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RADIONUCLIDE MIGRATION IN GROUNDWATERS: REVIEW OF THE BEHAVIOUR OF ACTINIDES

(Technical Report)

Prepared for publication by

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Radionuclide migration in groundwaters : Review of the behaviour of actinides (Technical Report)

Abstract

The most likely process that can lead to the release of radionuclides from a radioactive waste repository in a geological formation is transport by groundwaters.

Because of this, the migration of radionuclides in groundwaters is extensively studied ; consequently works and studies to be performed in the evaluation of this phenomenon must deal with aqueous chemistry, geochemistry, hydrology, physics and modeling.

The current state of the art concerning actinide migration is given in this report in order to highlight the various aspects of the subject and to point out the research required to bridge the gaps in our current knowledge.

INTRODUCTION

The safety of a radioactive waste or spent nuclear fuel repository is related to its capacity to confine radioactivity and isolate it from the biosphere. The most likely process that can lead to the release of radionuclides from a repository to the geosphere is transport by groundwater. Consequently, waste disposal-related safety analyses must assess the importance of the migration of radionuclides (i.e., their mobility) in the conservative assumption of leaching by groundwater (i.e., after the destruction of the engineered barriers).

The evaluation of the mobility of radionuclides in groundwaters requires :

- Knowledge of their mobile species, i.e., knowledge of radionuclide aqueous chemistry and knowledge of the environmental waters, which condition the nature and concentration of their soluble species. This study can be carried out with a thermodynamic approach, which considers the system at steady state (reasonable approximation, taking into account the very low water velocity expected in the vicinity of a geological repository). The chemical species are calculated (with the assistance of computer based methods) by solving the equilibrium reactions which can occur between the water constituents and the nuclides. This procedure assumes that reliable thermodynamic data are available for every major reaction, including data for conditions that differ greatly from standard conditions (such as temperature up to 200°C in the near field of vitrified waste disposal and ionic strengths different from zero). Unfortunately, these data are not always available...

- Knowledge of transport processes and their kinetic, convection and diffusion characteristics within the water, of sorption and of desorption from rocks and minerals in contact with the aqueous phase. The effect of these processes on radionuclide mobility and changes in sorption behaviour, as a function of time due to rock aging phenomena, are also required. Research in this field has led to both

experimental determination of sorption coefficients and retardation factors and to modeling work.

- Finally, the influence of the specific conditions of a high level waste or spent fuel disposal (establishment of an oxidizing environment near the waste canister due to radiation, very high temperatures etc...) must also be taken into account when estimating radionuclide mobility from a repository, and hence, the safety of the latter.

Consequently, studies to be performed in the evaluation of the long term ability of specific disposal conditions to confine radioactivity must then deal with aqueous chemistry, geochemistry, hydrology, physics and modeling.

In view of the importance of the subject as regards the long-term effectiveness of underground repositories and the complexity of the problems to be solved, it is not surprising to find a very wide range of literature concerning the major aspects of this topic. These are :

- the determination of thermodynamic data relative to solubility, hydrolysis and complexation,
- the determination of sorption data on various materials,
- the influence of colloids and humic substances on the transport of radionuclides,
- the application of new analytical spectroscopic techniques for detection and determination of speciation in aquatic systems (particularly for actinides).

An assessment of the current state-of-the art concerning migration of plutonium, americium and mainly of neptunium will be given here in order to highlight the various aspects of the question and to underline the research required to bridge the gaps in our current knowledge.

MIGRATION OF ACTINIDES IN GROUNDWATERS

Long-lived actinides, such as ^{237}Np , ^{239}Pu , ^{240}Pu , ^{241}Am , as well as the daughter products will dominate (with the fission products ^{99}Tc and ^{129}I) the long term biological risk from disposal of spent nuclear fuel or high level wastes.

Transport by groundwaters represents the most likely pathway of activity into the geosphere ; because of this, the migration behaviour of long-lived actinides is extensively studied. In particular, the evaluation of the transport properties of ^{237}Np is of great interest, due to the high ingestion radiotoxicity of that isotope.

Many laboratories and organisations are currently studying the migration of actinides in groundwater, either in the framework of national programs of research, in relation with national projects of geological waste disposal, or in the framework of international research programmes, such as the MIRAGE programme of the Commission of the European Communities.[1]. As examples, we can mention the following organisations or universities :

Canada : Whiteshell Nuclear Research Establishment (Atomic Energy of Canada Limited)

France : Commissariat à l'Energie Atomique

Germany : Institut für Radiochemie der Technischen Universität, München ; Technische Hochschule, Darmstadt

Sweden : Chalmers University (Goteborg) ; The Royal Institute of Technology (Stockholm)

Switzerland : NAGRA (Baden) ; Paul Sherrer Institut

U.K. : United Kingdom Atomic Energy Authority, Harwell Laboratory

U.S.A. : Argonne National Laboratory ; Lawrence Berkeley Laboratory ; Lawrence Livermore Laboratory

Aqueous chemistry including solubility, sorption behaviour and transport mechanisms are the three main fields of research.

1. AQUEOUS CHEMISTRY: THERMODYNAMIC BEHAVIOUR OF ACTINIDES

1.1. Oxidation state

The actinides of the serie U--> Am exhibit multiple oxidation states (from III to VII).

Neptunium

The most important feature of the chemistry of Np in aqueous solutions is the wide range of stability of Np^V. In this respect, Np differs markedly from its neighbouring elements U and Pu that exhibit only small ranges of stability in the oxidation state V. Np^{VI} is only formed at very high redox potentials that may be created by highly oxidizing reagents or by radiolysis products [2]. Np^{III} is easily oxidized.

Plutonium

Plutonium can exist in four oxidation states, III, IV, V and VI, in aqueous solutions with the pH and Eh ranges found in nature. States III and IV may be present as simple hydrated cations, while states V and VI form dioxo cations, PuO₂⁺ and PuO₂²⁺ respectively. As expected, the lower oxidation states are stabilized by acidic conditions and as basicity increases so does the stability of the higher states. This generalization can be negated by factors such as complexation which can modify the relative stability of the different oxidation states.

Disproportionation reactions are also a common feature of the IV and V states but are unlikely to be of concern at environmental concentrations. It is important to note that plutonium may coexist in several oxidation states in the same solution.

Whatever the oxidation state, plutonium cations interact with anionic species by ionic bonding, the normal trend in complexation strength being :



Americium

Am^{III} is the most stable oxidation state in solution, although the easily reducible Am^{VI} and Am^V can also exist in aqueous systems, as well as Am^{IV} in the presence of high concentrations of complexing agents. Americium would be expected to be in the III oxidation state in aerated waters in the absence of oxidants other than oxygen from the air [5].

1.2. Solubility and aqueous dissolved species

Actinide concentration in groundwaters outside the waste package can be limited by two mechanisms : the low dissolution rate of the solid waste form or the solubilities of individual nuclides. Solubility establishes an upper limit for the source term for radionuclide transport from a repository [6]. The estimates of the solubilities and the speciation of the actinides (nature and concentration of the dissolved species) are predicted from thermodynamic data, taking into account the presence of inorganic ligands in the groundwaters studied, mainly OH⁻, HCO₃⁻, CO₃²⁻, (Cl⁻ in case of disposal in rock-salt formation) and the properties of these waters (redox potential).

