SIGNIFICANCE OF ACTINIDE CHEMISTRY FOR THE LONG-TERM SAFETY OF WASTE DISPOSAL

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A geochemical approach to the long-term safety of waste disposal is discussed in connection with the significance of actinides, which shall deliver the major radioactivity inventory subsequent to the relatively short-term decay of fission products. Every power reactor generates transuranic (TRU) elements: plutonium and minor actinides (Np, Am, Cm), which consist chiefly of long-lived nuclides emitting alpha radiation. The amount of TRU actinides generated in a fuel life period is found to be relatively small (about 1 wt% or less in spent fuel) but their radioactivity persists many hundred thousands years. Geological confinement of waste containing TRU actinides demands, as a result, fundamental knowledge on the geochemical behavior of actinides in the repository environment for a long period of time. Appraisal of the scientific progress in this subject area is the main objective of the present paper.

Following the introductory discussion on natural radioactivities, the nuclear fuel cycle is briefly brought up with reference to actinide generation and waste disposal. As the long-term disposal safety concerns inevitably with actinides, the significance of the aquatic actinide chemistry is summarized in two parts: the fundamental properties relevant to their aquatic behavior and the geochemical reactions in nanoscopic scale. The constrained space of writing allows discussion on some examples only, for which topics of the primary concern are selected, e.g. apparent solubility and colloid generation, colloid-facilitated migration, notable speciation of such processes, etc. Discussion is summed up to end with how to make a geochemical approach available for the long-term disposal safety of nuclear waste or for the performance assessment (PA) as known generally.

KEYWORDS : Actinides, Aquatic Chemistry, Colloids, Safety of Waste Disposal

1. INTRODUCTION

Nuclear energy makes the resourceful generation of electricity available for sustaining our well-being. This benefit is however counterbalanced by side effects, i.e. the extensive safety measures for operation and the generation of long-lasting radioactive elements. Use of every energy resource has a lasting aftereffect in the environment, for example, use of fossil resource produces CO_2, NO_x, SO_2 and harmful aerosols and also exploiting photovoltaic solar energy generates substantial chemical waste in the course of material production and afterwards [1]. As a matter of fact, there is no "clean" energy available for the industrial development. Likewise, exploiting nuclear energy generates a lasting radioactivity inventory that has to be dealt with utmost precaution and subsequently disposed safely in a geologic confinement for many hundred-thousands years [2].

The long-lasting radioactivity inventory of spent fuel from nuclear power plants (NPP) is mainly attributed to actinide isotopes, i.e. ^{237}Np, ^{239,240}Pu and ^{241,243}Am, after the adequate decay of the major fission products, i.e. ^{90}Sr and ^{137}Cs for a period of about 200 years or somewhat over [3]. In spent fuel, the atomic content of these actinides is relatively small, about 1% or less, but their radioactivity inventory is prevalent up to a million year period and beyond [3]. Therefore, insightful knowledge on the chemistry of actinides is indispensable not only for nuclear fuel reprocessing but also for safe disposal of waste, either direct disposal of spent fuel or indirect disposal of processed waste only. For obvious reasons, the chemistry of actinides relevant to the safety assessment of waste disposal is fundamentally different from that involved in fuel reprocessing [4,5]. While the former is engaged in the nano-scale chemistry in the multi-component geological environment at near neutral pH, the latter entails the macro-scale chemistry in strong chemical media with remote handling systems. Since in natural aquatic media of near neutral pH the solubility of actinide is in general very low [6], the nanoscopic chemical speciation is inevitable for appraising their chemical behavior.

