

# **Complexes of actinides with naturally occurring organic substances – Literature survey**

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Denna rapport utgör redovisning av ett arbete som utförts på uppdrag av KBS-projektet. Slutsatser och värderingar i rapporten är författarnas och behöver inte nödvändigtvis sammanfalla med uppdragsgivarens.

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## SUMMARY

Properties of naturally occurring humic and fulvic acids and their formation of actinide complexes are reviewed. Actinides in all the oxidation states III, IV, V and VI would form complexes with many humic and fulvic acids, comparable in strength to the hydroxide and carbonate complexes. Preliminary experiments have shown, that the presence of predominantly humic acid complexes would significantly reduce the sorption of americium on geologic media. This does not, however, necessarily lead to a potentially enhanced mobility under environmental conditions, since humic and fulvic acids carrying trace metals also would be strongly bound to e.g. clayish material.

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## 1. INTRODUCTION

The sorption of actinides on various rocks and minerals has been studied in many waste programs, in order to allow predictions of the migration behaviour of these elements, e.g., when released from an underground waste repository. One objection to the conclusions drawn from laboratory experiments under idealized conditions and e.g. using artificial groundwaters is that effects of colloidal particles and macro molecular organics rarely are simulated or taken into account.

In analyses of Swedish groundwater both humic and fulvic acids have been found at a total concentration in the mg/l-level, and concentrations even as high as 10-20 mg/l have in a few occasions been indicated. In Table 1 the proportions of humic acid and low molecular weight organics from some deep groundwaters are given.

Table 1. The molecular weight distribution (%) of humic acids (HA) and other organic constituents in deep groundwaters (1).

Sample	Molecular weight				
	HA	>1000	1000-700	700-300	<300
Finnsjön 4, 260 m	6	2	8	19	65
Finnsjön 4, 382 m	6	2	6	13	73
Finnsjön 4, 562 m	6	3	←—————	91	—————→
Stripa Mine	0	2	10	45	43
Grande Ronde, DC-6	0	10	53	34	3

Thus it seems to be important to get information on the interaction between radionuclides and organic matter and the migration of organic complexes in the groundwater-rock environment as a part of any evaluation of the feasibility of long-term deposition of radioactive waste underground.

Previously, Marinsky has studied the interaction between europium and fulvic acid (2) within the Swedish KBS program. The present literature survey is intended to be a starting point for further studies of the interaction

between the actinides and organic matter present in the groundwater, particularly of the transport and sorption of organic actinide complexes that may exist in deep granitic groundwaters.

## 2. CHARACTERIZATION OF HUMIC AND FULVIC ACIDS

Organic substances such as humics occur in nature in most soils, peat bogs, etc. and in natural waters. There are no general formulas for humic substances. Their compositions vary with vegetative source and geographical location, but in general they contain phenolic, and carboxylic acids as well as hydroxy groups, which give these compounds strong metal complexing capacities (3). Many different suggestions of probable structures have been presented, as exemplified in Fig. 1 (4).

Humic substance is a common name for at least four different kinds of organic compounds: humic acid, fulvic acid, humatmelanic acid and humin. These groups may, somewhat arbitrarily, be differentiated by their solubilities. By definition, humic acid is soluble in alkali but not in acid. Fulvic acid is soluble in both alkali and acid. Humatmelanic acid is the alcohol-soluble fraction of the humic acid and humin is insoluble in alkali.

The humic acid fraction can be subdivided into two groups using the solubility in an electrolyte under alkaline conditions as a criterion. "Brown humic acid" is not coagulated in the presence of an electrolyte whereas "grey humic acid" is.

In terms of chemical composition, the fulvic acids are generally less crosslinked and polymerized, have lower molecular weights and contain more oxygen than humic acids. Also the hydroxyl and carboxyl contents are higher (3).

Humic acids can be transformed to fulvic acids, i.e. transferred from an acid insoluble to an acid soluble form through oxidation. Thus, humic and fulvic acids belong to similar groups of substances and differ mainly in the molecular weight.

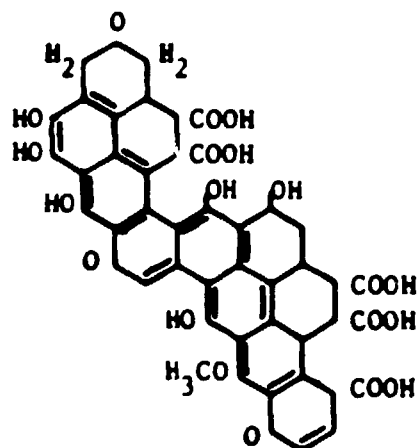
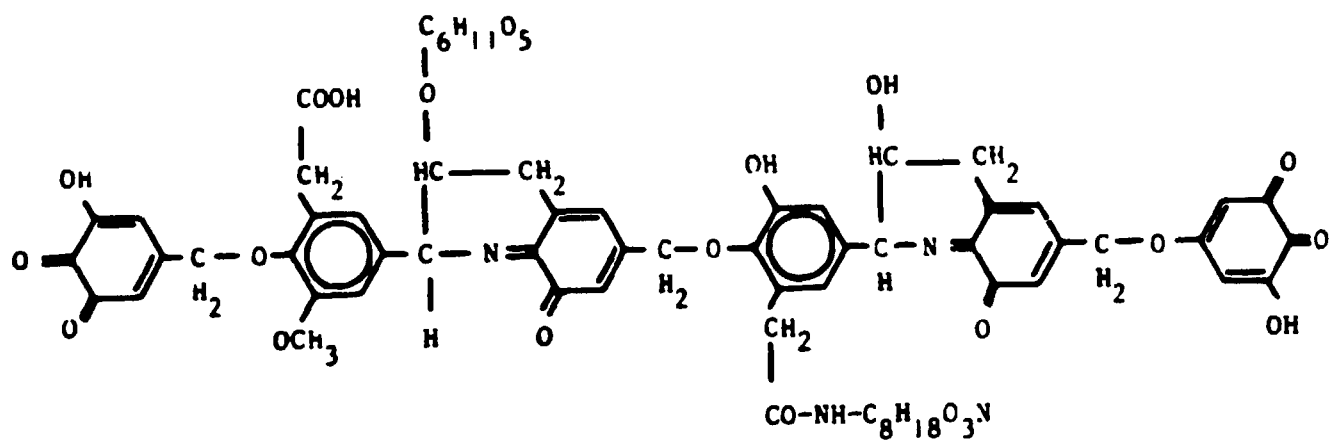


Figure 1. Suggested humic acid structures (4)

### 2.1. Separation and purification of humic and fulvic acids.

Choppin and Bertha (5) used a modification of the standard methods (6) to isolate the humic and fulvic acids. A crushed, air-dried mud sample was treated with 0.5 M NaOH for 22 hours. It was then filtered through glass-wool, centrifuged at 8000 rpm for 15 min to eliminate the solid mud particles, centrifuged at 36000 rpm for 30 min to precipitate colloidal clay particles, and acidified to pH 2.0 with dilute mineral acid to precipitate the humic acid. This humic acid was separated by centrifugation, dissolved in 0.1 M NaOH and reprecipitated with dilute acid at pH 2.0; this was repeated three



times. To eliminate traces of iron and aluminum the humic acid was shaken with 2 M HCl for 30 min, centrifuged and washed until a negative test for chloride ion was obtained. The wet humic acid was lyophilized and determined to have an ash content of less than 1%. The supernatant solution from the precipitation of humic acid contained the fulvic acid. This solution was passed through a column of hydrogen form Dowex 50 W x 8 resin to remove metal ions. The acidic eluant was dialyzed against distilled water four times, for three hours each time. The solution was then rotoevaporized and lyophilized and its ash content was determined to be less than 1%.

Means (1) fractionated the humic and fulvic acids from groundwater using a procedure shown in Fig. 2. The samples were fractionated in 5 different groups.

Willin (4) and Yamamoto (7) used similar methods to separate humic and fulvic acids from water and e.g. peat bogs.

