The Chemical Behavior of the Transuranic Elements and the Barrier Function in Natural Aquifer Systems

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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THE CHEMICAL BEHAVIOR OF THE TRANSURANIC ELEMENTS AND THE BARRIER FUNCTION IN NATURAL AQUIFER SYSTEMS

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Das chemische Verhalten der Transuranelemente und die Barrierefunktion in natürlichen Aquifersystemen

by J.-I. Kim and R. Klenze

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THE CHEMICAL BEHAVIOR OF THE TRANSURANIC ELEMENTS AND THE BARRIER FUNCTION IN NATURAL AQUIFER SYSTEMS

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1. INTRODUCTION.

The use of nuclear energy worldwide leads to appreciable production of fission nuclides and transuranic elements. Based on the known data, [and] using a KORIGEN calculation [1], it may be estimated that, for the annual worldwide production of 213 GW_e·a (total capacity: 320 GW_e) of electric energy by nuclear fission [2], 240 t of fission products, as well as 77 t of plutonium, 1.0 t of americium, 4.3 t of neptunium and 0.3 t of curium are formed. In the Federal Republic of Germany, with an installed capacity of 23 GW_e, about one-third of the electrical output is produced in nuclear reactors [3]. The annual production rates resulting from this amounts to 20 t of fission products, 6.5 t Pu, 0.08 t Am, 0.36 t Np, and 0.025 t Cm.

The present plan in the Federal Republic of Germany for disposing the radioactive wastes from nuclear power plants [4] is to process the spent fuel elements through the French COGEMA plant or the British BNFL plant. The heat-producing high-active waste (HAW) arising from reprocessing will be immobilized by vitrification in a borosilicate matrix and returned to Germany for final storage starting in 1994. Direct repository storage of the spent fuel elements is considered as an alternative to this concept [4]. The change in the atomic regulatory law required for this is in discussion for the present, so safety analysis of the two waste forms, glass matrix and spent fuel elements, must take place.

In Figure 1, the activities of important fission products and transuranic elements arising during the production of 1 GW_e·a per year in a light-water reactor are plotted over a time span of more than 10^6 years [5]. The activities are given in radiotoxicity equivalents (ALI unit: the limit set by the international radiation protection commission for the annual uptake of activity permitted for workers in nuclear facilities [6]). In Figure 1, the activities with and without reprocessing are shown vs. time. The amounts of plutonium and uranium in the waste are reduced by two orders of magnitude by separation during reprocessing. As may be seen from the figure, most of the activity of the fission products has decayed away after 500 years and the [fission products] play no role in long-term safety, except for a few long-lived nuclides (^{99}Tc, 2.1×10^5 a). On the other hand, the greatest hazard is due to the transuranic elements, which are primarily alpha emitters with a radiotoxicity 20 times greater than beta and gamma emitters, and [which] frequently also have long half-lives.

Plutonium is produced in larger amounts than any other transuranic element. With respect to the long-term behavior of this element in the natural environment, the following isotopes are important: ^{238}Pu (87.7 a), ^{239}Pu (2.41×10^4 a), ^{240}Pu (6.4×10^3 a), and ^{241}Pu (14.4 a). Likewise, for very long times, a long-term safety risk is discussed for neptunium, since it has one long-lived isotope ^{237}Np (2.14×10^6 a) [7], and it exists as the highly mobile NpO_2^+, oxidation state V, under aerobic conditions [8]. For americium, the two long-lived nuclides ^{241}Am (433 a) and ^{243}Am (7370 a) are relevant. Because of Am formation due to beta decay from the short-lived ^{241}Pu, the amount of Am increases during storage, and is the second-most prevalent transuranic element after Pu. Curium is formed in only small amounts, but [it] is responsible for most of the alpha activity, after Pu, at the beginning of storage, due to the short half-life of ^{244}Cm (18.1 a).

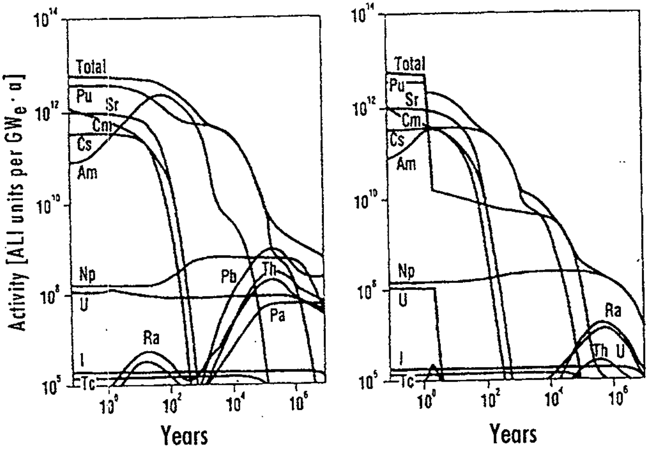

Figure 1. The radiotoxicity potential of various elements arising during the production of 1 Gw$_e$·a, expressed in ALI units (annually permitted limit of activity uptake by work forces) for light-water reactors *[5]*.

2. THE CHEMISTRY IN THE NATURAL AQUATIC SYSTEM.

The significance of the transuranic elements as potential environmental pollutants depends upon various factors, such as amount, half-life, chemical behavior in a given transport medium, dispersion mechanism, and biological availability. For obvious reasons, water is frequently the transport medium in question. The inorganic and organic constituents present in various amounts in natural groundwater undergo complex multi-component reactions with the dissolved radionuclides. The main reactions occurring this way are hydrolysis, complexation with various inorganic and organic anions, redox reactions, and the formation of colloidal species *[8]*. The combination of these parallel reactions determines the geochemical interaction of the radionuclides with the geomatrix *[9]*. It is all-important in the migration behavior of the radionuclides in the aquifer system whether they are present as mobile or as immobile species. Evidently the transuranic ions, except for the pentavalent neptunium ion, are mobile only as anionic complexes or as colloids.

