutions for radioactivity measurements were placed into glass ampoules containing 0.5 ml of 4M HCl to prevent adsorption of radium on the walls of the ampoules. Their activity was measured using a well-type NaI(Tl) crystal and nuclear counter NZQ-714 T (Tesla, Liberec, Czechoslovakia), after the establishment of radioactive equilibrium between radium and its decay products.

Results and discussion

Adsorption of radium was studied as a function of several variables, whose changes might affect the behaviour of radium in waste and natural waters. Conditions of the experiments were chosen so as to simulate as closely as possible the conditions prevailing in real systems. The ionic strength of the solutions and the original concentration of radium were similar to those common in contaminated surface waters.⁵

The ratio of the solution volume to the amount of adsorbent (liquid to solid ratio, $V/m = 500-10,000 \text{ cm}^3 \cdot \text{g}^{-1}$) used was lower than that usually encountered in surface waters, for instance $50000 \text{ cm}^3 \cdot \text{g}^{-1}$ corresponding to $20 \text{ mg} \cdot \text{l}^{-1}$ suspended solids. However, measurement of radium adsorption at higher V/m ratios is less accurate and convenient and some waste waters or river waters under intense flow conditions contain rather high concentrations of suspended solids.

Preliminary experiments have shown that radium adsorption on ferric hydroxide and quartz is very rapid. The adsorbed amount does not change from 1 hr to 17 hrs contact, most of the radium being adsorbed during the first 10 min of shaking.

It can therefore be assumed that the adsorption values resulting from 17 h experiments represent equilibrium (or pseudoequilibrium, if the adsorption is not completely reversible) values of radium distribution. Furthermore, kinetics of radium adsorption on ferric hydroxide and quartz in natural water systems will be more probably determined by the transport of radium to the surface of particles (diffusion, eddy diffusion) than by the adsorption process itself.

Ferric hydroxide

The results of the study of radium interaction with ferric hydroxide are shown in Figs 1 and 2. As can be seen, the interaction strongly depends on pH and liquid to solid ratio, V/m . Calcium and sulfate ions at concentrations typical for natural waters do not affect the adsorption, and the ionic strength has only a small effect. The increase of the ionic strength from 0.003 to 0.03M slightly suppresses the adsorption in the pH region 6–8, whereas the addition of sodium chloride to increase its concentration from 0.03 to 0.3M brings about no decrease in the adsorption. The age of the precipitate influences the adsorption but slightly. The adsorption decreases in the first 14 days of ageing, probably due to a decrease in the surface area of the originally amorphous precipitate in the course of its partial crystalliza-

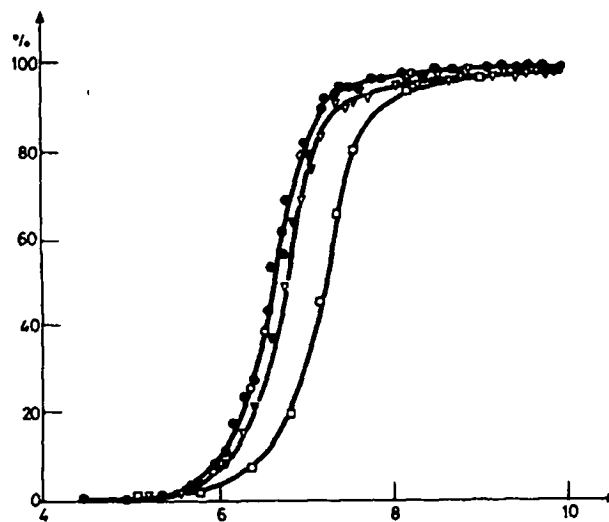


Fig. 1. Adsorption of radium on, or coprecipitation with, ferric hydroxide from 0.03M NaCl as a function of pH, age of the precipitate (T) and liquid to solid ratio (V/m). Curves: 1 – $V/m = 1000 \text{ cm}^3 \text{ g}^{-1}$, fresh precipitate ($T < 1 \text{ h}$), adsorption (\bullet) and coprecipitation (\circ); 2 – adsorption, $V/m = 1000 \text{ cm}^3 \cdot \text{g}^{-1}$, $T = 14 \text{ d}$ (\blacktriangledown) and 28 d (\triangledown); 3 – adsorption, $V/m = 10000 \text{ cm}^3 \cdot \text{g}^{-1}$ (\square)