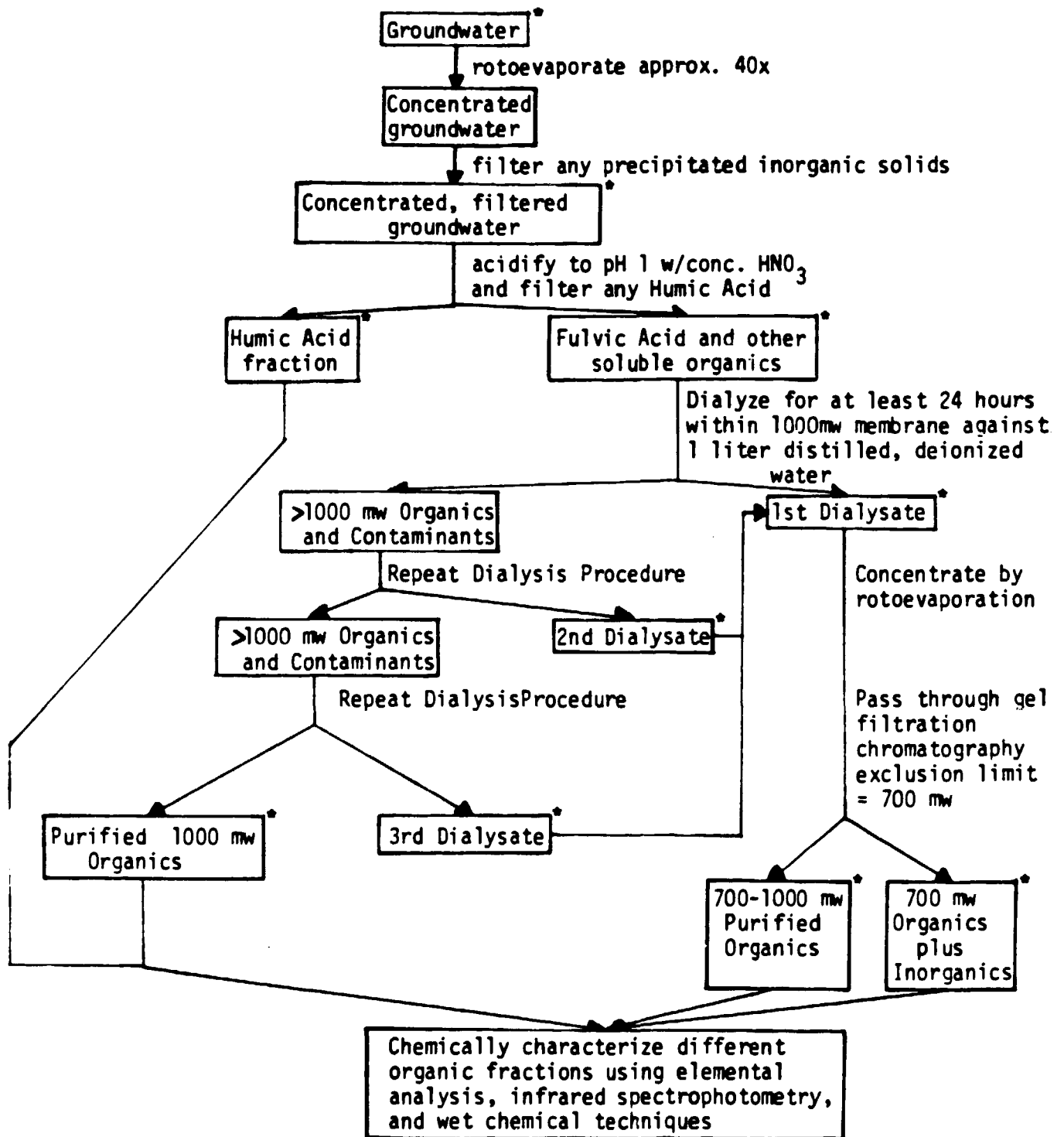


Figure 2. Flow chart for separation and purification of hydrophilic organic compounds in groundwater (1).

## 2.2. Protonation of humic and fulvic acids.

Humic acids are polybasic with at least two types of proton releasing groups. They act as weak, acidic cation exchangers.

Choppin and Kullberg (8) have determined the capacity and  $pK_a$ -values of a humic acid from Lake Bradford. Fig. 3 shows a titration curve with first end point at  $5.90 \pm 0.1$  ml, which corresponds to a capacity of 2.95 meq/g.

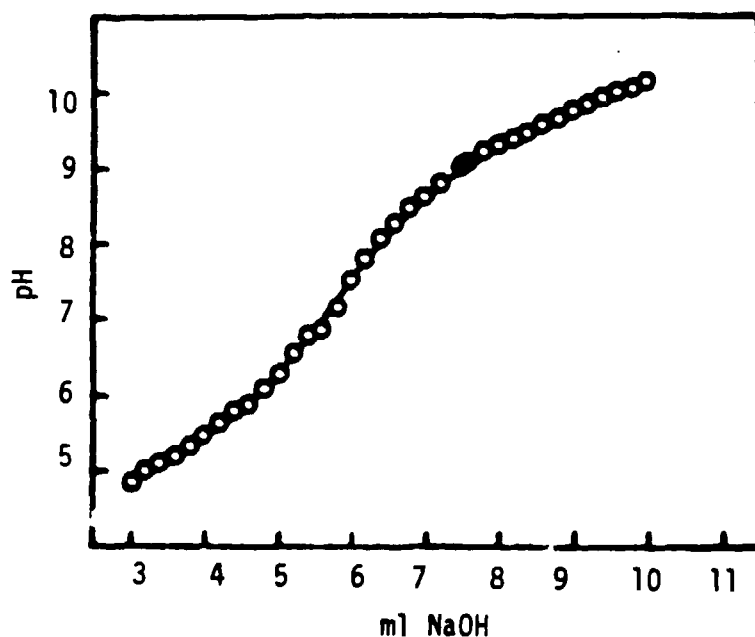


Figure 3. A titration curve of 0.040 g Lake Bradford humic acid by 0.02 M NaOH at a constant ionic strength of 0.1 M (8).

If more alkali was added a second protonation step was observed, but due to the weak acidity in this step no definitive end point could be established. A preliminary measurement of the same humic acid a year earlier gave a capacity of 4.16 meq/g. This difference shows that the capacity may decrease during storage.

The two kinds of functional groups observed were protonated in pH ranges of 4-7 and >8 respectively. The dissociation can be described by

$$pK = pH - \log \frac{\alpha}{1-\alpha}$$

where  $\alpha$  is the degree of dissociation. Fig. 4 shows a plot of  $pK_a$  as a function of  $\alpha$ . By extrapolation to  $\alpha = 0$  values of  $pK_a^0$ , corresponding to  $4.0 \pm 0.1$  and  $9.0 \pm 0.2$  were obtained. The less acidic group was only 75% as abundant and gave  $pK_a^0 = 8.9 \pm 0.2$ .