The chemistry of the radionuclides in natural solutions differs in many aspects from the known chemistry of these elements in the laboratory or in industrial processes. The essential characteristics of natural aquatic systems are:

a) In the pH range of natural water (pH 4 to 9) the more highly charged metal ions ($Z \geq 3+$) are unstable due to hydrolysis. Because of this, for all oxidation states, except for the pentavalent actinyl ions, these ions have small solubilities, amounting to much less than 10^{-6} mol/L.

b) Natural aquatic media contain various dissolved heavy-metal ions of higher oxidation states ($Z \geq 3+$) in amounts that correspond to the solubility concentrations of the transuranic elements. This results in synergistic or interacting reactions of the transuranic ions with multiple components of the natural water.

c) Anions present in groundwater, such as carbonate and humate and/or fulvate ions, stabilize the more highly charged metal ions by formation of mobile anionic complexes. The relative importances of these reactions are delicately balanced with each other and with hydrolysis and are dependent on the ligand concentration, the pH, and the Eh value.

d) There are always colloids present in natural waters, especially [ones] with particle diameters less than 30 nm *[10]*. The more highly charged radionuclide ions are sorbed onto these colloids, forming so-called pseudocolloids *[8, 10]*. Therefore, the radionuclides assume the migration properties of the natural colloids.

e) The [above-] mentioned geochemical reactions of the radionuclides depend primarily on the prevalent oxidation states, which are characteristic of the chemical properties of the water for each element. The kinetics of the redox and disproportionation reactions that occur depend on the groundwater composition and are mostly very slow, so that unequilibrated redox [conditions] may remain over long times.

f) Because of the small solubility, most geochemical reactions proceed in the sub-micromolar concentration range. For the most part, the transuranic ion concentrations relevant to safety are much less than their natural solubilities. To follow and quantify the geochemical reactions at these small concentrations, and to understand the migration mechanisms, very sensitive and interference-free speciation methods are required; these [methods] are yet to be developed for the most part *[11, 12]*.

To better understand the microchemical behavior of the transuranic elements in various natural aquatic systems, it is necessary to have a basic understanding of the reactions that are likely to occur. These are: dissolution, hydrolytic reactions, complexation with various ligands, redox reactions, formation of colloids, and surface reactions. In this report, the present state of knowledge of these basic geochemical reactions is described. For now, the first four of these reactions are discussed; colloid formation is handled later in its own chapter because of its special importance in natural waters.

2.1. Solubility.

Solubility is the most important quantity that affects the mobility of the transuranic elements and thus their dispersion in the aquifer. The concept of "solubility" cannot be defined [as] exactly for a transuranic compound in natural aquatic medium, as [it could be] in a well-defined laboratory system, i.e., [one] in thermodynamic equilibrium. The dissolution process involves a multiplicity of many-component reactions, such as multi-ligand complexation, polynucleation, and formation of colloidal species, for which thermodynamic description is not yet possible.

The first reaction step associated with the dissolution of a metal compound in natural water is hydrolysis, which leads to formation of mononuclear and oxygen-bridged polynuclear and colloidal species *[8, 13]*. These hydrolysis products are in dynamic equilibrium; they are unstable in the aquatic system and are sorbed on both mineral surfaces and groundwater colloids *[10]*. The transuranic ions may be stabilized, and thus mobilized, in the dissolved form by complexation with the anions contained in natural waters, such as carbonate, humate/fulvate, etc.

Besides reactions occurring during dissolution of the transuranic elements, formation of colloids plays a large role in natural aquifer systems. Finally, by hydrolysis and polynuclear reactions, the transuranic ions may form so-called "true" colloids through cross-linking due to oxygen bridging *[13]*. The so-called pseudocolloids are formed *via* sorption of the transuranic ions or their hydrolysis products onto the colloids [which are] always present in the natural water *[14]*. If colloids play a role in the dissolution of transuranic ions in the natural water, and this is usually the case, then determination of the "solubility" is indeterminate. Accordingly, calculation of the solubility from experimentally determined thermodynamic quantities, such as solubility products and formation constants for complexes, may be carried out only by placing limitations on the natural system. The highly charged transuranic ions ($Z \geq 3+$) exist in natural aquatic systems either complexed in the anionic form or bound to colloids. Cationic species, except for pentavalent actinyl ions, are not stable under these conditions. Therefore, the mobilities of the transuranic elements in the aquifer are determined by complexation reactions and the formation of colloids.

As a typical example, the equilibrium solubility of solid $^{241}Am(OH)_3$ is shown in Figure 2 in two different groundwaters from an aquifer in the area of the planned repository site at Gorleben *[15]*. The most important difference between the waters is their salinity: Gohy-1061 is not saline, Gohy-2122 is strongly [saline] (2.5 M NaCl). After equilibration, the waters are filtered with ultrafilters of various pore sizes from 450 down to 1 nm. The Am concentration in the filtrate of Gohy-1061 decreases continually over nearly four orders of magnitude. This substantiates that Am is present nearly exclusively on groundwater colloids. Based on the ambient atmospheric partial pressure of CO_2 and the measured pH of 8.2, the thermodynamically calculated solubility for $Am(OH)_3$ amounts to 2×10^{-7} mol/L *[16]*. In the saline water Gohy-2122, formation of groundwater colloids with larger particle [sizes] (>5 nm) is completely suppressed by the high ionic strength. Nevertheless, smaller particles, so-called microcolloids, still exist in solution, to which 68% of the dissolved Am is bound. Thus, in a colloid-rich groundwater, such as Gohy-1061, the solubility of a transuranic ion is not a well-determined quantity, but depends on whether and which pseudocolloids of the dissolved species are to be considered. The mobility of the transuranic ions is determined by which particles are removed from the geomatrix by filtration.

