

ACTINIDES IN THE ENVIRONMENT

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The influence of the following parameters is discussed: oxidation state (Eh), hydrolysis (pH), solubility, complex formation, colloid formation, sorption and filtration effects. The oxidation states of the actinides in neutral aqueous media are plotted as a function of the redox potential. Hydrolysis, stability of 1 : 1 carbonato complexes, of humic acid complexes and solubilities of the hydroxides in the various oxidation states are considered. Mobility is investigated as a function of pH by paper chromatography. Partition of the actinides in groundwaters on the molecular fraction, the fine particle (colloid) fraction and the coarse particle fraction is determined as a function of pH by filtration and ultrafiltration. Sorption ratios are measured as function of pH, salt concentration and of EDTA concentration. When the groundwaters are passed through the sediments, mainly the coarse particle fractions are retained by size filtration. The pronounced influence of the redox potential on sorption is demonstrated for Np.

Introduction

The behaviour of the actinides in the environment depends on many parameters:

- Oxidation state (which for many actinides is a function of the redox potential Eh),
- Hydrolysis, depends on the oxidation state and pH,
- Complex formation (other than hydroxo complexes), depends on the presence of complexing agents and on their concentration,
- Solubility, depends on the kind of solid formed, on complex formation and on colloid formation,
- Colloid formation, depends on actinide concentration, the presence of carrier colloids and the sorption of the actinides on these carrier colloids,
- Sorption, depends on the actinide species present in the water (ionic species, complexes, colloids),
- Filtration effects, depend on the size of particulate matter carrying the actinides and the size of the pores in the sediment.

This great number of interdependent parameters has to be taken into account, in order to understand the behaviour of actinides in the environment properly.

Complex formation by humic substances may be very important in groundwaters,¹ in particular near the surface. Solubility data are valid only for well defined solids. However, traces of actinides cannot be expected to form such well defined solids, and complex or colloid formation may increase the solubility or apparent solubility considerably.

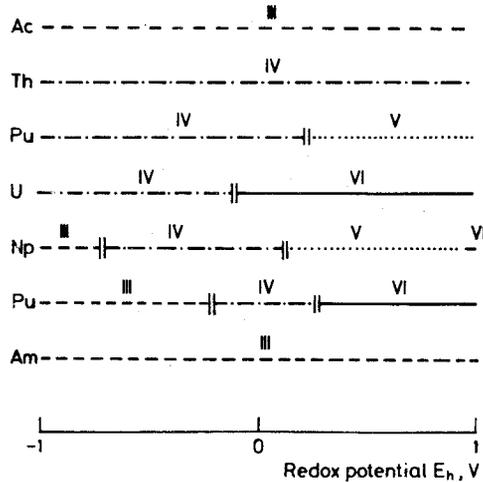


Fig. 1. Oxidation states of the actinides Ac to Am at pH 7 in absence of complexing agents as a function of the redox potential E_h

Colloids are metastable states of matter. At very low concentrations of actinides the formation of intrinsic colloids (“Eigenkolloide”) is very improbable, and in groundwaters the actinides will mainly be present in form of carrier colloids (“Fremdkolloide”) in which colloidal polysilicic acid, colloidal iron hydroxide or colloidal clay particles serve as carriers. It is well known that these kinds of colloids abound in groundwaters.²

The oxidation states of the actinides Ac to Am in neutral aqueous media in absence of complexing agents are plotted in Fig. 1 as a function of the redox potential E_h . It is evident from this figure that under reducing conditions which are found in deep groundwaters ($E_h < -0.1$ V) only the oxidation states +3 and +4 are of interest for all actinides. Above $E_h \approx -0.1$ V, U^{4+} is oxidized to UO_2^{2+} and above $E_h \approx 0.1$ V, Np^{4+} is oxidized to NpO_2^+ . Oxidation of Pu^{4+} occurs at appreciably higher redox potentials. Therefore, in groundwaters the oxidation states +3 and +4 play the most important role. In case of U and of Np, the oxidation states +6 and +5, respectively, have to be taken into account.

The tendency of hydrolysis of the various oxidation states of the actinides decreases as follows: $M^{5+} > M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$. In neutral media all forms except MO_2^+ are strongly hydrolyzed.