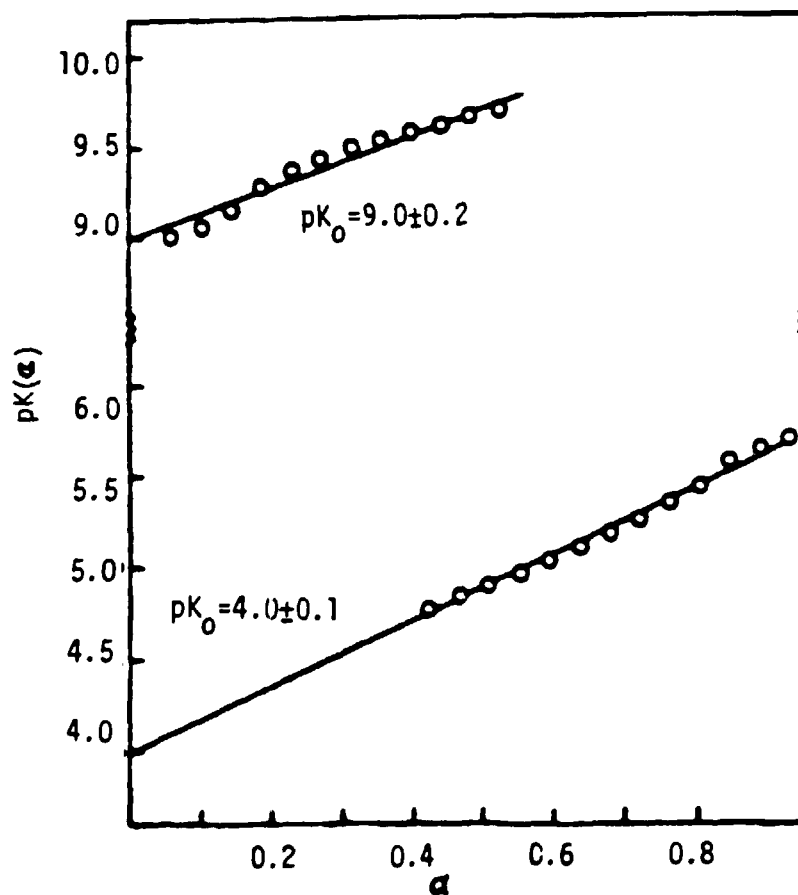


Figure 4. Plots of the apparent  $pK_a$ -values as a function of the degree of dissociation,  $\alpha$  for Lake Bradford humic acid (8).

Choppin and Kullberg also determined the heat changes on protonation for the same humic acid from Lake Bradford and for a commercial humic acid (8). Fig. 5 shows changes of enthalpy as a function of pH from calorimetric measurements. These experiments indicate that the protonation reactions are fast. The enthalpy curves for the two humic acids are very similar and their shapes support the assumption that two types of functional groups are present.

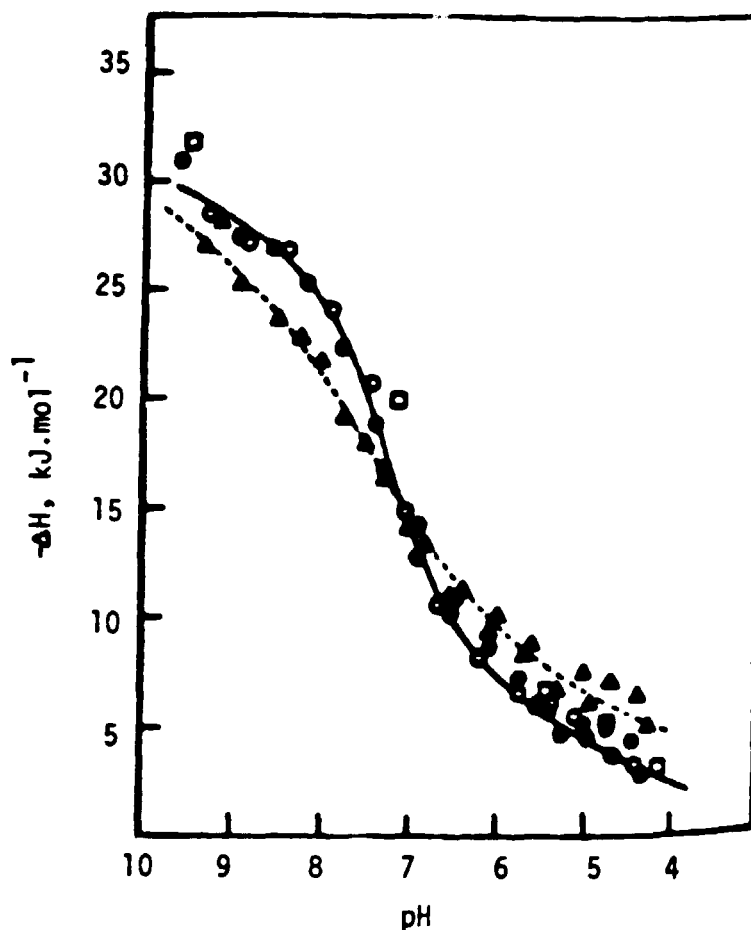


Figure 5. Variation of the enthalpy of protonation as a function of the pH of the measurement (8).

The commercial humic acid values are shown as  $\Delta$  and  $\blacktriangle$  for two different calorimetric titrations. The Lake Bradford humic acid samples are designated by  $\circ$ ,  $\bullet$ ,  $\bullet$  for three titrations (8).

A comparison of the  $pK_a^0$  values for humic acid with those for simple monomeric acids indicates that the two functional acidic groups are carboxylic and phenolic.

However, for other humic acids, e.g. in the humic acid from Hohlosee (4), only one type of acidic group was observed ( $pK_a = 4.08 \pm 0.03$ ).

Marinsky (2) made potentiometric studies of Farmadale fulvic acid and made the following observations:

- o This particular fulvic acid exists as a small molecule in solution.
- o The tendency for the fulvic acid to aggregate is reduced as the concentration of the fulvic acid and the ionic medium containing it are decreased.

- o For non-aggregated fulvic acid  $pK_a$  vs  $\alpha$  is independent of the initial fulvic acid concentration and of the ionic strength of the electrolyte, Fig. 6.
- o The fulvic acid loses capacity with time.

Halbach et. al. (9) carried out IR-measurements of humic and fulvic acids. Fig. 7 shows an IR-spectrum of a fulvic acid. The C:H:O relation of 1.0:1.8:1.0 indicates that fulvic acids are acid derivatives of carbohydrates.

