

The geochemistry of radionuclides with long half-lives. Their expected migration behaviour

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The Geochemistry of Radionuclides with Long Half-Lives

Their expected migration behaviour

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November 1980

THE GEOCHEMISTRY OF RADIONUCLIDES WITH LONG HALF-LIVES
Their expected migration behaviour

B. Skytte Jensen

This report has been worked out according to the agreement between Risø National Laboratory and ELSAM/ELKRAFT concerning advisory assistance from Risø to ELSAM/ELKRAFT's waste management project.

Abstract. The geochemical behaviour of the actinides and technetium is discussed on a thermodynamic basis. The compositions of ground water in deep underground formations are discussed.

The components in ground water which may enhance migration by complexation are found to be primarily bicarbonate and carbonate ions; but organic acids, if present, may similarly enhance migration.

Based on available data, stability-diagrams for the transuranium elements from uranium to americium under diverse conditions have been calculated. The diagrams identify the dominant species in solution, and in an accompanying diagram iso-concentration cur-

(continued on next page)

November 1980

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ves have been calculated, which show that the actinides may be expected to be very slightly soluble under the conditions existing in deep geological formations. The same is found to be the case for technetium.

The adsorption of selected radionuclides onto clay components from Danish soils is discussed, and recent experimental data are presented.

INIS Descriptors: ACTINIDES, ADSORPTION, AMERICIUM 241, CARBONATES, CHEMICAL COMPOSITION, COMPLEXES, DIAGRAMS, GEOCHEMISTRY, GROUND WATER, HIGH-LEVEL RADIOACTIVE WASTES, NEPTUNIUM 237, PLUTONIUM 239, RADIONUCLIDE MIGRATION, REDOX POTENTIAL, SOILS, SOLUBILITY, STABILITY, TECHNETIUM, TECHNETIUM 99, TRANSURANIUM ELEMENTS, UNDERGROUND DISPOSAL.

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INTRODUCTION

High-level radioactive waste contains several radionuclides whose lifetimes vastly exceed the time spans humankind has had experience in handling.

It is obvious that no one can secure that geological or artificial structures will remain undisturbed for several hundred thousand years or more. One cannot be sure, therefore, that some of the activity in geologically disposed waste will not be released from the repository at some remote future time.

It is generally agreed that the only medium for transporting eventually released activity to the biosphere is ground water. Therefore, it is important to be able to predict the behaviour of the long-lived radionuclides under the conditions in ground waters which may be found in diverse geological formations now and in the future.

Although ^{90}Sr is potentially the most dangerous radionuclide in the waste, its rather short half-life (29 years) secures that reasonable delays in its release will reduce its possible impact on the surroundings to a negligible level.

The long-lived radionuclides that are formed in larger amounts in the waste, are found among the transuranium elements, i.e. ^{239}Pu , ^{237}Np , ^{241}Am , etc. In addition the long-lived fission product ^{99}Tc needs also to be considered because it is one of the major components of the waste.

Most of the chemistry of these compounds has been studied under conditions which deviate appreciably from those encountered in nature, but at present new information is published which supports predictions based on theoretical considerations.

The detailed chemical conditions in geological formations naturally vary from site to site and a migrating radionuclide may experience different compositions of ground water in its path and may take part in different chemical reactions.

Present-day knowledge of the hydrology at a chosen site, the velocity and direction of flowing ground water, is naturally of utmost importance for estimating the extent of transport of immediately released radionuclides towards the biosphere. However, because of the probabilistic nature of geological changes, it is not applicable with certainty to releases caused by events occurring at a distant future time.

The final "barrier" towards the migration of radionuclides is based on the chemical reactions of the waste components under the conditions encountered in nature, i.e. their solubility, their sorption on minerals and soil colloids, etc. These properties may vary, depending on conditions, but the underlying chemical reactions will operate during any chosen second now and in the future with equal probability.

Ground water is the first medium which eventually will attack a body of glass containing radioactive waste. This will occur only after a series of other barriers have been degraded. Exposed to water the glass will corrode, a process which usually has been characterized by a leaching rate. The leaching rate is probably a good measure of the dissolution process when the glass is attacked by a large amount of flowing water, but if the water available is restricted, the maximum solubility of the waste components in the water can be assumed to be the more relevant limiting factor.

The solubility of the different radionuclides depends primarily on their chemical nature, being iron, cobalt, plutonium, technetium, etc., but also on the composition of the ground water in which they are dissolved. In the next section ground-water composition will be discussed together with its probable influence on the migration behaviour of different chemical elements.

GROUNDWATER COMPOSITIONS

Ground waters are characterized by their pH, redox potentials and specified concentrations of cations and anions. To a large extent the magnitudes are determined by reactions between water and the minerals of the formation and may have approached equilibrium conditions if the time of contact has been long enough.

Very many chemical analyses of groundwater composition have been made throughout the years; however, these have not always been of sufficient quality and detail to be useful in estimating the effect of the composition of a given ground water on the behaviour of the radionuclides. Notably, reliable measurements of the redox potentials in ground waters are often lacking, and these parameters play a very important role in determining the chemical state of the transuranium elements and hence of their migration properties.

In a very comprehensive analysis of available data Baas-Becking, Kaplan and Moor:¹⁾ classified ground waters according to their redox potentials and pH values. From their data compilation it can be concluded that below the water table the environment can be assumed to be reducing and slightly alkaline except in local distances of high rates of water flow.

Reducing and slightly alkaline conditions are therefore those one primarily should consider when studying the migration behaviour of radionuclides released from a geological repository.

If some radionuclides are released under near-surface conditions their migration behaviour may be drastically different from that occurring in deep soil because of the prevailing oxidizing conditions exposed to the atmosphere. This is especially true for the transuranium elements, which can attain many different oxidation states depending on the chemistry of the environment. Laboratory or field observations on their migration behaviour in the biosphere can therefore not be transferred uncritically to the conditions found in deep geological formations.

For by far the largest part of their migration path, released radionuclides will, in the Danish concept, experience the slightly alkaline reducing condition mentioned above, because of the high groundwater level in Denmark.

The different components of ground waters, anions and cations, may both enhance the migration of radionuclides although by different mechanisms.

The anions, i.e. chloride, sulphate, carbonate, bicarbonate, etc., may react with the radionuclides forming complexes which either are not adsorbed at all or only slightly so onto clays or other colloids.

The cations, on the other hand, compete with the radionuclides for available adsorption sites on the sorbing mineral surfaces, and may thereby enhance nuclide migration if present in large concentrations.

The acidity, i.e. the pH, of the ground water will determine the solubility of many of the heavier elements to a large extent, and will also determine the extent of complexation with, for example, carbonate; it is, therefore, an important parameter.

The redox potential determines the oxidation state in which a given element will be found, and as the chemical properties of an element depend very much on its oxidation state, variations in redox potentials may have a profound influence on the migration properties of a radionuclide.

The analysis of ground water for its macro-components, i.e. Na, K, Ca, Cl, SO₄, etc., is straightforward, and published data are usually of adequate precision. The same need not be true for the published data of redox potentials, because
1) samples may have been oxidized by air during collection
and 2) the determination of reliable redox potentials is not without experimental difficulties, i.e. the instrument reading may correspond to different electrode processes than the one being searched for.

It seems relevant, therefore, to get independent estimates of the conditions which can be expected to be encountered in nature. To this end a collection of analytical data on deep water compositions²⁾ has been analysed as follows.

The data analysed comprise waters from different geological formations such as granites, sandstones, shales, etc., and notably those where pH and total soluble iron, C_{Fe} , were recorded. When $\log C_{Fe}$ versus pH is plotted, as in Fig. 1, it is seen that all the ground waters were undersaturated

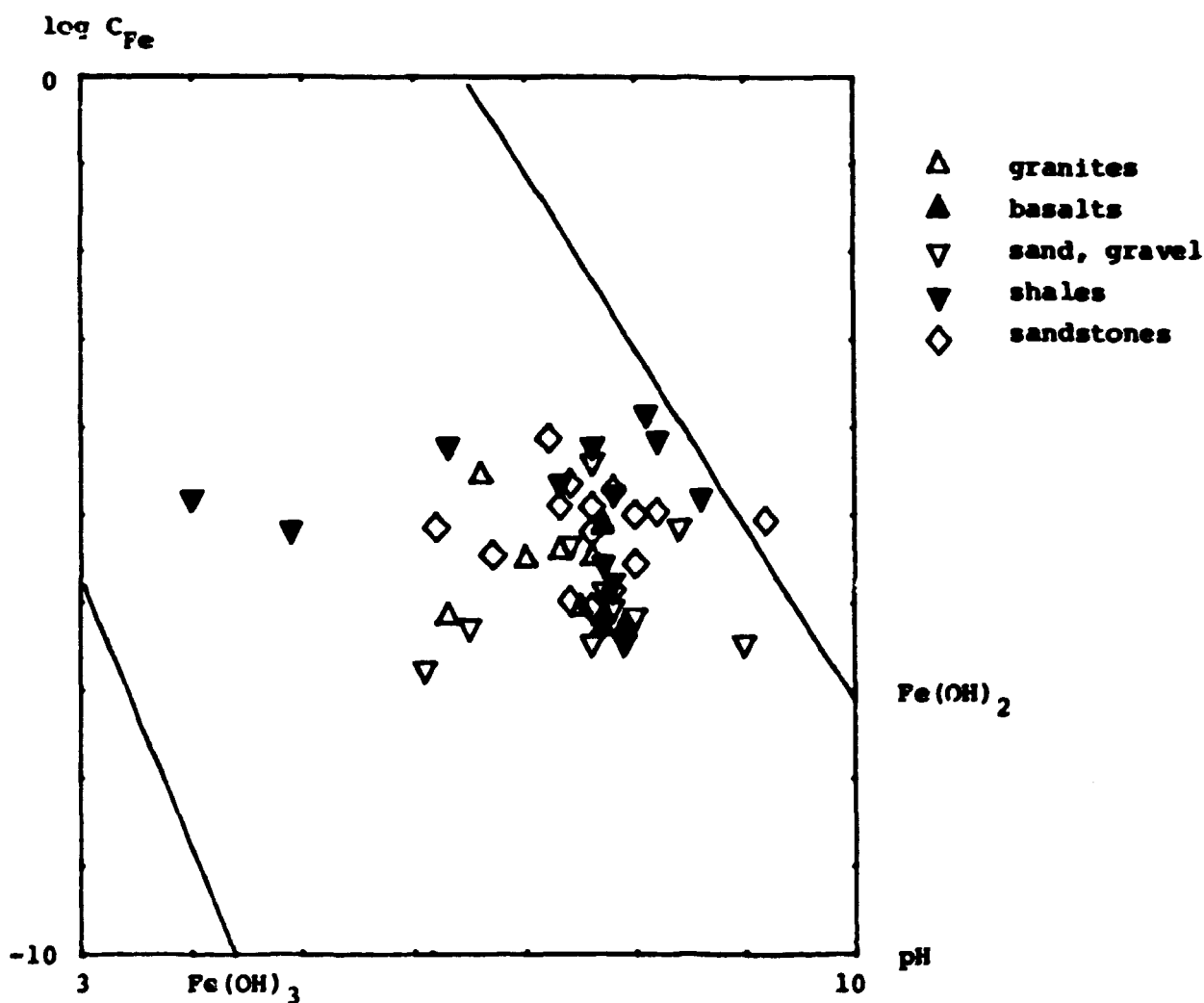


Figure 1

with respect to ferrous hydroxide ($Fe(OH)_2$), but highly oversaturated with respect to ferric hydroxide ($Fe(OH)_3$). One may, therefore, conclude with confidence that the iron in solution

in ground water is almost solely found in the ferrous state if major amounts of complexing agents can be excluded.