The stability of the 1:1 carbonato complexes decreases in the order: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$. The same order is found for the stability of the humic acid complexes: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$. This is not surprising, because carboxylic groups are the main functional groups of humic acids.

For the solubility of the hydroxides in neutral aqueous solutions the following order is valid: $M(OH)_4 < MO_2(OH)_2 < M(OH)_3 < MO_2OH$. Solubility values calculated from solubility products^{3,4} at pH 7 are: For $M(OH)_4$: 10^{-19} to 10^{-35} mol/l, for $MO_2(OH)_2$: 10^{-8} to 10^{-10} mol/l, for $M(OH)_3$: 10^{-2} to 10^{-4} mol/l, and for $MO_2(OH)$: 10^{-1} to 10^{-2} mol/l. It should be emphasized, however, that these values have to be used with great care, because of the following reasons: Solubility of a solid depends on its chemical composition, the modification and the size of the particles. Thus, on the basis of our knowledge of the properties of sparingly soluble oxides and hydroxides, solubility of crystalline PuO_2 , hydrous $PuO_2 \cdot xH_2O$ and amorphous plutonium(IV) hydroxide must be expected to be different by several orders of magnitude. Furthermore, by electrochemical measurements only ionic species are detected, and solubility calculations based on solubility products give values which are, in general, too low, because the contribution of undissociated species or ion pairs is neglected. Erroneous solubilities are also obtained if complexation is not taken into account. The influences of undissociated species and of complexation on solubility have been demonstrated in detail for the silver halides.⁵

Finally, colloid formation may also increase appreciably the apparent solubility of hydroxides, and the tendency of the hydroxides of actinides, in particular of plutonium hydroxide, to form colloids is well known.⁶

The various species of the actinides are sorbed on sediments by different mechanisms. Free ions (aquo complexes) are preferentially sorbed by ion exchange. However, free ions of the actinides are present only at relatively high acidity at which H^+ ions compete strongly with other ions in the ion exchange reactions. Therefore, ion exchange is of minor importance for the sorption of actinides.

Beginning at about pH 2 to 3 increasing amounts of actinides in the oxidation states +3 and +4, respectively, are present in form of hydroxo complexes which interact strongly with hydroxy groups at the surface of solids (e.g. $>SiOH$, $>AlOH$ groups). This kind of chemisorption is called hydrolytic adsorption.⁷ It is very effective in the pH range in which hydroxo complexes of low molecular mass dominate and has been used for separation of di- and trivalent ions.⁸ In the range of higher pH when condensation reactions of the hydroxo complexes proceed and particles of higher molecular mass or colloidal particles are formed, hydrolytic adsorption becomes less effective.

The interaction of other complexes of the actinides with sediments is generally weaker than that of hydroxo complexes. Humic or fulvic acid complexes are mainly bound by physical adsorption, and bridged complexes in which carbonate groups serve as bridging ligands may also be formed, in particular at high concentrations of carbonate or humic acids, respectively. Colloids, in general, show relatively weak interaction with sediments by physical adsorption.

Experimental results and discussion

Information on the mobility of actinides as a function of pH can be obtained in a relatively simple way by paper chromatography: Water is adjusted to a certain pH by addition of small amounts of HCl or NaOH. 1 ml of this solution is spiked with a small volume of actinide solution and pH is adjusted again, if necessary. 25 μ l of the spiked solution is put on the starting point of a suitable chromatographic paper which is transferred into a closed chromatographic box, dipped into water of adjusted pH and left there for about 1 hour. Various chromatographic papers from Schleicher and Schüll (2043, 2045 and others) were tested and the most suitable papers were selected. At the end of the experiment the activity distribution on the paper was measured by use of a windowless scanning proportional counter. The relative amount of activity transported with the front of the solution was taken as a measure of the mobility.

Results obtained for the mobility of Ac^{3+} as a function of pH are plotted in Fig. 2. The water was spiked with ^{227}Ac . Retention on the paper is due to the interaction of actinium with the reactive groups of cellulose, mainly the Cell-OH groups. As the reactivity of these groups may vary with the preparation of the chromatographic paper, the results of the chromatographic separation depend to some extent on the quality of the paper. They also depend on the concentration of the hydrolyzing element, or more precisely, on the ratio of hydrolyzed species to sorption sites.