The present paper deals with the radiochemical aspect

of nuclear waste disposal, primarily relevant to the long-term safety assessment. A shared wisdom lays emphasis on that the sustained exploitation of nuclear energy stipulates a sound solution for the long-term safety of waste disposal. Answer to such an issue can only be sought-after fundamental knowledge on the actinide chemistry in natural aquifer systems. Because of the complexity of aquatic chemistry [4,5], particularly trace actinides eventually involved, the aquatic actinide chemistry has experienced a tedious development since the monitoring of fallout Pu in the natural environment in 1960/70s [7]. Nonetheless, in the last two decades a worldwide growing interest is attended to the aquatic actinide chemistry in conjunction with the safety-assessment of nuclear waste disposal [8,9]. In the course of time, various nanoscopic speciation methods have been developed [10-13] and hence insightful knowledge on the migration behavior of trace actinides in a variety of aquifer systems has been accrued up to date. The present paper summarizes the recent knowledge on the aquatic actinide chemistry pertinent to the long-term safety assessment of nuclear waste disposal. For the reason of space constraints, discussion concentrates on notable examples only.

2. ACTINIDES IN THE ENVIRONMENT

Sources of actinides in the environment can be divided into four categories: natural occurrence, nuclear technology, nuclear weapon testing and accidental re-entry of satellite isotope batteries.

Natural occurrence is well known to be Th and U, which are wide spread in lithosphere as well as in ocean. Estimated amounts of both elements, together with natural radioactive ^{40}K, are illustrated in Fig. 1, which provides the total activity inventories in lithosphere and ocean [14,15]. Considered for calculation are mother isotopes: ^{232}Th and ^{238}U only, which amount thus to 1.8×10^{14} and 4.7×10^{13} tons, respectively. Distribution ratios of three elements in ocean relative to lithosphere appear to be about 1.2×10^{-3} for ^{40}K, 9.5×10^{-5} for U and 3.9×10^{-7} for Th. These numbers reflect the migration of each element in the course of geologic time scale in agreement with each oxidation state: K(I), U(VI) and Th(IV) or to each charge state: K^+, UO_2^{2+} and Th^{4+}, respectively. The distribution ratio is an instructive sign of the long-term chemical behavior of each element concerned. To the natural radioactivity inventory, a comparison can be made for the total radioactivity of long-lived actinides produced worldwide, i.e. 5×10^{19} Bq, in spent fuel accumulated until 2005 [3]. This number indicates that an activity fraction of 4×10^{-5} (40 part per million) has been hitherto produced from the worldwide NPPs operation relative to the total natural Th and U activity.

Naturally occurring transuranic element is mainly ^{239}Pu in an extremely small amount, which is produced by neutron capture in uranium ores. The natural content of ^{239}Pu relative to uranium is in the range of $10^{-11} - 10^{-12}$ [4]. However, in volcanic rocks the occurrence of ^{239}Pu appears many orders of magnitude higher: $4.7 \times 10^{-9} - 1.7 \times 10^{-5}$ [4]. The cause for this is not yet known.

