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Actinide Colloid Generation in Groundwater

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Actinides / Colloids / Groundwater / Migration

Abstract

Recent progress in the study of actinide colloid generation in groundwaters is summarized and discussed with particular examples relevant to an understanding of the migration behaviour of actinides and natural aquifer systems. The first part deals with the characterization of colloids: groundwater colloids, actinide real-colloids and actinide pseudocolloids. The second part concentrates on the generation processes and migration behaviour of actinide pseudocolloids, which are discussed with some notable examples available in the literature. Importance is stressed more on the chemical aspects of the actinide colloid generation in groundwater.

1. Introduction

Natural colloids are ubiquitous in all groundwaters. The chemical composition, structure and particle size of natural colloids vary widely depending on the geochemical nature of given aquifer systems [1, 2] and their particle concentration likewise varies to a great degree from 10^8 to 10^{17} particles per liter of water [2, 3].

These colloids are chemically surface-active and therefore readily adsorb metal ions of higher charge ($Z \geqq 2+$) through complexation and/or ion exchange processes [1, 4, 5]. The actinide ions with high electric charges ($Z \geqq 2+$) are unstable in groundwater due to their strong hydrolysis reactions [1] and thus easily adsorbed on natural colloids. The generation of such colloids, called "pseudocolloids" of actinides, may increase the amount of actinides in groundwater much higher than their thermodynamic solubilities [1] and may thus enhance the possibility of their migration in a given aquifer system [4, 6].

For these obvious reasons, much attention has been attracted recently to the chemistry of groundwater colloids in the field of the migration study of actinides [1 – 17] and environmental contaminants [18] in the geosphere. The role of colloids is being appraised as of critical importance for the near and far field assessment of the migration behaviour of actinides [4, 6, 7, 9, 11, 19]. Failure to account for colloid transport, as a carrier of actinides, can lead to serious underestimates of the actinide migration. For example, at Los Alamos, plutonium and americium were detected in monitoring wells over a kilometer from a liquid waste outfall and the transported radionuclides were characterized as being bound on colloids of 25 nm to 450 nm particle size [20].

This paper reviews the present state of the groundwater colloid chemistry, the potentially critical role of groundwater colloids for transport of actinides, generation processes of actinide pseudocolloids, their geochemical interactions and migration of actinide pseudocolloids.

2. Characterization of colloids

The colloids under discussion are classified into three kinds: "groundwater colloids", "real colloids" of actinides and "pseudocolloids" of actinides [1, 4, 10, 14]. Groundwater colloids are naturally occuring in all groundwaters, real colloids are produced by the aggregation of hydrolysed actinide ions and pseudocolloids are generated by sorption of actinide ions, or colloids, on groundwater colloids. Whether or not the naming of pseudocolloids is appropriate is contended by some authors [17], on the grounds that the prefix "pseudo" may perceptibly misrepresent the state of the colloid under discussion. For the clear distinction between the colloid of an actinide itself and a groundwater-colloid-borne actinide [4 – 14], we are going to use the above given classification for different kinds of colloids in the text throughout. The three kinds of colloids in question are distinctively different from one another from a chemical viewpoint [5, 8, 14, 17]. The proper characterization of each of these colloids is an essential prerequisite for understanding their role in the migration process of actinides in a variety of aquifer systems.

2.1. Groundwater colloids

Groundwater colloids are composed of inorganic and organic molecular constituents [4, 5, 15, 17, 18, 21, 24, 26], a mixture of both [5, 21], or microorganisms [18]. They include detritus of weathering mineral products [15, 26], hydrolysed precipitates of mixed metal ions [4, 24], macromolecular components of dissolved organic carbon (DOC), e.g. humic substances, loaded with metal ions [1, 5], and biocolloids composed probably of microorganisms [18]. Experiences show that colloids of inorganic or organic nature, besides biocolloids, are relatively small in size (<450 nm diameter) [3, 7, 15, 19, 21], so that the characterization of these

Table 1. Major ions and trace elements in Gorleben groundwaters with different DOC concentrations [5, 23, 24] (an average accuracy of analytical data given here is 5%)

Element		Gohy-73 (pH = 7.8)	Gohy-1012 (pH = 8.2)	Gohy-1011 (pH = 7.9)
DOC (mg C/l)*		97.3	7.8	< 0.5
Major ions (mol l^{-1})				
Na^+	(10^{-3})	25.3	10.9	0.8
Ca^{2+}	(10^{-4})	2.6	2.6	16.5
Mg^{2+}	(10^{-5})	10.5	6.2	2.2
Cl^-	(10^{-3})	8.2	9.4	1.7
NO_3^-	(10^{-5})	96.8	< 0.5	2.2
SO_4^{2-}	(10^{-5})	0.3	18.4	60.4
SiO_3^{2-}	(10^{-4})	2.6	6.0	2.7
HCO_3^-	(10^{-3})	16.3	3.3	1.4
Trace element (mol l^{-1})				
Ba	(10^{-8})	37.0	7.0	54.5
Cr	(10^{-8})	39.1	4.2	0.23
Ce	(10^{-8})	70.4	3.2	–
Eu	(10^{-9})	10.9	1.8	0.05
Fe	(10^{-6})	48.6	3.7	0.16
Hf	(10^{-9})	6.2	0.4	–
La	(10^{-8})	26.3	1.6	0.04
Nd	(10^{-8})	27.0	2.3	–
Sm	(10^{-9})	45.0	4.2	0.24
Sr	(10^{-7})	20.7	8.4	15.8
Th	(10^{-9})	105.0	3.2	2.4
U	(10^{-9})	11.0	5.5	–
Zr	(10^{-8})	128.0	12.0	–

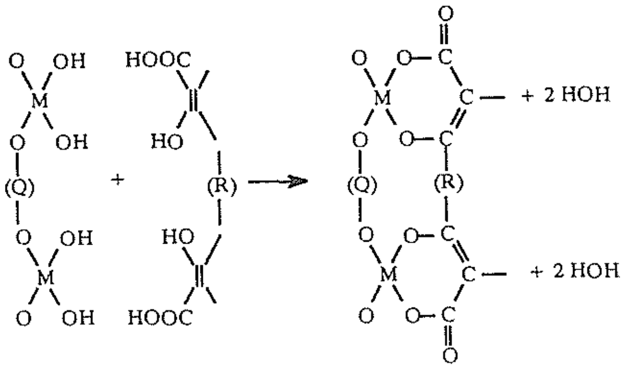
* DOC is mainly composed of humic and fulvic acids [23].

colloids requires modern ultrafiltration techniques or high power ultracentrifugation. In Gorleben aquifer systems the major part of colloids is found to have an average size smaller than 100 nm [2, 3, 21]. Colloids composed of microorganisms might be relatively large in size (> 450 nm) [18, 22] and therefore can be easily distinguished from other groundwater colloids. A little knowledge is available for such biocolloids in deep aquifer systems. For this reason, this paper deals only with colloids of inorganic and organic constituents.