With a given redox couple like the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion-pair the redox potential is described by the following expression

$$E = E_0 + 0.06 \log\left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}\right) \text{ with } E_0 = 0.771 \text{ volt.} \quad (1)$$

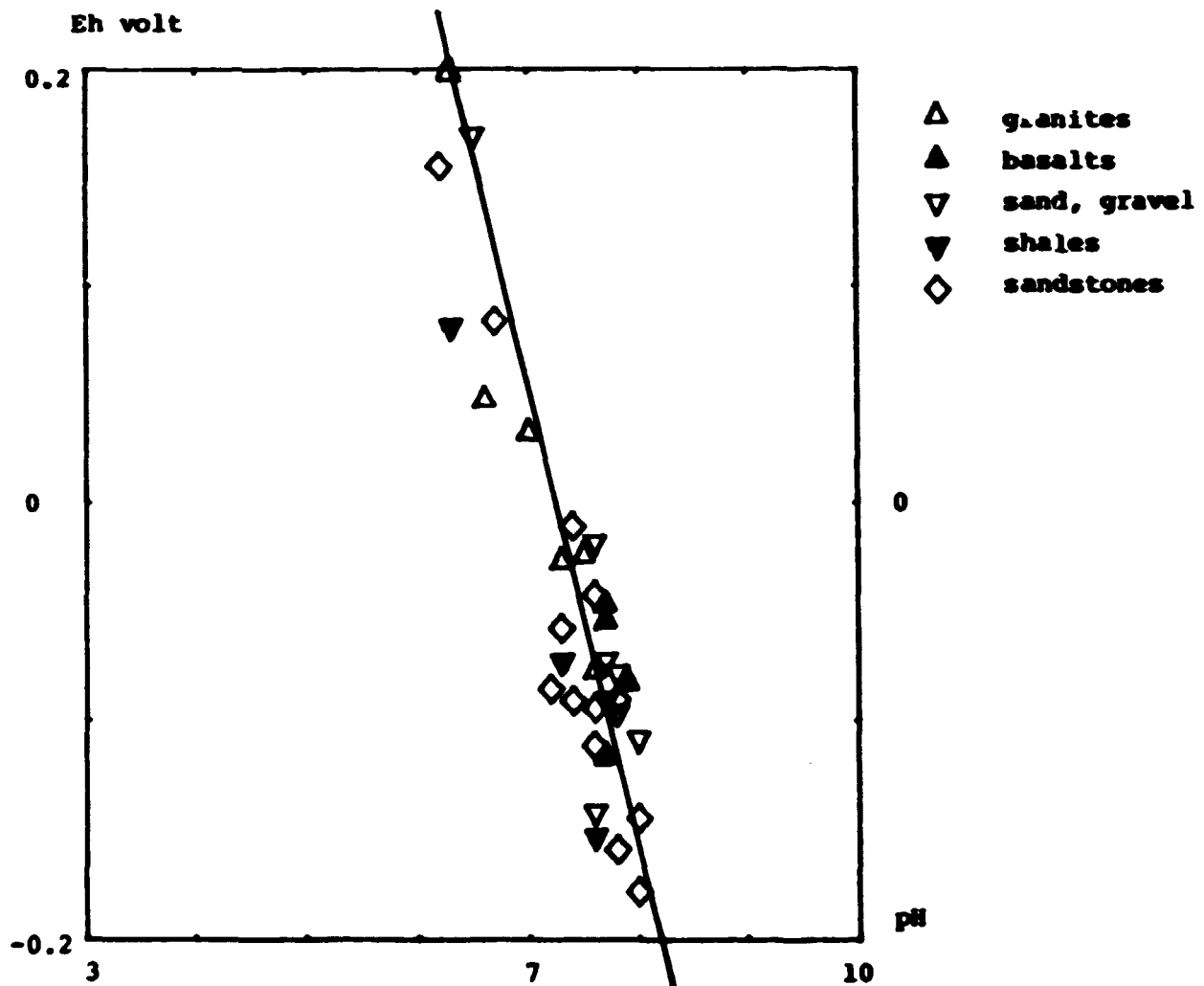
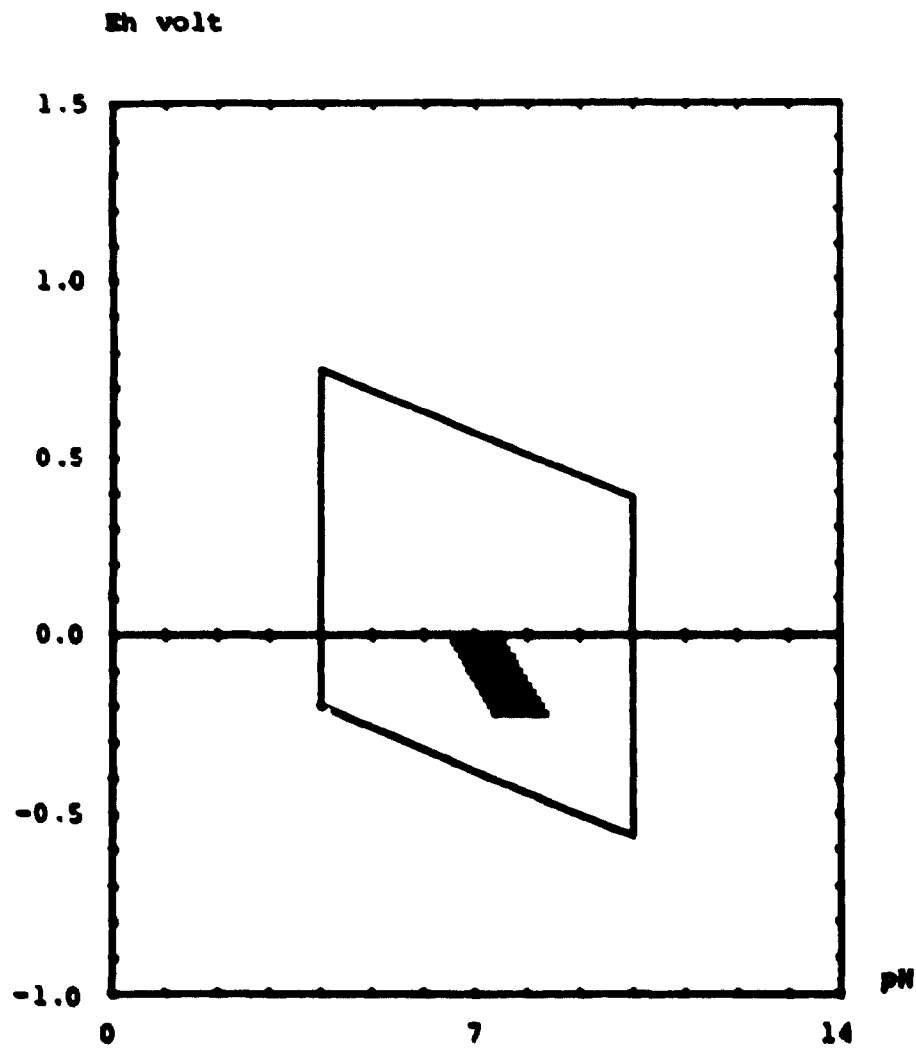


Figure 2

If it is assumed that $\text{Fe}(\text{OH})_3$ is the solid phase controlling the concentration of ferric ion, $[\text{Fe}^{3+}]$, in ground waters, the following expression is derived from which one may calculate the redox potential:

$$E = 0.962 - 0.18 \text{ pH} - 0.06 \log C_{\text{Fe}} \text{ volt.} \quad (2)$$



Hatched area corresponds to expected subsurface conditions.

The parallelogram circumscribes conditions found in more than 90% of all terrestrial waters.

The uppermost border of the parallelogram corresponds to conditions experienced in formations exposed to the atmosphere.

Figure 3

The redox potentials calculated by means of Eq. 2 are plotted in Fig. 2 and show a variation which is well in accordance with the few experimental data available¹⁾.

If the oxide, Fe_2O_3 , is assumed to be the solid phase controlling the Fe^{3+} concentration, the calculated redox potentials are approximately 200 mV lower.

By assuming that the redox potentials of granitic rock are determined by solid solutions of Fe^{2+} and Fe^{3+} in chloritic minerals, Swedish scientists³⁾ estimated the redox potentials in granites, based on mineral analyses of the rock material. Their calculations coincide with those presented here, and confirm that reducing conditions as a rule are to be found at larger depths in rocks.

In the diagram, Fig. 3, the expected subsurface groundwater domain is shown as a hatched area in the Eh versus pH landscape. In the same figure the borders circumscribing the conditions experienced in the majority of terrestrial waters (data from Ref. 1) are also shown. The uppermost border will correspond to conditions found in near-surface soils, and these will in turn determine the chemical forms of the elements exposed to the influence of the oxidizing atmosphere. As shown later, the migration of some elements will be appreciably enhanced when they are oxidized.

COMPLEX CHEMISTRY

Cations like M^{z+} may react with anions like L^- forming complexes exemplified by the following reaction schemes



each reaction being characterized by a complexity constant K_i or a complexity product β_i

$$\frac{[ML_i]}{[ML_{i-1}][L]} = K_i \text{ and } \frac{[ML_i]}{[M][L]^i} = \beta_i \quad (4)$$

Complex formation will influence such important parameters as solubilities and adsorption phenomena of elements and need to be seriously considered when discussing radionuclide migration phenomena.

The influence of a complex formation on the solubilities of a slightly soluble compound can be calculated as follows:

The solubility, s , of a compound can be expressed as the sum of concentrations of all types of species found in solution in chemical equilibrium with the slightly soluble compound MX_2 ; thus

$$s = [M] + [ML] + [ML_2] + [ML_3] \dots + [ML_i] + \quad (5)$$

with the additional condition

$$[M][X]^2 = K_s, \text{ the solubility product of } MX_2. \quad (6)$$

The combining of Eqs. 5 and 6 leads to an expression for the solubility as a function of the concentration of L as

$$s = (K_s/[X]^2) (1 + \beta_1[L] + \beta_2[L]^2 \dots + \beta_i[L]^i) = \quad (7)$$

$$s_0 (1 + \sum \beta_i [L]^i)$$

which, for $L = 0$, reduces to the simple solubility-product restriction.

To be able to estimate the effect of complex formation on solubilities one therefore needs to know, apart from the magnitude of L, the values of all the complexity products. These data are determined by laboratory experiments and are known for very many reactions. In a recent four-volume com-

TABLE 1 C

log $\beta_{r,x}$

Sulphate complexes, L = SO ₄ ²⁻					Carbonate complexes, L = CO ₃ ²⁻				
r.x,	1.1	1.2	1.3	K _s		1.1	1.2	1.3	K _s
Sr	1.14			-6.5					- 9.03
3+									
U	---								
Np	---								
Pu	1.26					9.6	12.9	16.2	
Am	1.57	2.66							
Cm	1.86	2.70							
La	1.43	2.86							-33.4
Eu	1.54	2.73							-32
4+									
U	3.42	5.82							
Np	3.41	5.42							
Pu	3.66								
Am	---								
Cm	---								
5+									
UO ₂ ⁺	---								
NpO ₂ ⁺	---								
PuO ₂ ⁺	---								
AmO ₂ ⁺	---								
6+									
UO ₂ ²⁺	1.81	2.5	3.7			10.1	17.1	21.4	-14.46
NpO ₂ ²⁺	1.82	2.62							
PuO ₂ ²⁺	---								
AmO ₂ ²⁺	---								

In addition the following mixed carbonate-hydroxide complex has been recorded and its existence found probable.

	log β
Pu(OH) ₃ CO ₃ ⁻	41

By similar reasoning one may estimate the effect of complex formation on adsorption processes. If it is assumed that each complex is adsorbed with its own distribution coefficient

$$K_{D(i)} = \frac{[ML_i]_{ad}}{[ML_i]} \quad (8)$$

the following expression, valid for tracer concentrations, for the average distribution coefficient, \bar{K}_D , can be derived

$$\bar{K}_D = \frac{([M]_{ad} + [ML]_{ad} + \dots + [ML_i]_{ad})}{([M] + [ML] + \dots + [ML_i])} = \frac{K_{D(0)} (1 + \sum \alpha_i \beta_i [L]^i)}{(1 + \sum \beta_i [L]^i)} \quad (9)$$

with $\alpha_i = \frac{K_{D(i)}}{K_{D(0)}}$

If the sorption process is ion-exchange, $K_{D(i)}$ will diminish with increasing i , and eventually become zero. For sufficiently large concentrations of L , the average distribution coefficient, \bar{K}_D , which corresponds to the observation value, may therefore approach zero; this means that the retention properties of the soil groundwater system are upset.

CRITICAL ANION CONCENTRATION IN GROUND WATERS

The complex forming anions in ground waters comprise the OH^- , F^- , Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} ions. In addition, ground waters may contain organic compounds in minor amounts, which may have a strong tendency for complexing cations.

The organic compounds are decay products from biological material and, if found in deep formations, may indicate the presence

of nearby deposits of biological origin. They are found in the largest concentrations in topsoils where biological activity predominates.

The organic compounds may be insoluble like the humic acids whose presence will retard the migration of radionuclides, or they may be soluble like the fulvic acids or fermentation products as lactic- or citric acids, whose presence could enhance migration by forming soluble complexes.

The inorganic anions mentioned above are found in all ground waters if they are looked for. Their concentrations vary within wide limits, but below some critical concentrations their presence may be considered insignificant.

The extent to which a given concentration of an anion may influence the migration of a radionuclide can be estimated by comparison with the hydroxide ion, whose presence is unavoidable. If a complex $M(OH)_iX$ is formed with the anion X simultaneously with the formation of hydroxide complexes $M(OH)_j$, the fraction

$$F = \frac{[M(OH)_iX]}{[M] + [M(OH)_iX] + [M(OH)_j]} \quad (10)$$

is then a measure of the importance to be placed on the formation of complexes with the anion X.

If $F \lesssim 0.5$, the effect of complex formation would be that a given distribution coefficient K_D would be reduced to some value between K_D and $D_D/2$ due to the interaction of X with the system. This effect would be barely noticeable compared to the uncertainties involved in the migration calculations, but for $F > 0.5$, the effect on K_D will be important.

By solving Eq. 10 for the concentration X with $F = 0.5$, one may therefore calculate a limiting concentration of X, below which the presence of the anion X in ground waters may be neglected.

$$F = 0.5 = \frac{[M(OH)_i X]}{[M] + [M(OH)_i X] + \sum [M(OH)_j]} = \frac{\beta [OH]^i [X]}{1 + \beta [OH]^i [X] + \sum \gamma [OH]^j} \quad (11)$$

hence

$$\log[X] = \log(1 + \sum \gamma [OH]^j) - \log(\beta [OH]^i) \quad (12)$$

Figs. 4-8 indicate the calculated limiting concentrations for fluoride, chloride, sulphate, and carbonate ions using the actinide ions, MO_2^{2+} , M^{4+} , M^{3+} and the strontium ion Sr^{2+} as indicators, and with pH as variable. The constants used in the calculation are tabulated in Tables 1A, B, and C.

The limiting concentration determined in this way should be taken only as a warning limit, which indicates that more attention should be paid to the problem. Superimposed on the effect of complex formation is the competitive effect of concentrations of cations, Na^+ , Ca^{2+} , etc., which may be decisive in determining the distribution coefficients of radionuclides between minerals and ground water. Complex formation may be the more decisive reaction at low cation concentrations, i.e. in soft waters, whereas its effect may be hidden under the dominant displacement reactions at high cation concentrations.