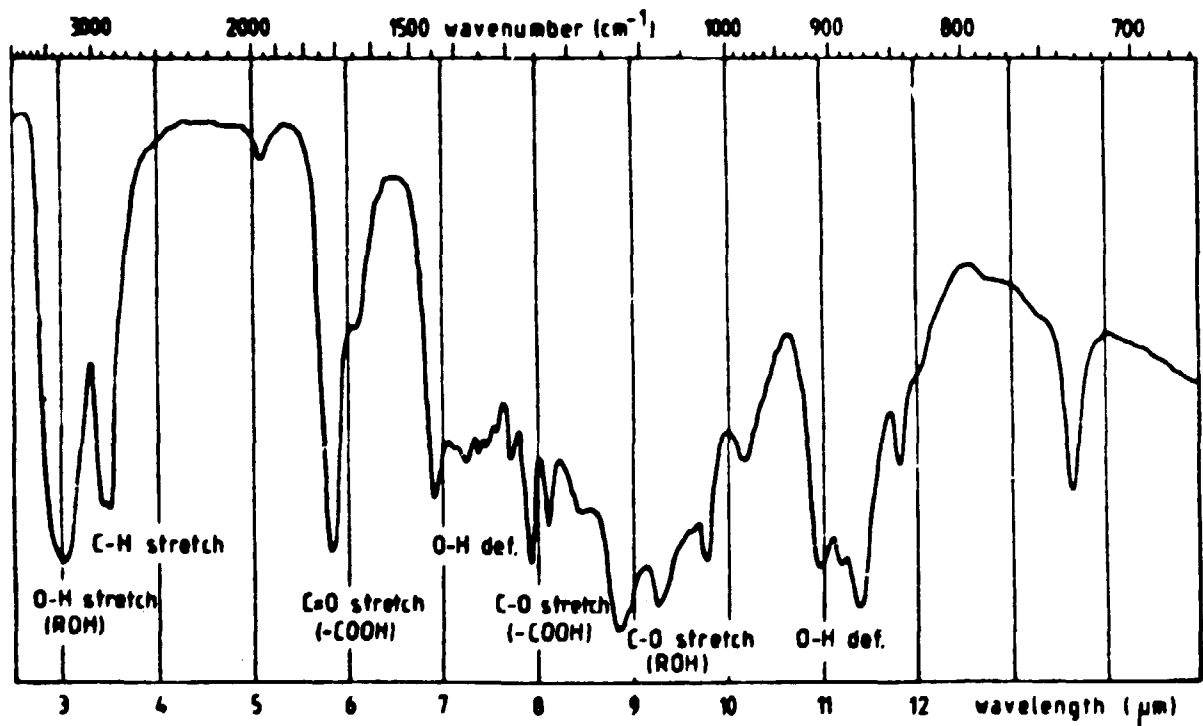
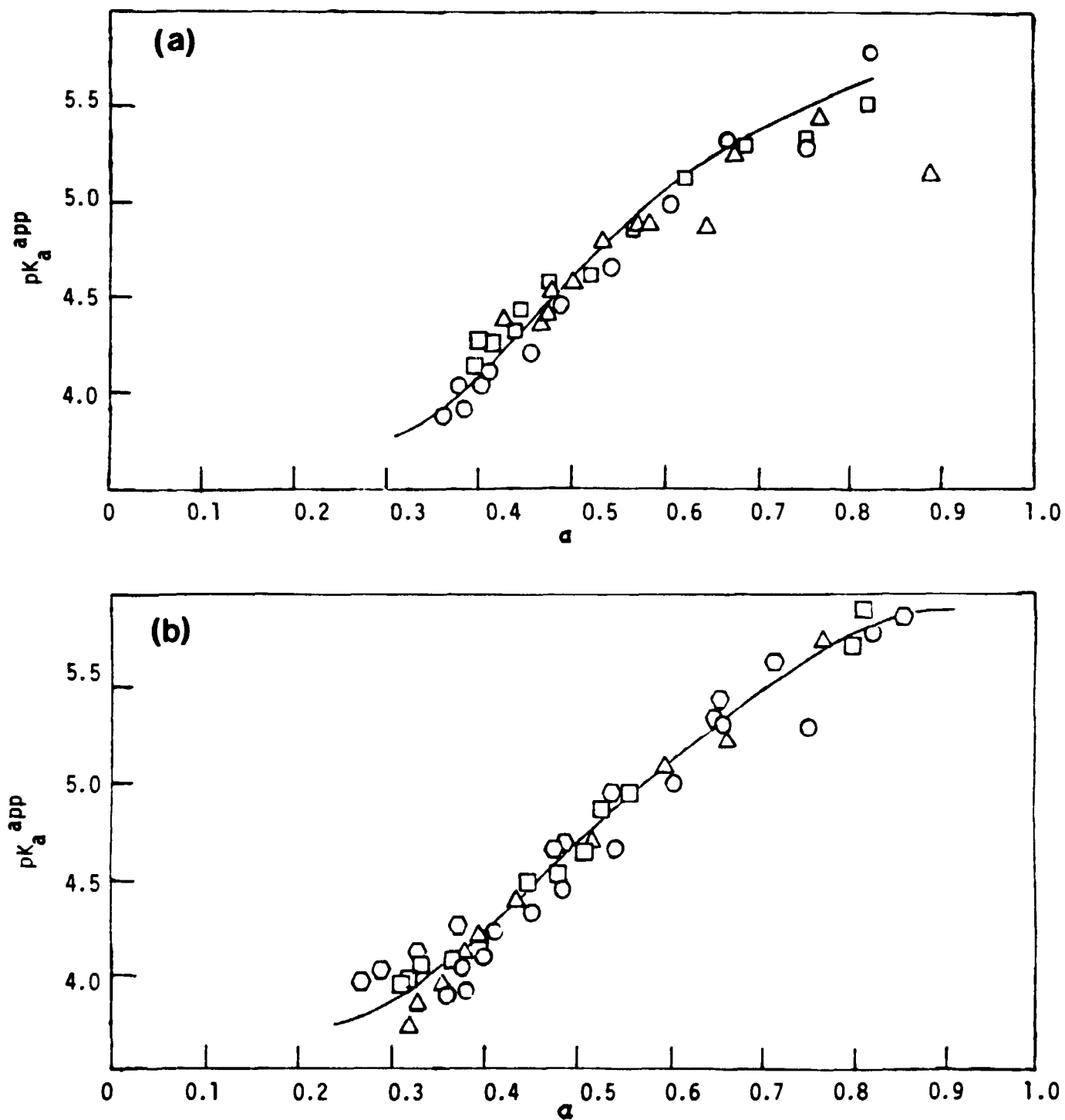


Figure 7. IR spectrum of a fulvic acid (9).

IR spectra of humic acids are usually less differentiated than those of fulvic acids. There exist only broad peaks with a low resolution, mainly caused by O-H and C-O stretching vibrations. The C:H:O relation of 1.0:1.4:1.0 in the humic acids indicates the presence of aromatic constituents.

The acidic properties of eleven humic and three fulvic acids are shown in Table 2 (9).



**Figure 6.** Plots of the apparant  $pK_a$ -values as a function of the degree of dissociation,  $\alpha$ , for Armadale fulvic acid (2)  
 (a)  $\circ$   $1.3 \times 10^{-4}$  g/ml;  $\square$   $6.0 \times 10^{-5}$  g/ml;  $\triangle$   $3.0 \times 10^{-5}$  g/ml; initial capacity ( $6.7 \pm .3$  meq/g) and ionic strength (0.1 M NaCl) kept essentially constant.  
 (b)  $\circ$  0.10 M NaCl;  $\square$  0.030 M NaCl;  $\triangle$  0.010 M NaCl;  $\odot$  0.0050 M NaCl; initial capacity ( $7.1 \pm 0.5$  meq/g) and initial concentration ( $1.2 \pm 0.08 \times 10^{-3}$  M) kept essentially constant.

Table 2. Acidities of humic and fulvic acids (9)

		Total acidity (meq./g)	Strong acid groups (meq./g)	Weak acid groups (meq./g)
Humic acids	range	5.61-6.77	1.79-2.52	3.17-4.55
	mean	6.00	2.17	3.82
Fulvic acids	range	5.11-6.04	3.25-4.32	1.72-2.12
	mean	5.64	3.74	1.90

In these humic acids the weak acid groups, partly resulting from phenolic OH-groups, are dominating, while in the fulvic acids investigated the strong acid groups predominate.

In another type of humic acid Schebetovskii et. al. (10) found  $pK_a$ -values of about 4.2 and 9.2 for the carboxylic and phenolic groups, respectively.

### 3. INTERACTION WITH ACTINIDES

#### 3.1. The strength of interactions between actinides and humic substances.

Trivalent actinides would form strong complexes with humic acids, as indicated from studies of Eu(III) and Am(III)(5). For Th(IV) strong complex have been observed both for humic and fulvic materials (11). The binding constants increase with increasing ionization of the humic substances, Fig. 8.