For the purposes of demonstration, three particular groundwaters from the Gorleben area, which shall be the future German repository site, are chosen to characterize colloids in these waters and later to elucidate geochemical interactions of groundwater colloids with actinide ions [4, 23, 24].

The analytical data of the major ions and trace elements in the groundwaters of different DOC concentrations are given in Table 1. DOC in these groundwaters are found to be composed of humic and fulvic acids [23]. Taking into account an average carbon content of humic or fulvic acid, i.e. 57% [25], the aquatic humic substance concentrations in each of the groundwaters are 170.7 mg in Gohy-73, 15.7 mg in Gohy-1012 and < 0.9 mg in Gohy-1011 [23, 24]. With its exceptionally large concentration of humic substances, Gohy-73 does not represent an ordinary groundwater. However, its content of heavy trace elements, particulary tri- and tetravalent elements, are of interest for comparison with those in Gohy-1012 and Gohy-1011. As shown in Table 1, the concentrations of trace elements (valence states of III and IV) show a certain proportionality to the amount of humic substances (or DOC) in the three groundwaters. This fact implies that many of the trace elements are bound on humic substances through either complexation or ion exchange.

Since actinide ions bound on aquatic humic substances cannot be characterized spectroscopically as humate complexes [23], their chemical state can only be colloidal [5]. Such pseudocolloids of actinides are called "humic colloids" [5, 23] in order to distinguish from other colloids. This kind of colloid is composed of large organic polyelectrolyte molecules with carboxylic, phenolic and other minor functional groups with a certain proton exchange capacity [25]. Metal ions can be sorbed on humic colloids by monodentate or multidentate complexation. Real colloids of actinides can also be sorbed on humic colloids in accordance with the following dehydration process [26]:



Wherein (Q) and (R) are the cores of the polynuclear metal hydroxide and humic substance, respectively. By their chemical nature humic colloids thus produced are more stable in aqueous solution than colloids of inorganic composition, since the latter are composed of oxygenbridges with hydroxide surfaces and hence tend towards sorption on mineral surfaces.

As shown in Table 1, concentrations of heavy elements in Gohy-1011 are much lower than in other groundwaters because of a very small amount of humic substances (or DOC). However, there is a substantial amount of colloids to be observed by laser induced photoacoustic spectroscopy (LPAS) with its light scattering measurements [3, 24]. The number of colloid particles counted, taking into account an average size of 100 nm diameter, is 3.4×10^{11} particles l^{-1}. This number is comparable with that in the granitic groundwater from Grimsel Switzerland [15] measured by the same technique, i.e. 3.2×10^{11} particles l^{-1}. Since the average sizes of groundwater colloids are smaller than 100 nm, the actual numbers in both groundwaters would be at least one or two orders of magnitude larger [3, 15].

In the presence of humic substances the particle number of colloids increases substantially. Semiquan-

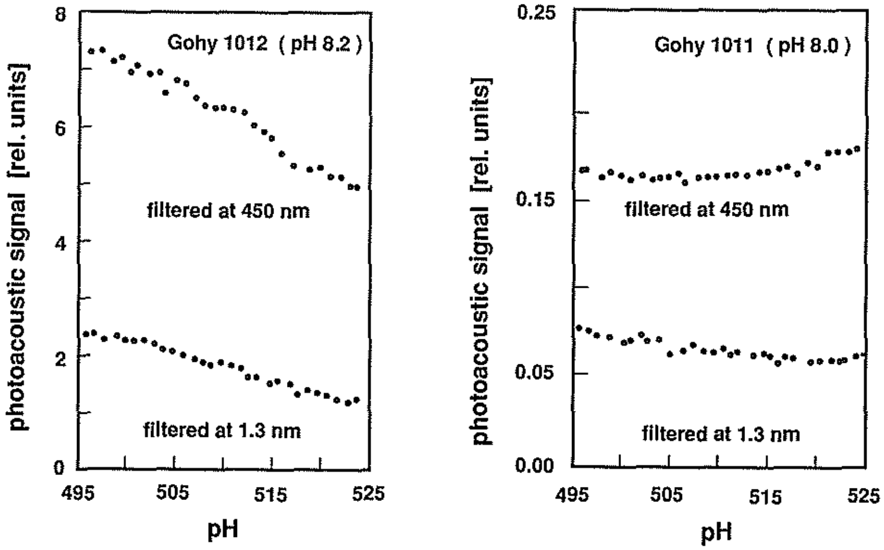


Fig. 1. Colloid characterization by photoacoustic measurement of light scattering in two different Gorleben groundwaters: one with organic colloids (Gohy-1012) and another with inorganic colloids (Gohy-1011): Filtration at different pore sizes shows a decrease of colloids in filtrates [24].

Table 2. Analysis of trace elements in the Gohy-1012 groundwater and colloids (concentration in mol l^{-1}) [1, 4]

Element	Groundwater (0.45 μm)	Groundwater-colloids*			
		XM 300** (15 nm)	XM 100 A (5 nm)	XM 50 (3 nm)	YM 5 (~1 nm)
Ba	7.0×10^{-8}	ND	2.7×10^{-8}	ND	3.7×10^{-8}
Br	1.9×10^{-6}	7.7×10^{-9}	1.1×10^{-8}	1.1×10^{-8}	1.2×10^{-8}
Ca	2.6×10^{-4}	2.5×10^{-5}	3.7×10^{-5}	5.7×10^{-5}	7.9×10^{-5}
Ce	3.2×10^{-8}	0.7×10^{-8}	1.2×10^{-8}	1.3×10^{-8}	1.6×10^{-8}
Co	2.2×10^{-8}	ND	3.4×10^{-9}	1.3×10^{-9}	2.2×10^{-9}
Cr	4.2×10^{-8}	1.0×10^{-8}	1.4×10^{-8}	1.5×10^{-8}	1.6×10^{-8}
Eu	1.8×10^{-9}	6.7×10^{-10}	9.4×10^{-10}	8.2×10^{-10}	1.1×10^{-9}
Fe	3.7×10^{-6}	3.1×10^{-6}	3.4×10^{-6}	3.5×10^{-6}	3.6×10^{-6}
Hf	3.8×10^{-10}	0.7×10^{-10}	1.2×10^{-10}	1.2×10^{-10}	1.5×10^{-10}
La	1.6×10^{-8}	3.1×10^{-9}	4.8×10^{-9}	5.2×10^{-9}	6.2×10^{-9}
Nd	2.3×10^{-8}	5.1×10^{-9}	ND	5.4×10^{-9}	6.3×10^{-9}
Sb	1.6×10^{-9}	1.3×10^{-10}	2.3×10^{-10}	3.1×10^{-10}	1.2×10^{-9}
Sm	4.2×10^{-9}	6.3×10^{-10}	1.0×10^{-9}	1.1×10^{-9}	ND
Th	3.2×10^{-9}	1.5×10^{-9}	2.2×10^{-9}	2.6×10^{-9}	2.7×10^{-9}
U	5.5×10^{-9}	6.3×10^{-10}	5.3×10^{-10}	5.4×10^{-10}	2.1×10^{-9}