1.2.1. Available thermodynamic data

There are several compilations of thermodynamic data for the formation of solid and soluble actinide compounds [7-25]. Among these, we can mention the reviews carried out by J. PAQUETTE, R. LEMIRE and his co-workers (Canada [7-9]) ; B. ALLARD and his collaborators (Sweden [10-13]) ; M.R. SCHWEINGRUBER (Switzerland [14-15]) ; J.F. KERRISK (USA [16]) ; C. RIGLET, P. VITORGE et P. ROBOUCH (France [17-21]) ; C.A. PHILLIPS (USA [22]).

The compilation of R. LEMIRE and J. PAQUETTE concerning plutonium [7-8] and neptunium [9] is virtually complete. They critically reviewed standard Gibbs energies of formation ($\Delta_f G^\circ$), entropy data (S°) and heat capacities (C_p°) for neptunium and plutonium oxides, hydroxides, phosphates, fluorides, sulphates, carbonates (solids and complexes) ; selected values were used in a modified Criss-Cobble

extrapolation scheme [26] to estimate thermodynamic values for plutonium and neptunium equilibria at temperatures as high as 150°C (for Np) and 200°C (for Pu).

For more efficiency, the necessary thermodynamic data for predicting the aqueous behaviour of the elements important to radioactive waste disposal are now compiled more and more frequently in computerized data bases. This procedure allows a better comparison of the values obtained in the literature, and thus brings to the fore the possible discrepancies between data. (In this case, procedures of refinement of the formation constants are usually applied).

Let us mention, for instance, the HATCHES data base compiled at Harwell Laboratory in the framework of the "Nirex Safety Assessment Research Programme" and associated with the geological model "PHREEQE" [28], the data base developed at Lawrence Livermore National Laboratory for use with the EQ3/6 modeling package [27], or the data base elaborated in the framework of the CHEMVAL project [29], ...

The elaboration of such databases requires considerable contributions in order to compile the numerical values, to discuss them and verify their compatibility either among themselves or with the values recommended by different international organisations (i. e., CODATA or NEA - see section 5.1.). This is why the different teams often work in close collaboration.

1.2.2. Use of thermodynamic data

The above-mentioned thermodynamic data allow the calculation of the Gibbs energies of reaction $\Delta_r G^\circ(T)$ and equilibrium constants $K(T)$, using the following expressions :

$$\Delta_r G^\circ(T) = \Delta_r G^\circ(298.15) + (\Delta_r C_p^\circ - \Delta_r S^\circ) (T/298.15) - T\Delta_r C_p^\circ \ln (T/298.15)$$

$$\log_{10} K(T) = -\Delta_r G^\circ(T)/(2.3026 RT).$$

(the equilibrium constants for Pu and Np at different temperatures (25°C, 60°C 100°C, 150°C, (200°C for Pu)) are reported in [8-9] respectively).

It is also possible to calculate the equilibrium constants by means of an electrochemical approach, as done by C. RIGLET in [19].

Knowledge of $K(T)$ for all chemical reactions which can occur within the considered system (here actinide/inorganic constituents of water) enables prediction of the chemical behaviour of the system at equilibrium.

Potential Eh/pH diagrams are a convenient, compact, pictorial method of representing the behaviour of aqueous systems for a wide range of different pH and Eh conditions, and are often used. However, these representations present two drawbacks :

- They define areas in which one compound (or one species) is predominant and thus the other species coexisting in these fields, in lower concentrations, do not appear on the diagram. Only plotting of species distribution curves versus pH can show the existence of these species for a given Eh-pH dependence. For instance, the curves in figure 6 thus complement figure 5 for groundwater under reducing and oxidizing conditions (see figures below).
- The kinetics of chemical reactions are not taken into account ; Eh-pH diagrams only indicate the thermodynamically feasible reactions. Therefore some reactions may not occur, though they are indicated in the Eh-pH diagrams.

1.2.3. Use of Eh-pH diagram, example: prediction of neptunium behaviour in aquatic systems

The interpretation work carried out by R. LEMIRE [9] will be quoted in this chapter as an example, with reference to the Eh-pH diagrams, species distribution curves, and solubility contour diagrams for neptunium, with the aim of showing all of the information that can be gathered from such diagrams. Similar work has been done in the literature for plutonium [7] and americium [17-18] but will not be described here.

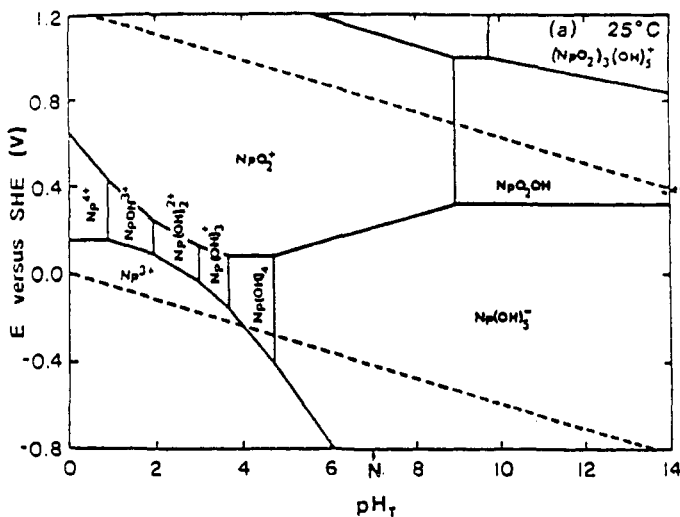
R. LEMIRE [9] gives the Eh-pH diagrams for pure water and two model "groundwaters" of differing ionic composition : the first one is similar to deep groundwater found in contact with granitic rocks and used for leach testing, and the second one is representative of granitic water containing higher concentrations of ions, in particular chloride, fluoride and phosphate. Compositions of both artificial groundwaters are given in the following table. It is to be noted that the author only considered in his selection of groundwater composition ions that could form species for which data were available and no attempt was made to maintain electroneutrality in this "open system". In particular, concentrations of additional ions such as Ca^{2+} , which would undoubtedly occur in real groundwaters, are not given.

Table 1 : Ionic Composition of two Artificial Groundwaters [9]

Ions	Ionic Activity (molal Scale)	
	Groundwater N° 1	Groundwater N° 2
Chloride	1.4×10^{-4}	0.10
Carbonate (total)	1.0×10^{-3}	1.0×10^{-2}
Fluoride (total)	1.0×10^{-5}	5.0×10^{-5}
Phosphate (total)	-----	2.0×10^{-6}
Sodium	3.6×10^{-4}	0.10
Sulphate (total)	9.0×10^{-5}	1.0×10^{-2}

Fig. 1 to 7, extracted from [9], present different curves and diagrams obtained by calculation, and allow, for instance, examination of the effects of changing parameters relative to the aqueous media, such as its nature (chemical composition), characteristics (temperature), properties (redox properties, pH) ... We can thus draw the following observations from these figures :

. In pure water (artificial case), within the stability field of water, and for the entire temperature range from 25 to 150°C, the predominant solid is NpO_2 . The solution chemistry is dominated by Np^{V} (NpO_2^+ and NpO_2OH) for oxidizing conditions (e.g. near the upper stability line for water) and by Np^{IV} hydrolysis species for reducing conditions, especially at high pH (see fig. 1). There is little difference in behaviour over the temperature range 25-150°C .



as the oxidation potential of the solution increases, but exceeds 10^{-6} mol.L⁻¹ only for acidic oxidizing conditions (see fig.2) (for $pO_2 = 101$ kPa = limit of thermodynamical stability of water).