2.2. Hydrolysis reactions.

Hydrolysis is the primary reaction common to all the transuranic ions in a natural aquatic system. Experimentally, it is found that the tendency for hydrolysis increases with the effective charge of the ions *[17]* in the series

$$\begin{array}{c} An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+} \\ (An = \text{actinide}) \end{array} \qquad (1)$$

AnO_2^+ [sic] exhibits a greater tendency toward hydrolysis than An^{3+}, since an effective charge of 3.3±0.1 results in the linear molecular structure $(O\text{-}An\text{-}O)^{2+}$ due to the strongly electronegative oxygen atoms in the equatorial bonding plane of the metal ion *[17, 18]*. Similarly, an effective charge of 2.3±0.2 is given for AnO_2^+. The following first hydrolysis constants determined experimentally by us *[21, 22, 19, 20]* for the various oxidation states of the transuranic elements follow the effective charge trend [just] mentioned:

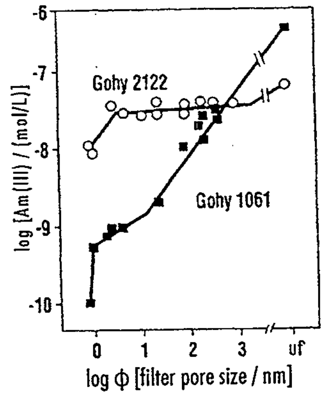

Figure 2. Solubility of ^{241}Am hydroxide in a non-saline (Gohy-1061) and a saline (Gohy-2122, 2.5 mol/L NaCl) groundwater from Gorleben as a function of the pore size of the ultrafilter used for phase separation (uf. = unfiltered) *[15]*.

$$\begin{array}{llll} \text{An(IV)} & \text{Pu(OH)}^{3+} & \log \beta_{11}=12.3\pm0.3 & (I=1.0) \\ \text{An(VI)} & \text{PuO}_2\text{(OH)}^{+} & \log \beta_{11}=8.3\pm0.3 & (I=0.1) \\ \text{An(III)} & \text{Am(OH)}^{2+} & \log \beta_{11}=6.3\pm0.3 & (I=0.1) \\ \text{An(V)} & \text{NpO}_2\text{(OH)} & \log \beta_{11}=2.7\pm0.2 & (I=0.1) \end{array} \qquad (2)$$

Similar to the series found for hydrolysis, stability of the transuranic ions in aquatic solution actually shows the opposite tendency, so that, under certain conditions, An(V) is the most stable. The trend for formation of colloids also parallels the hydrolysis behavior, so that the tendency for stabilizing the transuranic ions as aquo ions can be compensated by stabilization as colloids. The primary hydrolysis products of the transuranic ions are not stable in aqueous solution and tend to interact further with the OH binding sites of available surfaces. This is especially true for An^{4+}, which exhibits a great tendency for formation of colloidal species as well as [for] strong sorption *[21]*. AnO_2^+ is an exception to this *[20]*, being stable in solution at up to pH 10.

2.3. Complexation.

Under natural conditions, complexation occurs simultaneously with hydrolysis. Every natural water, especially groundwater, contains considerable amounts of complexing anions such as carbonate, chloride, sulfate, phosphate, and others *[23]*. The strength of complexation of transuranic anions increases according to the series

$$CO_3^{2-} \geq (\text{Humate})^{n-} > SO_4^{2-} > H_2PO_4^- > Cl^- \tag{3}$$

Because of the omnipresence of CO_3^{2-} in nature and its great complexing strength, complexation of transuranic ions with carbonate is the most important geochemical reaction, especially in deep groundwaters *[24, 25]*. Complexation with other inorganic anions such as chloride, sulfate, phosphate, etc. is normally negligible because the tendency for complexation [is] slight or the concentration [is] small.

In contrast to this, humic and fulvic acids are of special significance as organic complexants for stabilizing more highly charged metal ions *[26, 27]*. These humic materials are ubiquitous in natural aquatic systems and are present in a wide range of concentrations. In addition to the natural organic complexants, man-made chelators, such as EDTA, which are used as decontamination agents, and therefore get into the repository, also play an important role in complexation.

The first complexation constants of the transuranic ions in various oxidation states are plotted in Figure 3 for a series of relevant anions *[8]*. The complexation constants exhibit the same dependence on oxidation state as observed for the hydrolysis reaction. Thus, in addition to destabilization due to hydrolysis and stabilization due to colloid formation, the transuranic ions can undergo further stabilization due to complexation. This applies especially for reaction with the strongly complexing ligands CO_3^{2-} and humate/fulvate.

The extents of these individual reactions may be simply compared by the following relationship:

$$R = \log(\beta_{11}C + \beta_{12}C^2) \, , \tag{4}$$

where β_{11} and β_{12} represent the first and second mononuclear complexation constants, respectively, and C, the ligand concentration. [Using] Am^{3+} as an example, comparing the range of variation observed for the Gorleben aquifer yields the following values for R:

$$\begin{array}{ll}
\text{Hydrolysis:} & \\
\log \beta_{11} = 6.3 \pm 0.3 \quad [19] & \\
\log \beta_{12} = 12.2 \pm 0.4 \quad [19] & \\
C = 10^{-8} \text{ to } 10^{-5.5} \text{ mol/L} & -1.7 \leq R \leq 1.4
\end{array} \tag{5}$$

$$\begin{array}{l} \text{Carbonate complexation:} \\ \log \beta_{11} = 6.35 \pm 0.1 \quad [16] \\ \log \beta_{12} = 9.54 \pm 0.2 \quad [16] \\ C = 10^{-9.3} \text{ to } 10^{-2.8} \text{ mol/L} \qquad -3.0 \leq R \leq 4.1 \end{array} \tag{6}$$

$$\begin{array}{l} \text{Humate complexation:} \\ \log \beta_{11} = 6.42 \pm 0.11 \quad [28] \\ C = 10^{-5} \text{ to } 10^{-4} \text{ mol/L} \qquad -1.4 \leq R \leq 2.4 \end{array} \tag{7}$$