Main anthropogenic source, particularly of plutonium

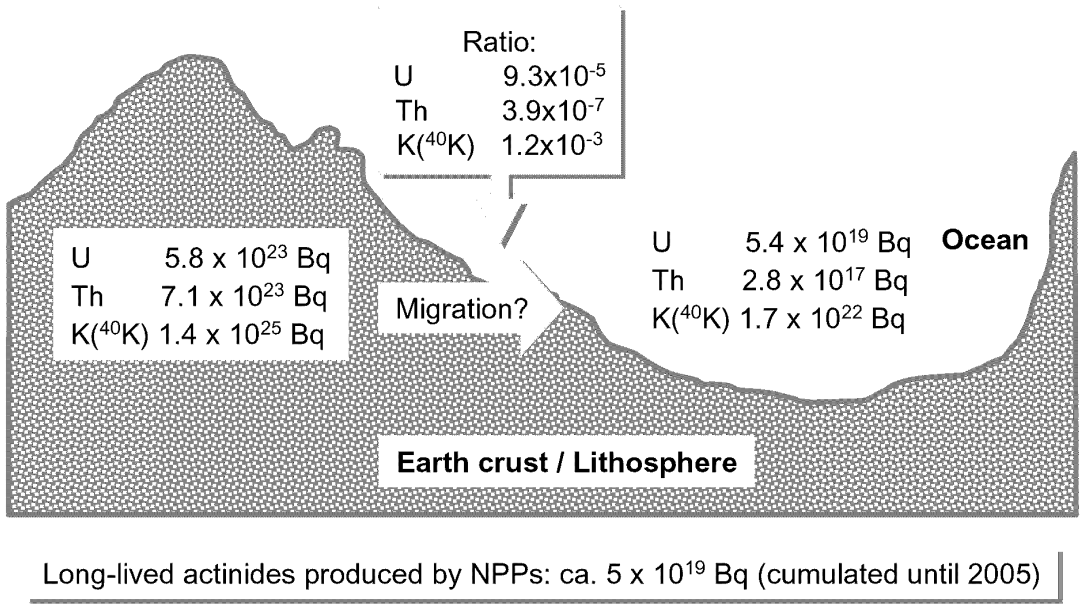


Fig. 1. Natural Radioactivities (^{238}U, ^{232}Th, ^{40}K) in Lithosphere and Ocean, and Element Specific Ratios Between the Two Compartments. Also Given is the Anthropogenic Alpha-emitting Actinides Generated from Worldwide NPPs Until 2005

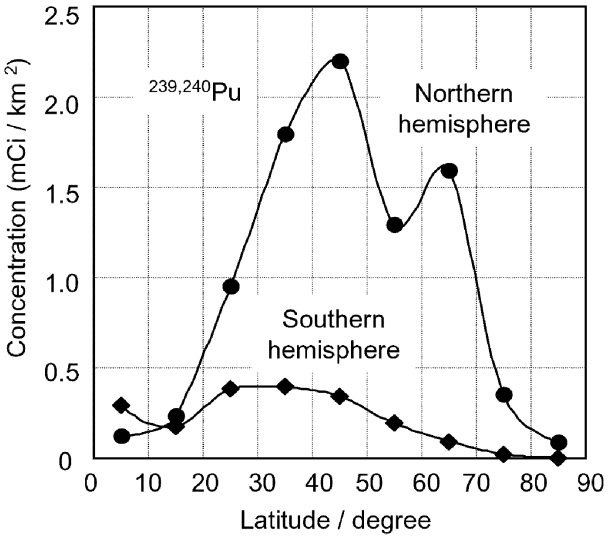


Fig. 2. Distribution of Fallout ^{239,240}Pu in Northern and Southern Hemispheres as a Function of the Latitude

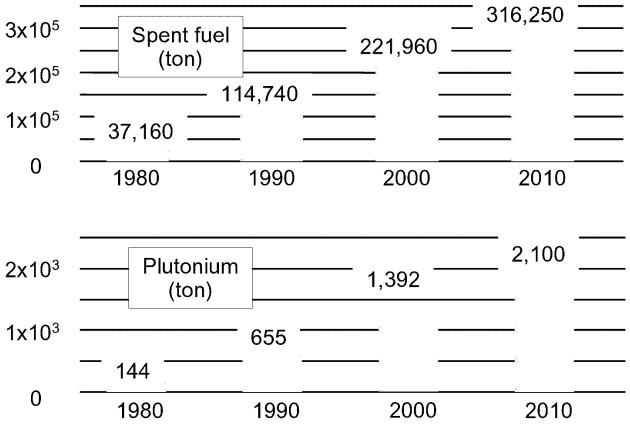


Fig. 3. Worldwide Accumulation of Spent Fuel and Plutonium Produced from NPPs

spread widely in the environment, is nuclear weapon testing. According to announced nuclear tests that recapitulate approximately 230 Mt of fission yield, Harley [16] estimated about 360 kCi of ^{239,240}Pu, corresponding to about 4,200 kg Pu and lesser amounts of other transuranic elements that might be introduced into the atmosphere. Another estimation made by Hardy et al. [17] is 480 kCi ^{239,240}Pu, equal to around 5,500 kg Pu, which is based on the assumption of a worldwide distribution (on the surface of 4.8×10^8 km^2) of ^{239,240}Pu that persists at an average level of 1 mCi/km^2.