. In groundwaters : solubility contour diagrams and potential - pH diagrams for neptunium in groundwaters 1 and 2 are represented in figures 3 and 4 respectively.

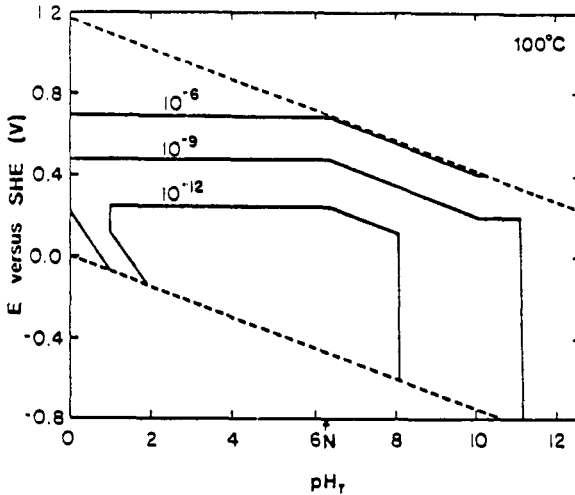


Fig 3 : Solubility Contours for Neptunium in Groundwater N°1 at 100°C as a function of potential and pH [9]

"As can be seen in fig. 4, neptunium solubility does not increase substantially in groundwater n°1 ; the only complex solution species that cuts significantly into the stability field of NpO_2 is $NpO_2CO_3^-$ (field of predominance increases with the temperature).

In groundwater No. 2 it is again apparent (see fig. 5) that carbonate complexation is a major process in the increase of the neptunium solubility. For oxidizing solutions, Np^V carbonate species increase their range of stability at the expense of Np^{VI} species as the temperature is increased. $Np(SO_4)_2$ ($NpCl_2^{2+}$ at 150°C) supplants NpF^{3+} as the major aqueous neptunium species for low pH and reducing conditions. Nevertheless, the overall behaviour of neptunium in groundwater No. 2 does not differ greatly from the behaviour predicted for pure water.

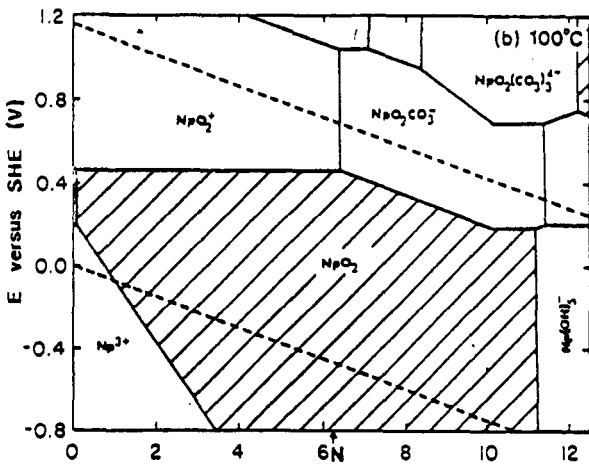


Fig 4

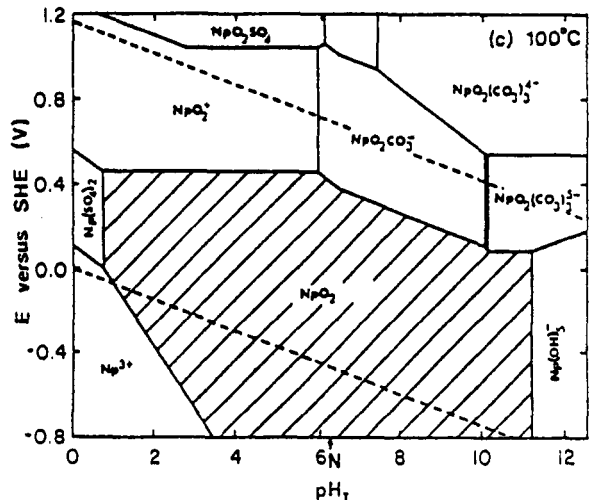


Fig 5

Potential-pH Diagrams for Neptunium at 100°C for Groundwater N°1 (Fig 4) and Groundwater N°2 (Fig 5) ; Boundaries = 10^{-9} mol.L⁻¹ [9]

Figure 6 shows the distribution of neptunium species at 100°C as a function of pH for both oxidizing and moderately reducing conditions. This further emphasizes that hydrolysis species and carbonate complexes are of primary importance. The predominance of Np^{IV} and Np^V as the major oxidation states of neptunium is also apparent.

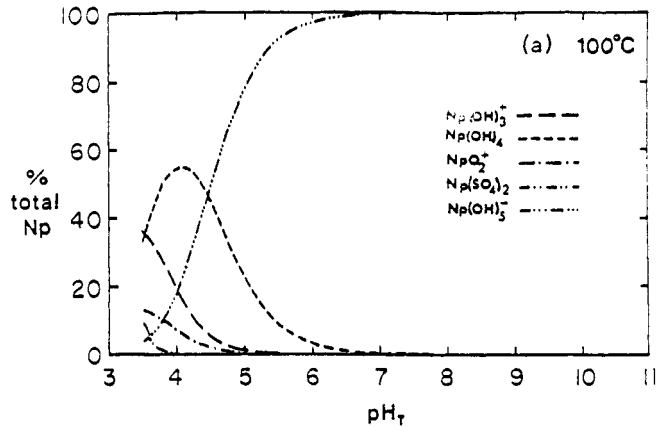


Fig 6 : Neptunium Species Distributions for Groundwater N°2 at 100°C →
 (a) $E = (0.200 - 0.074pH)V$;
 (b) $E = (0.840 - 0.074pH)V$ [9].

Figure 7 shows the temperature dependence of neptunium solubility under the oxidizing and reducing conditions used in figure 6. The solubility only increases with increasing temperature for oxidizing solutions that are neutral or basic. Under other conditions, the solubility of neptunium is essentially temperature independent in groundwater No. 2" (extract [from [9]).

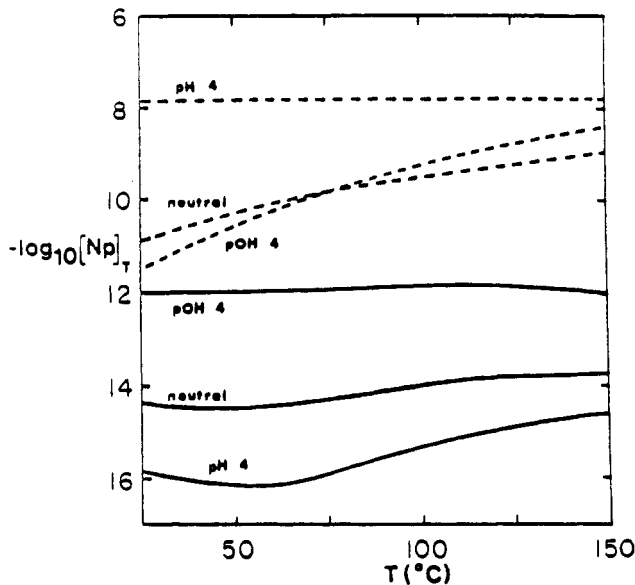
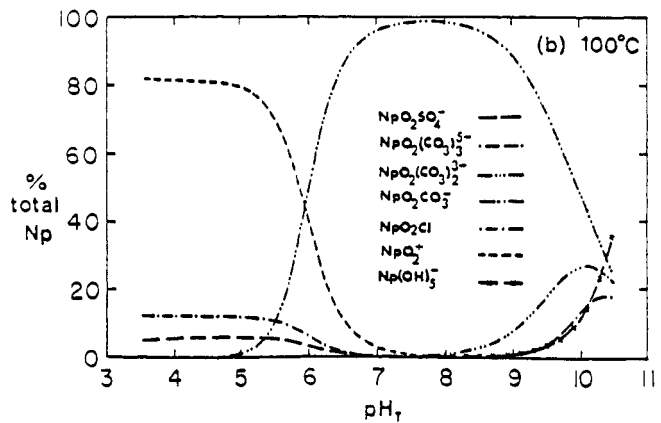