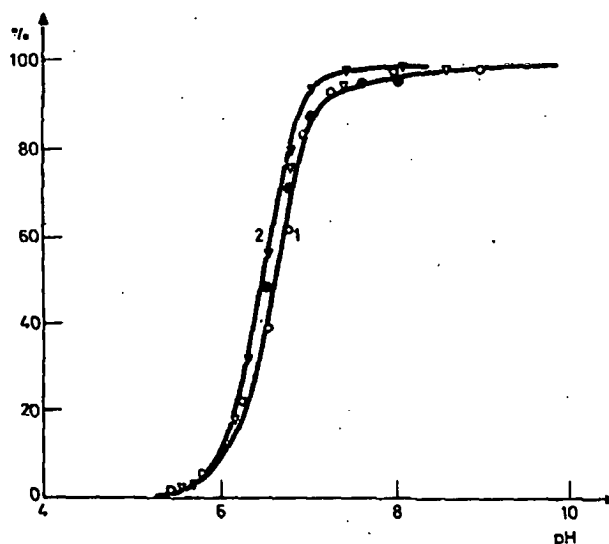
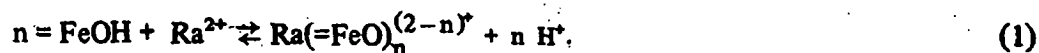


Fig. 2. Adsorption of radium on freshly prepared ferric hydroxide as a function of pH and composition of the solution ($V/m = 1000 \text{ cm}^3 \cdot \text{g}^{-1}$). Curve 1 – (\circ) 0.03M NaCl, 0.0015M CaCl_2 ; (∇) 0.03M NaCl, 0.001M K_2SO_4 ; (\bullet) 0.3M NaCl; curve 2 – 0.003M NaCl

tion. Adsorption on preformed hydroxide leads to the same distribution of radium as coprecipitation with the hydroxide. This suggests that the mechanisms of both processes are about the same, i.e. that coprecipitation proceeds by the adsorption of radium on the hydroxide being formed.

Radium was present in the solutions investigated almost exclusively as Ra^{2+} ion, only in the solutions containing sulfates about 6.7% of radium existed as RaSO_4 ion pair.¹⁰ The small effect of sulfates on the adsorption shows that the existence of RaSO_4 ion pair in surface waters will not affect the interaction of radium with ferric hydroxide. The adsorption of radium on ferric hydroxide can be explained by ion exchange of radium ions for hydrogen ions or atoms in dissociated or undissociated groups ($=\text{FeO}^- + \text{H}^+$ or $=\text{FeOH}$, respectively) existing at the surface of ferric hydroxide:



The ratio of adsorbed to nonadsorbed radium can be expressed as

$$\frac{[\text{Ra}(=\text{FeO})_n^{(2-n)+}]}{[\text{Ra}^{2+}]} = K \cdot [= \text{FeOH}]^n \cdot [\text{H}^+]^{-n} \quad (2)$$

where K is a constant and square brackets denote concentrations. The low effect of sodium and calcium ions on the adsorption indicates that these ions, at the concentrations studied, compete but slightly with radium in the ion exchange. This seems to support the concept of ion exchange in undissociated surface groups, as the ion exchange in dissociated groups (i.e. in an electric double layer) is usually more susceptible to competition of foreign ions.¹¹ The strong dependence of the adsorption on the pH and liquid to solid ratio directly follows from Eq. (2). The concentration $[=FeOH]$ is inversely proportional to V/m .