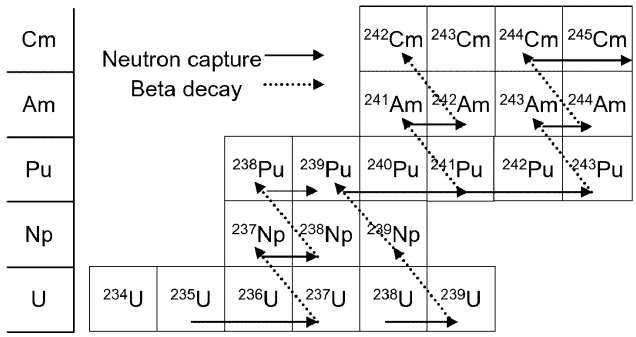


Fig. 4. Generation of Transuranic Actinides in a Power Reactor. Transcurium Elements are Produced in a Negligible Amount

Assuming a complete decay of ^{241}Pu to ^{241}Am, the amount of Am is expected to be around 1% of Pu, namely in the range of 42 – 55 kg. Global distribution of fallout plutonium was discussed comprehensively by Perkins and Thomas [18]. Fig. 2 illustrates the latitude dependent distribution of fallout plutonium [18]. As an example, in the lake Michigan (Chicago) a total amount of fallout ^{239,240}Pu deposited until 1977 was estimated to be 130 Ci [19], equivalent to 1500g, from which expected was a water concentration of 1.3×10^{-15} M. In contrast, an actual water concentration was found at 2×10^{-17} M. The difference suggests a distribution of the major fallout Pu (98.5%) into sediment, thus immobilized. The global distribution of fallout Pu is about 4 tons, or somewhat more, but as shown in the lake Michigan, its concentration in the hydrosphere is over million times lower than the plausible hazard-level to human life. Fortunately, the atmospheric weapon testing has been stopped-up since the last Chinese explosion in 1976 [18].

Another plutonium (^{238}Pu used for the isotope battery) to be found in the environment is attributed to three space flight aborts [20]. One of the three was burnt-up on re-entry in the atmosphere and dispersed in the upper atmosphere of the southern hemisphere in 1964 (SNAP-9A: 17 kCi ^{238}Pu). Another was recovered (34.4 kCi) and the last one remains in the Pacific Ocean (44.5 kCi). The advanced technology of today prevents burn-up on re-entry of such an isotope battery in the atmosphere.

A large amount of actinides are produced from world-wide commercial nuclear power plants, which add up to 440 for the moment and produce the electricity of around 2,400 TWhe per year, i.e. about 16% of the world electricity production [21]. Over the last two decades, the number of NPP has been continuously increased, consequently the amount of spent fuel cumulated steadily as shown in Fig. 3 [22-24]. According to this figure, the accumulation of spent fuel until 2005, whether reprocessed partly or not, comes to about 270,000 tons, which contain roughly 1750

tons of Pu. Additionally, the minor actinides comprising Np, Am and Cm are also produced, as a sum equivalent to about 10% of Pu. The production pathways of Pu and minor actinides by neutron capture and beta decay are shown in Fig. 4, in which relatively long-lived and very long-lived nuclides are marked by gray background. The amount of long-lived actinides produced until now adds up approximately to 5×10^{19} Bq (cf. Fig. 1) [3], from which a part of Pu has been recycled as a MOX (mixed U/Pu-oxide) fuel in some European countries and Japan. It is to note that once-through recycle reduces the worldwide Pu inventory only a little and its significant reduction entails multiple recycling [23,24]. All actinides hitherto produced from NPPs are not environmentally exposed but confined safely in the spent fuel storages or in the reprocessing plants.