Fig 7 : Total Neptunium Solubility in Groundwater N°2 as a function of temperature,
 — Reducing conditions, - - - - - Oxidizing Conditions [9]

1.2.4. Observations relative to the thermodynamic data of actinides and their ability to predict the actinide chemistry in groundwaters

As mentioned above, thermodynamic data can be used to establish the solubilities and speciation of aqueous dissolved species for a given system (here actinide/groundwater) at equilibrium.

Nevertheless, this procedure presents some limitations as mentioned by R. LEMIRE himself in [9] :

- a lack of thermodynamic data, especially in neutral or basic solutions ; (lack of information on the hydrolysis behaviour of Np^{IV} in these media with, besides, additional complications due to the presence of carbonates (by formation of strong complexes of Np^{IV} , Np^{V} , Np^{VI} ...).
- some uncertainties in the correction of the basic thermodynamic values in connection with the temperature or with the ionic strength of the aqueous phase ; uncertainties also, in the available thermodynamic data relative to the neptunium solubility in basic solution (see fig. 8).

Similar observations are related by C. RIGLET [19] who also points out :

- the existence (occasionally) of notable discrepancies among the published potentials of actinide couple redox systems,
- the few experimental data related to the influence of ionic strength on redox potential, and so the extrapolations made by some authors which do not seem to be supported by ratified arguments,
- some misreading concerning actinide complexation (stoichiometry, formation constants, activity factors) with inorganic ligands in carbonate media.

In view of the lack of data and the existence of discrepancies in existing data, further solubility studies must be undertaken. To ensure high quality and reliability of the derived data however, these studies must respect the following criteria, well defined by H. NITSCHKE in [6].

- (1) Equilibrium conditions.
- (2) Accurate solution concentrations, for which phase separations should be as complete as possible.
- (3) A well-defined solid phase (which ideally consists of crystalline material)
- (4) Knowledge of the speciation/oxidation state of the soluble species at equilibrium

Following these four principles as closely as possible however is not, as H. NITSCHKE says, "an easy task because the experimental conditions required in a particular study may complicate matters".

Specifically, experiments designed to describe conditions in the vicinity of the repository may not only have a radionuclide and groundwater present, but additional components such as high-level waste glass, spent fuel assemblies, cement, bitumen, backfill, and other geologic materials [6].

In particular, the presence of organic substances and/or colloids in the groundwater which were not taken into account in the previously cited compilations of data makes the system still more complex : It is proved that "actinides, in all their oxidation-states (III to VI) can form complexes with humic and fulvic acids comparable in strength to the hydroxide and carbonate complexes" [30], or interact with molecular components or colloidal particles [31].

These processes are of great importance because they can lead to extremely high apparent solubilities which have no relation to the thermodynamically defined solubilities.

1.2.5. Influence of humic substances

Humic substances formed by the degradation of plants and animals constitute a heterogeneous group of compounds with a complex forming capacity due to the presence of carboxylic, hydroxy and phenolic groups in simultaneous presence [32]. Dissolved humic substances (humic and fulvic acids) exist in surface waters and groundwaters in concentrations ranging from less than 1 mg(TOC)/L to more than 100 mg(TOC)/L. (TOC = Total Organic Carbon). They are strong complexing agents for many trace metals in the environment and are also capable of forming stable soluble complexes or chelates with radionuclides [33]. It has been shown that the binding of metals to humic acid apparently occurs at binding sites with relatively well defined complex formation constants [32].

Complexation of actinides (mainly Am^{3+}) has been studied in many laboratories, in particular in over ten laboratories working in close collaboration in the framework of the C.E.C. project MIRAGE II

launched in 1986 [1]. As an example, we can mention some of the results obtained at the CEA (France) by V. MOULIN and her co-workers :

V. MOULIN and her co-workers studied the complexation of americium by humic and fulvic acids (HA and FA, respectively) from various sources [34], and interpreted the results obtained in the system 0.1 M NaClO₄, pH 4.65, [Am^{III}]_t = 10⁻⁵M as the formation of a 1:1 complex (AmA) for which the calculated formation constant logβ₁₁ is the following [34]:

Ligand	Equivalent capacity (meq/g)	Logβ ₁₁ (β ₁₁ inL/eq)	Logβ ₁₁ (β ₁₁ inL/eq)
Fulvic acid			
- from groundwater	0.88	6.2 ± 0.2	3.1
- from surface water	1.22	6.0 ± 0.2	3.1
Humic acid			
- from surface water	1.20	7 ± 0.2	4.1
- from Lake Bradford sediment (HALB*)	1.03	7 ± 0.2	4.0

* HALB : Humic Acid from Lake Bradford

They also calculated the speciation for the system Am^{III}-OH-CO₃-HA, particularly for simulated granitic groundwaters where pH, pCO₂, and [HA] vary in the range : 10^{-3.5} < pCO₂ < 0.1 atm ; 6 < pH < 9 ; 0.1 < [HA] < 10mg/L.

It must be noted that all the speciation calculations are based on data for purified humic materials (HALB) and thus none of the competing cations usually found in natural waters (Ca²⁺, Mg²⁺, metal traces ...) were considered. Moreover, the sorption behaviour of americium and colloid formation were not taken into account in the complexation model used in this work (TORRES and CHOPPIN's model [35]).

The predominance diagrams for the Am^{III}-OH-CO₃-HALB system were drawn at a very low [HA] concentration (0.1 mg/L) for different pCO₂ values. These diagrams (see fig. 8) lead to the following conclusions :