In the case of carbonate complexes two presentations are shown, 1) with the partial pressure of CO_2 in a saturating gas phase as the limiting concentration, and 2) with the analytical concentration of HCO_3^- in the ground water as the dependent variable.

In the figures a rectangle circumscribes the conditions which have been found in actual ground waters in more than 90% of the analysed cases.⁵⁾ The published data, however, while mostly representing conditions near surface waters and under extreme concentrations, are not unexpectedly observed in some deep waters.

Although some groundwater compositions at the disposal site may be unfavourable with regard to migration in the immediate vicinity of the site, on its way back to the biosphere eventually released activity will invariably end in or pass through formations characterized by "normal" groundwater compositions. These formations will then represent the actual barriers against transport to the biosphere.

Inspection of Figs. 4-6 shows that under these "normal" conditions the effect of sulphate and chloride complexation may be neglected. Fluoride may have a slight enhancing influence on migration if found in higher-than-average concentrations under slightly acidic conditions, which therefore should be avoided.

Figures 7 and 8 on the other hand show a pronounced effect of carbonate complexation even at very low carbonate concentrations.

The effect of complex formation is generally to enhance migrations, its effect being counteracted by precipitation and/or sorption processes of a diverse nature. Actual migration behaviour of radionuclides depends on an interplay of these two processes of which complex formation is the best understood. A description of actual observations may be further complicated by the occurrence of slow chemical reactions, for example, among the different possible oxidation states of the trans-uranium elements.

Diagrams for complexing with organic compounds will resemble Fig. 7, and the presence of even small concentrations of compounds as lactic and citric acid may have a pronounced enhancing effect on the migration behaviour of certain radionuclides.

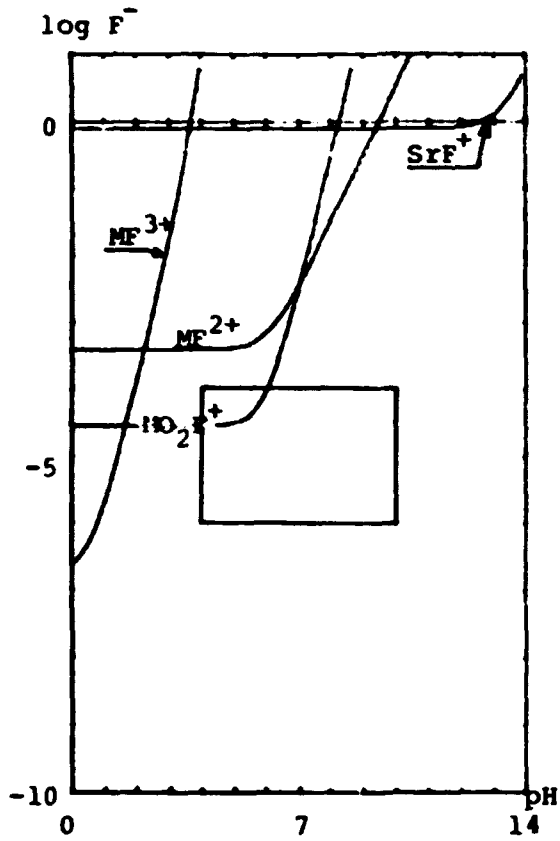


Figure 4

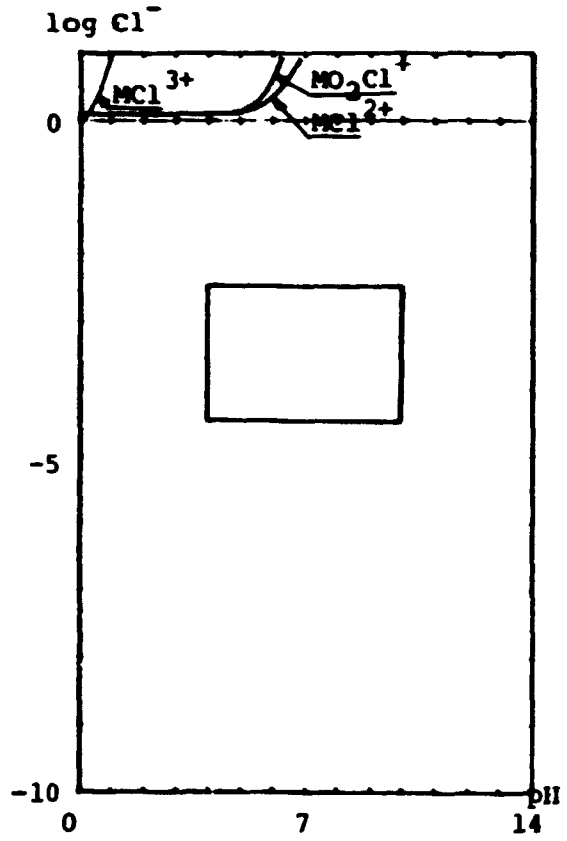


Figure 5

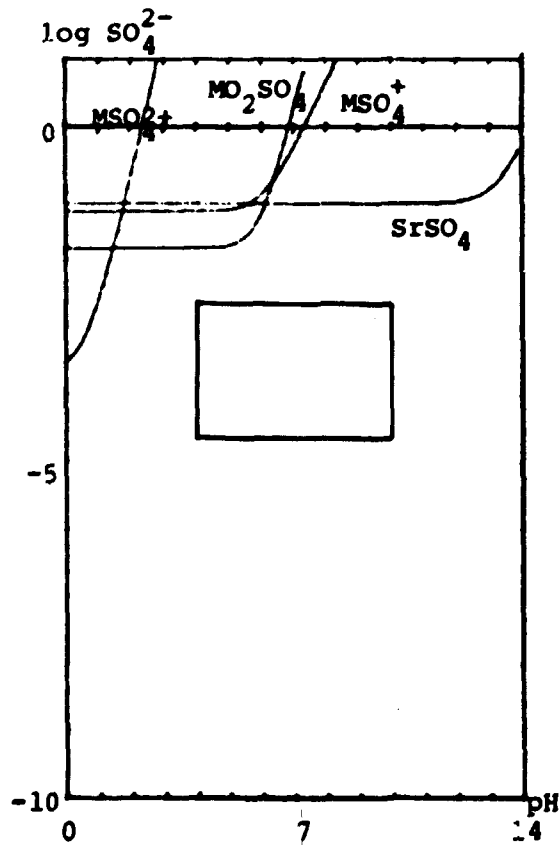


Figure 6

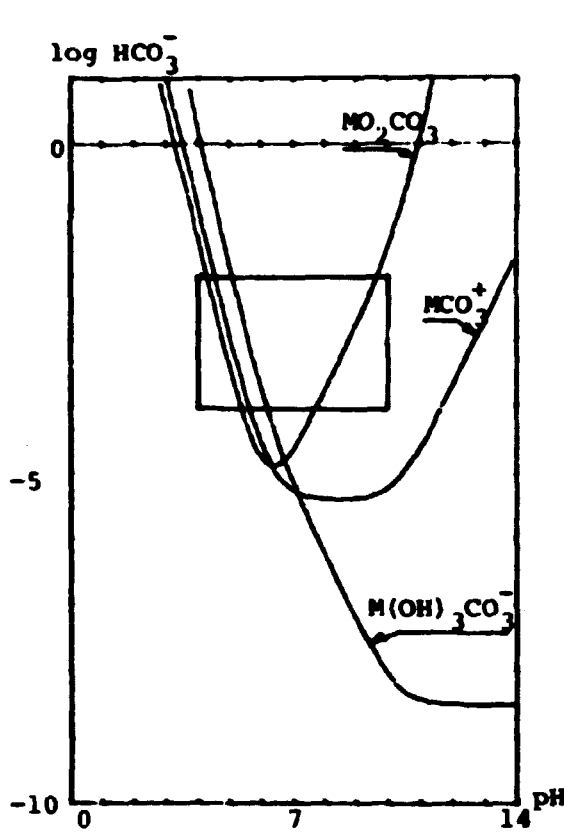


Figure 7

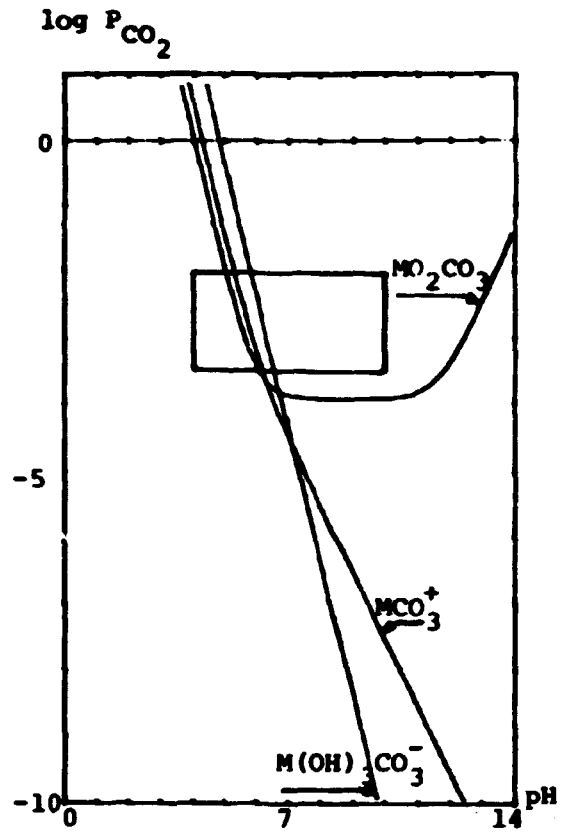


Figure 8

THE CHEMISTRY OF THE TRANSURANIUM ELEMENTS OF RELEVANCE FOR THE EVALUATION OF THE HAZARDS OF GEOLOGICAL DEPOSITION OF HIGH-LEVEL WASTE

The transuranium elements Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md and No are the heavy elements, which together with Ac, Th, Pa and U comprise the actinide elements.

Their aqueous chemistry has recently been surveyed by Ahrland, and Rydberg and Liljenzin⁶⁾; other recent articles⁷⁾ discuss topics of relevance in the present context.

The following table⁸⁾ shows the amounts of the actinide isotopes, in terms of activity level, which will be found in the waste from one ton of uranium fuel.

Table 2

Actinides in High-Level Waste

		Curie/ton uranium - after years				
		2	10	100	1000	10000
Curium	-246	0.061	0.061	0.060	0.053	
	-245	0.34	0.34	0.34	0.32	
	-244	1600	1200	34		
	-243	16	13	1.4		
	-242	1700	0.0069			
Americium	-243	15	15	15	13	0.0024
	-242m	12	12	8.0	0.13	
	-241	470	470	420	99	0.0001
Plutonium	-242	0.0092	0.0092	0.0092	0.0093	0.0083
	-241	520	340	3.4	0.32	0.0001
	-240	2.6	3.7	6.8	6.2	0.00017
	-239	1.5	1.5	1.5	1.8	0.5
	-238	9.3	17	8.3	0.0058	
Neptunium	-239	15	15	15	14	0.0024
	-238	12	12	8.0	0.13	
	-237	0.21	0.21	0.23	0.29	0.30
Uranium	-238	0.0003	0.0003	0.0003	0.0003	0.0003
	-236	0.0002	0.0002	0.0002	0.0004	0.0021
	-235	0.00002	0.00002	0.00002	0.00002	0.00021
	-234	0.001	0.001	0.0007	0.015	0.011
	-233				0.001	0.11

The radio toxicities of the transuranium elements are very large, and the potential hazards of the high-level waste are in the long term mostly due to their presence. Some of them have such long half-lives that the only barrier which one can safely calculate is their geochemical behaviour. This is especially true for the Pu-239 and Np-237 isotopes.

Their mere presence, however, is not an adequate measure of the actual risks involved in their disposal in geological formations.

In many respects these isotopes may be compared with naturally occurring thorium and protactinium. Under many conditions their chemistry is similar and their half-lives and alpha-energies are comparable.

The actual consequences of having potentially extremely hazardous amounts of thorium, protactinium, as well as radium in the uppermost soil-layer of the country are negligible, and with a high degree of certainty the same will apply to the presence of the transuranium isotopes in a geological repository.

The main reason for the minuteness of the actual hazards compared to the potential hazards no doubt lies in the chemical properties of the elements, which secure that very low concentrations are to be found in drinking water and foodstuffs.

Neglecting the sorption processes for the moment, it is possible in principle to identify the dominant species in solution under given conditions, i.e. Eh and pH (Figs. 9-16A), and to calculate the maximum total concentration of soluble species in equilibrium with a solid phase (Figs. 9-16B). This is, however, possible only if all the constants characterising the possible equilibria are known.

Unfortunately this is not the case for all the transuranium elements, but experience - as well as theory - has revealed that their chemical properties are so much alike that one may confidently use information from one species in a given oxidation state as a good estimate of the chemical properties of another transuranium element in the same oxidation state. This means that we may assume that the transuranium elements show the same solubility products, complexity constants, etc., when in the same oxidation states - being trivalent, tetravalent, pentavalent, or hexavalent. Experience with the chemical reactions of the uranyl-ion may therefore be applied to understanding the behaviour of the plutonyl- and neptonyl-ions, etc. The affinity for the electron, however, varies much among the different ionic species, as shown by the redox potentials in Table 4.⁶⁾

The information from the A-figures will be useful for estimating the sorption characteristics of the soluble species, and the information in the B-figures will permit an estimation to be made of the maximum total concentration in solution under given conditions.