*: Groundwater is filtered by a Millipore filter of 0.45 μm and groundwater-colloids are collected by different Amicon filters as indicated. The concentration of each element in colloids corresponds to its amount in 1 liter groundwater.
**: Amicon filter description (estimated pore size in parentheses) above columns.
ND: Not determined.

titative illustrations of colloid numbers measured by LPAS [24] for Gohy-1012 and Gohy-1011 are shown in Fig. 1. The relative intensities of light scattering measured by LPAS in filtrates from ultrafiltration at 450 nm and 1.3 nm pore sizes demonstrate unambiguously the amounts of colloids in both groundwaters. According to Fig. 1, the amount of colloids in a size group from 1.3 nm – 450 nm is approximately 50 times larger in Gohy-1012 than in Gohy-1011. The chemical composition of colloids in Gohy-1012 is found to be predominantly of organic nature whereas those in Gohy-1011 are of inorganic nature [24].

Most humic colloids contain a major part of metal ions of higher oxidation states ($Z \geqq 3+$) present in groundwater. This has been proved by analysis of metal ion concentrations in groundwater colloids collected on various ultrafilters with decreasing pore size [4, 21]. A typical example is shown in Table 2 for Gohy-1012 [4], which compares metal ion concentrations in groundwater with those in colloids separated on ultrafilters of different pore sizes. A substantial amount of each element ($Z \geqq 3+$) is found in colloids of sizes larger than ca. 1 nm, while Fe is present quantitatively in colloids. Since in this groundwater 3.3×10^{-3} M HCO_3^- and 1.4 mg C l^{-1} fulvic acid [1] are present, apart of metal ions ($Z \geqq 3+$) is complexed with them and remain unfilterable at a pore size of ca. 1 nm.

Humic colloids with their strong absorption capacity of metal ions of higher oxidation state ($Z \geqq 3+$)

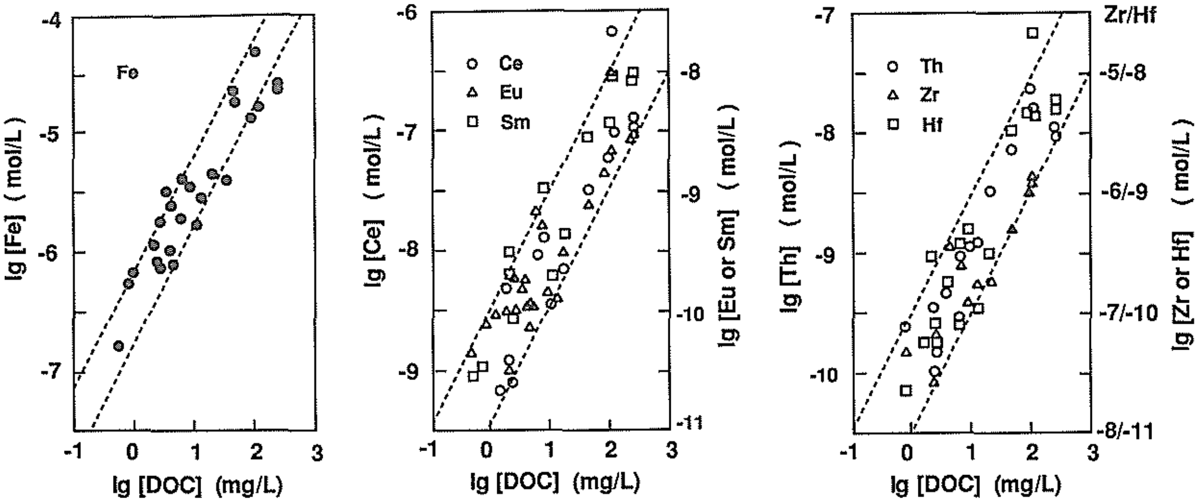


Fig. 2. Natural concentrations of elements (M(III) and M(IV)) as a linear function of the DOC concentration (mainly humic substances) in Gorleben groundwaters [23]: An average slope of one is found for each element.

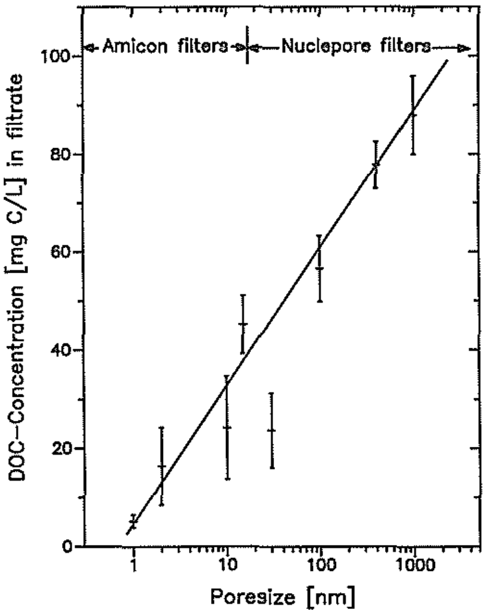


Fig. 3. A linear relationship of the DOC concentration (86% humic acid and 14% fulvic acid) with the filtration pore size in one of the Gorleben groundwaters (Gohy-2227) [21].

considerably increase concentrations of such elements in groundwater [5, 21, 23]. A typical example [5] is shown in Fig. 2, which illustrates a linear correlation between the concentrations of trivalent and tetravalent elements, i.e. Fe, Ce, Eu, Sm, Hf, Zr and Th, and the DOC concentration in various Gorleben groundwaters [23]. The linear correlation with an average slope of one found for all elements suggests that trivalent and tetravalent elements are present as being DOC-bound. This means, they are bound to aquatic humic substances [5], since in Gorleben groundwaters DOC is mainly composed of humic and fulvic acids [23]. The filtration characteristics of DOC in one of the Gorleben groundwaters are demonstrated in Fig. 3 [21]. About 94% of DOC can be filtered at a pore size of ca. 1 nm, infering that the major part of DOC is larger than 1000 Dalton in molecular size.