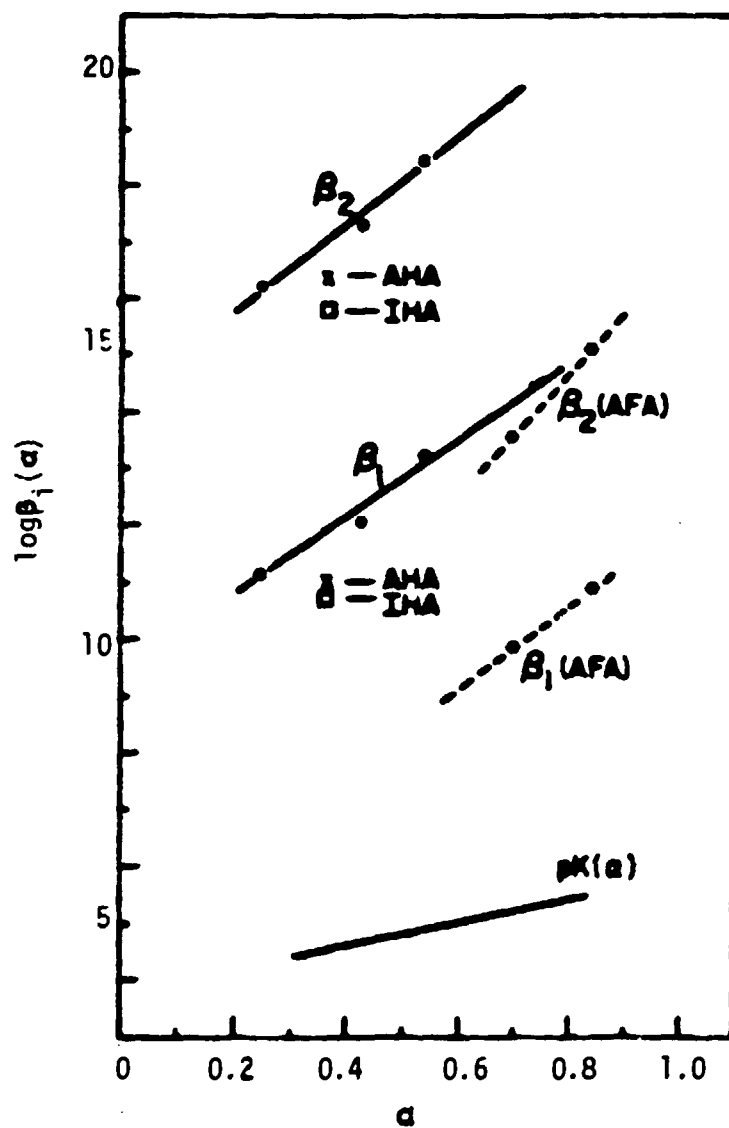


Figure 8. Variation of  $\log \beta_1$  and  $pK(a)$  with  $\alpha$  for thorium complexes with Lake Bradford humic acid (11).

In Table 3 some binding constants for actinide humates are given (12).

Table 3. Binding constants for actinide humates. ( $\mu = 0.10$  M;  
T = 25.0°C) (12).

Cation	$\alpha$	$\log \beta_1$	$\log \beta_2$
Eu(III)	0.40 <sup>+</sup>	7.78 <sup>+</sup> ±0.04	10.70 <sup>+</sup> ±0.05
Am(III)	0.40 <sup>+</sup>	7.26 <sup>+</sup> ±0.11	11.04 <sup>+</sup> ±0.02
Th(IV)	0.25 <sup>+</sup>	11.14 <sup>+</sup> ±0.01	16.17 <sup>+</sup> ±0.02
Th(IV)	0.43 <sup>+</sup>	12.03 <sup>+</sup> ±0.02	17.29 <sup>+</sup> ±0.04
Th(IV)	0.54 <sup>+</sup>	13.18 <sup>+</sup> ±0.04	18.43 <sup>+</sup> ±0.17
Th(IV)	0.37 <sup>-</sup>	10.74 <sup>+</sup> ±0.01	15.79 <sup>+</sup> ±0.04
Th(IV)	0.39 <sup>x</sup>	10.94 <sup>+</sup> ±0.02	16.43 <sup>+</sup> ±0.06
UO <sub>2</sub> <sup>+2</sup>	0.48 <sup>x</sup>	7.28 <sup>+</sup> ±0.03	10.69 <sup>+</sup> ±0.04
UO <sub>2</sub> <sup>+2</sup>	0.67 <sup>x</sup>	8.20 <sup>+</sup> ±0.03	11.55 <sup>+</sup> ±0.04

<sup>+</sup> Humic acid from a lake

<sup>-</sup> Soil humic acid

<sup>x</sup> Humic acid from Aldrich Chem. Co.

It is probable that Pu exists primarily as Pu(IV) in the presence of organic material like humics and thus it may be bound very strongly by humic acid. Fig. 9 shows an estimate of the fractional concentration of Pu(IV) as a function of the humate concentration for a concentration range representative of marine water or groundwaters.

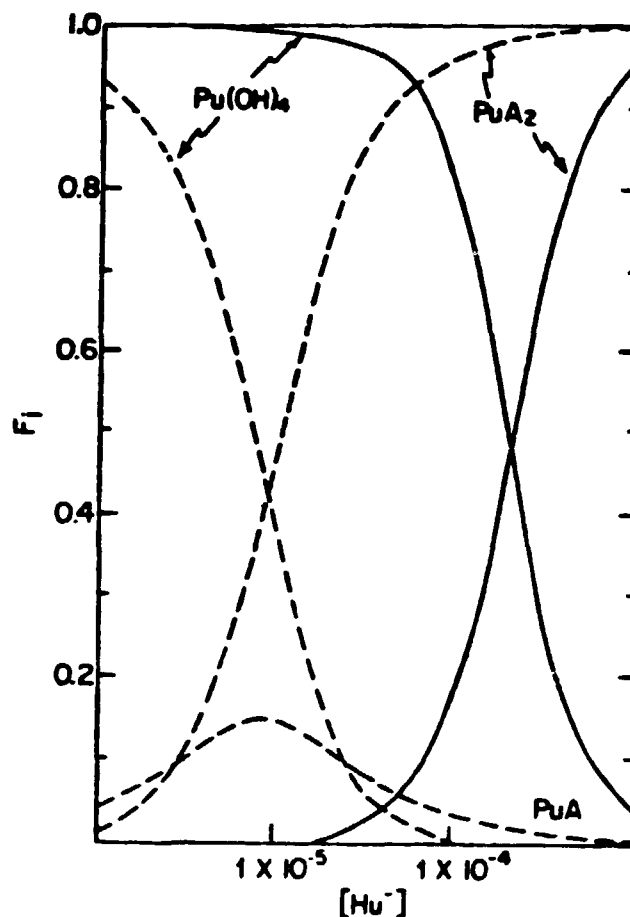


Figure 9. Calculated fractional ( $F_i$ ) concentration of a hypothetical plutonium(IV) humate complex as a function of the humate concentration at pH 5.5 (---) and 7.5 (—) (12).

In the presence of carbonate, hydrolysis decreases, but humate binding is still dominant for humate concentration  $>10^{-5}$  eq/l.

From studies of the complexation between Eu(III) and fulvic acid the following conclusions have been suggested (2):

- o Eu(III) is strongly complexed by the carboxylate units in the fulvic acid over a pH range of 3.5 to 9.5.
- o At the lower pH-value the dominant Eu(III)-complexed species involves one carboxylate unit.
- o In the pH-range from 7.5 to 9.5 the dominant complex is most probably a chelate involving the oxygen in phenolic groups or highly aromatic carboxylic acids that are present in the molecule.

From studies of the mobility of Th(IV) in the "Morro do Ferro"-environment some observations were made (13):

- o When the water was acidified to pH 2, humic acids would precipitate and carry about 64% of the thorium.
- o The fulvic acid fraction contained about 16% of the thorium.

Also plutonium has been reported to be strongly absorbed by natural humus substances from acid media (7,10,14). The interaction between plutonium and humic materials would either be through ion exchange with undissociated carboxyl groups, but also chelation may occur.

Also for americium similar observations have been made (7,14).

Li and coworkers (15) studied the interaction of U(IV) and U(VI) with humic and fulvic acids and have reported the existence of two different binding sites on the organic ligands. The stability constants vary about two orders of magnitude, as shown in Table 4.

Table 4. Stability constants ( $K_1$ ) for uranium-organic complexes (15).

Uranium ion	Ligand <sup>a</sup>	$K_1$	$n_i$ , mmol/g
Uranium(VI)	HA	$5.4 \times 10^6$	1.0
		$5.3 \times 10^4$	9.5
Uranium(VI)	FA	$2.7 \times 10^7$	0.2
		$3.6 \times 10^5$	3.8
Uranium(VI)	TA	$2.3 \times 10^6$	0.6
		$9.2 \times 10^4$	11.4
Uranium(IV)	HA	$9.5 \times 10^6$	0.5
		$3.2 \times 10^4$	4.5
Uranium(IV)	FA	$4.4 \times 10^6$	0.3
		$8.8 \times 10^4$	1.8
Uranium(IV)	TA	$8.5 \times 10^6$	0.9
		$1.1 \times 10^5$	4.5

<sup>a</sup> HA = humic acid  
 FA = fulvic acid  
 TA = tannic acid

### 3.2. Effects of pH on the complex strength.

The interactions of actinides with humic and fulvic acids are highly dependent of the pH-value, because both the hydrolysis of the nuclides and the dissociation of the acids are pH-dependent.