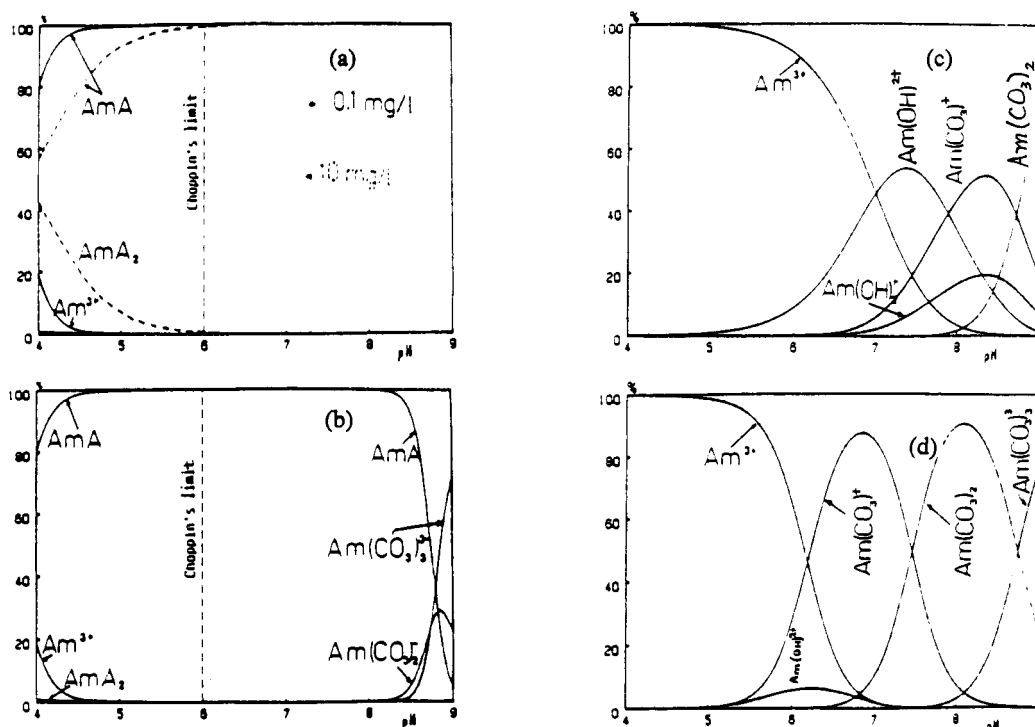


Fig 8 : Predominance Diagrams ; Species distribution plot for the systems :
 Am(III)-OH-CO₃-HALB (fig. 8a, 8b) ; Am(III)-OH-CO₃ (fig 8c, 8d)
 at I = 0.1 M NaClO₄ ; pCO₂ = 10^{-3.5} atm (fig 8a, 8c), or pCO₂ = 0.1 atm (fig: 8b, 8d). [34]

- humate complexation (AmA) is the major reaction occurring between pH 5 and 8,
- carbonate species such as $\text{Am}(\text{CO}_3)^+$ and $\text{Am}(\text{CO}_3)_2^-$ would compete with humate complexes only at $\text{pH} > 8$ and $\text{pCO}_2 > 0.1$ atm.

An increase of humic acid concentration implies an increase of the 1 : 2 complex (AmA_2) as shown in figure 8a at the expense of the 1:1 complex in the acidic pH range (up to pH 6). This humate complexation should entirely dominate Am speciation under atmospheric conditions, even for a very low concentration of humic acids.

The comparison of the species distribution curves shows the influence of humic materials on actinide solubility and therefore on actinide mobility even if, in reality, other phenomena tend to decrease this effect :

- indeed humic acids show a strong tendency to interact with solid surfaces [36] and to bind to clay minerals [30] ; this probably would imply low resulting mobility of actinides (retardation due to the sorption process).
- in addition, binding metal ions onto humic acids leads to a molecular aggregation and/or coagulation which finally results, whatever the mechanism (binding to large single macromolecules of humic acids, binding or sorption on colloidal humic acids, binding or sorption on humic-clay colloids [37]), in the formation of colloids holding actinides. (It must be noted however, that formation of colloids holding actinides depends on concentration levels. Competition of actinides with main cations (e.g. Ca^{2+} , Mg^{2+} , Sr^{2+} ...) does also occur.

Therefore the presence in groundwaters of humic substances must be taken into account both in the studies relative to the thermodynamical behaviour of actinides in groundwater, and in the studies relative to the physico-chemical processes of sorption on rocks and minerals and of colloid transport (see below).

Several groups conduct laboratory investigations designed to measure the stability constants of actinide-humic complexation [32, 37-47] ; but G.R. CHOPPIN in [37] emphasizes that "such studies are not easy as many experimental difficulties may lead the unwary experimenter astray". Indeed, difficulties are encountered in both of the following fields :

- Experimentation in natural water conditions ;
- Modeling of actinide complexation with organic matter : as pointed out by P. JACQUIER in [48], "we can model radionuclide complexation with very simple carboxylic acids, i.e. short chains, like citric or tartaric acid. For more complex molecules, the modeling today is quite intractable, because the configuration of these molecules is very variable : the short and long distance interactions between molecular groups imply that the configuration depends upon ionic strength, pH etc..."

Accurate chemical information on humic substances is needed to allow discussion of potential radionuclide complexing properties. Studies on the characterization of humic materials (and thus also on the isolation of these compounds from natural waters) with the above-mentioned objective are in progress [49-52].

2. SORPTION OF ACTINIDES

In the nuclear waste literature, the various physical or chemical processes (ion exchange, adsorption, precipitation of secondary phases, ion exclusion etc...) responsible for the retardation of radionuclides along their migration paths have received the generic name of "sorption".

The experimental approach generally applied for sorption studies such as these consists in determining either :

- the partition or distribution or sorption coefficient K_d of a specific element between the solid (unaltered or altered rock, unconsolidated fracture filling minerals, clays or backfill materials...) and the solution (spiked groundwater or simulated groundwater), or:
- the retardation factor R_f , defined as the ratio between the velocities of the groundwater and the radionuclide being studied.

2.1. Determination of the sorption coefficient

The sorption coefficient is expressed as the ratio between sorbed $[M]_s$ and solution $[M]_l$ concentrations of the element M considered :

$$K_D \text{ (ml/g)} = [M]_s \text{ (mol/g)} / [M]_l \text{ (mol/ml)} \text{ for unconsolidated material, and as}$$

$$K_A \text{ (cm)} = [M]_s \text{ (mol/cm}^2\text{)} / [M]_l \text{ (mol/ml)} \text{ for fracture flow systems.}$$

Corrections must be applied if competing sorption occurs on the vial walls [53].

Static batch tests and dynamic experiments (crushed-rock columns and crushed-rock circulating systems [40]) are used to determine K_D . Usually K_D is determined from the results of static batch tests by periodically measuring decrease in radionuclide concentration in solution. This straightforward approach leads to an experimental value for the ratio :

$$(1) \quad \frac{C - C_0}{C} \times \frac{V}{m}$$

Where C_0 and C are the concentration of the studied radionuclide, at the start of the experiment and at time t respectively, V is the volume of the liquid phase and m is the mass of the solid phase.

Most researchers identify this ratio (1) with the distribution coefficient K_D expressed in mL/g [54].

This interpretation of the experimental value (1) must be done carefully : the decrease of the radionuclide concentration in solution is not necessarily due to the sorption process ; it can be, for instance, the consequence of a chemical reaction occurring between the radionuclide and some ions of the solution, or of a redox reaction for a multivalent ion [53]. (This should be checked by a careful investigation).

The experimentally determined ratio (1) can be wrong if certain experimental precautions have not been taken, the most important precaution being to equilibrate the solution with the rock before starting the sorption-test : if the solution is not equilibrated with the solid, a dissolution process occurs in the first period of the sorption-test (dissolution of the solid by the aggressive solution), and the system eventually studied is different from the one initially selected !

2.2. Determination of the retardation factor

This factor, defined as the ratio between the velocities of the solution and the radionuclide in solution, is usually determined by means of dynamic tests (percolation of the solution through a column filled with the crushed materials) [55, 56].

In this experimental procedure, as in the case of K_D determination, the studied parameter (here R_f) can be measured directly, but, as for the K_D , the experimentally determined value will be misleading if the following two elementary precautions are not taken :

- equilibrating the column with the solution before starting the test (for the same reason as mentioned previously), and
- choice of the velocity of solution percolation through the column, in accordance with the physical characteristics of the column, and the sorption/desorption characteristics of the radionuclide in the system studied.