The interesting facts revealed in Fig. 2 (see also Table 2) are the association of heavy metal ions ($Z \geqq 3+$) with DOC (mainly humic substances in the case of Gorleben groundwaters), especially trivalent and tetravalent ions. These elements are chemically analogous to actinides in aquatic solutions, as regards to their hydrolysis and complexation reactions. A close examination of such natural analogues under in-situ natural conditions is of cardinal importance for the assessment of the migration behaviour of actinides in a given aquifer system [21].

2.2. Actinide colloids

The hydrolysis properties of actinide ions under aquatic conditions are mainly governed by the effective charge of a given ion, so that the tendency to hydrolysis of actinide ions follows [27]:

$$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+}.$$

A linear configuration of the $(O=An=O)^{n+}$ ion localizes a relatively high effective charge at the equatorial space. Hydrolysis is a primary step to polynucleation and thus generation of actinide colloids, which are known as real colloids [1, 13]. The relative tendency to generate real colloids of actinide ions is the same as the hydrolsis order indicated above.

Tetravalent actinide ions are most unstable in aqueous solution and readily undergo colloid generation [28–31] even at pH = 1 [30]. Colloids of An(IV), particularly Pu(IV), are rather intractable to revertion to monomer species. As the colloids age the decomposition process entails increasingly rigorous treatment [29]. The ageing process of An(IV) colloids is pictured by a simple model [27], wherein hydroxo bridges are replaced by oxo bridges. For example, Pu(IV) colloids give a distinctive absorption spectrum which remains the same, unaffected by the nature of the solutions in

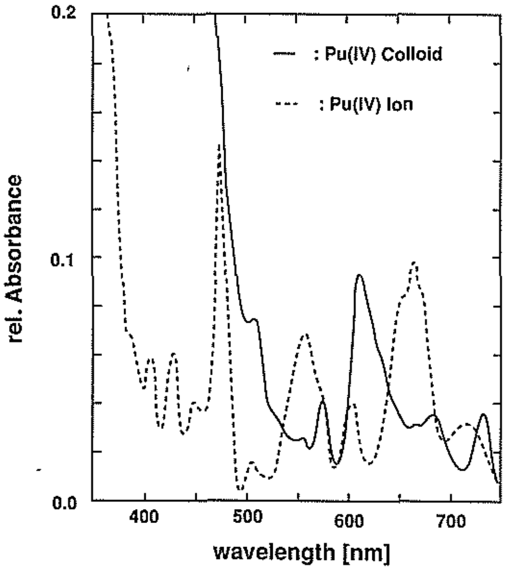


Fig. 4. Absorption spectrum of the Pu(IV)-colloid compared with that of the Pu^{4+} ion [1].

which the colloids are produced [1, 28, 30]. A typical spectrum of Pu(IV) colloids [1] is shown in Fig. 4.

Such a colloid generation increases the solubility of Pu hydroxide or oxide, many orders of magnitude higher than expected thermodynamically in a wide range of pH [30, 31]. Therefore, the dissolution of Pu hydroxide or oxide in aqueous solution involves a quasi equilibrium among three components: ions-colloids-precipitates [30, 31]. A further complication arises from disproportionation or redox reactions of Pu(IV) [28, 31]. Such a chemical system results in great difficulties for the theoretical prediction of Pu(IV) solubilities in natural aquatic solutions. The same situation applies, though to a lesser extent, to other actinides of tetravalent oxidation state.

Following the hydrolsis properties of tetravalent actinide ions, the second strong hydrolsis tendency goes with hexavalent actinyl ions, AnO_2^{2+} [27], which is also conducive to colloid generation. The polynucleation of hydroxides of AnO_2^{2+} in aqueous solution has been reported in the literature [32], but its real colloid generation has not been discussed. In the solubility experiment of $PuO_2(OH)_2$(am) [33], it is observed that Pu concentrations in near neutral solutions of $NaClO_4$ and NaCl (pH=4−9) remain stable at $10^{-4}-10^{-3}$ mol l^{-1}, which is much higher than expected thermodynamically. Spectroscopic verification suggests no involvement of redox reactions, but presumably the generation of Pu(VI) colloids [33]. The study is still in progress for positive verification.

As for trivalent actinide ions, there is clear evidence of their colloid generation. Experimental evidence is available only for Am^{3+} [1, 24]. Am(III) colloids are normally observed from dissolution of the Am hydroxide precipitate in neutral solutions (pH>6) and can be separated by ultrafiltration at a pore size of ca. 1 nm. A typical absorption spectrum of the Am^{3+} solution containing its colloids [24] is illustrated in Fig. 5 together with the spectrum of the Am^{3+} ion. A consecutive ultrafiltration with decreasing pore size reveals the gradual appearance of the Am^{3+} ion in spectra [1]. Am(III) colloids are found to be much less stable in aqueous solution than Pu(IV) colloids and prone to sorption on solid surfaces, especially on experimental vessels. This is the reason why difficulties arise in keeping the Am^{3+} solution at neutral pH.

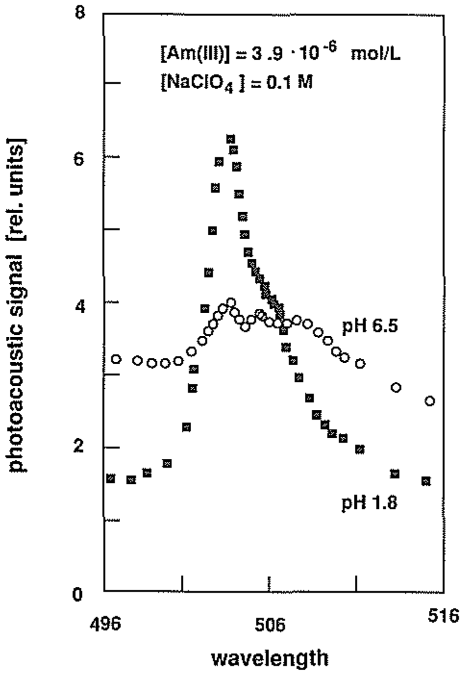


Fig. 5. Comparison of photoacoustic spectra (equivalent to absorption spectra): The Am^{3+} ion and Am(III)-colloid [24].

With respect to colloid formation, pentavalent actinyl ions, AnO_2^{+}, are the most stable against hydrolysis among all actinide ions in aqueous solution. Because of their low effective charge, pentavalent actinyl ions are not hydrolysed up to pH=10 [34], so that these ions, if not undergoing redox reactions, remain very stable in neutral solution. For example the NpO_2^{+} ion appears stable as an unhydrolysed ion up to 10^{-2} mol l^{-1} at pH=7 in $NaClO_4$ without undergoing polynucleation or colloid formation [34].