The value of R indicates the relative extent of each reaction. From the estimated ranges of R it is possible to say that all three reactions may have comparable effects in aquatic systems. For the Gorleben groundwaters studied by us, carbonate and humate/fulvate complexation dominates over hydrolysis. From this basis, these reactions are discussed in detail below.

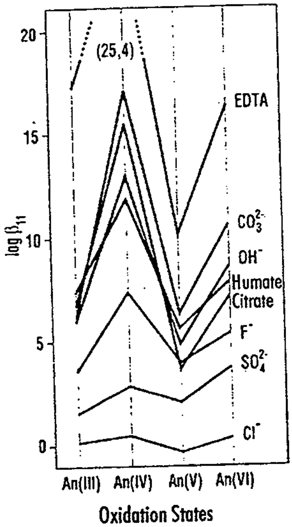

Figure 3. Primary complexation constants (β_1) of the actinides in oxidation states III, IV, V, and VI for various ligands *[8]*.

1. Carbonate complexation

In the pH range of natural water, carbonate is present nearly exclusively as bicarbonate, HCO_3^-. The concentrations in various waters range between 1×10^{-4} and 1.3×10^{-2} *[29]*, [and] in groundwaters, between 1×10^{-3} and 1.3×10^{-2} mol/L *[30]*. The concentration of bicarbonate, $[HCO_3^-]$, is tied directly to the partial pressure P_{CO_2} of CO_2 over the solution and the pH through the following relationship *[23]*:

$$\log\ [HCO_3^-] = \log K^* + \log P_{CO_2} + \mathrm{pH}\ , \tag{8}$$

where K^* includes the first protolysis constant of carbonic acid and the Henry constant. As shown in Figure 4, the partial pressure of CO_2 in groundwaters from the Gorleben area, just as in other aquifer systems, is generally greater than the atmospheric partial pressure of 0.035%, reaching a maximum of 10% and averaging 1%.

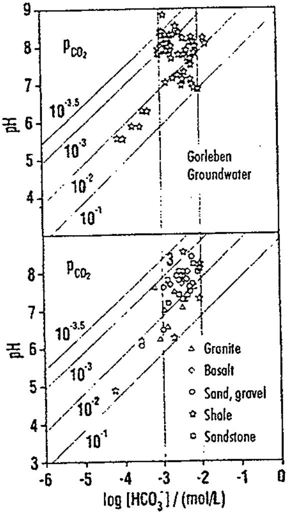

Figure 4. Correlation of pH with $[HCO_3^-]$ according to Eq. 8 for groundwater from Gorleben (top) *[31]* and various aquifer systems (bottom) *[30]*.

Experimental investigation of the thermodynamic equilibrium of transuranic ions in the carbonate system is very difficult, since simultaneous control of pH and P_{CO_2} is difficult to obtain. That is the reason that the published complexation constants *[8, 24, 25, 33]* exhibit appreciable differences among themselves. To obtain reliable information about the chemical behavior of the transuranic elements in the natural environment, a better understanding of the carbonate complexation in those media, both in the aqueous and in the solid phase, cannot be avoided.

2. *Humate complexation*

The significance of heavy metal ion complexation by humic materials has been well recognized in the fields of agrochemistry, aquatic chemistry, and geochemistry in recent years *[23, 26, 34, 35]*. Humic materials, which are present everywhere in the natural environment, behave like amorphous, polydisperse polyelectrolytes of variable structure. The molecular weight varies between a few hundred up to a few tens of thousands *[26]*. Operationally, they may be divided into three main classes: the humic acids, which are soluble in dilute alkaline aqueous solution, but precipitate in acid media; the fulvic acids, as the part remaining in solution during acidification; and finally, the humus, which is not extractable into either alkaline or into acidic media. Structurally, these fractions are very similar and differ from each other mainly in their molecular weights and their functional group content *[26]*. Fulvic acid has a smaller molecular weight than humic acid. The low solubility of humus results from strong bonding to inorganic components of the soil *[34]*.

Aromatic carboxylate and phenolate groups are regarded as the two functional groups responsible for complexation of heavy metals *[26]*. At least two different types of interaction between humic materials and metal ions are known *[36, 37]*: electrostatic bonding to the polyelectrolyte and "inner sphere" complexes due to chelate formation. The complexation of transuranic ions with higher charge ($Z \geq +3$) seems to fall into both categories. Aquatic humic materials, consisting of humic and fulvic acids, are in general strongly laden with more highly charged ($Z \geq +3$) metal ions of the substances contained in the groundwater *[10]*. In groundwaters where there is an apparent long-term geochemical equilibrium with the humic materials, all available bonding sites of the humic materials are loaded to saturation with metal ions *[38, 39]*. The humic materials are partially hydrophobic and undergo a structural contraction due to neutralization of the functional groups by complexation. Finally, they are present in colloidal form and are characterized as humic colloids *[38-40]*.