As can be seen from Fig. 2, beginning at about pH 2 increasing amounts of Ac are bound on the cellulose along the pathway of the upwards moving solution, and increasing amounts are held back on the starting point. On approaching pH 4, partially all of the Ac is retained at and near the starting point.

The results of another set of experiments with Ac are plotted in Fig. 3. A groundwater of low salinity taken at the Gorleben site (FRG, Weichsel glacial, depth of 12 to 15 m) was equilibrated with the sediment taken at the same site for one week, separated from the sediment, left at rest for one week and filtered through a membrane filter of 0.45 μm pore size. All operations were carried out under anaerobic conditions in a glove box filled with 99% Ar + 1% CO_2 . This precaution

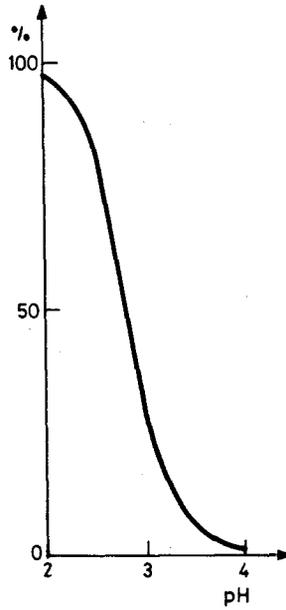


Fig. 2. Mobility of Ac^{3+} in water as a function of pH [paper chromatography, $c_0(\text{Ac}) \approx 10^{-9}$ mol/l]

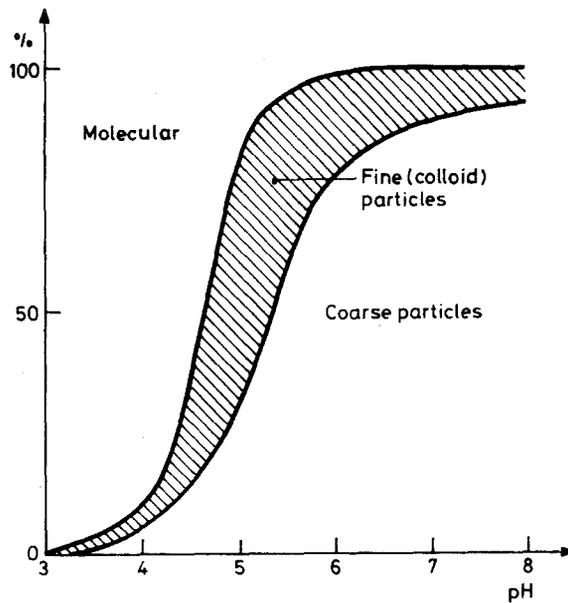


Fig. 3. Partition of Ac in groundwater of low salinity [pH 7.4 ± 0.2 , $c_0(\text{Ac}) \approx 10^{-9}$ mol/l]

is important with respect to redox reactions of other elements, in particular of iron, which may influence the behaviour of Ac. pH and the redox potential E_h were measured. pH was 6.6 ± 0.1 and E_h was 70 ± 15 mV. The groundwater was spiked with small amounts of ^{227}Ac and pH was adjusted by addition of small amounts of HCl or NaOH, respectively. After one week of standing at rest, pH and E_h were checked and the groundwater samples were passed successively through a membrane filter of $0.45 \mu\text{m}$ pore size and an ultrafilter of $0.002 \mu\text{m}$ pore size (Amecon filter sets). The relative activities in the unfiltered, the $0.45 \mu\text{m}$ filtered and the $0.002 \mu\text{m}$ filtered samples were measured by use of the liquid scintillation technique.⁹ From the results the partition of Ac on the molecular fraction ($< 0.002 \mu\text{m}$), the fine particle (colloid) fraction (0.002 to $0.45 \mu\text{m}$) and the coarse particle fraction ($> 0.45 \mu\text{m}$) was calculated and plotted in Fig. 3. The following features are evident from Fig. 3. Beginning at about pH 3, increasing amounts of Ac are found in the fine particle (colloid) fraction, and at about pH 5 more than 50%. At the same time the percentage of Ac in the coarse particle fraction increases and dominates above pH 6.