In the figures the hatched area indicates the conditions expected to be dominant in deep geological formations in solid rock or sediments.

The following "best" data for the transuranium elements were used in the calculations.

Table 3

Species	L = OH ⁻			L = CO ₃ ²⁻		
	log β ₁	log β ₂	log β ₃	log β ₁	log β ₂	log β ₃
MO ₂ ²⁺	8.7	17.0	21.3	10	17	21
MO ₂ ⁺	4.3					
M ⁴⁺	13.45	26.8	37.5			
M ³⁺	8.0			9.6	12.9	16.2

The mixed complex M(OH)₃CO₃⁻ has also been taken into account.

$$\frac{\log \beta}{M(OH)_3CO_3^-} \quad 41$$

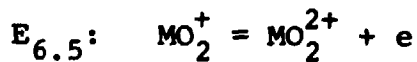
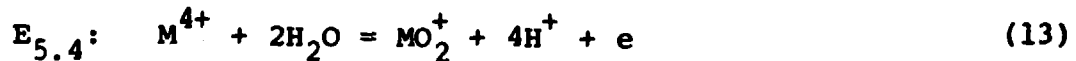
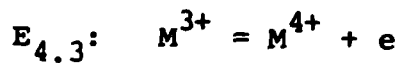
The other possible complexes mentioned previously have been found to contribute negligibly to the overall behaviour of the transuranium elements.

The standard potentials used in the calculations are the following

Table 4

	$E_{4.3}$	$E_{5.4}$	$E_{6.5}$
U	-0.596	0.558	0.080
Np	0.190	0.684	1.153
Pu	0.017	1.115	0.933
Am	2.38	1.10	1.62
Cm	3.28	--	--

defined by the reactions



thus

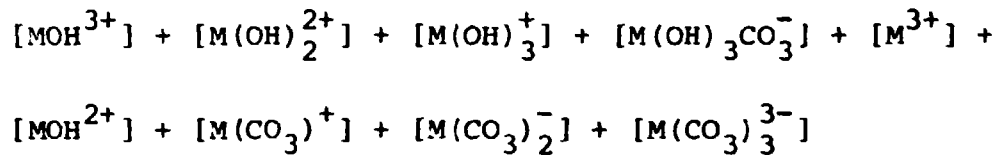
$$[M^{4+}]/[M^{3+}] = 10^{((E-E_{4.3})/0.06)} \quad (14)$$

$$[MO_2^+]/[M^{4+}] = \frac{10^{((E-E_{5.4})/0.06)}}{[H^+]^4}$$

$$MO_2^{2+}/MO_2^+ = 10^{((E-E_{6.5})/0.06)}$$

By assuming all the reactions of Table 3 to occur, the total concentration C_t of a transuranium element in solution is expressed by

$$C_t = [MO_2^{2+}] + [MO_2OH^+] + [MO_2(OH)_2] + [MO_2(OH)_3^-] + [MO_2CO_3] + [MO_2(CO_3)_2^{2-}] + [MO_2(CO_3)_3^{4-}] + [MO_2^+] + [MO_2OH] + [M^{4+}] + \quad (15)$$



For any selected species one may calculate the curve in the E versus pH coordinate system, where the species accounts for half the total concentration. The curves found in this way identify domains where the different species are predominant in the E/pH diagram.

The equation

$$\frac{[\text{M}(\text{OH})_i(\text{CO}_3)_j]}{C_t} = 0.5 \text{ is solved by inserting the expressions}$$

defining the complex equilibria

$$\frac{[\text{M}(\text{OH})_i(\text{CO}_3)_j]}{[\text{M}][\text{OH}]^i[\text{CO}_3]^j} = \beta_{i,j} \tag{16}$$

and the expressions relating the relative concentrations of the species in a redox couple to the redox potential E.

The resulting equation becomes a third-order polynomial in 10^E , which is solved by iteration. It was found that the species, $\text{MC}_2(\text{CO}_3)_2^{2-}$, did not contribute significantly to the total concentration of dissolved species.

The resulting diagrams show the distribution of species in solution, only.

If the concentration of some of the species exceed some level, precipitates may be formed. When well-defined solids exist the concentrations of their components are determined by the solubility product of the solid. The new relation thus established allows for the determination of the total concentration C_t of the radionuclide.

D. Rai and R.J. Serne⁷⁾ considered the case of solids in equilibria with solutions for a series of important radio-nuclides. They compiled available constants, more or less critically, and compared deductions based on these data with actual observations.

In the present approach we consider only oxides or hydroxides as precipitates, and assume, as before, that the chemistry of each transuranium element is so similar to the others in the same oxidation state, that all their reactions are governed by the same equilibrium constants.

Some ground waters may contain silicate, phosphate, vanadate, etc. in concentrations high enough to compete effectively with the hydroxide ion thereby forming precipitates which, under the given conditions, are more stable than the hydroxides. On the other hand, the presence of the hydroxide ion is unavoidable, and the total concentrations calculated according to the assumptions above will therefore represent the maximum concentrations to be expected under any conditions with regard to pH and Eh.

Figures 9-15B indicate the domains in the Eh versus pH diagrams where the solids $\text{MO}_2(\text{OH})_2$, MO_2OH , MO_2 , and $\text{M}(\text{OH})_3$ are stable. The line bordering two domains corresponds to the conditions in which the two solid phases may exist simultaneously in equilibrium.

With the solid phase present, which is underlined in the figures, contour lines have been calculated at total concentrations of 10^{-3} to 10^{-5} M for uranium, neptunium, plutonium and americium. The solid phase considered is that which will dominate the equilibria under the conditions to be found in nature, i.e. within the indicated parallelogram in the figures.

The following solubility products have been chosen as typical for the oxides and/or hydroxides of the transuranium elements in their different oxidation states.

Table 5

<u>Compound</u>	<u>log K_s</u>
MO ₂ (OH) ₂	-23
MO ₂ OH	- 9.0
MO ₂	-56
M(OH) ₃	-19.5

The diagrams in Figs. 9,11,13,15,17 have been calculated for a carbonate-free medium and Figs. 10,12,14,16 for a medium saturated with carbon dioxide at a partial pressure of $10^{-3.5}$ atm, corresponding to atmospheric conditions.

A general observation which can be made from the diagrams is that most of the species encountered in solution at near neutral to basic reactions should have moderate to negligible affinity for ion-exchangers, even under reducing conditions, and therefore show slight adsorption.

This is contrary to experience from laboratory studies, where trivalent actinides invariably are strongly adsorbed on to clays even when exposed to an ambient atmosphere.

The reason for the discrepancy could be that unrealistically large complexity constants for the carbonate complexes were used in the calculations. The tabulated constants for the trivalent species were not actually measured, but their magnitudes were estimated by comparison with oxalate complexes⁹⁾, and, therefore, may be in error.

There is certain qualitative evidence for the formation of carbonate complexes of trivalent actinides, but recent work at Risø¹⁰⁾ indicates that the complexity constants are smaller than those recorded in Table 1.

Alternatively, the experiments may be explained if the uncomplexed ions have unusually large affinities for the soil

minerals. This is not unreasonable because the purely electrostatic bond-energy between ion and ionised surface can be expected to be proportional to z^2/r , where r is the distance of closest approach. For the larger ions the less strongly bound water of hydration may be expelled with the ion actually being incorporated into the surface structure of the mineral. The phenomenon of charge reversal of colloids by ion-adsorption and the very slow adsorption kinetics measured by Allard¹¹⁾ support the last hypothesis, although other explanations may also be found.

The last hypothesis may also "explain" the often observed irreversibility of adsorption of polyvalent cations because they will be released only by processes dissolving the whole surface layer.

Geochemically, uranium is known to be highly mobile under near-surface conditions exposed to both oxygen and carbon dioxide but to become immobilised under reducing conditions precipitating as UO_2 . Although the distribution of species in solution for both neptunium and plutonium differs from that of uranium in detail, the same general pattern of behaviour should be expected. For Np and Pu, immobilisation should occur at much lower reducing conditions than those necessary for the immobilisation of U, according to the diagrams.

On the average both Np and Pu should therefore be less mobile in nature than U and immobilisation be easy to accomplish by the proper choice of geochemical conditions at a disposal site.

At near-surface conditions, i.e. along the upper side of the parallelogram enclosing commonly encountered natural conditions, both Np and Pu should be quite mobile with flowing water. Unattended disposal of Pu-containing material under near-surface conditions, i.e. shallow burial, should therefore be avoided.

For americium (and curium) the solid phase existing under natural conditions is the trihydroxide $M(OH)_3$. In a carbonate-

free medium the soluble species should have high-to-moderate affinity to ion-exchanging material in the environment, and their migration would be effectively retarded. Exposed to carbon dioxide, carbonate complexes with less affinity to ion exchangers should be formed and migration would be enhanced. The data on carbonate complexes are rather uncertain, however, but there exist plenty of qualitative observations which show that carbonate complexation must play an important role in nature. The calculated total concentrations of Am at $P_{CO_2} = 10^{-3.5}$ exceed $10^{-3}M$ under all conditions.

Both americium and curium exist in nature solely in the trivalent state independent of the redox potential. Their migration behaviour or geochemical mobility may be deduced by comparison with the rare earth elements.

Under strongly reducing conditions plutonium is found in solution in the trivalent state and, as for americium, its migration should therefore be effectively retarded by ion-exchange processes.

Due to the uncertainties in the constants applied in the calculations one must not overemphasize the content of the diagrams; it is safe to draw the conclusion, however, that even at the point of release, the actual concentrations of transuranium species in solution will be very small. After the release their concentrations will be diminished additionally by sorption and dispersion processes to an extent that they will probably never exceed the maximum permissible concentrations in ground waters.

Uranium

The diagram indicates that under deep-soil conditions uranium should be extremely insoluble even in the presence of carbonate. However, even a slight increase in the redox-potential should increase the solubility drastically, leading to the formation of highly mobile carbonate complexes.

These predictions agree well with observations of the geochemical behaviour of uranium.