A typical example of the complexation of various trace metal ions in groundwater by aquatic humic materials is shown in Figure 5 *[39, 41]*. A number of Gorleben groundwaters were analyzed for tri-, tetra-, and hexa-valent trace metal ions and dissolved organic carbon (DOC). The DOC is present in these waters nearly entirely as humic and fulvic acid *[38, 41]*. The heavy metal ions analyzed in the groundwaters are homologs of the transuranic ions. The concentrations of the trivalent lanthanides shown in Figure 5a exhibit a logarithmic correlation with the DOC concentration. The average slope of 1 [which was] found demonstrates that the heavy metal ions are present in the groundwaters as humate/fulvate complexes. The graphical representation for the tetravalent heavy metal ions in Figure 5b leads to the same result. The same correlation is apparent for uranium (Fig. 5c) as for the tri- and tetra-valent ions. Figure 5 unquestionably shows that the higher valence metal ions in groundwaters rich in humic materials are present as humus complexes, and their concentration is proportional to the humus concentration.

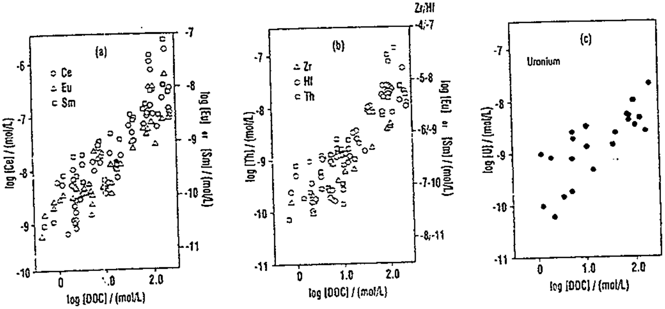

Figure 5. Concentration of various trace elements in oxidation states III (a), IV (b) and IV/VI in Gorleben groundwaters as functions of the humic substance concentration, expressed as the concentration of dissolved organic carbon (DOC) *[39, 41]*.

Therefore, it is expected that the transuranic ions are stabilized in humus-rich groundwaters as humus complexes and thus can be made mobile. If a solubility for ^{239}Pu corresponding to that found for the homologous Zr in the Gorleben groundwaters is assumed, then specific alpha activities between 2×10^4 and 6×10^6 Bq/L are obtained. Similarly, activities between 3×10^4 and 3×10^7 Bq/L are derived for ^{241}Am from the concentrations of the homolog Ce. These values lie many orders of magnitude above the 0.1 Bq/L WHO guideline for alpha activity in drinking water *[42]*. The necessity for barriers to retain transuranic ions [and] to retard [their] dispersion in the biosphere results from this simple evaluation.

The quantitative description of the chemical interaction between transuranic ions and aquatic humic materials is of overriding importance for completely understanding the chemical behavior of the transuranic elements in the aquifer system. In the literature, a series of constants is given for the complexation reactions of humic materials with actinide ions, such as Th(IV), U(IV), and U(VI) (overview in *[41, 43]*), Am(III) (overview in *[28, 44]*), Cm(III) *[44, 45]*, and Np(V) *[46]*. Except for Np(V), these data were all determined at pH≤6, so as to eliminate simultaneous hydrolysis and carbonate complexation. Since the humic and fulvic acids are polyelectrolytes with various proton-exchanging functional groups *[26]*, an unequivocal description of the complexation is not possible as [would be] for well-defined ligands. Therefore, various models were used for interpretation *[47]*. Thus, the published constants differ considerably from one laboratory to the next, according to the interpretation of the data and the experimental methods used *[47]*. Therefore, an actual, rigorous comparison of results for the same metal ions turns out to be difficult.

Thus, a general concept for interpretation and quantification of the metal-humus complexes is imperative. The resulting data must be comparable with one another and must have practical application. Individual studies *[28, 45, 46]* have shown that consideration of the true loading (or exchange) capacity of the particular humic material for the metal ion to be studied leads to complexation constants that are comparable to one another. The constants developed in this way are independent of pH and ionic strength and therefore are applicable to groundwater.

The complexation of humic materials with transuranic elements is best studied with spectroscopic methods *[28, 45, 46]*. Other methods used in the literature, such as ion exchange *[48]*, solvent extraction *[49]*, gel chromatography *[50]*, etc. do not permit direct speciation of the complexes present and lead to large differences among the complexation constants obtained. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) is a simple direct spectroscopic speciation method for complexes of humic material with the trivalent actinides *[45]*. This method makes it possible, for example, to study the complexation of Cm(III) at concentrations down to 10^{-9} mol/L. The interfering fluorescence of the humic materials may be completely discriminated out by time-resolution. The fluorescence emission spectra of the hydrated Cm^{3+} ion and of Cm fulvate are shown in the sub-nanomolar range in Figure 6 *[44]*. The species present may be unequivocally quantified at these small concentrations using peak-shifting.

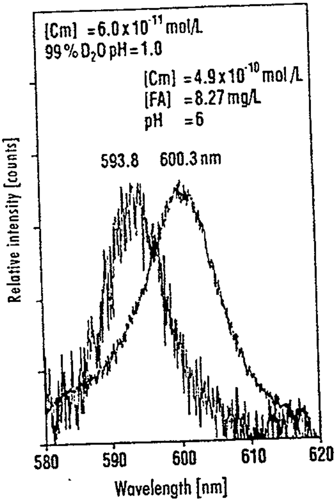

Figure 6. Fluorescence spectra of Cm^{3+} (6.0×10^{-11} mol/L) in 0.1 M DCl in D_2O and of Cm fulvate (4.9×10^{-10} mol/L) in 0.1 mol/L $NaClO_4$ at pH 6 *[44]*.

Since humic materials play a role in natural aquatic systems, they have a large influence on the aquatic chemistry of transuranic ions and therefore their mobility. The geochemical reactions of humic materials with transuranic ions are, for the most part, only partially understood; [this is true] especially in the submicroscopic region.