The question about the nature of fine particles and of coarse particles is to be answered as follows. It is extremely improbable that Ac present in concentrations of about 10^{-9} mol/l is able to form coarse particles by condensation of hydroxo complexes. The amount of Ac present at this concentration in 1 ml solution would give about 40 particles of $1 \mu\text{m}$ diameter and of 1 g/cm^3 density. However, by autoradiography of the filters through which the spiked groundwaters were passed, no single particles were detected, but a practically continuous layer of material containing the ^{227}Ac was observed. That proves that the main constituents of the coarse and the fine particle fraction carrying the ^{227}Ac must be of other origin. Chemical analysis of the groundwater has shown that it contains appreciable amounts of silicic acid (about 12 mg/l of SiO_2 $< 0.002 \mu\text{m}$ and about 3 mg/l of SiO_2 in the range between 0.002 and $0.45 \mu\text{m}$), smaller amounts of iron (about 0.3 mg/l $< 0.002 \mu\text{m}$, about 0.7 mg/l in the range between 0.002 and $0.45 \mu\text{m}$ and about 2.5 mg/l $> 0.45 \mu\text{m}$), and small amounts of colloidal clay. Thus, the concentration of silicic acid is about 5 to 6 orders of magnitude higher than that of Ac. These relatively high concentrations of silicic acid are found in all natural waters.¹⁰ Reaction of the hydroxo complexes of Ac with the various forms of silicic acid, with colloidal iron hydroxide or with colloidal clay minerals is very probable. Investigation of the filters in the electron microscope by means of an X-ray microprobe revealed that Si, minor amounts of Fe and some clay particles are the main constituents of the material filtered off from the groundwater.

It is remarkable that a coarse particle fraction is found in the groundwater samples after one week of standing at rest, although the samples had been filtered before

through membrane filters of $0.45 \mu\text{m}$ pore size. This shows that the fine particles interact with each other forming coarse particles and that after filtration a new distribution between fine and coarse particles is established by this interaction. Accordingly, Ac which is bound by sorption on the particles is found in the fine as well as in the coarse particle fraction.

It should be mentioned that in saline groundwaters the formation of colloids is considerably suppressed with the consequence that different partition is observed.

The sorption ratio of Ac on the corresponding sediment taken at the same site is plotted in Fig. 4 as a function of pH. For this set of experiments the same ground-

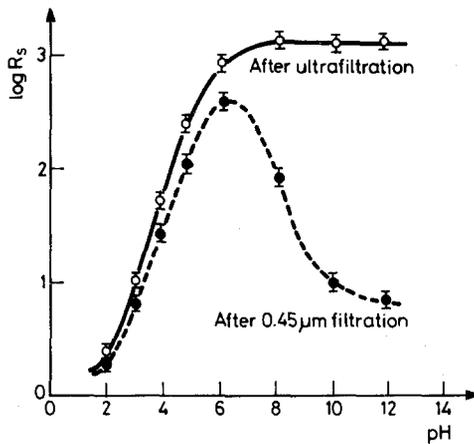


Fig. 4. Sorption ratio R_s (R_s in ml/g) of Ac as a function of pH

water and the same sediment were used as for the previous set of experiments. Groundwater and sediment were equilibrated in the volume to mass ratio 2.5 ml/g for one week and pH was adjusted by addition of HCl or NaOH, respectively. Because of the buffer capacity of the system, several additions were necessary to obtain the pH wanted. Then the groundwater was spiked with ^{227}Ac and equilibration was continued for another week. Only very smooth agitation was applied to avoid setting free of large amounts of suspended matter into the groundwater. Again, all operations were carried out under anaerobic conditions. pH and E_h were checked. After filtration and subsequent ultrafiltration the activity was measured in a liquid scintillation spectrometer and the sorption ratio R_s was calculated.