The adsorption of radium on ferric hydroxide strongly changes in the pH region critical for surface waters. Because the adsorption also depends on the concentration of ferric hydroxide, it is difficult to unambiguously decide whether ferric hydroxide or oxides represent important adsorbents for radium in surface waters. An extrapolation of the data presented suggests, however, that at pH less than 7 and at concentrations of suspended ferric iron less than $5 \text{ mg} \cdot \text{l}^{-1}$ [e.g. $<100 \text{ mg} \cdot \text{l}^{-1}$ suspended solids with $\leq 5\%$ content of Fe(III)] ferric hydroxide has a negligible effect on the state and migration of radium in surface waters. This conclusion can probably be extended also to ferric oxides for it is known that fresh amorphous ferric hydroxide is more reactive than the crystalline oxides. Additional support can be found in the negative effect of the precipitate ageing shown above.

Orientative experiments with desorption of radium from ferric hydroxide at pH 6 and 7 have shown that the adsorption process is reversible: the distribution of radium between the adsorbent and solution after two hours of desorption was approximately equal to the distribution after the preliminary adsorption, if the pH and composition of the adsorption and desorption solutions were the same.

Quartz

Results of the study of radium adsorption on quartz are given in Figs 3 and 4 and Table 1. The adsorption increases with pH in a broader pH region than that on ferric hydroxide and the increase is less steep. The effect of solution composition on the adsorption is demonstrated in Fig. 4, where curve 1 is identical with curve 1 of Fig. 3. Consequently, the presence of sulfate ions ($60 \text{ mg} \cdot \text{l}^{-1}$) and the change of sodium ion concentration from 0.01 to 0.001M do not significantly affect the adsorption. On the other hand, addition of calcium chloride and sodium chloride to increase the concentration of calcium and sodium ions to $30 \text{ mg} \cdot \text{l}^{-1}$ and 0.1M, respectively, brings about a pronounced decrease in the adsorption. This effect suggests that radium is adsorbed on quartz by ion exchange for counter ions in an electric double layer which exists on the surface of quartz due to dissociation¹² of $\equiv \text{SiOH}$ groups at $\text{pH} \geq 3$.

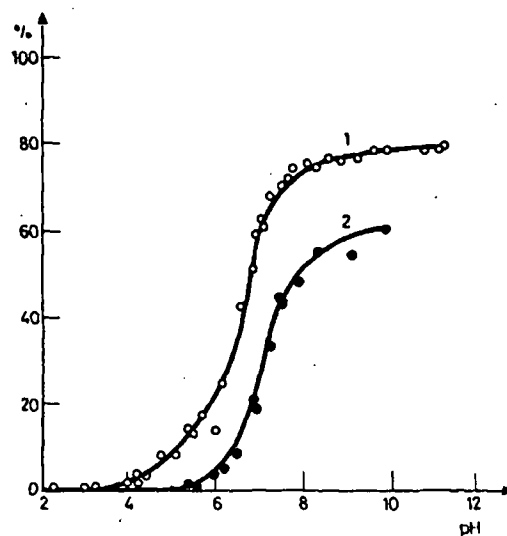


Fig. 3. Adsorption of radium on quartz from aqueous solutions of 0.01M Na⁺ as a function of pH and liquid to solid ratio (V/m). Curve 1 – V/m = 500 cm³ · g⁻¹; curve 2 – V/m = 5000 cm³ · g⁻¹

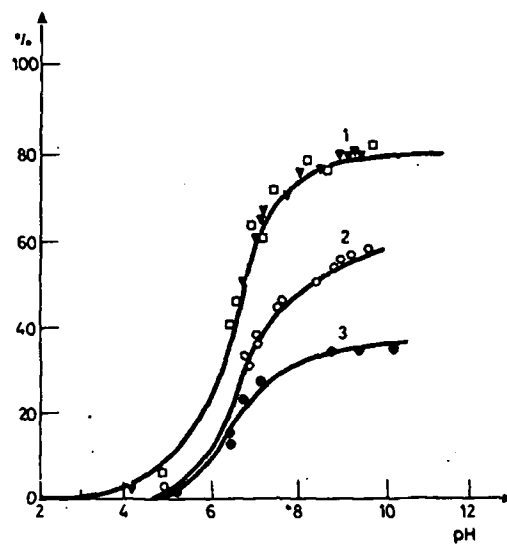


Fig. 4. Adsorption of radium on quartz as a function of pH and composition of the solution (V/m = 500 cm³ · g⁻¹). Curves: 1 – 0.001M Na⁺ (□) and 0.01M Na⁺, 60 mg l⁻¹ SO₄²⁻ (▼); 2 – 0.01M Na⁺, 30 mg l⁻¹ Ca²⁺; 3 – 0.1M NaCl