The effect of pH on the interactions of U(IV) and U(VI) with organic ligands has been studied by employing dialysis and ultrafiltration techniques (15). Fig. 10 and 11 show that humic acid can bind both U(IV) and U(VI) at lower pH-values than fulvic acid. At  $\text{pH} \leq 4$  U(IV) forms stronger complexes than U(VI). At  $\text{pH} \geq 7$  the complexes are very strong for both U(VI) and U(IV) with both acids. The complexation increases with increasing pH-values.

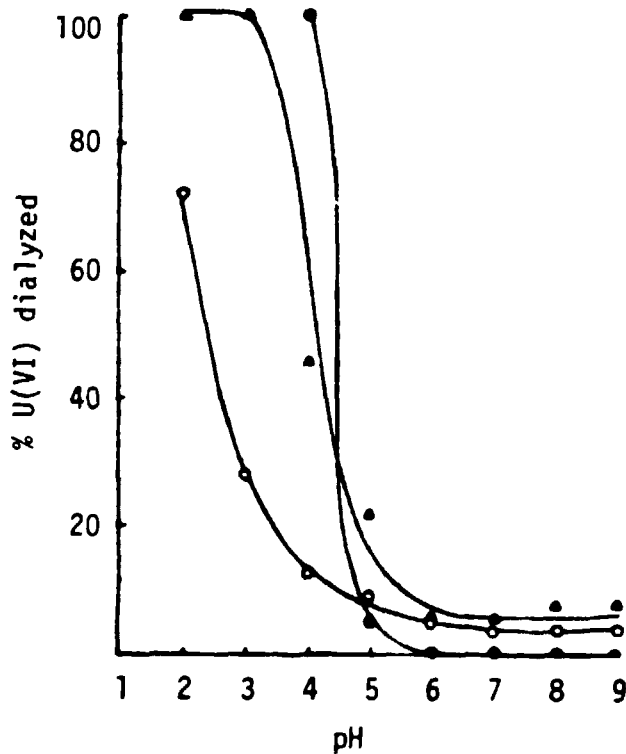


Figure 10. Dialysis of an aqueous solution of U(VI) in 0.01 M  $\text{KNO}_3$  as a function of pH (15).

○humic acid,  
△fulvic acid,  
●tannic acid.

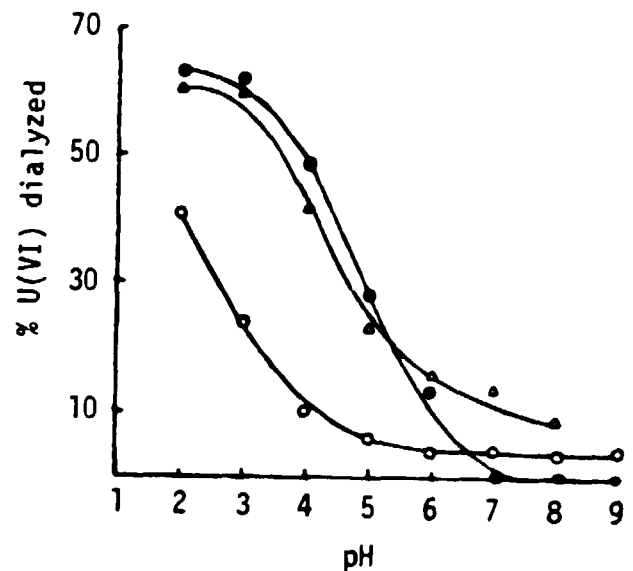


Figure 11. Dialysis of an aqueous solution of U(IV) in 0.01 M  $\text{NaCl}$  as a function of pH (15).

○humic acid,  
△fulvic acid,  
●tannic acid.

Studies of the absorption of Pu(IV) by humus substances as a function of pH have showed that the distribution coefficient ( $K_d$ ) increases with increasing pH, Fig. 12, according to eqn.

$$\log K_d = apH + b$$

where a and b are constants.

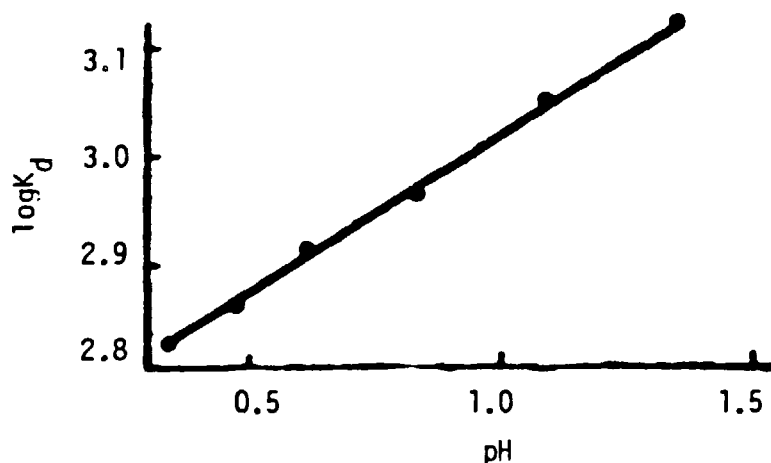


Figure 12. The sorption of plutonium by humus substances as a function of pH (10).

### 3.3. Redox reactions of actinides in the presence of humic substances.

Bondiatti and coworkers (16) studied the interaction of plutonium with complexing substances in soils and natural waters, particularly with respect to the plutonium redox behaviour. Under acidic conditions, plutonium can in principle exist in four oxidation states in aqueous solution. At low pH (<3) plutonium is readily reduced from the tetravalent to the trivalent states by humic material. However, the acidity of the solution affects the relative stability of the various oxidation states through the competing hydrolysis. Thus a reduction of Pu(IV) to Pu(III) by humic or fulvic acids does not occur at pH > 3.1 under aerobic conditions. Possibly there can be a reduction at higher pH-values under anaerobic conditions, but not very likely above pH 6, due to the

stabilizing effect of the strong hydroxide complexes formed in the tetravalent state.

The oxidation potentials for the Pu(IV)-Pu(VI) and Pu(IV)-Pu(V) couples are low enough at environmental pH that a reduction by phenolic materials like humic substances readily occurs. Since such material is abundant in the environment oxidation states of plutonium higher than Pu(IV) are not likely to dominate.

Thus, Pu(IV) seems to be the predominant oxidation state in most environments and the chemistry of plutonium will be strongly affected by complex formation. Inorganic complexing agents, like hydroxides, are dominating, but organic ligands may be of importance in maintaining plutonium in forms which are more mobile in the environment.

Nash et. al. (17) have investigated the redox behaviour, complexing and adsorption of hexavalent actinides by humic acid. They found that hexavalent plutonium and neptunium are readily reduced by humic acids to Np(V) and Pu(IV), although U(VI) is not reduced.

The humic acids complex with actinides in the tetra- and hexavalent states are strong enough to compete with carbonate complexation. Complexes between  $\text{NpO}_2^+$  and humic acid occur in the neutral and alkaline pH-ranges.

#### 3.4. Dissociation kinetics.

Choppin and Nash (18) studied the dissociation kinetics of thorium and humic acid. The kinetic data could be resolved by applying a first order rate equation, as shown in Fig. 13, into three parallel first order processes.