2.4. Redox reactions.

Among the various geochemical variables, the pH and the redox potential (Eh) have a direct influence on the redox reactions of the transuranic elements in the natural aquatic system. The Eh and pH values (points) determined for groundwater from the Gorleben aquifer are plotted against each other in Figure 7 *[31]*. The surrounding curve approximately defines the Eh-pH region of naturally occurring water. The stability limits of water with respect to oxidation to O_2 and reduction to H_2 are also displayed.

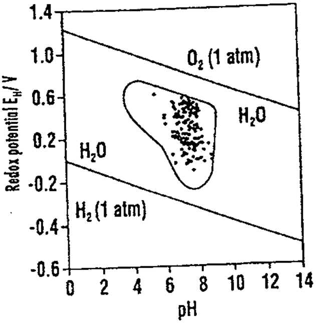

Figure 7. Correlation of Eh and pH values in various Gorleben groundwaters (points); the surrounding curve represents the range of natural water *[8]*.

The redox potentials of Np, Pu, and Am in 1 M $HClO_4$, as well as for pH 8 and pH 14, are displayed in Figure 8 *[51]*. Because of the uncertainty of the thermodynamic data used for the derivation, the values given for pH 8 and 14 are only approximately valid. In the Eh-pH region of natural water, Am exists as the trivalent ion, Np predominantly as pentavalent, and as tetravalent only in strongly reducing waters. Pu, on the other hand, may exist in the tri-, tetra-, penta-, and hexa-valent oxidation states, which are in equilibrium through combined redox and disproportionation reactions. The stabilization of pentavalent Pu observed in natural aquatic systems *[52]* may be related to the strong tendency toward hydrolysis in the tetra- and hexa-valent oxidation states. Trivalent Pu may be present in natural waters only in exceptional cases. Reduction of mobile penta- and hexa-valent actinyl ions to An(IV) and An(III) first leads to the formation of species of [only] slight mobility. Of course, the mobility may be increased again by subsequent complexation and colloid formation.

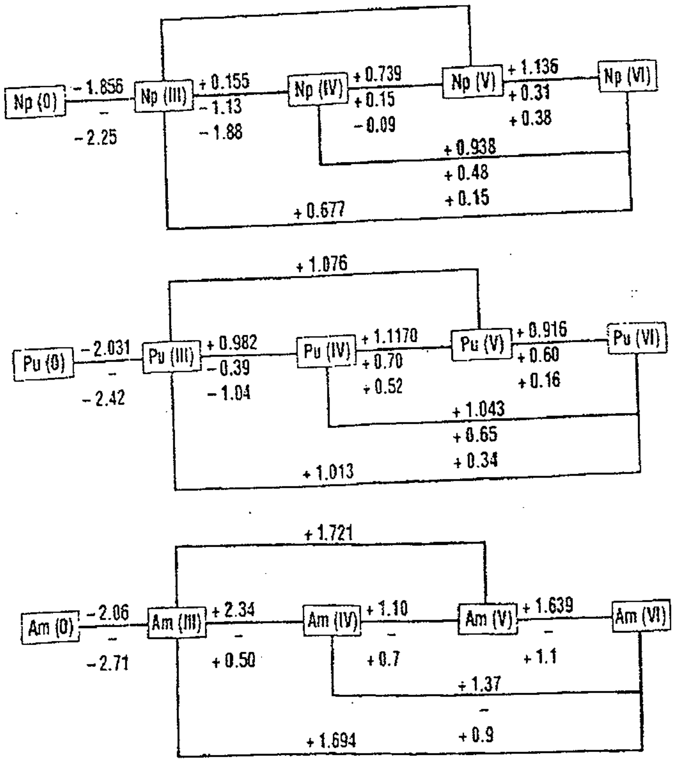

Figure 8. Redox potentials (in V) for Np, Pu, and Am in 1 mol/L $HClO_4$ (upper values), at pH 8 (middle values), and at pH 14 (lower values) *[51]*.

A drastic change in the redox potential may occur due to radiolysis under the influence of the strong radiation field near the repository site *[53]*. Particularly in saline solutions (≥3 M NaCl) and a high alpha activity (≥1 Ci/L), the redox potential increases to 1200 mV due to formation of strongly oxidizing Cl species *[54]*. Under such conditions, the transuranic elements are stabilized as Np(VI) *[55]*, Pu(VI) *[54]*, and Am(V) *[53]*. Up to now, the chemical behavior of the transuranic elements in these oxidation states in the natural environment has been studied only a little.

It is possible to maintain persistent reducing conditions in the repository, for example by an excess of Fe (container material). Thus, an additional barrier may be established for the easily mobile species NpO_2^+ and TcO_4^- by reducing [them] to the slightly mobile species Np(IV) and Tc(IV). The formation of a redox front for immobilizing the transuranic ions by insertion of an "intelligent" barrier is one of the most important subjects to be studied for the safety investigation of the HAW repository.

3. COLLOID FORMATION.

Aquatic colloids are always present in natural waters. The chemical composition, structure and particle size of the natural colloids varies greatly with the geochemical nature of the particular aquifer system *[10]*. The particle concentration also fluctuates between 10^8 and 10^{17} particles/L depending on the source *[47, 56]*. Formation of pseudocolloids due to sorption onto natural colloids may lead to transuranic solubilities that are greater or less than the thermodynamic equilibrium concentration. Depending of the size distribution of the colloid and the natural filtering effect of the geomatrix, the migration of transuranic ions bound to colloids may be accelerated or retarded in a particular aquifer system. Therefore, the chemistry of natural colloids and their interaction with radionuclides has been given extra attention in recent years *[10, 57-60]*.