$P_{CO_2} = 0$

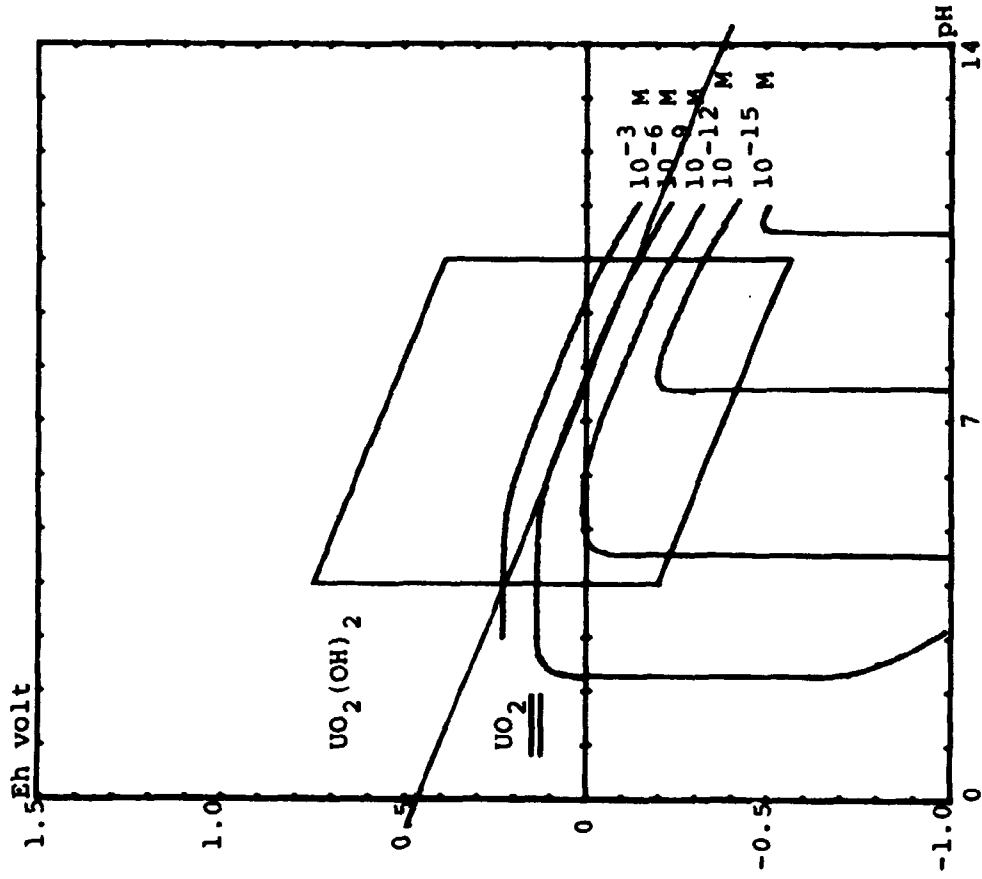


Figure 9A

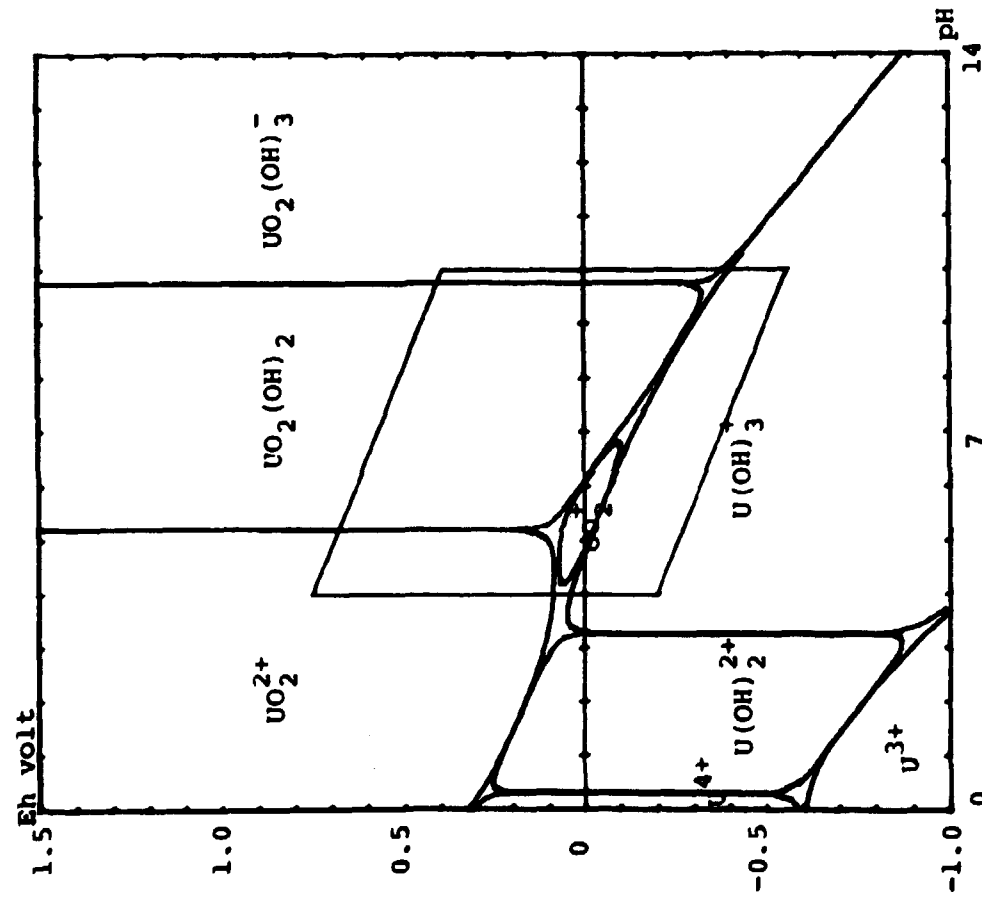


Figure 9B

$P_{CO_2} = 10^{-3.5}$ atm.

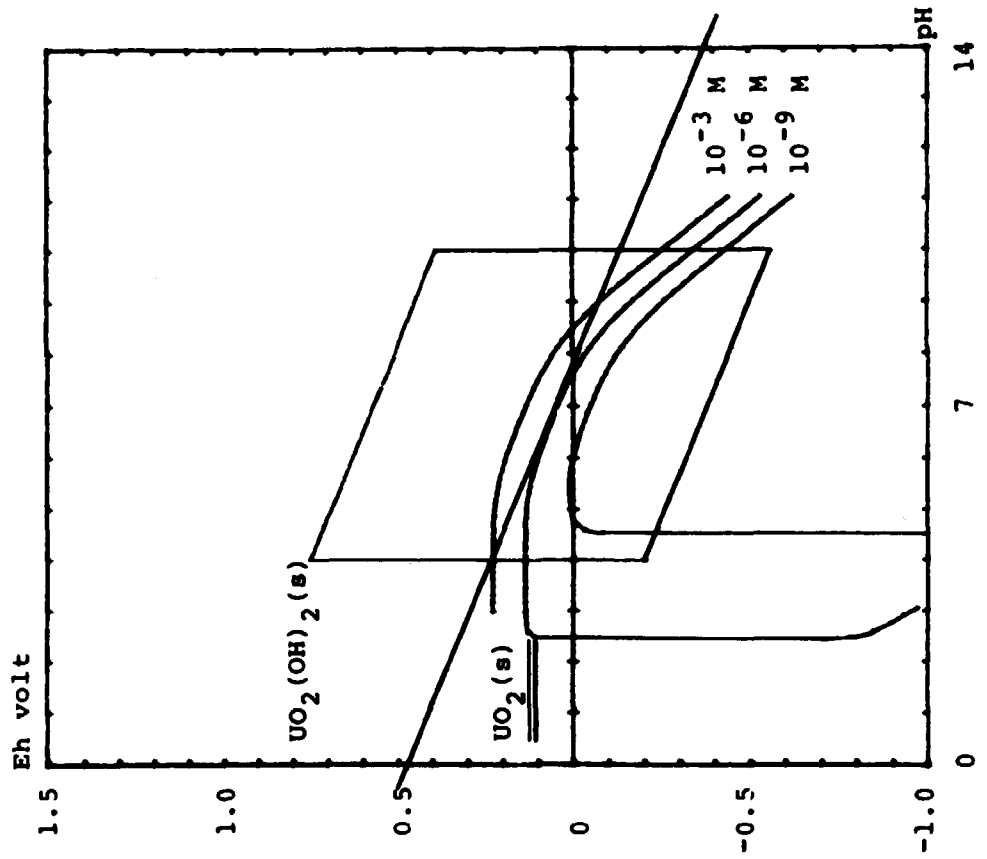


Figure 10A

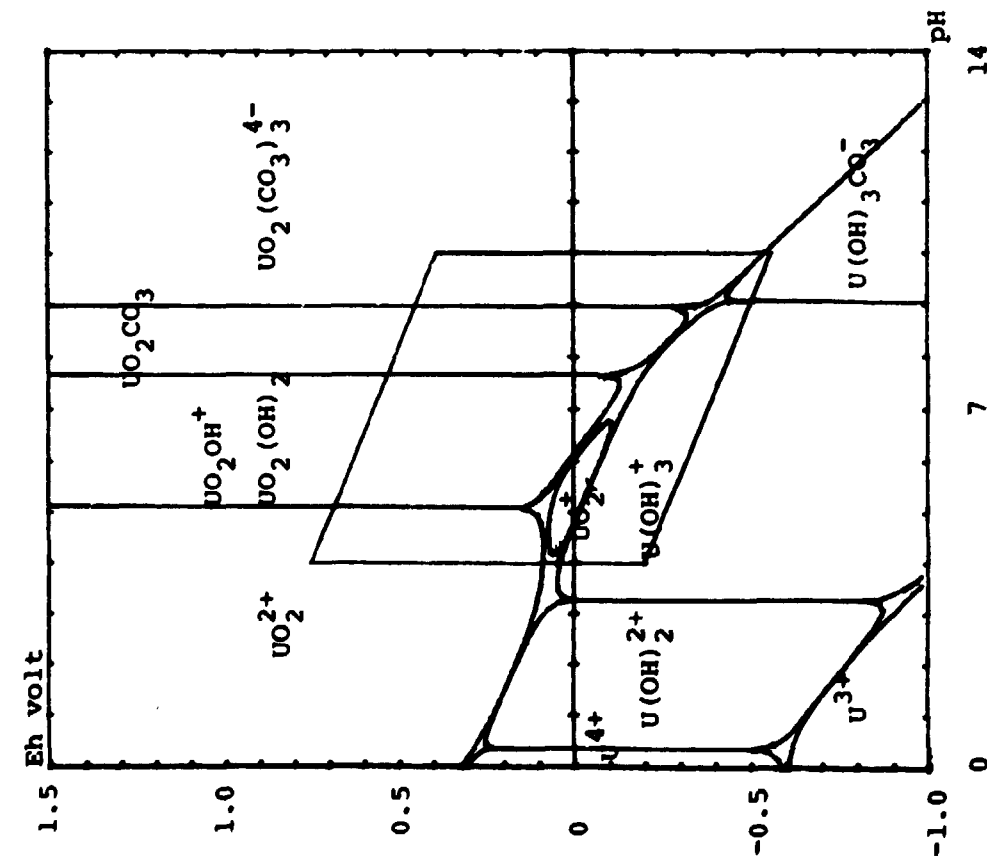


Figure 10B

Neptunium

The diagram indicates that neptunium is extremely insoluble under deep-soil conditions, even in the presence of carbonate. Neptunium doesn't seem to form carbonate complexes under any conditions that normally are encountered in nature.

When exposed to the atmosphere the neptonylion, NpO_2^+ , is the dominant species in solution. This species is only slightly adsorbed onto clays, and a certain mobility of Np under top-soil conditions is expected, as is actually also observed.¹²⁾

The extreme insolubility of Np under the conditions expected around a repository indicates that its concentration in ground water will never exceed the maximum permissible concentration, even at the point of leaching.

Subsequent adsorption reactions will reduce the groundwater concentrations to negligible magnitudes.