For the experiments xylenol orange was used as a complexing ligand, due to its ability to form complexes with thorium, which are much stronger than thorium complexes with humic acid. The rate of decom-

position was dependent on the pH, but not on the xylenol orange concentration. The resolved rate equation was obtained as

$$R = k_1 [ThH\bar{U}] + k_2 [ThH\bar{U}] [H^+]^{0.3} + k_3 [ThH\bar{U}] [H^+]^{0.7}$$

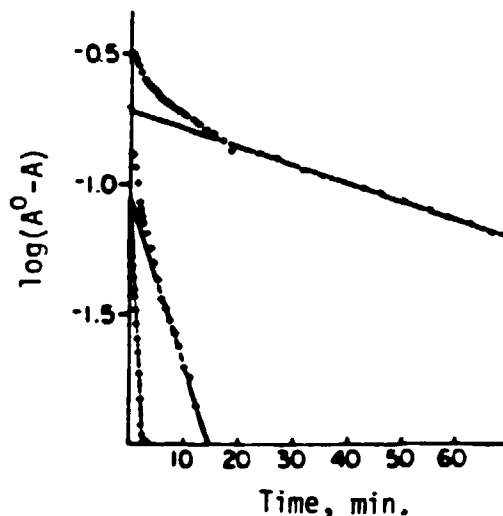


Figure 13. Resolution of the observed curve of the dissociation of thorium-humate with time.  $[ThH\bar{U}] = 5.77 \times 10^{-6}$  M,  $[H\bar{U}] = 1.20 \times 10^{-4}$  M,  $[xy1. Or] = 9.85 \times 10^{-5}$  M,  $[Ac_T] = 0.01$  M, pH = 4.33 (18).

In 24 hours only 15-50% of the total thorium dissociated. Thus, the rate expression does not represent the dissociation kinetics of all thorium bound to humate. An extraction experiment showed that only 34% of the thorium was extracted from the thorium-humate solution. These results indicate the existence of a fraction of the thorium bound to humate in a kinetically inert state. It appears that Th(IV) is bound to humate by at least four types of sites with different basicities and different local polymer structure.

Bondietti and coworkers (16) found that a fraction of the plutonium bound to humic substances could not be sorbed by ion exchange resins. After a contact time of 14 weeks between a soluble plutonium



humate solution and the chelating resin Chelex 100, only about 20% of the total humate bound plutonium was sorbed by the resin. No further exchange was observed with increased contact time. Thus, even plutonium seems to have a fraction bound to humate in a kinetically inert state.

#### 4. MOBILITY OF ACTINIDE-HUMIC ACID COMPLEXES

The formation of actinide-humic acid complexes is likely to have a significant impact on the actinide mobility in natural aqueous systems (5,16-18). Since humic acids are strongly bound to clay minerals, this probably would imply low resulting mobility of the actinides in waters contacting humic substances. The migration of Th(IV) through soil rich in humic materials is slow. A similar behaviour would be expected for plutonium (as Pu(IV)) considering the similarities in chemical properties.

At pH 9, both americium and plutonium exist predominantly as hydrolyzed species at a low total concentration and are not significantly solubilized and transported by the humic compounds dissolved in the groundwater. However, in acid soils the possibility of e.g. americium transport may be greater than that of plutonium, since Am(III) hydrolyzes to a less extent than Pu(IV).

Marinsky (2) found that the stability constant of the bidentate Eu(III) complex is several orders of magnitude larger than that of  $\text{Eu}(\text{CO}_3)_n^{3-2n}$  species and therefore suggests that migration behaviour of the trivalent actinides and the rare earths will be very significantly influenced by the formation of a chelated complex with fulvic acid, e.g. in a groundwater which would contain  $2 \times 10^{-4}$  to  $10^{-2}$  M total carbonate and pH values ranging from 7.5 to 9.5. This has, however, not been confirmed experimentally.

As general conclusions can be stated that

- o Actinides in all oxidation states would form strong complexes with certain humic material.

- o This complexation may only become significant at low pH, in comparison with hydrolysis and carbonate complexation.
- o Since much of the humic material in natural waters would be bound to clay particles also the actinide-humic acid complexes would be associated with such particulate fractions.
- o Although complex formation should be a reversible process very slow kinetics in the breaking of metal-humate bonds have been observed in some cases.
- o The effect of the presence of soluble humic materials not bound to suspended clayish material would act as a potential complexing agent that could yield soluble species with poor sorption properties on geologic media. Quantitative data on the sorption of actinide-humates, e.g. on oxide and silicate-surfaces, are not available.

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SORPTION OF AMERICIUM ON GRANITE IN  
THE PRESENCE OF HUMIC ACID

The sorption of americium on granite has been studied in batch experiments under the following conditions:

Solid:	Granite from Stripa (19), (particle size 0.090-0.125 mm)
Liquid:	Synthetic groundwater (19)
Solid/liquid:	0.2 g/20 ml
Contact time:	6 w
Temperature:	25±1°C
Nuclide conc.:	2.9×10 <sup>-7</sup> M ( <sup>241</sup> Am)
Parameters:	pH (3-11) Humic acid (HA) concentration (0, 0.1 mg/l, 10 mg/l)

The humic acid (from Lake Bradford, c.f. ref. 8, 12) had the following chemical properties:

Capacity:	2.95 meq/g
pK <sub>a</sub> :	4.0±0.1, 9.0±0.2
Binding constant for Am:	logβ <sub>1</sub> = 7.26±0.11, logβ <sub>2</sub> = 11.04±0.02

Some preliminary distribution coefficients (K<sub>d</sub>; (concentration in the solid phase)/(concentration in solution); m<sup>3</sup>/kg) are given in Fig. 1-1.

The speciation in a saturated americium solution is given in Fig. 1-2, assuming the following formation constants (log K) (21):

AmOH <sup>2+</sup>	6.5	
Am(OH) <sub>2</sub> <sup>+</sup>	11.5	
Am(OH) <sub>3</sub>	15.5	
Am(OH) <sub>4</sub> <sup>-</sup>	19	
Am(OH) <sub>3</sub> (s)	-23.5	(log K <sub>s</sub> )

$\text{AmCO}_3^+$	6	
$\text{Am}(\text{CO}_3)_2^-$	10	
$\text{Am}(\text{CO}_3)_3^{3-}$	13	
$\text{Am}_2(\text{CO}_3)_3(\text{s})$	-31	(log $K_s$ )
AmHA	7.3	(12)

and a HA-concentration of 0.1 or 10 mg/l.

The AmHA- and the  $\text{Am}^{3+}$ -concentrations are comparable at the low total HA-concentration level (0.1 mg/l). At the high concentration (10 mg/l HA), AmHA-complexes would be expected to dominate in the low and intermediate pH-range (c.f. Fig. 1-2). The distribution coefficient is reduced by one order of magnitude at the high HA-concentration, while no significant effect is observed at the low concentration.

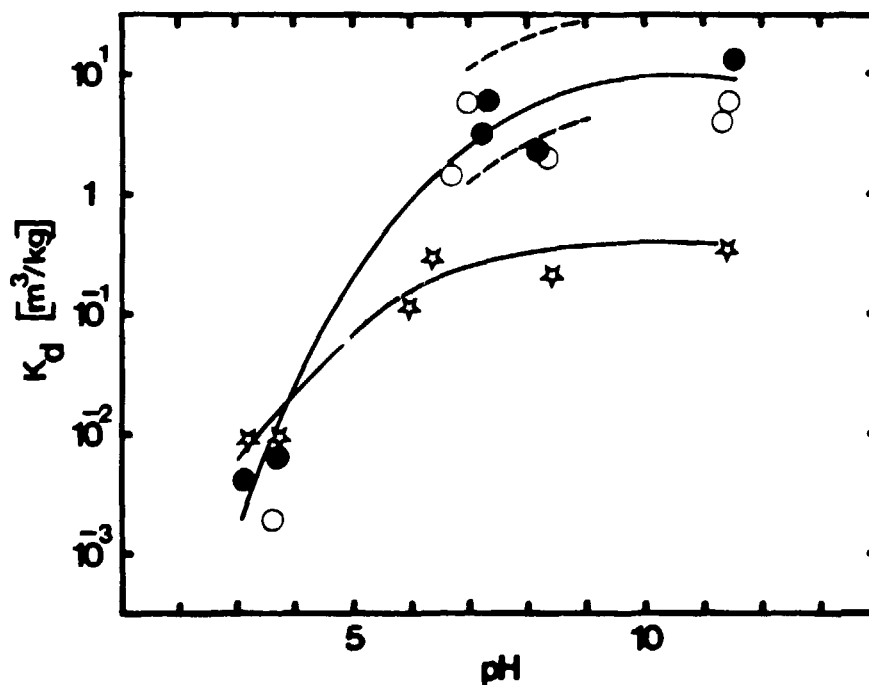


Figure 1-1. The distribution coefficient ( $K_d$ ) vs pH for americium. (Synthetic groundwater, granite).