Table 1
Adsorption (A) of radium on quartz from a solution of
pH 7.37 (0.005M Na₂B₄O₇, 0.005M HCl)
as a function of liquid to solid ratio (V/m)

V/m, cm ³ · g ⁻¹	A, %	K _D , cm ³ · g ⁻¹	K' _D , cm ³ · g ⁻¹
5000	28.1	1954	2116
3333	33.7	1694	1847
500	73.0	1352	1698
200	83.2	990	1473
100	89.2	826	1683
50	91.7	552	1637
25	94.5	430	—
10	94.5	172	—

The effect of the liquid to solid ratio (V/m) was studied in more detail in this case, the results given in Table 1 represent average values from 4 determinations. In accordance with literature data on radium adsorption by sediments^{1,3} it has been found that the adsorption increases with decreasing V/m to a maximum value A_{max}, which is significantly lower than 100%. The distribution coefficient K_D defined as

$$K_D = \frac{m_a}{m_s} \frac{V}{m} \quad (3)$$

where m_a and m_s are equilibrium amounts of radium adsorbed and remaining in the solution, respectively, decreases with decreasing V/m. MANSFELD and HANSLÍK^{1,4} suggested to use a modified distribution coefficient K'_D defined as

$$K'_D = \frac{A}{A_{\max} - A} \frac{V}{m} \quad (4)$$

The K'_D values calculated for our system using Eq. (4) and A_{max} = 94.5% are fairly constant (see Table 1), the average value of K'_D is equal to 1742 ± 89. Our results thus corroborate the conclusion drawn by the above authors that K_D is independent of V/m and therefore suitable for quantitative characterization of radium adsorption by minerals. The average value found by us lies between the values, determined by

Table 2
Desorption (D) of radium from quartz by 0.1M NaCl and 1M HCl
as a function of pH during the preliminary adsorption, and
reversibility (R) of the adsorption

pH	D, % 0.1M NaCl	pH	D, % 1M HCl	pH	R, %
5.4	91.0	5.6	100	4.2	94.3
6.5	83.2	6.8	100	5.5	75.2
7.1	77.2	7.5	99.7	7.0	76.4
7.8	73.1	7.8	100	7.8	74.9
8.5	73.6	9.2	99.5	9.0	68.5
9.2	73.8	—	—	11.2	68.4

MANSFELD and HANSLÍK¹⁴ for radium adsorption on quartz from distilled and tap water 3020 ± 290 and 480 ± 200 , respectively.

For the adsorption of radium on quartz in surface waters a similar conclusion can be drawn as for the adsorption on ferric hydroxide. At pH less than 7 and concentration of quartz lower than $100 \text{ mg} \cdot \text{l}^{-1}$ the adsorption of radium on the quartz component of suspended solids will not play an important role.

Desorption of radium from quartz was studied as a function of pH during preliminary adsorption and of the composition of desorbing solution. The ionic strength of the solution during preliminary adsorption was 0.01M (NaCl, $\text{Na}_2\text{B}_4\text{O}_7$), the liquid to solid ratio was equal to $500 \text{ cm}^3 \cdot \text{g}^{-1}$ during both adsorption and desorption. The results of this study are presented in Table 2 as average values of 2 or 4 determinations. As can be seen, radium is quantitatively desorbed with 1M HCl. Its desorption with 0.1M NaCl is also rather high but depends on pH during the preliminary adsorption. These findings suggest that radium adsorbed on the quartz component of aquatic sediments can be easily desorbed by an increase in the salinity or acidity of water. A significant release of adsorbed radium can occur even without a change in water composition, as follows from the comparatively high reversibility of radium adsorption on quartz. The easiness of radium desorption supports our conclusion that radium is adsorbed on quartz by ion exchange in the surface electric double layer.

Financial support of this work by the International Atomic Energy Agency under research contract 2893/RB is gratefully acknowledged.

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AR-028