$P_{CO_2} = 0 \text{ atm.}$

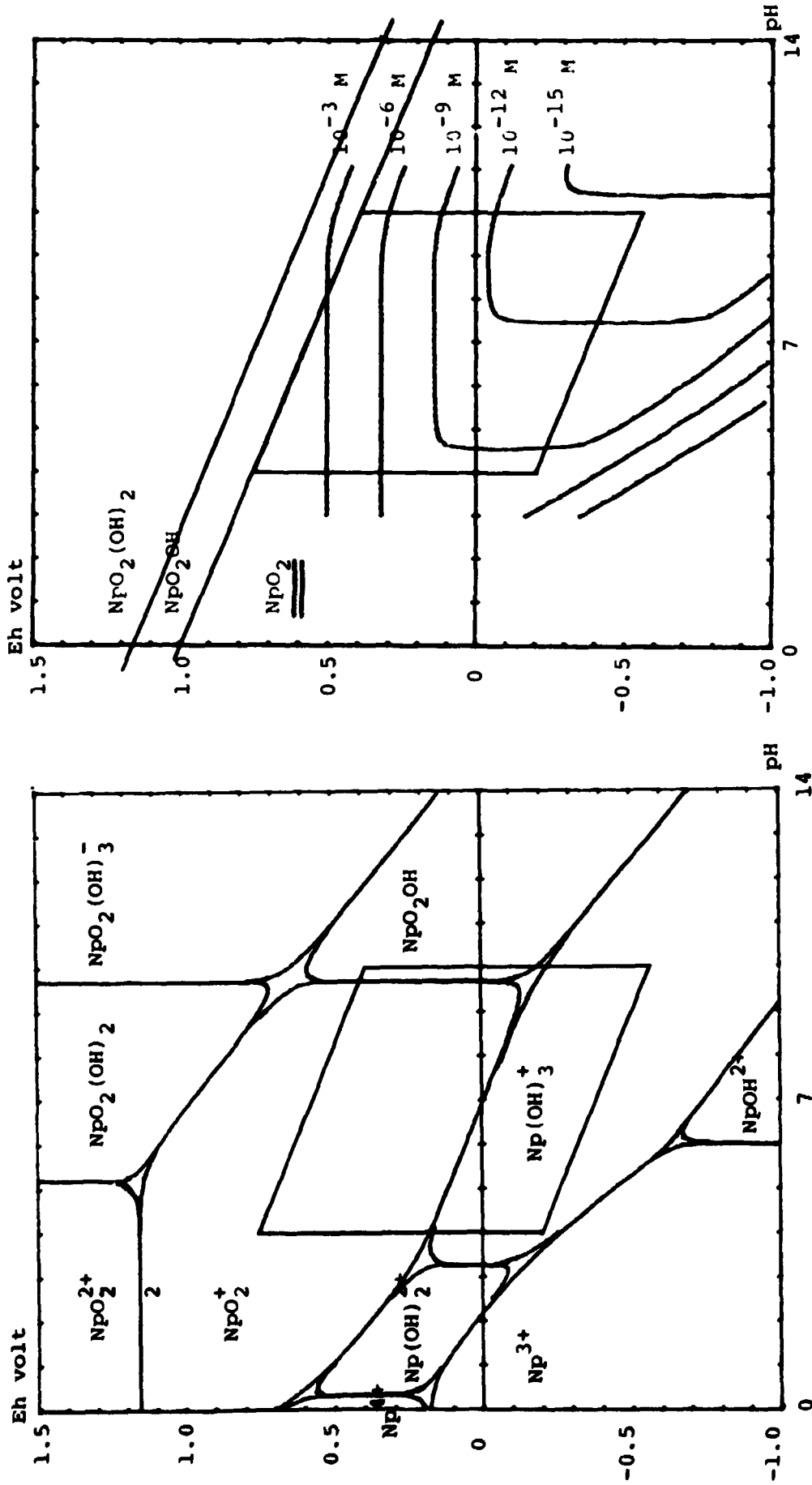


Figure 11B

Figure 11A

$P_{CO_2} = 10^{-3.5} \text{ atm.}$

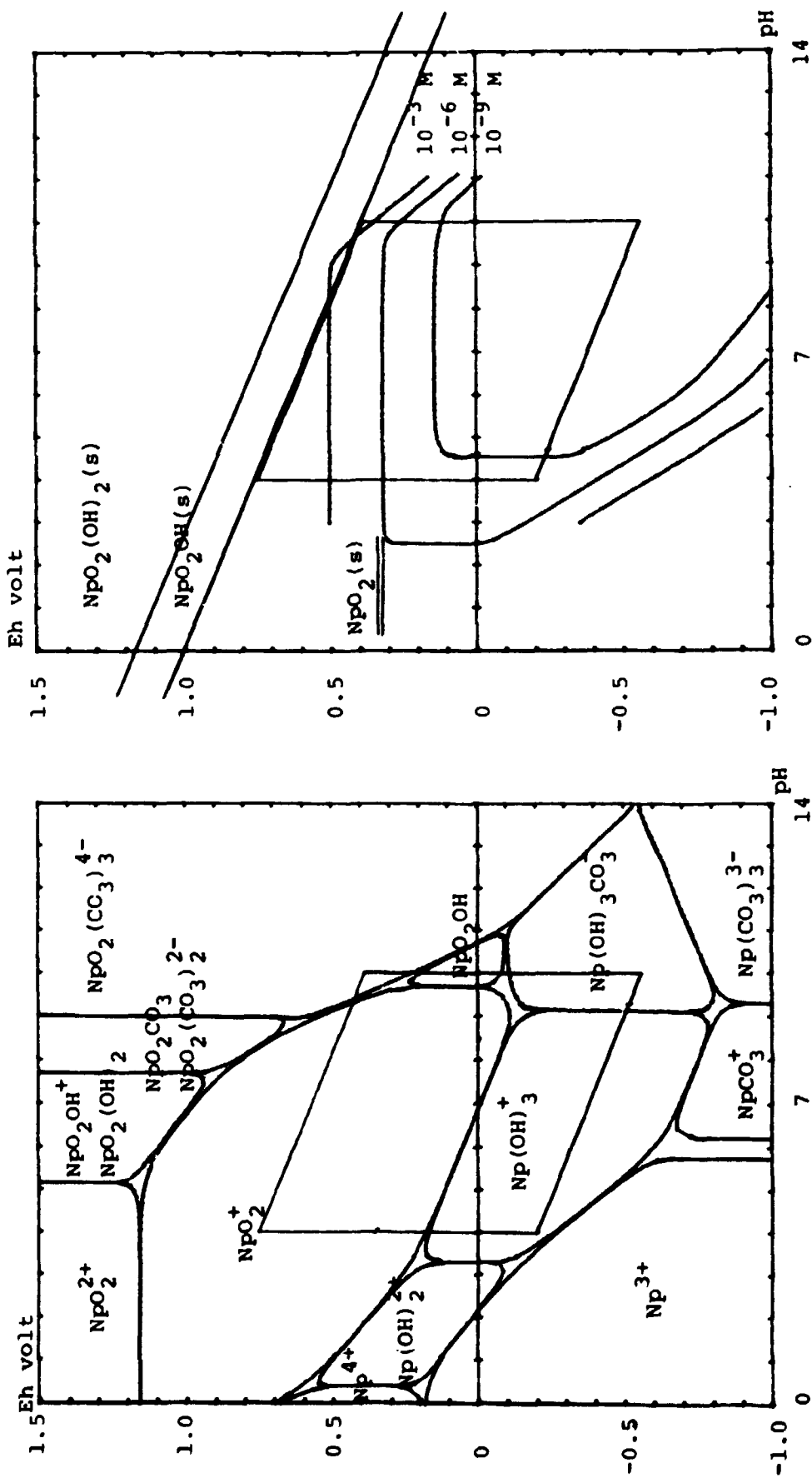


Figure 12B

Figure 12A

Plutonium

The diagram indicates that at the repository, Pu should be extremely insoluble. The presence of carbonate may have some enhancing effect on the migration behaviour of the element due to the formation of carbonate complexes of trivalent plutonium.

Under repository conditions the behaviour of plutonium in solution should resemble that of the trivalent americium, apart from its much lower solubility.

When exposed to the atmosphere, plutonium is expected to be found as the plutonyl species, PuO_2^+ , or as a hydroxy-carbonate complex of the tetravalent ion. The strong adsorption of the tetravalent ions onto clays may displace the equilibrium with carbonate such that the latter is effectively scavenged from solution. The slight adsorption of the PuO_2^+ species may account for the often-observed migration of very minute amounts of plutonium under topsoil conditions.

At the repository, plutonium will be found mainly as the extremely insoluble PuO_2 species and in solution mainly in the trivalent state, wherein it resembles americium. This suggests a closer study of the behaviour of americium under a variety of chemical conditions.

$P_{CO_2} = 0 \text{ atm.}$

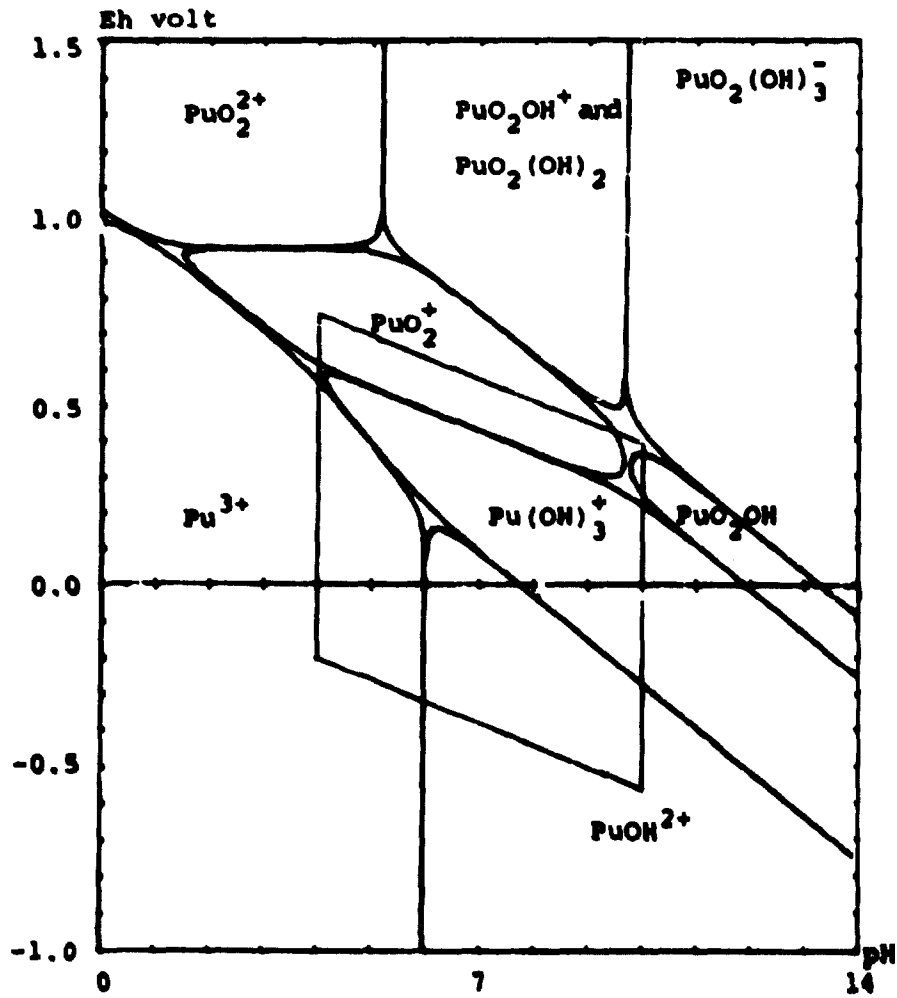


Figure 13A

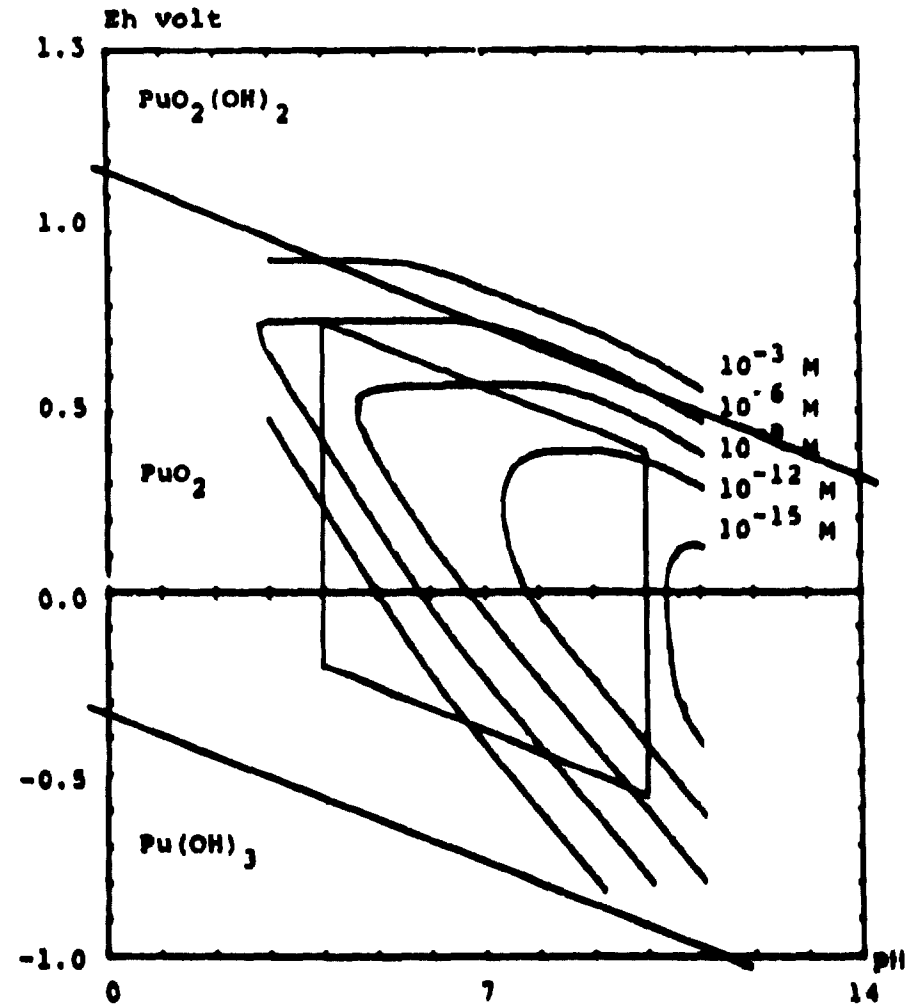


Figure 13B

$P_{CO_2} = 10^{-3.5}$ atm.

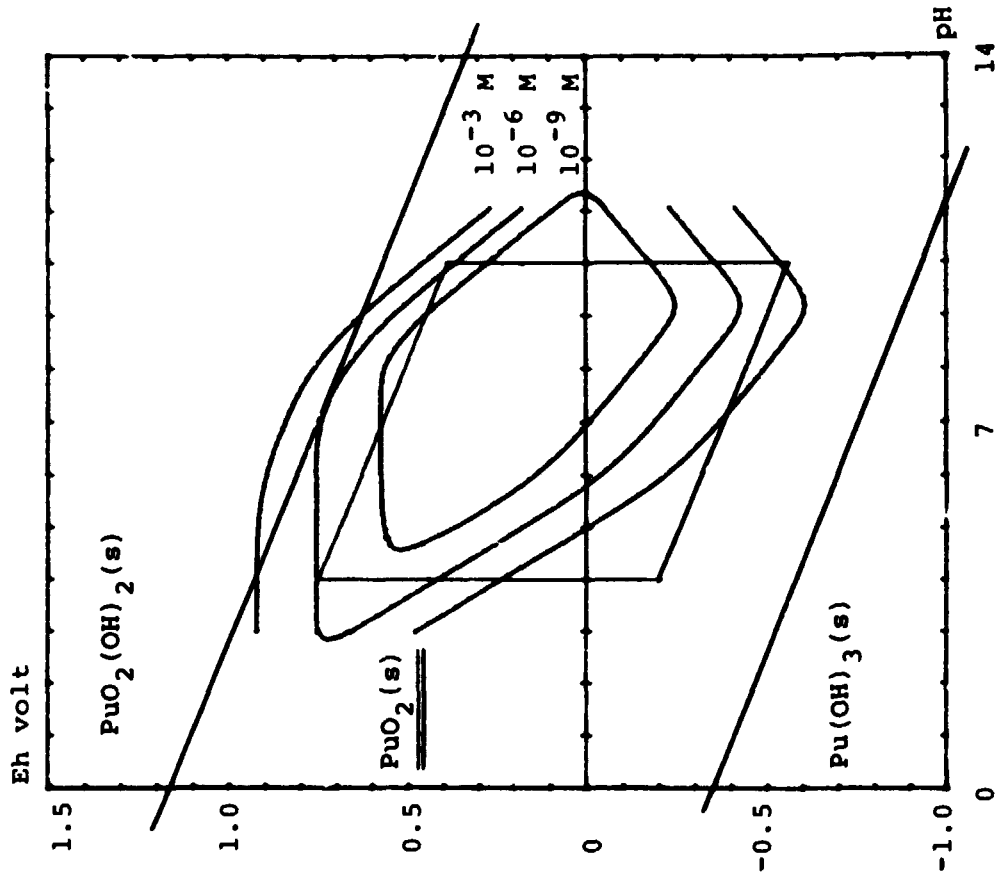


Figure 14B

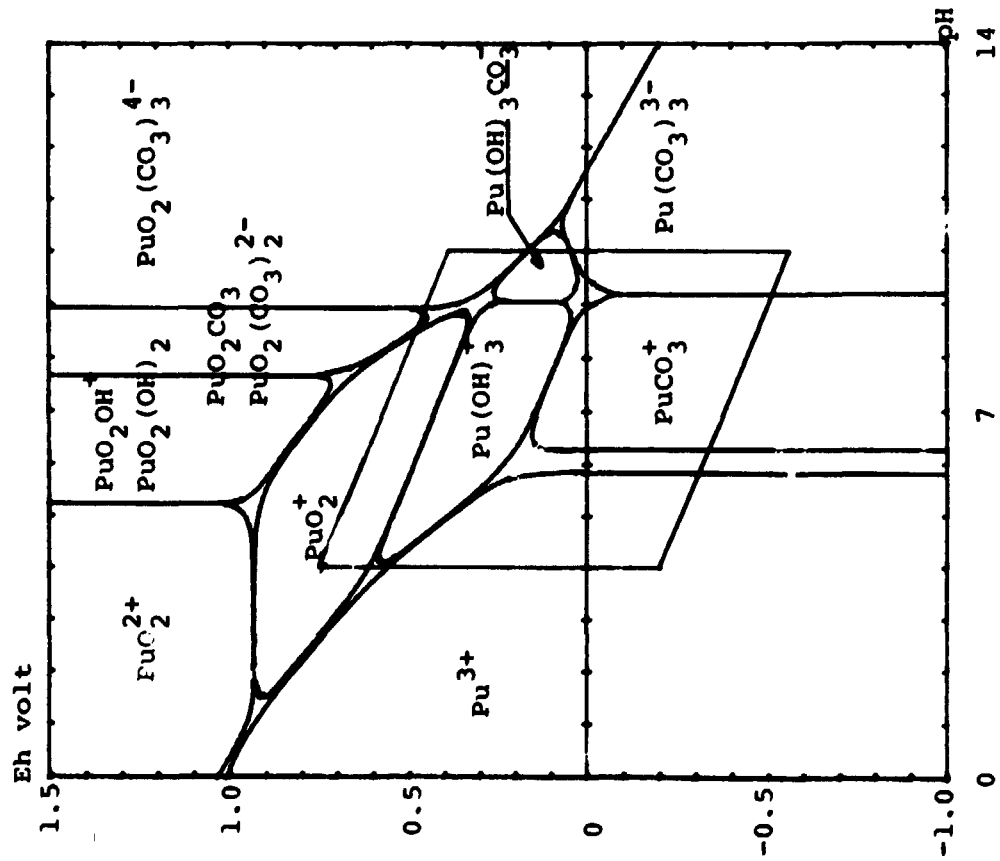


Figure 14A

Americium

The diagram shows that americium, as well as the higher actinides, will be found solely in the trivalent state under conditions encountered in nature.