If this last precaution is not complied with (percolation velocity too high or too low with respect to radionuclide migration velocity) the retardation factor, determined by experiment, has no significance.

Some of these precautions are often not taken (in particular with regard to the equilibrating of the systems), and this fact, amongst others, adds to the great variety of experimental results found in the literature.

2.3. Sorption behaviour of actinides

Many experiments conducted to examine the sorption of actinides onto rocks and minerals are reported in the literature, but they often concern particular soils or minerals, e.g., finnish granites and gneiss

[57], sandstone and tuff materials from interbed layers between basalt flows from the Columbia River basalt formation [58], shales of various origins [59]... Thus the comparison of experimental results is not easy, the more so as the latter depend on various test parameters, e.g., pH, temperature, groundwater composition ... [60].

The results obtained by B. ALLARD and his co-workers, reported in [5], are presented later as an example of laboratory sorption experiments. They used a batch technique under the following conditions :

Solid sorbents	=	cryst. Al_2O_3 and SiO_2 grain size 0.090 - 0.125 mm,
Solution	=	0.1 and 0.01 NaClO_4 mol.L ⁻¹ variation of pH (with NaOH)
Temperature	=	$25^\circ \pm 1^\circ\text{C}$
Solid/liquid	=	0.20 g/20.0 m (aerated systems)

The measured distribution coefficients (K_D) versus pH for Am^{III} , Np^{V} and Pu are given in figures 9-11. The authors point out that [5] :

"For Am and Pu, the K_D vs pH-curves exhibit three separate stages :

- increasing K_D with increasing pH ; from very low values in the low pH-region to a high level within a fairly narrow pH-range, e.g. from 0.005 to 1.9 (corresponding to 5 % and 95 % sorption, respectively) within three pH-units
- high and fairly constant K_D in the intermediate pH-region,
- slightly decreasing K_D with increasing pH in the high pH-region.

Only the K_D -increase stage is observed for Np^{V} within the pH-range of the present study (pH < 12).

Obviously, the degree of hydrolysis determined by the pH of the system has considerable influence on distribution between the solid and aqueous phases. The increase in sorption with increasing pH seems to reflect progressive hydrolysis, and the maximum sorption roughly corresponds to the pH-range where neutral species would exist.

According to B. ALLARD and his co-workers, this significant decrease in distribution with the increasing pH observed for Am^{III} and Pu could reflect the formation of anionic species. They also note a quite different sorption curve for the Np^{V} - system. Their conclusions are :

"The observed actinide sorption behaviour indicates a predominantly physical adsorption mechanism.

The major chemical parameters that would have a significant influence on the actinide distribution between a solid and aqueous phase are : the redox conditions (determining the oxidation state), pH (determining the degree of hydrolysis), presence of complexing agents (e.g. carbonate).

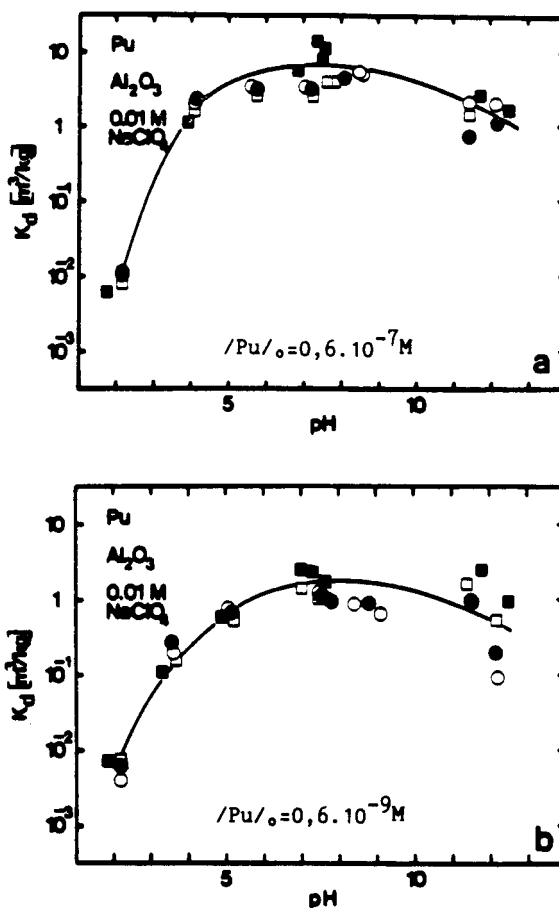
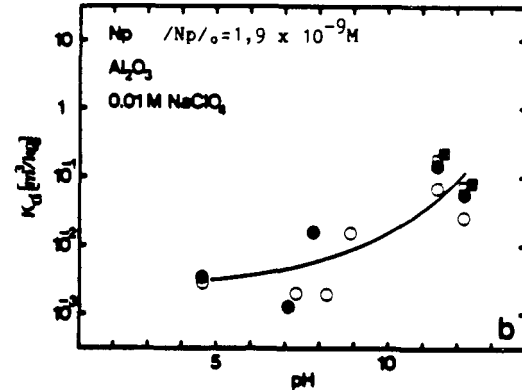
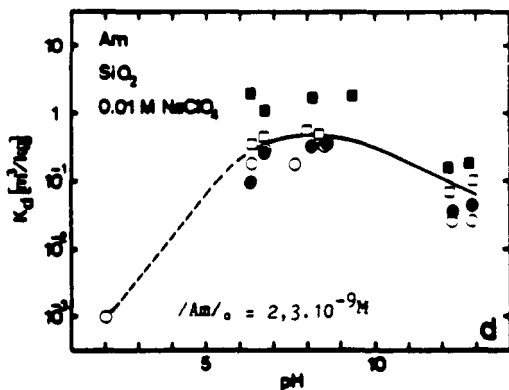
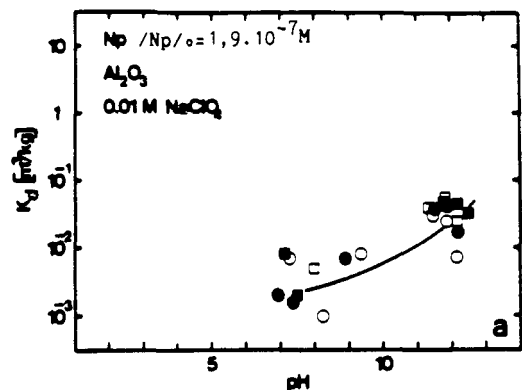
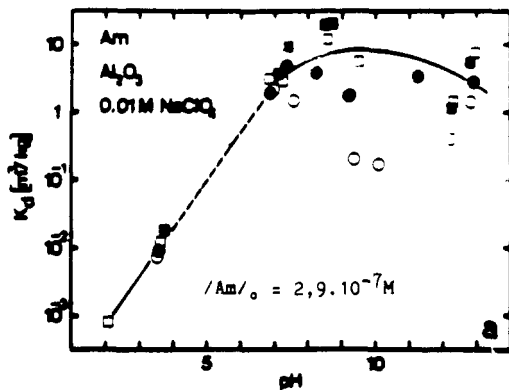


Fig 9 : Distribution Coefficients for Plutonium [5]
○ 6 h ● 27 h □ 1 w ■ 6 w

The sorption of cationic or neutral hydrolyzed actinide species would be pronounced on exposed solid phases, even when the exchange capacity of these solids is low. However, the formation of anionic species (hydroxides, carbonates) would reduce the sorption".