3.1. Characterization of colloids.

Natural colloids consist of inorganic and organic components *[38, 40, 57-59]*, a mixture of both *[39]*, or of microorganisms *[61]*. They include residual products of minerals *[34]*, hydrolyzed precipitates of mixed metal ions *[40, 60]*, macromolecular organic compounds, such as metal-laden humic materials *[38, 39]*, and biocolloids made up of microorganisms *[61]*. Except for the biocolloids, the colloids of inorganic and organic nature are relatively small (<450 nm) *[10]* and, in deep groundwaters, still smaller (<30 nm) *[56]*. The colloids may be separated by modern ultrafiltration methods or by ultracentrifugation *[40]*.

The size distribution of the particles present in the water, including the natural colloids, is compared with the pore size of various filter types in Figure 9 *[62]*. The 1 nm lower particle size of the colloid is given from the pore size of the available filter; the upper particle size is determined by instability of the colloid due to sedimentation. The particle size of groundwater colloids is comparable to that of viruses and lies far below the size of the smallest bacteria.

The population of natural colloids varies dramatically from one water to another. For the groundwaters from the Gorleben aquifer, differences in the total particle count of three orders of magnitude were determined. These colloids are almost exclusively humus colloids, i.e. humic material loaded with metal ions, so the colloid particle count correlates with the DOC *[56]*. In Figure 10, the colloid population for a series of Gorleben groundwaters is compared with a granitic water (Grimsel), as determined by laser-light scattering measurement (photoacoustic detection of scattered light: PALS *[12]*). To compare the values with one another, the particle count was normalized to a particle diameter of 100 nm. In contrast to the absolute particle counts, the size distribution of the particle diameters in the individual Gorleben groundwaters is quite similar. The size distribution of the colloid determined by PALS in combination with ultrafiltration is shown for one such groundwater in Figure 11.

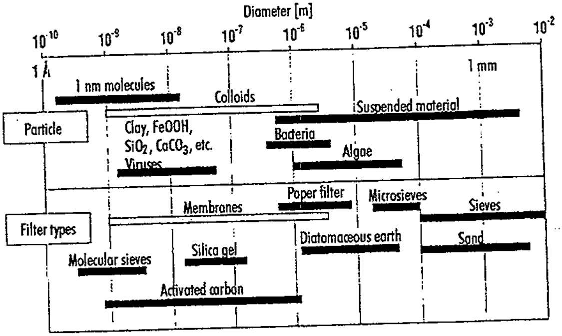

Figure 10. Size distribution of particular water components, and for various filter types of differing pore sizes, modified according to Stumm *[62]*.

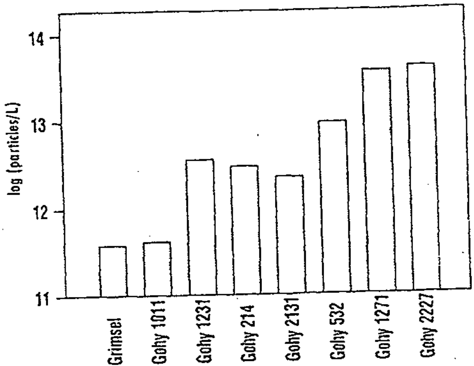

Figure 9. Colloid particle concentrations in various groundwaters from Gorleben (Gohy) and Switzerland (Grimsel). The values, determined by PALS, are normalized to a particle diameter of 100 nm *[56]*.

It shows that particles smaller than 30 nm, which are measurable only with much difficulty, comprise the predominant mass fraction of the colloid.

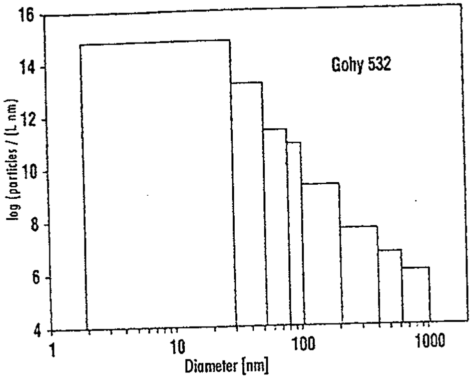

Figure 11. Size distribution of the colloids in a Gorleben groundwater *[56]*.

3.2. Geochemical interaction.

The question of what roles the natural colloids play as carriers for radionuclides is still very unclear. The mobility of the natural colloid in a fissured or porous matrix may be higher than in the aqueous medium or may be considerably lower due to a filtration effect. A distinction between mobile and non-mobile colloids may be obtained only individually for the particular aquifer system. Because of this, site-specific studies in the area of the repository are necessary to clarify this question.

As has already been discussed above, (see Fig. 2), the definition of a "practical" solubility of the transuranic elements in a particular aquatic solution is completely frustrated because of the formation of pseudocolloids. The same difficulty occurs in the determination of the geochemical sorption coefficients *Rs* of a transuranic ion. This coefficient is usually interpreted as the *Kd* value (cm^3/g) and is often used as a physical parameter for quantifying the retention process of radionuclides in the natural environment. A typical example is shown in Figure 12 *[15]*, in which the sorption coefficients *Rs* of Cm(III) after ultrafiltration are plotted for the same groundwaters as in Figure 2. As in Figure 2, the *Rs* values are displayed in a log-log plot against the pore size of the filter used for the ultrafiltration. The *Rs* value for the non-saline groundwater Gohy-1061 depends on the pore size and varies by 2.5 orders of magnitude. In contrast to this, and in agreement with the solubility of Am, the sorption coefficient for Cm in the strongly saline Gohy-2122 shows only a small dependence on the pore size employed.