3. NUCLEAR FUEL CYCLE AND WASTE DISPOSAL

3.1 Generation of Spent Fuel and Actinides

Development of a nuclear fuel cycle started shortly after the discovery of ^{239}Pu in 1941 by Seaborg et al. [25], at first with heterogeneous phase separation by precipitation and shortly later with homogeneous phase separation by solvent extraction [26]. The latter technology has been spread to many countries and refined continuously in each country involved. A simplified scheme of the conventional fuel cycle is shown Fig. 5 (left side). Each country with own option has adopted one or both of two different schemes of waste disposal policy. Direct disposal without recycling is optioned by many countries to dispose spent fuel permanently after apposite cooling. Another direct disposal reserves a retrieval option for the possible recycle by the future generation. Indirect disposal after recycling abides to recover Pu and U for subsequent use as fuel (MOX) and dispose all the rest as waste in different categories separately. The latter scheme recovers over 99% of Pu for recycle and as a result the waste to be disposed of contains all minor actinides (MA) with a small amount of Pu (< 1% of total) and fission products (FP) as well as activation products (AP). Some European countries adopt a combined option of direct and indirect disposal. Regardless of any fuel cycle optioned, the long-term safe disposal of nuclear waste is inevitable.

To minimize a long-lasting safety predicament of high-level waste disposal, a new technical option is under investigation in a number of countries. The preference is to burn-up long-lived radioactive nuclides, particularly actinides, in a high neutron flux, while allowing the generation of energy at the same time [27-30]. The concept is called the accelerator driven system (ADS), which generates a high neutron flux by spallation of a heavy element (e.g. Pb) induced by energetic protons from an accelerator. Operation of the system demands a new generation of actinide separation techniques (partitioning) and also development of actinide fuel for burning via neutron-induced transmutation. An advanced accelerator for sustained operation is of course an essential prerequisite for implementing the ADS concept. As sketched in Fig. 5 (right side), the ADS nuclear fuel cycle is going to generate, besides fission products, actinide-bearing waste that has to be also disposed of inevitably. Different from the conventional fuel cycle, the ADS cycle is anticipated to generate waste containing a less amount of actinides. Nonetheless, the main concern of the long-

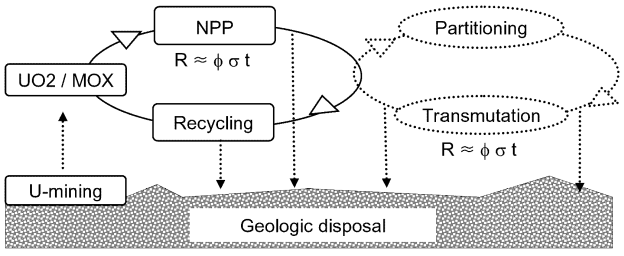


Fig. 5. Nuclear Fuel Cycles: a Conventional Fuel Cycle (left) and an Accelerator Driven System (ADS) Cycle (right). Waste Disposal is Inevitable for both Cycles

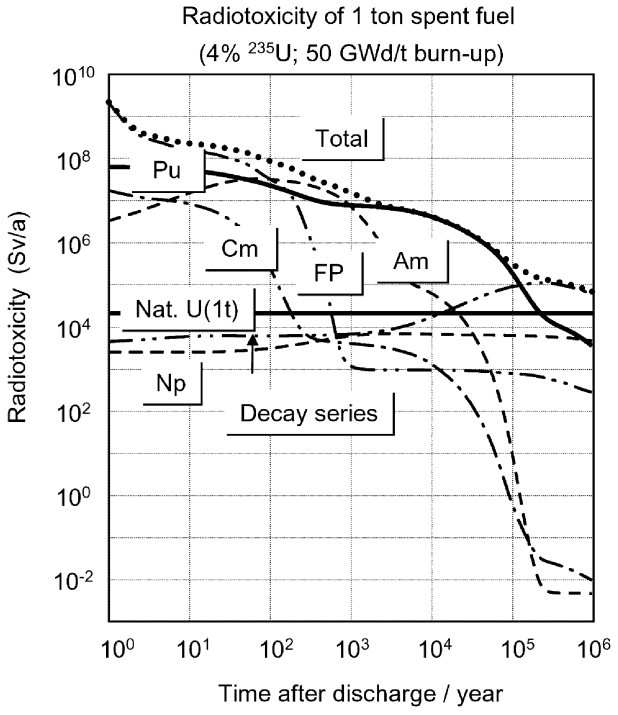


Fig. 6. Radiotoxicity (Sv/a) of Different Elements in 1 ton Spent Fuel as a Function of Time. A Com-parison is Made to 1 ton Natural Uranium Including Decay Chains