Solubilities are rather high, and insolubilities of hydroxides have no effect as a retardation mechanism.

If they exist, other insoluble compounds may naturally play that role, but, as for most other elements, retardation of americium migration may be ascribed mainly to sorption processes.

Although laboratory experiments made under atmospheric conditions indicate that the adsorption is hardly influenced at the prevailing partial pressure of CO₂, i.e. 10^{-3.5} atm, more extreme conditions may exist in deep geological formations and there is good reason to make a closer study of the migration behaviour of americium under a variety of chemical conditions.

$P_{CO_2} = 0 \text{ atm.}$

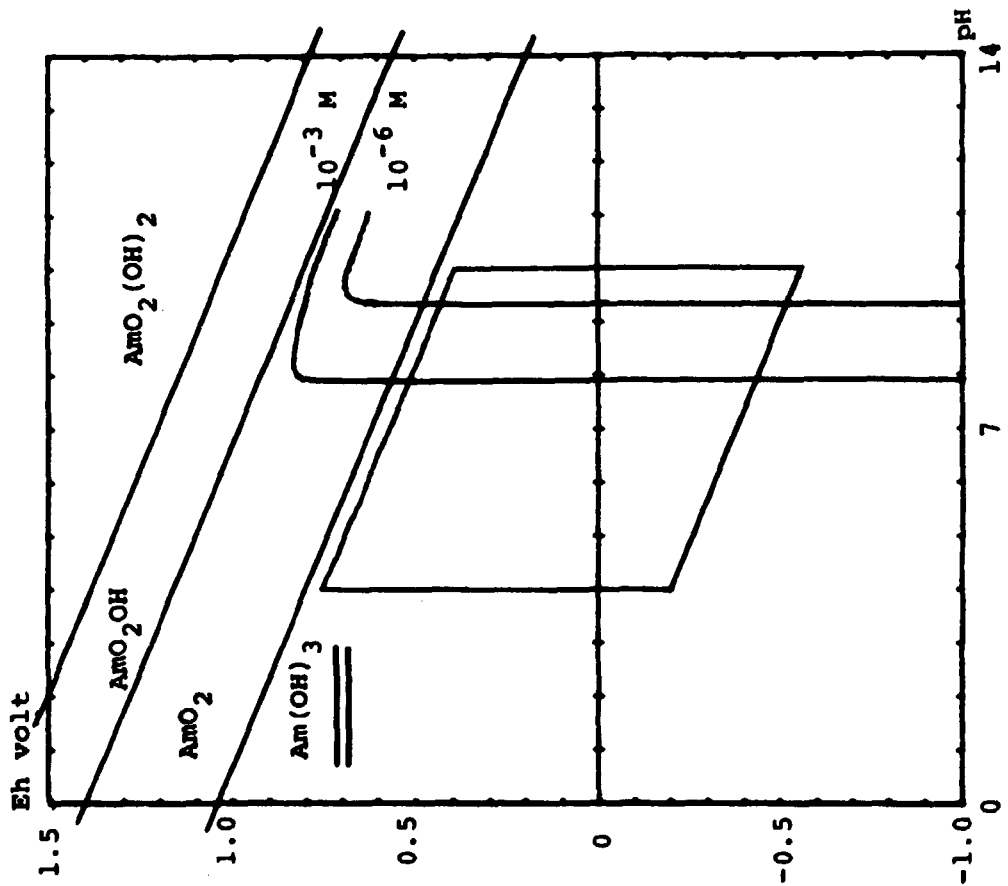


Figure 15B

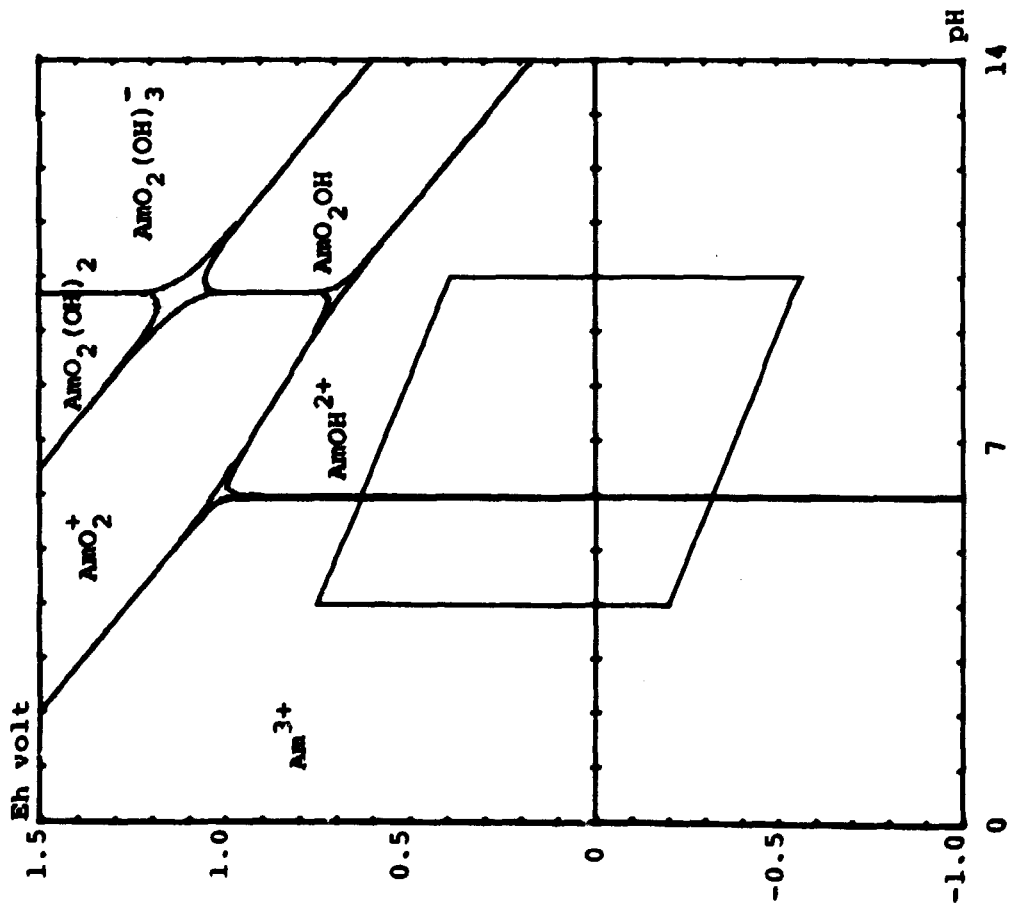


Figure 15A

$$P_{\text{CO}_2} = 10^{-3.5} \text{ atm.}$$

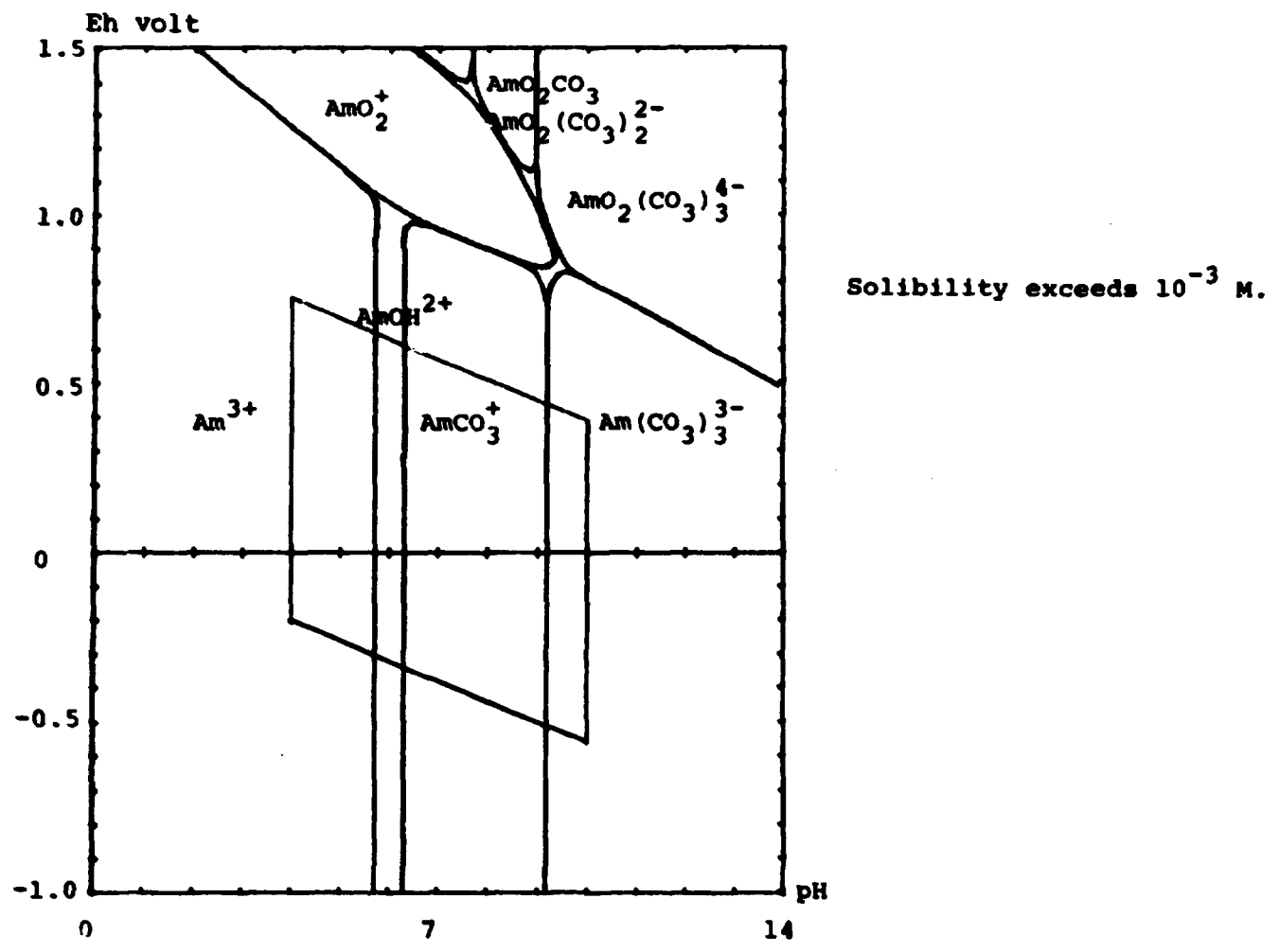


Figure 16

CHEMISTRY OF TECHNETIUM

The technetium isotope, Tc-99, is one of the major fission products of uranium (yield 6.3%). It is a weak beta-emitter of low radio-toxicity. The MPC_w value is 0.007 Ci/L, which corresponds to appr. 0.004 M/L.

Due to its long half-life (210,000 years) special attention should be paid to its geochemical behaviour, which must be presumed to be the final effective barrier against its migration to the biosphere.

Technetium is a metal resembling platinum in appearance. In solution it can attain all oxidation states from 2+ to 7+. In oxidation states 3+, 4+, and 6+, the solutions of Tc are unstable, even in the presence of complexing agents, and possible species in these oxidation states have only a transient existence.

In a recent paper¹³⁾ the chemistry of technetium of relevance for its behaviour in the geosphere has been discussed. The data presented herein together with other recent data on technetium chemistry¹⁴⁾ have been used to construct the stability diagrams of Figs. 17A and B.

The reaction schemes with equilibrium data used in the calculations are shown in Table 6.