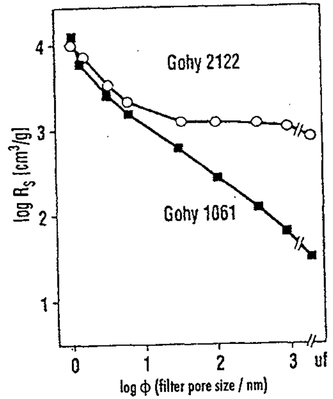

Figure 12. Sorption coefficients *Rs* of Cm^{3+} in a non-saline (Gohy-1061) and a saline (Gohy-2122, 2.5 M NaCl) groundwater from Gorleben, as functions of the pore size used for phase separation by ultrafiltration (uf: unfiltered) *[15]*.

When natural colloids are present in the aquatic system, a three-component system of interactions must be considered for the migration of the transuranic elements:

(1) the pure transuranic solution consisting of ionic, molecular, and polynuclear species that are well-defined by thermodynamics;

(2) colloids, which are made up of mobile and non-mobile fractions, and which may be considered as dissolved solids, and

(3) the actual non-mobile solid material of the geomatrix.

A schematic diagram of this three-component interaction is shown in Figure 13, in which the colloids are shown as simple spheres, enlarged for clarity. In an actual aquifer system, the apparent phase boundary between solution and solid is variable and its value depends on the mobility of the colloid present. This phenomenon is the actual basis for the difficulty of determining the migration behavior of the transuranic elements. Further investigations are still needed to elucidate and quantify this phenomenon.

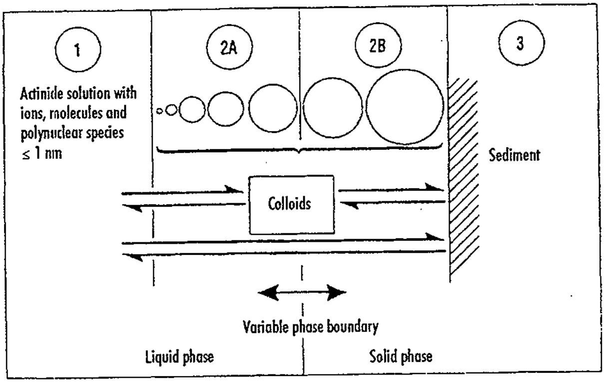

Figure 13. Schematic representation of the phase boundary between liquid and solid phases in a natural aquifer system containing colloids *[10]*.

4. SPECIATION OF AQUATIC TRANSURANIC COMPOUNDS.

The expression "speciation" here means the characterization of the chemical and physical state of the transuranic elements in the natural environment. Most importantly, knowledge of the transuranic species in a particular aquatic system gives insight into the submicrochemistry of these elements in the multicomponent system. Therefore, this is an important prerequisite for predicting the long-term behavior of the transuranic elements and, thus, the safety analysis of the repository for them. A method of speciation with the greatest possible sensitivity not only makes it possible to estimate the migration behavior correctly, but [it] also helps to verify the applicability of laboratory results, such as thermodynamic data, solubilities, retention phenomena, colloid formation, etc., to the natural system. Moreover, quality assurance of the various safety models requires satisfactory validation from laboratory experiments. Direct speciation of the transuranic elements is regarded as the most important method.

The slight solubility of most transuranic compounds in natural aquatic systems ($<10^{-6}$ mol/L, except for An(V)) demands a very sensitive speciation method. Chemical speciation methods *[52, 63-65]* exhibit the extremely high sensitivity of radiometric methods, but may be applied only to determining the oxidation states that are present, not the form of complexation. All chemical methods require pretreatment of the sample, such as dilution, evaporation, pH adjustment, etc. This process may cause the redox equilibrium to shift and thus change the distribution of the species in the original sample. This basic weakness of all chemical speciation methods diminishes the reliability of their results.

Optical spectroscopy of transitions within the non-filled 5f shell provides a direct, interference-free method for speciation for the transuranic ions. [The 5f shell] not only is sensitive to the oxidation state, but also provides information about chemical coordination *[66]*. Of course, conventional absorption spectroscopy does not attain the required sensitivity. Consequently, various highly sensitive laser spectroscopic methods have been developed and applied in recent years *[11, 12]*. The methods of photothermal absorption spectroscopy, such as laser-induced photoacoustic spectroscopy (LPAS) *[11]* and "thermal lensing" spectroscopy (TLS) *[67]* are applicable for most of the oxidation states that exist for the transuranic elements; the detection limit for Am(III) is 10^{-8} mol/L. Time-resolved fluorescence spectroscopy (TRLFS) *[12]* is only applicable to a few transuranic ions, but is distinguished by an extremely low detection limit (Cm(III): 10^{-12} mol/L *[68]*, see Fig. 6). Photoacoustic detection of scattered light (PALS) *[12]* has been developed for quantification of colloids. The use of laser spectroscopic methods for speciation of transuranic ions is experiencing further development.

5. SUMMARY.

In a geological repository for long-lived radioactive wastes, such as actinides and certain fission products, most of the stored radionuclides remain immobile in the particular geological formation. If any of these could possibly become mobile, only trace concentrations of a few radionuclides would result. Nevertheless, with an inventory in the repository of many tonnes of transuranic elements, the amounts that could disperse cannot be neglected. A critical assessment of the chemical behavior of these nuclides, especially their migration properties in the aquifer system around the repository site, is mandatory for analysis of the long-term safety. The chemistry required for this includes many geochemical multicomponent reactions that are so far only partially understood and [which] therefore can be quantified only incompletely. A few of these reactions have been discussed in this paper based on present knowledge. If a comprehensive discussion of the subject is impossible because of this [lack of information], then an attempt to emphasize the importance of the predominant geochemical reactions of the transuranic elements in various aquifer systems should be made.

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