2.3. Actinide pseudocolloids

Actinide ions are readily sorbed on groundwater colloids in natural aquifer systems [4−9] and thus generate their pseudocolloids. Experiment with colloidal alumina of 20 nm average diameter has demonstrated that trace quantities of ^{228}Th(IV), ^{241}Am(III) and ^{273}Np(V) are quantitatively sorbed on alumina in the pH range studied, where each ion becomes strongly hydrolysed [8]. Fig. 6 shows the sorption behaviour of the ions on alumina colloids as a function of pH [8]. The results from this study indicate that the generation of actinide pseudocolloids is closely related to the hydrolysis process of each ion of different oxidation states and available surface charge and area of alumina

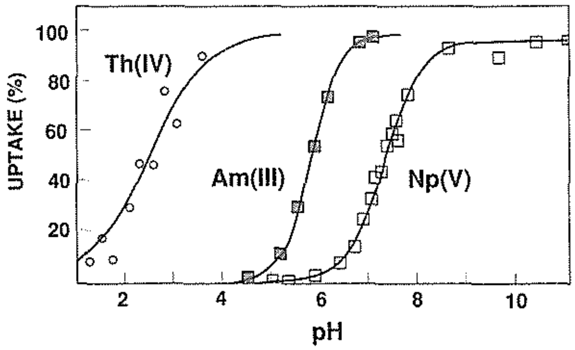


Fig. 6. Sorption of actinide ions on Alumina colloids (actinide pseudocolloid generation) as a function of pH: 10 ppm Alumina for Th(IV) and Am(III), and 200 ppm for Np(V) in 0.1 M $NaClO_4$ [8].

colloids. A similar investigation with different mineral colloids is in progress under the CEC project MIRAGE [2]. Further discussion on actinide pseudocolloids will be made extensively in the following section, as this subject is of great importance for the migration of actinides.

3. Generation and migration of actinide pseudocolloids

3.1. Generation

The generation of actinide pseudocolloids is easily examined by introducing trace quantities of actinide ions in groundwater containing natural colloids [4–8, 14, 23, 24]. As discussed in section 2.3, on surface active mineral colloids (alumina), actinide ions of trivalent and tetravalent oxidation states are sorbed quantitatively at acidic or neutral pH, whereas the AnO_2^+ ion is sorbed quantitatively only at alkaline pH (> 8) [8]. Thus adsorbed actinide ions can be desorbed partially by addition of 50 mM $NaHCO_3^-$ at pH > 8, while the desorption by humic acid takes place with a high humic acid concentration (50 ppm) also at pH > 8 [9]. These results suggest a strong binding of the actinide ions on alumina colloids.

The water leaching of simulated HLW-glasses (high level waste) [7,19] or cement products [10] results in actinide pseudocolloids in leachates, which can be characterized by ultrafiltration. In leachates of a simulated HLW-glass actinide pseudocolloids with sizes smaller than ca. 1 nm are also observed [19]. The presence of such colloids is verified by laser induced photoacoustic spectroscopy (LPAS) and ultrafiltration. The average size of colloids generated in cement leachates is normally larger than that in glass leachates [10]. The long term stability of both kinds of colloids is still not well known.

The generation of actinide pseudocolloids has been demonstrated by a number of experiments in groundwater [4–9, 14] as well as in surface water [35]. The colloid-borne natural radioactivities, e.g. Th and U [21, 36], or fall-out activity, e.g. $^{239/240}Pu$ [35], have also been investigated in groundwater and surface waters, respectively. Actinide ions are readily sorbed on groundwater colloids of either organic [23] or inorganic [8, 24] nature.

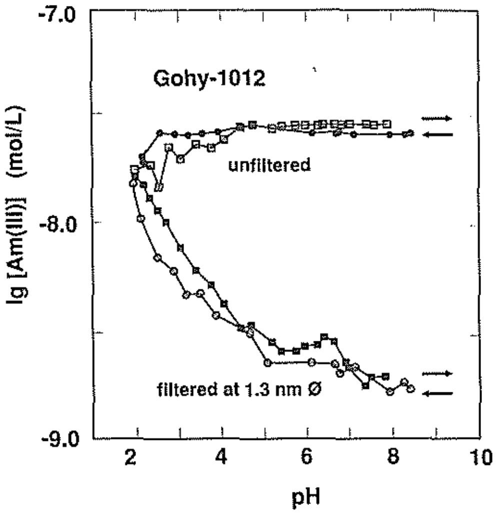


Fig. 7. Reversible exchange reaction of the Am^{3+} ion on natural humic colloids in Gorleben groundwater (Gohy-1012): The Am(III) concentration in unfiltered and filtered (at 1.3 nm pore size) groundwaters as a function of pH [5].

The generation of actinide pseudocolloids can be a reversible reaction, as though the reaction takes place with a soluble ion exchanger [5]. A typical reversible reaction of the actinide pseudocolloid generation [5] is illustrated in Fig. 7. This experiment involves the $^{241}Am^{3+}$ ion and humic colloids in the Gohy-1012 groundwater from Gorleben. The groundwater traced with the Am^{3+} ion of 2.63×10^{-8} mol l^{-1} at pH = 8.4 is titrated with 0.1 M HCl down to pH = 2 and back titrated with 0.1 M NaOH up to pH = 7.8. Along with titration, Am concentrations are determined both in unfiltered solutions and filtrates at a pore size of 5000 Dalton (ca. 1.3 nm) at each given pH. The concentration profiles of Am(III) as a function of the pH in filtrates and unfiltered solutions suggest conclusively a reversible ion exchange process for the Am ion involved. Such a reaction process can be explained as a complexation of the Am^{3+} ion with humic acid, which is the major constituent of the organic colloids in the Gohy-1012 groundwater.