Figure 4 shows the strong increase of the sorption ratio above pH 2, that is where also the mobility of Ac decreases due to hydrolysis (Fig. 2). After ultrafiltration, an increase of the sorption ratio by about 3 orders of magnitude is observed. After filtration through filters of $0.45 \mu\text{m}$ pore size, however, an increase and then a

decrease of the sorption ratio is observed with increasing pH under the conditions of these experiments. The explanation of this behaviour is as follows. Up to about pH 4.5, molecular species of Ac dominate in the groundwater, as can be seen from Fig. 3. These molecular species are mainly sorbed on the sediment by hydrolytic adsorption. Above about pH 4.5 the tendency of the hydrolyzed Ac species to react with molecular or colloidal species of silicic acid (and possibly with other compounds of low molecular weight like iron hydroxide) prevails and fine (colloidal) particles carrying the Ac (carrier colloids) dominate. This is also obvious from Fig. 3. These carrier colloids probably consist mainly of colloidal silicic acid on which Ac is bound by chemisorption. They are not filtered off by 0.45 μm filters, but only by ultrafiltration. At higher acidity (lower pH) stable bonds between the hydroxo complexes of Ac and the groundwater colloids are not formed.

The influence of increasing NaCl concentration is shown in Fig. 5. The experiments were carried out in the same way as described above and various amounts of NaCl were added at pH 7.5 ± 0.5 and at pH 3.5 ± 0.5 . Whereas at pH 7.5 no measurable influence of the NaCl concentration is observed, this influence is appreciable at pH 3.5. At pH 7.5 hydrolysis of Ac is practically complete. There is no contribution of ion exchange and the Na^+ ions do not compete with Ac for the sorption sites. At pH 3.5, however, hydrolysis is incomplete and ionic species of Ac prevail. At this pH, Na^+ ions compete with the ionic species of Ac in the ion exchange which leads to the negative slope of ≈ -0.8 in Fig. 5. This explanation is also in agreement with Figs 2 and 3. At pH 3.5 the partially hydrolyzed species of Ac are strongly retained by hydrolytic adsorption (Fig. 2), but they are mainly present in molecular form (Fig. 3).

The influence of complexing agents is demonstrated in Fig. 6. The experimental conditions were the same as in the other sorption experiments. pH was kept constant and EDTA was added in various concentrations. Even in presence of small concentrations of EDTA (10^{-5} mol/l) a drastic decrease of the sorption ratio is observed (Fig. 6). In discussing the influence of complexing agents it has to be taken into account that many cations which are present in the groundwater may compete with the trace elements for complexation. Therefore, the complexation of trace elements depends on the relative concentrations of these cations and on the stability constants of the various complexes. Furthermore, the sorption equilibria of the complexes have to be considered. At very low concentrations of complexing agents, the fraction bound on the surface of the sediment by physical adsorption is relatively high. The influence of complexing agents can be calculated only if all parameters (concentrations of cations, stability constants and sorption equilibria of the complex) are known.

In further experiments, groundwater of low salinity spiked with ^{227}Ac was passed upwards through columns containing 10 cm of the corresponding sediment at a

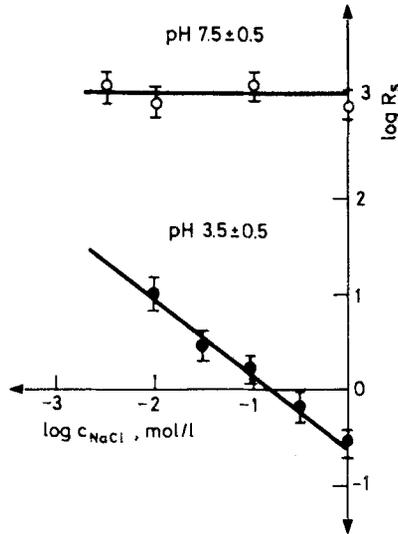


Fig. 5. Influence of NaCl concentration on the sorption of Ac at pH 7.5±0.5 and at pH 3.5±0.5 [$c_0(\text{Ac}) \approx 10^{-9}$ mol/l]