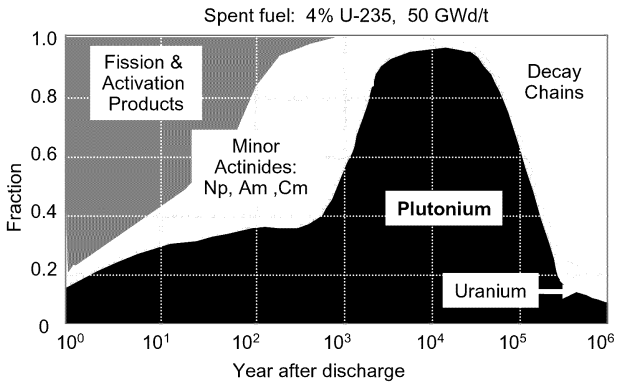


Fig. 7. Relative Fraction of Radiotoxicity of Different Components in Spent Fuel as a Function of Time

term disposal safety shall be inherent in the ADS cycle as well [29,30].

Radioactivity inventories (given as Sv) of 1-ton spent fuel (UO_2 with initial 4% ^{235}U) discharged after 50 GWd/t burn-up are illustrated individually for Pu, MA and FP in Fig. 6 as a function of the decay time [3]. For the purpose of comparison, the radioactivity inventory of 1-ton natural U in equilibration with daughter nuclides is also displayed. The decay time of the total inventory of spent fuel requires over a million year to reach the equivalent dose of natural U. The long-term inventory is prevailed by Pu, followed by Am. Fission products dominate at the beginning but fade away after a few hundreds years. To visualize individual fractions of the radioactivity inventory, the relative fractions are illustrated in Fig. 7 as a function of the decay time for Pu, MA, U, FP+AP and decay chains. The significant contribution of Pu to the total radioactivity inventory is obvious from the first year of spent fuel discharge until many hundred-thousands years. Additionally MA and decay chains unleash a foremost contribution after Pu. As is apparent from Fig. 7, the long-term safety of spent fuel disposal is entirely related to actinides generated within. Therefore, either direct or indirect disposal requires indeed a better understanding of the long-term geochemical behavior of actinides in a given repository.

To provide a comprehensible picture of the radioactivity inventory of spent fuel from a commonly operating PWR (pressurized water reactor) at present, the amounts of total and alpha activities are shown in Fig. 8 with ensuing numbers. For this purpose, the estimation is made for 1-ton of spent fuel (UO_2) after 50 GWd/t burn-up with an initial 4% ^{235}U [3]. At one year after discharge, FP and AP control the major activity, which emit beta and gamma radiation mostly. With time elapsing, the ratio of total to alpha decreases rapidly. Alpha emitters, predominated by actinides, decay slowly. After cooling for 200 years, the total activity decreases down to 0.4% of the initial level, while the alpha activity decays down to 21%. Afterwards, the total decay rate becomes slower due to long-lived actinides. A mid-term interim storage of spent fuel for such a time period under well-controlled conditions is therefore favored before optioning final disposal.

The NPP operation generates another kind of waste that is subject to conditioning on the spot for subsequent disposal. The operation waste is originated from cooling-water purification, off-gas cleaning, maintenance repair (debris), contaminated garments and some others. They contain relatively short-lived radionuclides of mostly beta and gamma emission. Fuel defect may set free some traces of long-lived radionuclides but such a case appears seldom. Generation of the operation waste is displayed in different

After 1 year		
Total activity	1.1×10^{17} Bq/t	100%
Alpha activity	1.2×10^{15} Bq/t	100%

After 20 years		
Total activity	1.4×10^{16} Bq/t	12%
Alpha activity	5.0×10^{14} Bq/t	42%

After 200 years		
Total activity	4.3×10^{14} Bq/t	0.4%
Alpha activity	2.5×10^{14} Bq/t	21%