3.2. Speciation

Groundwater colloids are polydispersive in their size and structure and consist of a wide variety of physical forms depending on their chemical composition [26]. The speciation of groundwater colloids involves the characterization of their chemical composition, determination of size distribution and particle number counting. The chemical composition of colloids can be analysed by a combination of diverse micro-analytical methods [4, 21, 23, 24], whereas the size distribution can be determined only by a limited number of methods, e.g. ultrafiltration, scanning electron mi-

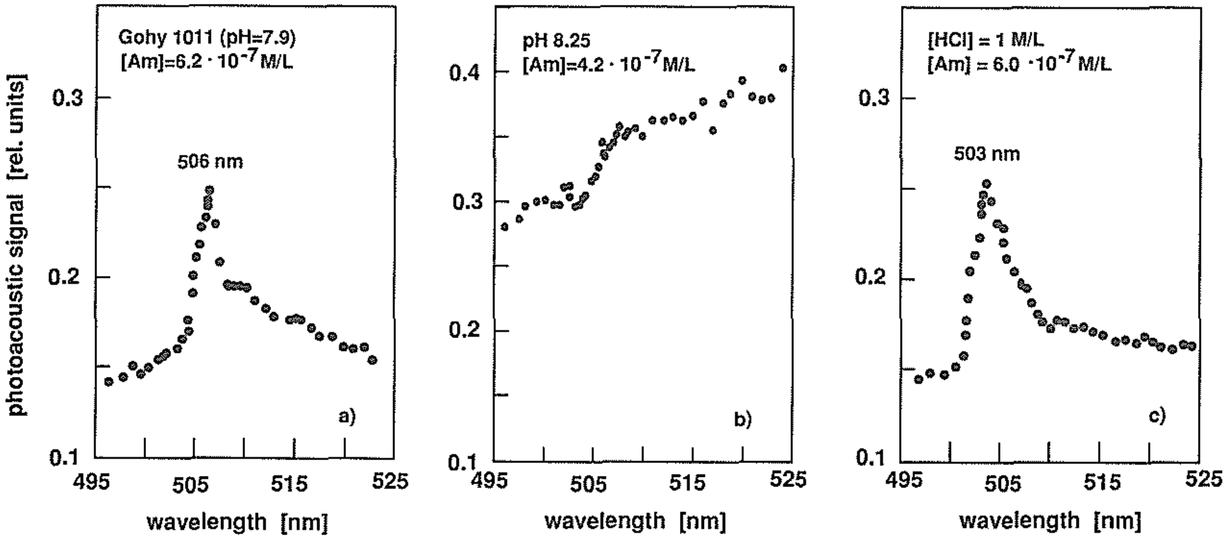


Fig. 8. Speciation of Am(III) in Gorleben groundwater (Gohy-1011) with a low DOC concentration (<0.5 mg C l^{-1}; see Table 1): a) Am carbonate (1% CO_2 partial pressure); b) Am colloid (0.035% CO_2); c) Am^{3+} ion (1 M HCl) [24].

croscopy (SEM) [15] and photon correlation spectroscopy (PCS) [10]. Ultrafiltration facilitates the characterization of a number of size groups, down to ca. 1 nm diameter, while SEM determines the particle number at different sizes down to ca. 50 nm. PCS is a useful technique for number counting of monodispersive colloids in relatively large concentrations but has not yet been successfully applied to the characterization of groundwater colloids. Apart from SEM (or TEM: transemission electron microscopy), the number counting of colloids can be performed by photoacoustic detection of light scattering (PALS) [3], which can provide, in combination with ultrafiltration, colloid numbers directly in solution in different size groups. The colloid number counted in the Grimsel groundwater by SEM and PALS is shown here as an example:

SEM: 3.3×10^{10} particles l^{-1} [15]
PALS: 3.2×10^{11} particles l^{-1} [3].

Both numbers are evaluated by assuming the average size of colloids to be 100 nm. If the average size is found to be smaller, the number counted by PALS will then increase. The number counted by PALS [3] is ten times larger than by SEM. Since the preparation of samples for SEM requires filtration and drying, colloid coagulation in the course of this process is inevitable and therefore the number counted by SEM can be smaller than in real groundwater [15].

The presence of actinide pseudocolloids can be verified by LPAS [24] with submitting the solution to some chemical alteration. For example, the Am^{3+} ion traced in the Gohy-1011 and Gohy-1012 groundwaters (cf. Fig. 1) is speciated in order to elucidate the behaviour of the ion in these groundwaters [24]. The Am traced groundwaters are stored under Ar atmosphere with 1% CO_2 partial pressure for six months. The applied CO_2 partial pressure approximately corresponds to the conditions found in Gorleben aquifer systems. Fig. 8 shows the chemical states of Am^{3+} speciated by LPAS in Gohy-1011. The LPAS spectrum (a) indicates that the Am carbonate ion ($AmCO_3^+$) is a predominant species under the given conditions, showing its absorption peak at 506 nm [24]. On releasing the CO_2 partial pressure by opening the cuvette and contacting with laboratory atmosphere (CO_2: 0.035%), as shown by spectrum (b), the Am carbonate ion decomposes and Am pseudocolloids are generated. Due to the change in partial pressure of CO_2, the groundwater pH is changed accordingly from 7.9 to 8.25. Am pseudocolloids are identified by recorded signals of light scattering as demonstrated already in Fig. 1. The process of changing the CO_2 partial pressure, as shown by spectra (a) and (b), is a situation comparable to normal sampling of deep groundwater. The CO_2 release during the sampling of groundwater will produce groundwater colloids, which will then falsify subsequent laboratory experiments. The Am concentration in the sample of spectrum (b) is decreased to about 32% of the original one [spectrum (a)]) presumably due to either precipitation or sorption on the cuvette surface. On acidification to 1 M HCl, the total amount of americium is transformed to the Am^{3+} ion, showing its absorption peak at 503 nm [24] [spectrum (c)]. The Am concentration diminished in the sample of spectrum (b), is recovered by acidification to 6.0×10^{-7} mol l^{-1}. A small difference from the original concentration of 6.2×10^{-7} mol l^{-1} is attributed to a slight dilution by acidification.

The other groundwater (Gohy-1012) containing humic colloids shows the different behaviour of Am [24]. LPAS spectra of Am traced Gohy-1012 are given in Fig. 9. The LPAS spectrum (a) illustrates the presence of colloids in the solution but the Am carbonate ion is not visible, unlike Am in Gohy-1011, although the CO_2 partial pressure is maintained at 1%. Since