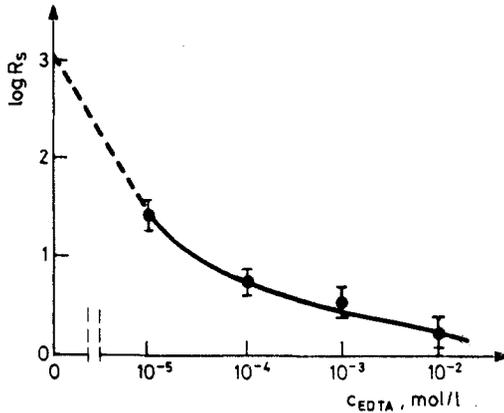


Fig. 6. Sorption ratio of Ac as a function of the concentration of EDTA [pH 7.6±0.3, $c_0(\text{Ac}) \approx 10^{-9}$ mol/l]

linear flow rate of 10 cm per day. Groundwater and sediment were preequilibrated for one week, and the groundwater was spiked by addition of ^{227}Ac . The partition of Ac in the groundwater on the coarse particle fraction ($> 0.45 \mu\text{m}$), the fine (colloid) particle fraction and the molecular fraction ($< 0.002 \mu\text{m}$) was determined by filtration ($0.45 \mu\text{m}$ filters) and ultrafiltration. Then the groundwater was passed through the column, 10 ml fractions of the effluent were sampled and the partition

of Ac was measured again. pH and E_h were checked in the initial and in the effluent groundwater. After throughput of about 30 ml of groundwater practically constant values were found. Again, all operations were carried out in an inert gas box (99% Ar, 1% CO₂). The results are summarized in Table 1.

Table 1
Partition of Ac in groundwater of low salinity in percent before
and after passing through 10 cm of sediment at a linear flow rate of 10 cm/day
(pH 6.5 ± 0.2, E_h 80 ± 15)

	Before	After
Coarse particle fraction (>0.45 μm)	95 ± 5	0.30 ± 0.05
Fine particle (colloid) fraction	4.5 ± 0.5	0.20 ± 0.05
Molecular fraction (<0.002 μm)	0.8 ± 0.5	0.15 ± 0.05
	100	0.65

Before passing through the column, the main part of Ac (\approx 95%) is in the coarse particle fraction. Less than 1% (0.65%) of the total amount of Ac is found in the effluent. That means retention in the column is very effective. The partition of Ac changes considerably while passing through the column (Table 1). In the effluent approximately equal amounts of Ac are in the three fractions. It must be concluded that the effective retention is mainly due to size filtration. Coarse particles carrying the Ac, and to a smaller extent fine particles, are very effectively retained in the pores of the sediment.

The mobility of Th in water, as found by paper chromatography, is plotted in Fig. 7 as a function of pH. The experimental conditions were the same as those described for Ac (Fig. 2). Due to its higher tendency of hydrolysis, the mobility of Th begins to decrease already at pH 1.

The partition of traces of Th (\approx 10⁻¹¹ mol/l) in groundwater of low salinity is plotted in Fig. 8. The experiments were carried out in the same way as in the case of Ac. ²³⁴Th separated from ²³⁸U was used as tracer and measured by means of liquid scintillation spectrometry. Figure 8 shows that at about pH 2.5 a relatively large percentage of Th is found in form of fine (colloidal) particles and that above pH 5 the coarse particle fraction of Th dominates. As in the case of Ac, single particles of Th compounds were not detected by autoradiography of the filters, and the electron microscope in combination with a X-ray probe revealed that the material carrying Th and retained on the filters consisted mainly of silicic acid, some iron hydroxide and some clay particles.

The chemistry of Th is much better known than that of Ac, and it is evident from

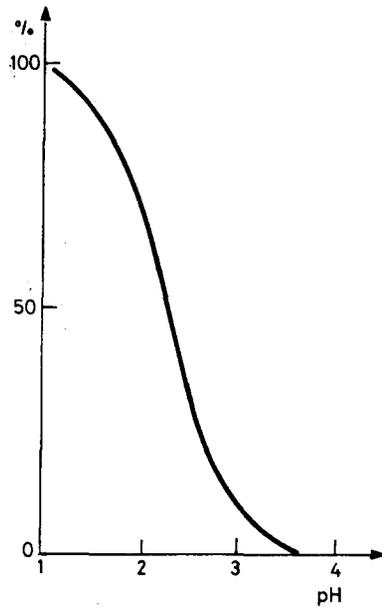


Fig. 7. Mobility of Th⁴⁺ in water as a function of pH [paper chromatography, $c_0(\text{Th}) \approx 10^{-11}$ mol/l]