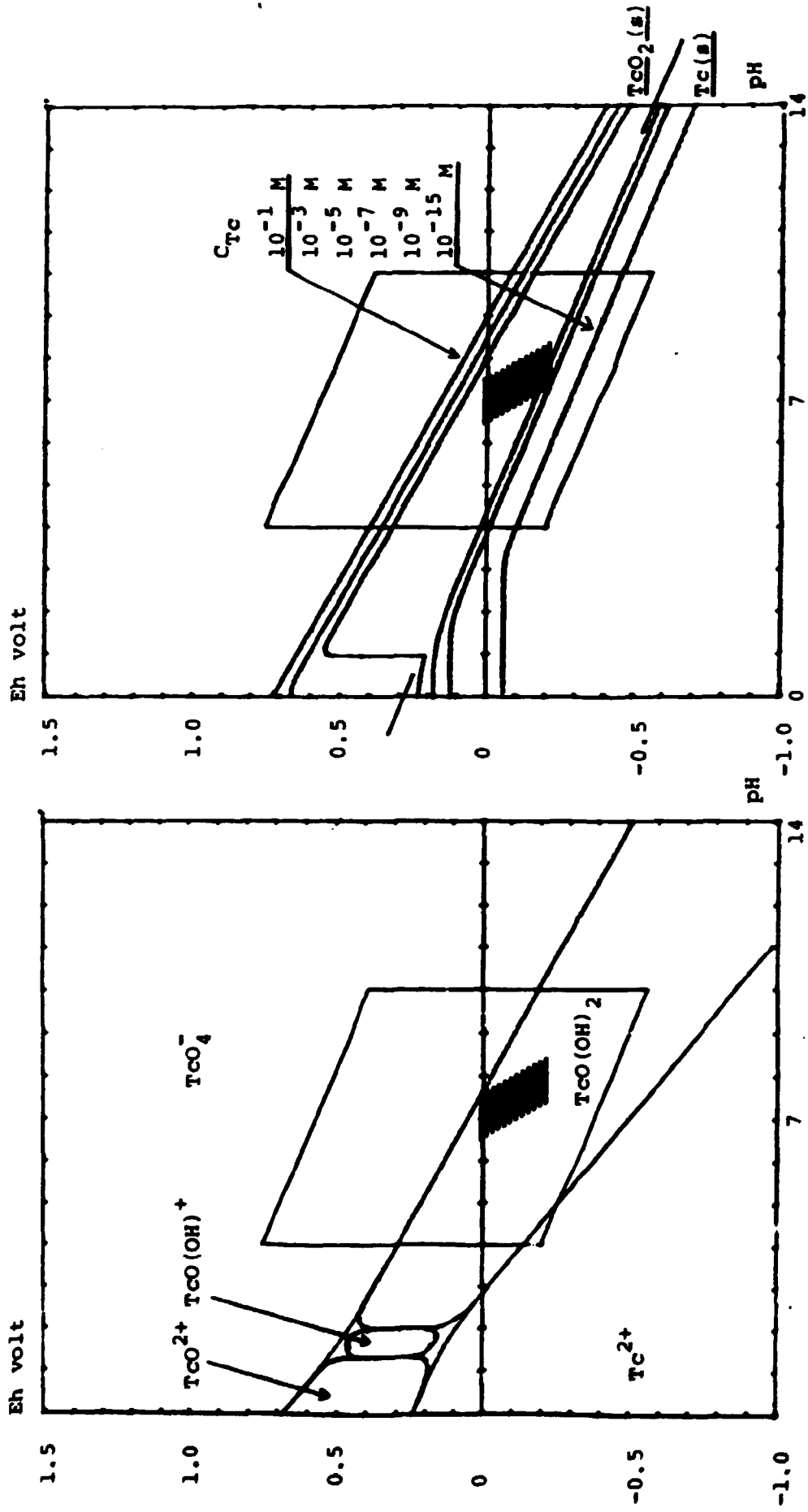


Figure 17B

Figure 17A

Table 6

Reaction schemes

1: $Tc^{2+} + 2e = Tc(s)$	0.400 E volt
2: $TcO_2(s) + 4H^+ + 4e = Tc(s) + 2H_2O$	0.272 - -
3: $TcO_2(s) + 4H^+ + 2e = Tc^{2+} + 2 H_2O$	0.144 - -
4: $TcO_4^- + 4H^+ + 3e = TcO_2(s) + 2 H_2O$	0.738 - -
5: $TcO_4^- + 6H^+ + 3e = TcO^{2+} + 3 H_2O$	0.68 - -
6: $TcO_4^- + 3 H_2O + 3e = TcO(OH)_2 + 4OH$	-0.50 - -
or	
6A: $TcO_4^- + 4H^+ + 3e = TcO(OH)_2 + H_2O$	0.62 - -
7: $TcO^{2+} + H_2O = TcO(OH)^+ + H^+$	-1.37 log K
8: $TcO(OH)^+ + H_2O = TcO(OH)_2 + H^+$	-2.03 - -
9: $2 TcO(OH)_2 = Tc_2O_2(OH)_4$	6.5 - -
From Eqs. 3, 4 and 5 it is possible to derive Eq. 10	
10: $TcO^{2+} + 2H^+ + 2e = Tc^{2+} + H_2O$	0.231 E volt
Other combinations are	•
11: $TcO_4^- + 8 H^+ + 5e = Tc^{2+} + H_2O$	0.500 - -
12: $TcO_4^- + 8 H^+ + 7e = Tc(s) + H_2O$	0.471 - -

Under atmospheric conditions Tc is found solely as the pertechnetate ion, TcO_4^- , which chemically resembles other XO_4^- -ions and, for example, forms slightly soluble potassium salts.

The solubility product of $KTcO_4$ is on the order of 10^{-2} . In saturated solutions of KCl, the solubility of $KTcO_4$ will therefore hardly exceed the MPC_w value.

The TcO_4^- ion should have little affinity for soil colloids and consequently migrates readily with flowing ground water.

This has often been observed^{12,13)}, but the same papers also describe how the migration of technetium is appreciably retarded under reducing conditions.

These observations are readily understood by inspection of the figures. It is observed that under the most probable chemical conditions near or at the repository the species $\text{TcO}(\text{OH})_2$ will be dominant in solution; it will be present only in concentrations from 10^{-7} to 10^{-5} molar, however, well below the MPC_w value.

By combining Eqs. 4 and 6, the free energy of hydration of technetium dioxide can be calculated. Thus



from which the solubility, s , of $\text{TcO}(\text{OH})_2$ can be calculated to

$$s(\text{TcO}(\text{OH})_2) = 1.2 \cdot 10^{-6} \text{ M} = 10^{-5.9} \text{ M.}$$

This value agrees well with the predictions from the stability diagrams.

At this concentration of the monomer, $\text{TcO}(\text{OH})_2$, the concentration of the dimer, $\text{Tc}_2\text{O}_2(\text{OH})_4$, is calculated to

$$s(\text{Tc}_2\text{O}_2(\text{OH})_4) = 4.9 \cdot 10^{-6} \text{ M.}$$

The total concentration of Tc, monomer + dimer, is therefore appr. $6 \cdot 10^{-6}$ M, when $\text{TcO}_2(\text{s})$ is present as precipitate.

Further polymerization either to colloids or precipitates of the hydrous dioxide has been suggested in Refs. 14 and 15, and appears to be probable. These colloids will most probably be adsorbed onto mineral surfaces and be filtered away by the passage of ground water through soils.

The predictions based on the foregoing analysis are supported by the observation¹⁶⁾ at the natural reactor at Oklo, that technetium has migrated only to a very limited extent during its decay period amounting to millions of years.

ADSORPTION PHENOMENA

In their migration path eventually released radionuclides will invariably contact mineral surfaces and there take part in adsorption reactions.

For a long time it has been known by soil scientists and geochemists that some soil colloids exhibit strong ion-exchange properties. The most studied are the clay minerals, but there are indications that many ill-defined intermediary weathering products also take part in ion-exchange reactions.

By ion-exchange there is competition between ions for the available adsorption sites. If only two ions, for example Na^+ and Ca^{2+} , are exchanged, the following relation has been found valid for a pure ion-exchanger

$$\frac{\sqrt{\bar{c}_{\text{Ca}^{2+}} \cdot [\text{Na}^+]}}{\sqrt{[\text{Ca}^{2+}] \cdot \bar{n}_{\text{Na}^+}}} = K \quad (17)$$

where $\bar{c}_{\text{Ca}^{2+}}$ and \bar{n}_{Na^+} are the concentrations in the solid phase, $[\text{Ca}^{2+}]$ and $[\text{Na}^+]$ the activities of ions in the equilibrating solution, and K an equilibrium constant.

If a radionuclide, m , with valency, z , in tracer concentration is introduced into the system, its distribution coefficient, K_D , between the solid and the solution depends on the activities of Na^+ and Ca^{2+} in the aqueous phase, as described by the following equation

$$A[\text{Na}^+](K_D)^{1/z} + B[\text{Ca}^{2+}](K_D)^{2/z} = \bar{c} \quad (18)$$

where \bar{c} is the total ion-exchange capacity of the solid, and A and B constants characteristic of the system.

This last equation has been found to describe actual observations for mono- and divalent ions with a fair degree of accuracy, although complications due to additional chemical reactions such as hydrolysis, etc. often make the investigations more difficult. With soil and sediment systems the sample is invariably composed of a mixture of minerals with different adsorption characteristics, wherefore, a study of its properties seldom can be described in detail by the previous simple equations. The overall tendency expressed by the equations do, however, clearly show up.

For ions of higher charge slow adsorption kinetics indicate the existence of additional reactions like, for example, direct chemical bonding into the surface layer (see p. 27).

The sorption processes are surface reactions, and the soil fines, clays and the like, contribute most to the available surface in a soil sample. The adsorption characteristics of soil samples may therefore in most cases be attributed to its content of soil fines.

The most common clay minerals in Danish soils are Montmorillonite, Illite and Kaolinite, whose sorption characteristics have been studied recently.¹⁷⁾ The following table shows the ranges for the distribution coefficients for several cations when the concentrations of Na^+ and Ca^{2+} in solution are varied between 10^{-3} to 10^{-1} M.

These results indicate that the clay minerals Illite and Montmorillonite are very effective in adsorbing trace elements under rather extreme chemical conditions, Kaolinite being less so.

Most Danish sediments contain several per cent of these clay minerals and should therefore be expected to be very efficient adsorbents for the trace elements mentioned.

As shown in Fig. 13, Pu^{3+} is the most stable species in deep formations, and should therefore behave like the Am^{3+} ion.

log K_D

	Kaolinite	Illite	Montmorillonite
Sr^{2+}	1 to 2.5	0.5 to 3	1 to 4.5
Cs^+	2.5 to 3.5	4 to 4.5	3 to 5
Eu^{3+}	0 to 4.5	4.5 to 5.5	4 to 5.5
$Fe^{2+/3+}$	2 to 4	3 to 5	3 to 5
Ce^{3+}	2.5 to 5	3.5 to 5	3 to 5
Ba^{2+}	1 to 4	3.5 to 4	2.5 to 3.5
Rb^+	1 to 2.5	3 to 3.5	2.6 to 3.4
Cc^{2+}	0.5 to 2.5	3 to 4	2 to 3.5
K^+	0.5 to 1.5	2 to 2.5	2 to 3
Ra^{2+}	1 to 4	3 to 4	2.5 to 4
Am^{3+}	2.5 to 5	4.5 to 5.5	3 to 5

The expected similarity between the lanthanides and trivalent actinides is observed by inspection of the data for Ce, Au and Am.

The only element which seems to behave critically at high salt concentrations is strontium.

The actual mobility of an element with flowing ground water depends also on other factors such as the porosity of the formation, the tortuosity of the groundwater path, etc.

With normally encountered numbers, the effect of the adsorption reaction will be that the ion in question moves approximately $10 K_D$ times slower than the ground water through the formation.

In a soil containing 1% Illite, Americium consequently can be expected to migrate with a velocity appr. 3000-30000 times slower than the pore velocity of ground water, and similar estimates can be made for other elements.

CONCLUSIONS

The calculations on the geochemical behaviour of some selected long-lived radionuclides contained in the high level waste indicate that under the most probable conditions at a repository their migration with ground water is highly retarded.

All the investigated elements, except americium, have a very limited solubility under deep-soil conditions, the maximum concentration hardly exceeding the MPC_w values for the dominant isotopes.

Except for Tc, all elements are found in chemical forms that are strongly adsorbed onto ion-exchanging minerals such as those found in clay. The electro-neutral Tc-species may, however, also be efficiently adsorbed, especially when found in a polymeric state.

Most geological formations found in the Danish underground contain sufficient clay material to be classified as efficient adsorbents for the investigated radionuclides.

High-cation concentrations have less enhancing effect on migration than complexation due to large concentrations of anions such as carbonates have. High carbonate concentrations may therefore be a critical parameter enhancing both solubility and migration.

The same effect may be expected from soluble organic acids, if present in large amounts. The presence of minor amounts of these organic acids in sedimentary formations cannot be excluded, and they may reach concentrations in the presence of coal, lignite, peat and the like, which are not negligible. In such cases the amount and nature of soluble organic matter need to be determined to secure that no adverse effect on migration can be expected.

By the very nature of migration phenomena the mechanisms presented cannot secure that very minute amounts of material do not travel some distance away from a repository; however, by far the major amount of material will be bound in the immediate vicinity of its release.

At normally encountered ground water velocities bulk migration will be so slow that radioactive decay together with mixing processes will secure that the radionuclides will never be found in the biosphere in concentrations approaching their maximum permissible values.

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