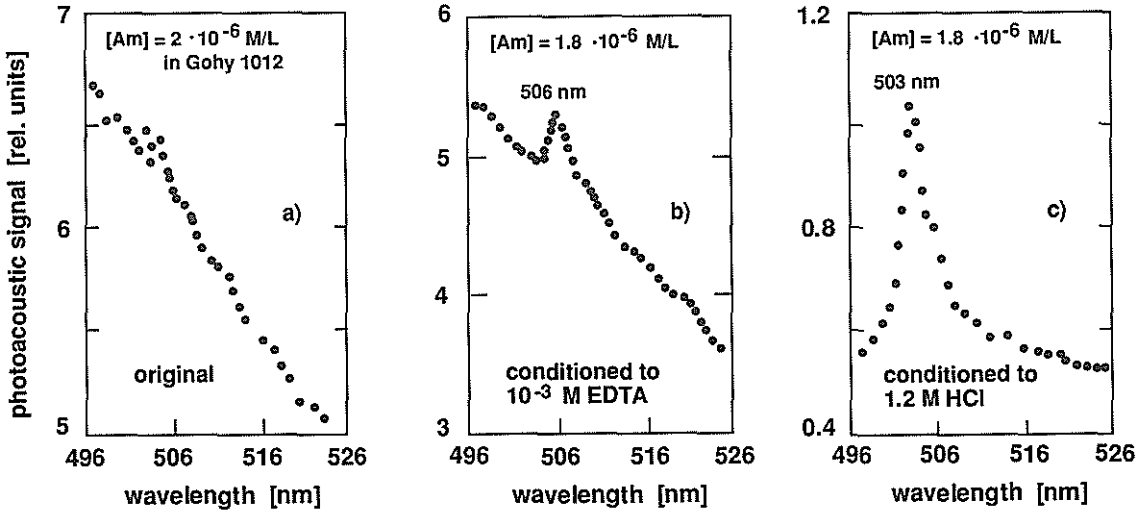


Fig. 9. Speciation of Am(III) in Gorleben groundwater (Gohy-1012) with a high DOC concentration (7.8 mg Cl^{-1}; see Table 1): a) humic colloid (Am pseudocolloid in original groundwater); b) Am-EDTA complex (10^{-3} M EDTA); c) Am^{3+} ion (1.2 M HCl) [5].

the Am concentration remains stable at 2.0×10^{-6} mol l^{-1} for a period of six months, the presence of Am pseudocolloids (humic colloid) is evident. To a portion of this solution EDTA is added to make a concentration of 10^{-3} mol l^{-1}. The reason for addition of EDTA is not to destroy humic colloids but to extract only the Am^{3+} ion out of colloids, because the complexation power of EDTA with Am^{3+} is much stronger [1, 2] than of humic acid in colloids. After six months of conditioning with EDTA, the Am-EDTA complex is observed in the LPAS spectrum (b) with its absorption peak at 506 nm [24]. A steep inclination of the base line with decreasing wave length suggests the presence of humic colloids in the solution. Another portion of the Am traced groundwater is at the same time conditioned to 1.2 M HCl. Again after a period of six months, the complete release of the Am^{3+} ion from humic colloids is observed [spectrum (c)] with its absorption peak at 503 nm. In the case of acidification, the humic colloids are precipitated by an excess protonation; the behaviour is comparable with the precipitation of humic acid by acidification [24]. Because of humic colloid precipitation, the spectrum (c) appears devoid of a high base line under the absorption peak.

The spectroscopic speciation shown above demonstrates the generation of two different kinds of actinide pseudocolloids in groundwaters with and without humic substances. As evidenced by Fig. 7, the generation of actinide pseudocolloids is reversible. Pseudocolloids of organic nature are more stable than those of inorganic nature. For the latter, the CO_2 partial pressure plays an important role in their generation.

3.3. Geochemical interactions and migration

Geochemical interactions of actinide pseudocolloids are of main interest to the migration study of actinides in natural aquifer systems [4, 6, 7, 10]. The challenge is how to quantify the migrational colloids, and subsequently how to use these quantities for the geochemical and hydrodynamic modelling. For the moment, neither quantification abilities nor modelling capabilities of the colloid migration are developed sufficiently to deal with the safety assessment of the actinide migration. However, much effort has been concentrated on solving these challenging problems [6, 12, 14, 17, 37] and experiments are underway at the moment in various laboratories [2].

Geochemical interactions of actinide pseudocolloids have been studied in laboratory systems by either static or dynamic processes, e.g. batch and column experiments. Colloidal Pu and Am leached from a simulated vitrified waste are examined for their retention in a glauconitic sand column [9, 12] and the retention process is adequately described by the Langmuir isotherm [12]. In a batch experiment for evaluating the retention processes of radiotraced metal ions, i.e. ^{137}Cs, ^{90}Sr and ^{144}Ce, only the trivalent cerium is found to be clearly associated with groundwater colloids [17]. The retention of colloidal Ce(III) on sediment is described mathematically. Geochemical interactions of actinide pseudocolloids in association with the migration study have been intensively investigated in Gorleben aquifer systems [4–6, 23, 24]. Regardless of different redox fronts, the soluble Pu and Am are always associated with colloids [4–6] and their pseudocolloids are found to play a major role in the migration or retention process. For the well known reason of redox properties, the involvement of Np in colloids is dependent on the redox potential of a given aquifer system.

The quantification of geochemical interactions of colloids is roughly pictured in Fig. 10. Assuming that a given aquifer system of a certain permeability is involved in the migration of actinides, there are three phases to be conceived [37], i.e. true actinide solution phase consisting of ionic, molecular and polynuclear species which can be well defined thermodynamically; colloids composed of migrational and non-migrational components, which can be considered as soluble-solid phases; immobile solid phases composed of various geomatrices. The actinide ions introduced into such an aquifer system undergo interactions with groundwater colloids as well as immobile solid phases and a part of the generated actinide pseudocolloids also interact with immobile solid phases. Colloid to colloid interactions as well as generation and regeneration of colloids are not considered for the moment. The soluble-solid phases (colloids) is a dynamic system which cannot be simply divided into mobile and immobile phases. For this reason, the phase boundary between solution and solid or migrational and non-migrational colloids is difficult to define for a given aquifer system.

A typical example of the three component interaction system is demonstrated in Fig. 11, in which the diagram on the left shows the solubilities (mol l^{-1}) of $Am(OH)_3(s)$ in two different Gorleben groundwaters while the diagram on the right shows the sorption coefficients ($cm^3\ g^{-1}$) of Cm^{3+} determined by batch experiment on the corresponding aquifer systems containing porous sediments. One groundwater is saline (Gohy-2122: 2.5 M NaCl) and the other is non-saline (Gohy-1061). Both solubility and sorption data are directly dependent on the phase boundary of the soluble-solid phases discussed above (cf. Fig. 10), namely the colloid separation. The colloid effects on solubilities and sorption data are reciprocal, e.g. in unfiltered systems the highest solubilities on the one hand and the lowest sorptions coefficients on the other hand. In the saline system (Gohy-2122), the colloid effect is smaller than in the non-saline system (1061). However, colloids are also present in the saline system [19] as verified below.

The presence of Am pseudocolloids in the saline groundwater is examined by LPAS [38] as shown in

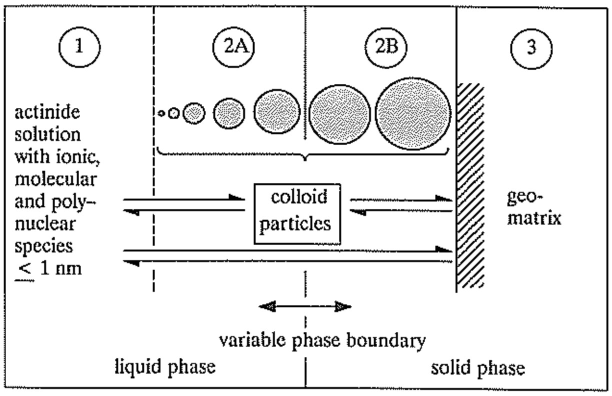


Fig. 10. A conceptional diagram of three component interactions in colloid-containing groundwater: (1) trace actinide solution phase; (2) colloid phase (soluble-solid phase); (3) immobile solid phase. The phase boundary is variable depending on the aquifer system [37].