○ No HA, ● 0.1 mg/l HA, ★ 10 mg/l HA

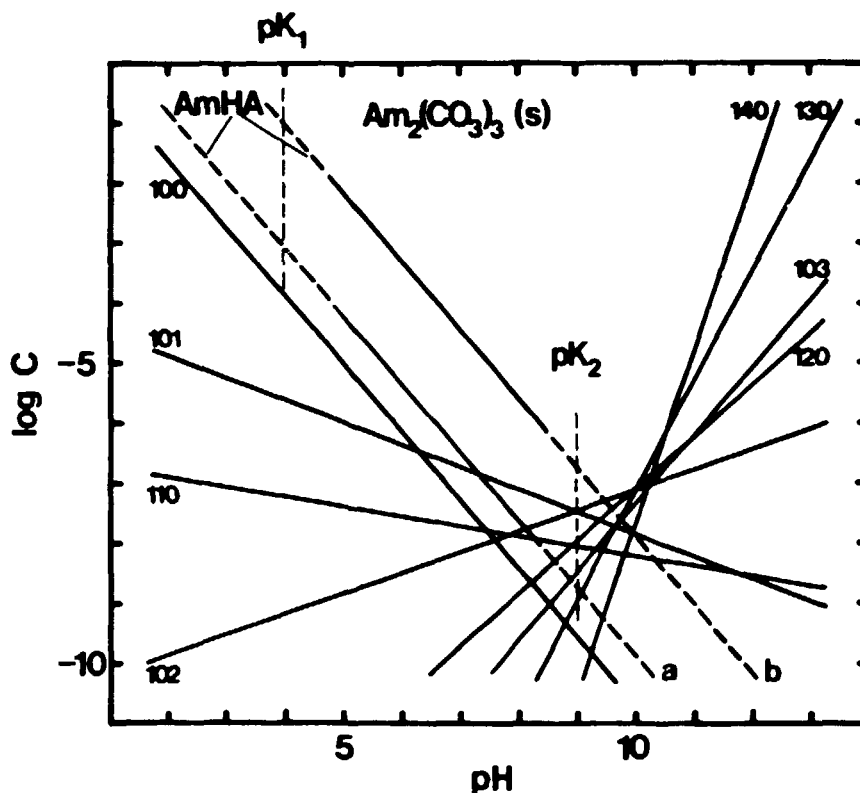


Figure 1-2. Speciation in a  $\text{Am}^{3+}$ - $\text{OH}^-$ - $\text{CO}_3^{2-}$ -HA-system  
 a. 0.1 mg/l HA      b. 10 mg/l HA

$$\log [\text{CO}_3^{2-}] = 0.76\text{pH} - 10.83 \quad (23)$$

Concentrations of macro-molecular complexing agents HA in deep Swedish groundwaters are estimated in Fig. 1-3, assuming

- o a capacity of 6 meq/g HA
- o a fraction HA in TOC (total organic carbon) of 0.1

Considering the hydrolysis constants and the formation constants for carbonate complexes and HA-complexes (c.f. Table 3 and 4) and  $\text{pH}/\text{CO}_3^{2-}$ -concentrations in deep groundwaters (23) it is likely that actinide-HA-complexes constitute a significant fraction of the soluble species of the actinides in their lower oxidation states (III, IV) at pH below 7-8. For the actinides in their higher oxidation states (V, VI) the carbonate complexation would dominate over HA-complexation in most waters.

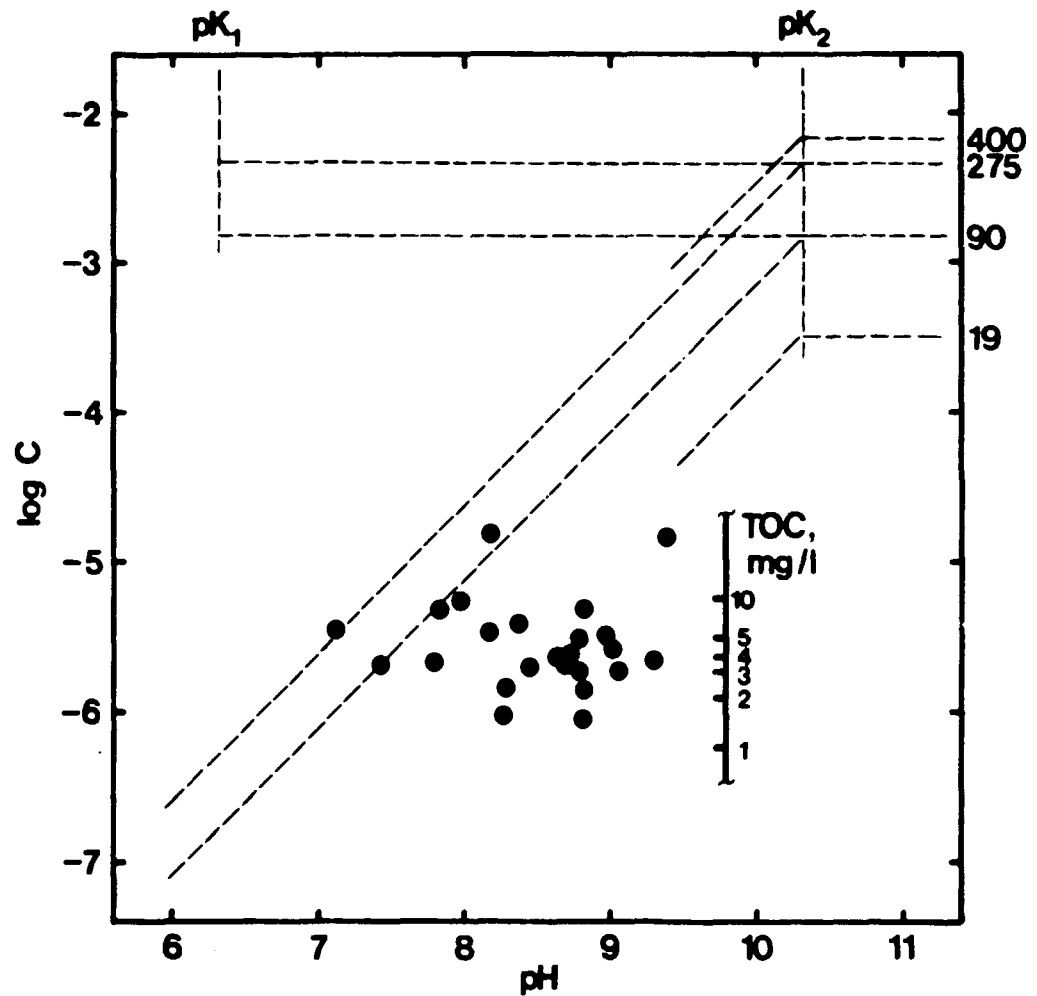


Figure 1-3. Concentration of organics (TOC) in deep groundwaters (22). The dashed lines represent the total carbonate concentrations 400, 275, 90 and 19 mg/l, respectively, and the corresponding  $\text{CO}_3^{2-}$ -concentrations (given by the lines with the slope + 1 crossing the  $\text{HCO}_3^-$ -concentration levels at  $\text{pH} = \text{pK}_2$ )

The HA-concentrations in the sorption experiments represent the extreme concentration levels in the Swedish deep groundwaters. No data are, however, available on the actinide complexing capacity of the organic fraction in these waters.

Further actinide sorption and mobility studies in the presence of humic and fulvic acids are in progress.



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