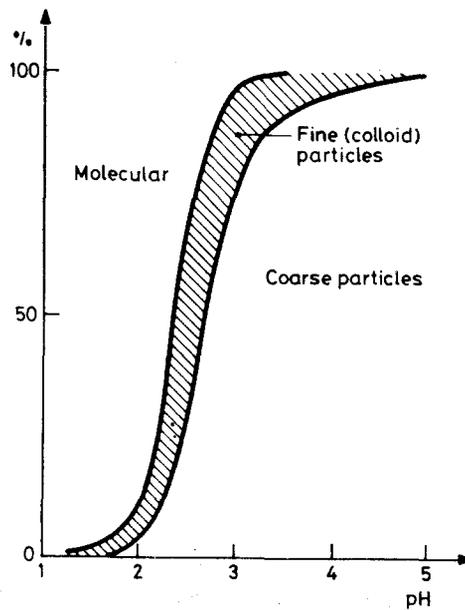


Fig. 8. Partition of Th in groundwater of low salinity [pH 7.4 ± 0.2 , $c_0(\text{Th}) \approx 10^{-11}$ mol/l]

the literature that Th reacts easily with silicic acid (silica gel) at relatively low pH.¹¹ At low concentrations of Th ($\approx 10^{-11}$ mol/l) and relatively high concentration of silicic acid (10^{-4} to 10^{-3} mol/l of SiO_2) in the groundwater, the chance of interaction of hydroxo complexes of Th with each other is very low, whereas the chance of interaction with silicic acid is high. Thus, the high tendency of formation of coarse particles ($> 0.45 \mu\text{m}$) of polysilicic acid on which Th is bound by hydrolytic adsorption is evident. Colloidal particles of iron hydroxide may also be involved in the formation of these particles.

The results of column experiments with Th are summarized in Table 2. The experimental procedure was the same as in the case of Ac (Table 1). Compared with

Table 2
Partition of Th in groundwater of low salinity in percent before
and after passing through 10 cm of sediment at a linear flow rate of 10 cm/day
(pH 6.5 ± 0.2 , E_h 80 ± 15)

	Before	After
Coarse particle fraction ($>0.45 \mu\text{m}$)	98 \pm 2	0.20 \pm 0.05
Fine particle (colloid) fraction	1.3 \pm 0.1	0.18 \pm 0.05
Molecular fraction ($<0.002 \mu\text{m}$)	1.0 \pm 0.5	0.20 \pm 0.05
	100	0.58

the results obtained for Ac, the amount of Th in the fine particle fraction is lower in the initial groundwater, but the other results are very similar. Less than 1% (0.58%) of Th are found in the effluent groundwater, and the amounts of Th in the coarse particle fraction, the fine (colloid) particle fraction and the molecular fraction in the effluent are practically the same. Again, the coarse particle fraction is reduced most drastically in the column due to effective size filtration of the particles in the pores of the sediment.

Insofar, sorption on natural sediments was considered. However, most sediments contain a great number of various substances, and sorption behaviour does not only depend on the properties of the species in solution, but also on the properties and the relative amounts of the solids. As a solid of definite properties, hydrous titanium dioxide was selected, and the sorption of UO_2^{2+} ions on this substance was studied in detail, because $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ is of special interest with respect to selective separation of uranium.^{1,2}

The main aspects of the sorption behaviour of UO_2^{2+} on $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ are evident from Fig. 9, in which the sorption ratio of UO_2^{2+} for 10^{-6} mol/l aqueous solutions under aerobic conditions is plotted as a function of pH. The experimental details are

given in the literature.¹² It is interesting to note that sorption of UO_2^{2+} goes parallel with the formation of the monohydroxo complex UO_2OH^+ and reaches its maximum near the isoelectric point of the TiOH groups. At higher pH where negatively charged polynuclear hydroxo complexes of U(VI) are formed, the sorption ratio decreases. From Fig. 9 it is obvious that the hydrolysis of MO_2^{2+} ions is of great importance for their sorption behaviour, similar as in the case of M^{3+} and M^{4+} ions.