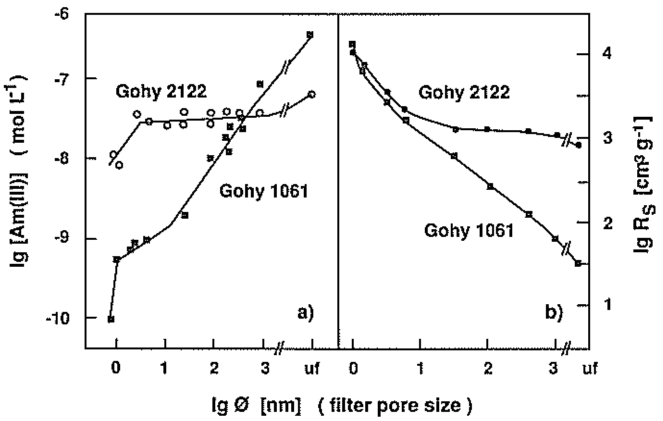


Fig. 11. Colloid effects on solubilities (mol l^{-1}) of Am(III) and sorption coefficients ($cm^3\ g^{-1}$) of Cm(III) determined in saline (Gohy-2122) and non-saline (Gohy-1061) aquifers by separation at different filter pore sizes (e.g. different phase boundaries as illustrated in Fig. 10) [6].

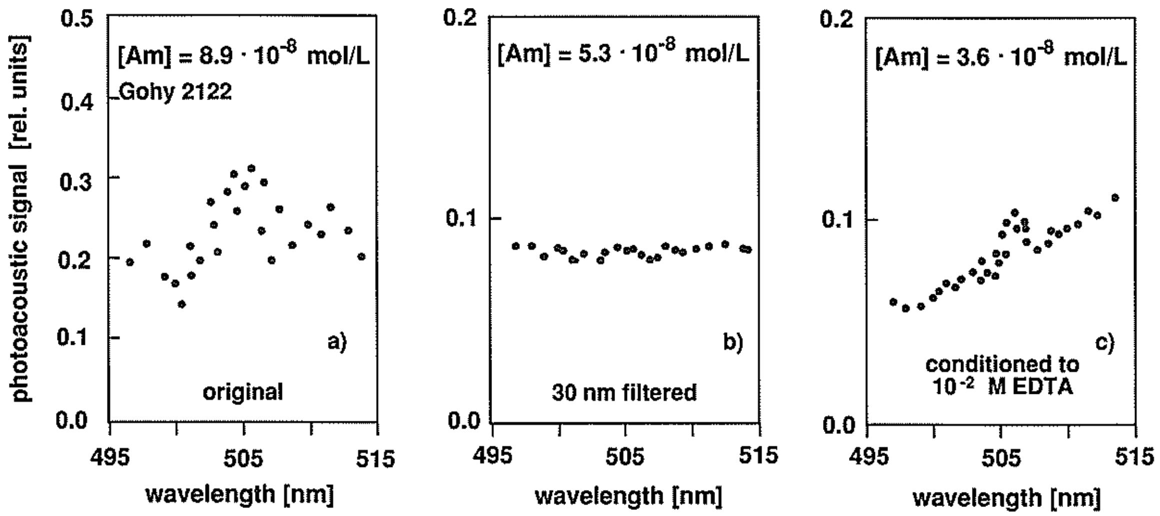


Fig. 12. Colloid confirmation in saline groundwater (Gohy-2122) (see Fig. 11) by LPAS: a) Am(III) pseudocolloids in original groundwater; b) Am(III) pseudocolloids after filtration at 30 nm pore size; c) Am-EDTA complex (506 nm) after addition of EDTA to the solution (b) [38].

Fig. 12. The spectrum (a) illustrates a relatively high base line due to light scattering with a fail indication of the broad peak at 505 nm. After filtration at a pore size of 30 nm the base line is decreased to less than one half of the unfiltered solution, but there is no indication of Am absorbances in the region of 503–505 nm (cf. Fig. 8). On addition of EDTA (10^{-2} mol l^{-1}) the peak of Am-EDTA at 506 nm is distinguished (spectrum (c)). The concentration decrease is due to dilution by the EDTA solution. Fig. 12 explains the presence of Am pseudocolloids even in the saline groundwater (Gohy-2122). As shown in Fig. 11 the colloid effects in this groundwater are to be observed only at smaller pore sizes of filters (< 10 nm). In the medium of high ionic strength, groundwater colloids of larger size are found to be unstable.

In a static batch experiment, due to the presence of actinide pseudocolloids, retention coefficients of actinides are variable within a determined modus operandi, e.g. ultrafiltration with different pore sizes [4, 6, 37]. A column experiment gives a better assessment of retention processes of actinides associated with colloids [9, 12]. However, a combination of both methods gives an insight into the geochemical interactions of actinide pseudocolloids and their migration behaviour.

The migration behaviour of actinide pseudocolloids can be understood only in conjunction with knowledge of the permeability of the colloids in a given aquifer system. Such a permeability is, by a first approximation, related to ultrafiltration as shown in Fig. 11. However, the permeability of an aquifer system over a long distance is difficult to assess especially for actinide pseudocolloids, because there are always geochemical multilayers involved even in a short aquifer distance. Much work is still necessary to understand the migration behaviour of actinide pseudocolloids in the real geochemical world.

Conclusions

- Groundwater colloids are ubiquitous; their amount and chemical composition differ from one groundwater to another.
- Colloids of inorganic and organic nature are present and organic colloids appear more stable in aqueous solution than inorganic colloids.
- A great part of M(III), M(IV) and M(VI) present in groundwater are colloid-bound (Actinide analogues).
- Actinides of all oxidation states generate their pseudocolloids unless they are stabilized by strong complexation (e.g. actinide carbonates etc.).
- Characterization methods especially for colloid size distribution and population counting have to be further improved.
- Geochemical interactions of actinide pseudocolloids with geomatrices (sorption, diffusion, filtration) are poorly understood.
- Quantification of the colloid-borne actinide migration requires basic knowledge of groundwater colloids as well as aquatic chemistry of actinides in general.
- Quality assurance of the safety analysis entails prediction capability of the colloid-borne actinide migration.

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