○ 6 h ● 27 h □ 1 w ■ 6 w

Fig 10: Distribution Coefficient for Americium

Fig 11 : Distribution Coefficient for Plutonium

2.4. Observations relative to the sorption behaviour of actinides

Unlike the study of chemical equilibria, the study of the sorption process is still empirical. The mechanisms of sorption, for an element as complex as an actinide in systems as complex as geological media is not perfectly known. At present, we are only able to note, a posteriori, the occurrence of a retention process and to quantify its importance by measuring a "distribution coefficient", strictly valid for well-defined conditions (those of the experimental procedure). We are not able to mathematically predict the exact sorption behaviour of an ion in particular conditions, or to extrapolate the sorption behaviour from a system experimentally studied to another system (obtained by modification of parameters such as initial radionuclide concentration, ionic strength, redox potential...). However, some models, known as "models of surface complexation" which take into account electrostatic interaction, reproduce sorption phenomena by means of surface complexation constants (Double Layer Model of J. LECKIE and J. DAVIS [61].

As long as the sorption mechanism is unknown, it will be impossible to accurately predict the importance and consequences of the sorption process, and to introduce this process into the modeling of aqueous species distribution, without introducing additional uncertainties.

It is clear that a knowledge of the sorption process will make predictions of the migration of actinides in soils and groundwaters easier and therefore this topic for research should be given priority.

3. ACTINIDE COLLOID FORMATION AND ACTINIDE TRANSPORT BY COLLOIDS

The term "colloid" in the nuclear waste field applies to any particle with a size in the 1mm - 1 μ m range which, due to special means of stabilization, remains in solution and does not settle over a long period of time. Colloid particles have a high specific surface area and a high specific surface energy. Therefore, the tendency to form particles of smaller specific particle area is strong and the small particles are metastable with respect to larger-ones. However the aggregation of small particles is countered by electrical charges of the same sign (preferably in case of hydrophobic colloids) or by a shell of water molecules (preferably in case of hydrophilic colloids) [31].

Two types of colloids are distinguished in colloid chemistry, identified in the literature by the following denominations :

- "intrinsic colloids" or "type I colloids" or "real colloids" as opposed to, respectively :
- "carrier colloids" or "type II colloids" or "pseudo-colloids".

The former consist essentially of compounds of the element considered (here actinides) whereas the latter are built up of compounds of other elements (here, actinides on or in colloids of mineral or organic origin). It must be noted, as mentioned by K.H. LIESER in [31], that the terms 'real colloids' and 'pseudocolloids' which are sometimes found in the literature are misleading, because both have the properties of real colloids".

3.1. Actinide colloids

Tetravalent and, to some extent, trivalent actinides tend to form polymeric colloidal hydroxides. According to B. ALLARD [13], these species could be composed of highly polymerized hydroxy complexes with large residual charges which prevent them from aggregation because of electrostatic repulsion. Thus, an apparent solubility which may exceed the expected equilibrium solubility by many orders of magnitude can be achieved. These colloids should be considered as metastable forms which will slowly convert to thermodynamically stable species. However, stable polymeric species could in fact also exist, particularly at low pH and high actinide concentrations. The species would carry a positive net charge.

The formation of actinide colloids is receiving growing attention, as recently reviewed by J.I. KIM [62, 63], or by K.H. LIESER [31].

3.2. Actinide carrier colloids

Colloids carrying actinides can be present naturally in groundwater or arise from the canister steel or the surrounding environment (backfill material such as bentonite clay or inorganic material in the host geology). Colloids can be inorganic compounds (fine clay particles, aluminium or iron hydroxides, silica, silicates, silicic acids resulting from mineral degradation) or organic substances (humic materials).

3.3. Influence on the migration of actinides (31, 38, 64–69)

J.D.F. RAMSAY and more recently K.H. LIESER and his co-workers [31] and J.I. KIM [68] reviewed experimental studies carried out in the fields of :

- the formation of colloids in an actinide solution of low concentration
- the effects of radiocolloid formation in enhancing the apparent solubility of actinides in solution (KIM's studies),
- the interaction of transuranic elements with humic and fulvic acids in natural groundwater...

J.D.F. RAMSAY points out that "although it is accepted that colloids may exist, their significance in affecting radionuclide migration rates in groundwaters is far from clear" ; little attention seems to have been given to this topic, although AVOGADRO and DE MARSILY [64] have recently developed a model which describes colloid transport under possible field conditions pertaining to vitrified high level waste" [38].

To complete the current situation admirably described by J.D.F. RAMSAY, it should also be stated that all investigations in the colloid field are difficult, due to the non-equilibrium state of the colloids, as pointed out by B. ALLARD [13] :

- "Much of the confusion concerning reported solubilities and solubility products of the actinide hydroxides, particularly for the tetravalent state, can be ascribed to the difficulties in properly defining the solid phase as well as what is in true solution and in the colloidal state, respectively. The slow kinetics of hydroxide dissolution and transformation and the strong tendency for hydroxy species and colloids to sorb strongly on exposed macro surfaces as well as on colloidal particles in solution (metal hydroxides, silica, etc...) can lead to experimental difficulties and possibly misinterpretations of experimental observations".

It should be mentioned that colloid generation in groundwater has been extensively studied these last few years in European Community countries in the framework of the coordinated project MIRAGE II, in the research area of "Geochemistry of actinides and fission products in natural aquifer system" (the two other subjects of this research being "complexation with natural and man-made organics" and "basic retention mechanisms in aquifer systems". [1]

4. MATHEMATICAL MODELING OF THE MIGRATION OF THE ACTINIDES IN GROUNDWATERS

Modeling is a way of estimating the consequences, over one million years or more, of actinides escaping from a geological repository into groundwaters with which spent nuclear fuel or vitrified high level waste could interact. Modeling must take into account :

- the speciation of the actinides in the groundwater systems, which is a function of the chemical composition of the aqueous phase and of local redox conditions which change with time and distance,
- the transport scenario (diffusion into the groundwater, convection, adsorption and transport on colloidal particles, [70, 71]) and retardation or retention phenomena such as sorption on rock and minerals, diffusion into the rock matrix, recrystallization of alteration minerals with incorporation of actinides or precipitation due to changing chemical environment [72].
- the hydrogeology of the host rock (variation of water velocity along a flow path especially if the flow path enters a much fissured zone) [73].

4.1. Geochemical computer calculation codes

The best known geochemical computer codes, capable of calculating the solubilities and concentrations of soluble species, resolving the coupled mass-action equations are at present MINELQ elaborated at the MIT BOSTON [74], PHREEQE [75], EQ3/6 [76], CHIMERE [77], DISSOL-EQUIL [78] ..., nevertheless, codes depend on the thermodynamic data used and are just tools ; the thermodynamic data bases are more important. Thus, D.P. HODGKINSON and his co-workers point out in a review [78] that "the limitations in this field come from the thermodynamic data rather than from any fundamental theoretical questions... However, the inadequacy of much of the data means that the calculations never achieve a truly predictive status"

Concerning sorption, the authors add that : "The prediction of nuclide sorption coefficients is in an even less happy state. There is no consensus on how to model what is probably a range of physical retention phenomena. It therefore remains an almost entirely empirical approach which produces linear sorption coefficients that can be used in transport modeling. Non-linear sorption processes could be modeled and used to predict repository data but current measurements and understanding would make such an approach little more than a fitting exercise".