The influence of the redox potential on the sorption behaviour of Np is shown in Fig. 10. In this figure the sorption ratios measured in 8 different groundwater/

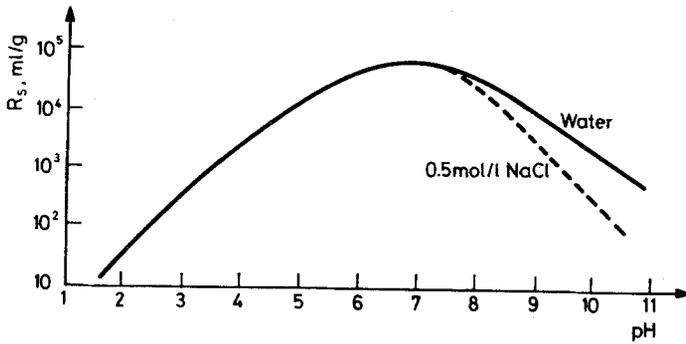


Fig. 9. Sorption ratio R_s (R_s in ml/g) of UO_2^{2+} on $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ as a function of pH in water and in 0.5 mol/l NaCl

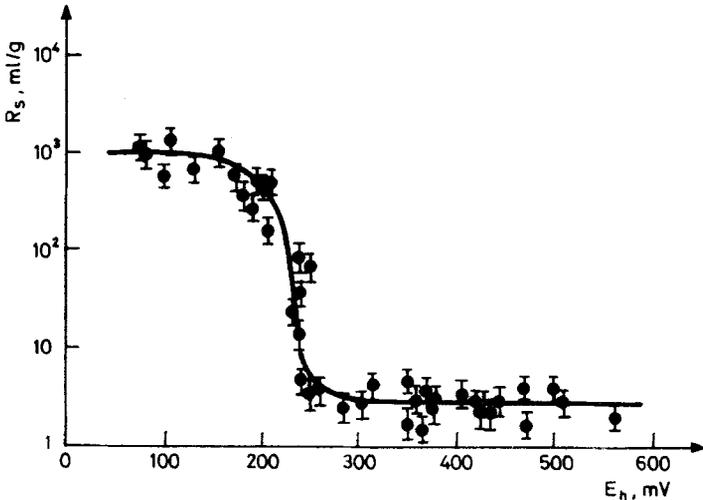


Fig. 10. Sorption ratios of Np in various groundwater/sediment systems, plotted as a function of the redox potential E_h

sediment systems, all taken at different depths at the Gorleben site (FRG), are plotted as a function of the redox potential E_h . The initial concentration of Np in the groundwaters was $\approx 10^{-7}$ mol/l. The redox potential was varied by varying the oxygen content in the inert gas box. Experimental details were given in a previous publication.^{1,3} The composition of the sediments, their specific surface area, the composition of the groundwaters, their salinity and their pH are different. Consequently, the sorption ratios must also be different. The sorption ratios vary between 2 and 5 at high E_h and they are of the order of 10^3 at low pH. With decreasing E_h the sorption ratio increases rather sharply at about $E_h = 240$ mV. At this redox potential, measurable amounts of Np(IV) are formed in the redox equilibrium. Due to the high sorption ratio of Np(IV) the reduced species are separated from solution by sorption, and in the redox equilibrium further Np(V) is reduced to Np(IV). At higher concentrations of Np, higher amounts of Np(IV) are separated from solution by sorption and precipitation, and due to the low solubility of neptunium(IV) hydroxide higher sorption ratios are measured.

Conclusions

Behaviour of actinides in the environment depends on hydrolysis, complex formation and colloid formation. At trace concentrations, the hydroxo complexes of tri- and tetravalent actinides react in certain pH ranges with other components present in solution (mainly silicic acid, some iron hydroxide and some colloidal clay particles) to give carrier colloids and suspended coarse particles carrying the actinides. When the groundwaters pass through sediments, the actinides are retained very efficiently by size filtration of coarse and to a smaller extent of fine particles which carry the actinides.

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