4.2. Migration computer calculation codes and coupled chemical/migration modeling

Among the migration codes we can mention the French computer codes MELODIE and CONDIMENT developed at the CEA, or STELE developed at the "Ecole Nationale Supérieure des Mines de PARIS". MELODIE models the migration of one ion taking into account filtration and sorption under the form of a linear isotherm [79] ; CONDIMENT, in its latest version , models diffusion-convection of several

ions taking into account the possibility of precipitate formation [80], i.e., chemical and migration modeling are coupled. STELE is a coupled model and was built by introducing the geochemical computer code CHIMERE into the existing computer code METIS. At this stage, the CHIMERE computer code can take into account : any chemical reaction in the aqueous phase (complexation, acid-base reaction, redox equilibrium), dissolution-precipitation of minerals and solid phases, dissolution-degassing of gas [77]. The CHEQMATE computer code , developed at HARWELL, also couples speciation calculation solving the chemistry by assuming local chemical equilibrium and transport mechanisms which in this computer code are : diffusion, advection and electromigration ; CHEQMATE is an iterative scheme that re-equilibrates the chemistry in each spatial cell, for each time-step [74]. In the Netherlands, a three-dimensional groundwater flow model called METROPOL has been developed at RIVM [81]. METROPOL, which stands for simulation M^Ethod for the T^Ransport Of P^Ollutants, consists of a family of packages used for mesh generation, computation of steady-state groundwater flow, simulation of transient flow, and the solution of the coupled flow and transport equation. Special care has been taken in treating the flow of groundwater containing a high concentration of solute (e.g. salt) correctly. Another package simulates the transport with groundwater of low concentration solutes undergoing decay and adsorption/desorption (assuming a linear adsorption isotherm with a time-independent distribution coefficient).

The chemical transport model CHEMTRN can also be mentioned which includes advection, dispersion/diffusion, complexation, sorption, precipitation of dissolution of solids, and the dissociation of water (with modeling of the sorption process by either ion-exchange or surface complexation) [82], or the THCC code, that simulates reactive chemical transport on which coupling of precipitation/dissolution reactions to diffusive mass transport via porosity changes has been implemented [83, 84]. The last two computer codes mentioned were both written at Lawrence Berkeley Laboratory.

D.P. HODGKINSON and his co-workers point out in [74] the current limitations of the coupled chemical/migration codes :

"Coupled chemical/migration codes suffer from all the disadvantages of the static chemical models such as inadequate thermodynamic data and an unsatisfactory treatment of sorption with the additional complications of treating simultaneously water flow and diffusion with potential numerical instabilities. Nevertheless, a coupled approach is the only way to address some of the complex chemical evolution problems of the near-field environment. It is also an appropriate way of addressing chemical transport in the geosphere when interactions are important".

5. CONCLUSIONS AND INTERNATIONAL COLLABORATION

Throughout this report certain gaps, inadequacies and limitations have been pointed out : inadequacies between the thermodynamic values obtained experimentally, gaps in basic thermodynamic data, gaps also in colloid behaviour and sorption mechanisms and hence limitations in transport modeling. A few years ago, the scientific community realized that a critical compilation of the thermodynamic data published in the literature, a comparison and a validation of the computer modeling codes had become a necessity.

5.1. Data selection and compilation

The OECD Nuclear Energy Agency (NEA) has undertaken the development of a chemical thermodynamic database for elements of interest to various areas of nuclear technology, especially to radioactive waste management research areas, such as the safety analysis of nuclear waste repositories.

Actinides are among the key elements considered. The development of this database involves not only a compilation of all relevant published thermodynamic data but also a detailed critical review of key elements resulting for each element in a selected data set which will then be recommended.

This critical review is performed for each element in question by a NEA specialists team, consisting of four to six internationally recognized experts in chemical thermodynamics. This work is carried out in connection with the CODATA Task Group on Chemical thermodynamic tables so as to ensure that the

review is performed in accordance with CODATA procedures and recommendations [85]. (CODATA =Committee on data for science and technology, interdisciplinary scientific committee of the International Council of Scientific Unions (ICSU)). The first report on data compilation is available, and concerns Uranium [88].

5.2. Comparison, validation of modeling codes

Although models of equilibrium chemistry have been in existence for a number of years, D. READ points out in [86] that in the nuclear waste field little effort has been expended in the past to validate the tools available, that is, to establish whether the models accurately predict the behaviour of the chemical system being simulated.

Furthermore, programs which couple transport of contaminants with both solute and host-rock chemistry are relatively new and untested ; they must also be subjected to rigorous verification and be shown to provide accurate results under the conditions anticipated in radioactive waste disposal. This is the reason why CHEMVAL, an international project concerned with the geochemical aspects of radioactive waste disposal, has been undertaken as part of the Commission of the European Communities "MIRAGE 2 research programme" ; it gathered participants from seventeen organisations in eight countries ; its overall objectives were :

- 1) to apply aqueous speciation and coupled chemical transport computer calculation codes to a range of realistic waste disposal situations, and hence to establish and/or confirm areas where research is required,
- 2) to provide some degree of validation for both aqueous speciation and coupled chemical transport computer codes,
- 3) to provide the best possible overall thermodynamic data base for use with aqueous speciation and coupled chemical transport computer codes, consistent with project resources and timescales.

This project covered the period 1987 - 1990. It is described in [86] which also refers to other recent or current international modeling projects that are reported in the following table.

Project	Assessment Aspect	Model Type	Objective	Project Organiser
MIRAGE	Nuclide migration	P,S	Ve	CEC / UK DOE
MIRAGE	Equilibrium chemistry	P	Ve	CEC / UK DOE
COSA	Geomechanics of rock salt	P	Ve, Va	CEC
PACOMA	Whole system	P, S	Ve, A	CEC
CHEMVAL	Chemistry / chemical transport	P	Ve, Va	CEC / UK DOE
INTRACOIN	Nuclide migration	P, S	Ve, Va	SKI
INTRAVAL	Nuclide migration	P, S	Va	SKI
HYDROCOIN	Groundwater flow	P	Ve, Va, A	NEA
BIOMOVS	Biosphere processes	P, S	Ve	NEA
PSACOIN	Probability safety assessment	S	Ve, A	NEA
NAWG	Natural geochemical processes	P	Ve, Va	CEC

Model type : P = "Process"

S = "Simple"

Objective : Ve = verification

Va = application

A = application

5.3. Future R & D needs

Concurrently with international collaboration, some R & D studies must be continued. Taking into account the complexity of the investigation field, a multidisciplinary approach is attractive. The French R and D programme, undertaken at the CEA, Department of Waste Management and Disposal, is based precisely on this multidisciplinary approach [87] :

- laboratory studies mainly dedicated to the speciation of transuranic elements, to the role of organic substances and colloids in complexing and transporting radionuclides, and to percolation experiments through columns and dynamic K_d measurements ;

- field studies directed towards the development of probes for in-situ estimation of important physico-chemical parameters of groundwaters ;
- analogue studies which intend firstly to derive reliable data from a thorough comparison of natural materials or geochemical systems with those found in a repository and assumed to be analogous, and secondly to check the validity of extrapolation to environmental systems or concepts or models developed from short-term small scale laboratory experiments ;
- modeling of the evolution of a whole disposal site and, in particular, of radionuclide migration.

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