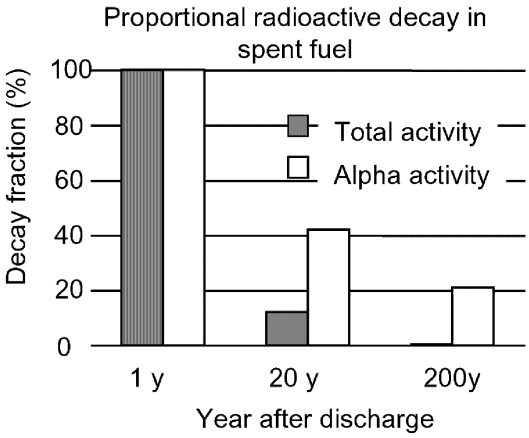


Fig. 8. Radioactivities (total and alpha emissions) of 1 ton Spent Fuel (4% ^{235}U; 50 GWd/t burn up) in Numbers after Different Cooling Periods. Also Shown are the Decay Proportionalities of Total and Alpha Activities

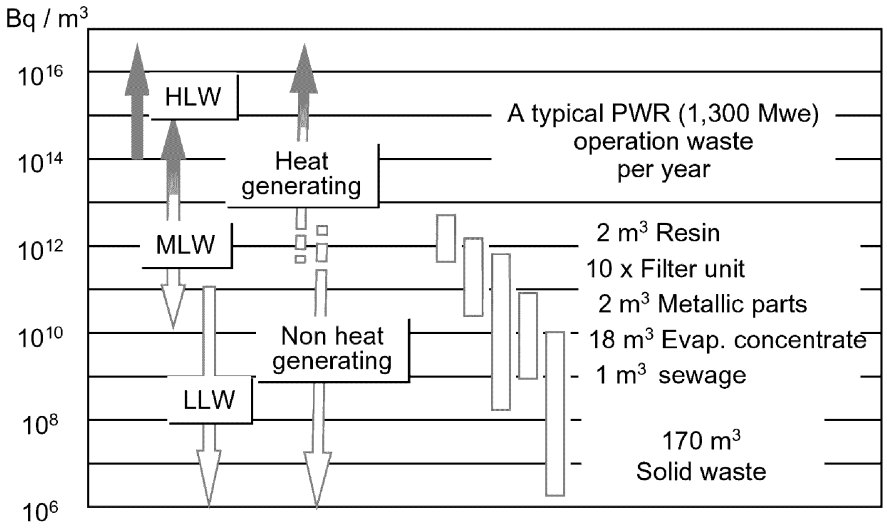


Fig. 9. Classifications of Nuclear Waste and Typical Operation Waste per Year from a PWR (1,300 MWe capacity) in Germany

categories in Fig. 9 for a typical PWR of 1,300 MWe capacity in Germany [31]. They are compared to general classifications of nuclear waste: high-level (HLW), medium-level (MLW) and low-level waste (LLW), or heat-generating and non-heat-generating waste (further refined classifications are left out). The latter classification is applied in Germany in quest of temperature difference to the geologic surrounding at 3°C. According to the two classifications, the operation waste belongs to a combined category of MLW and LLW, on the other hand, close to non-heat-generating waste. The operation waste as a whole appears voluminous, resulting in about 200 m^3 per year. This volume is in general reduced, as shown in Fig. 10, by high-pressure compaction or incineration, or by both processes combined [31]. The final product can be conditioned into an engineered barrier (normally cement) for long-term immobilization. The most advanced process envisaged in Korea resorts to a reduction of waste volume by plasma-incineration followed directly by on-line vitrification of resulting ashes. Disposal of the operation waste is subject to the medium-term disposal safety only, since there is no long-lived actinides involved; if any, only an inconsequential trace amount.

The spent fuel discharged every year from a PWR of 1,300 MWe capacity with 50 GWd/t burn-up is shown in Fig. 11, in which the radioactivity inventory is compared with that of the operation waste [3]. Ratio of both inventories (operation waste vs. spent fuel) is about 4×10^{-6} (4 parts per million). As the operation waste does not contain actinides; if any, only a trace amount, its disposal is practiced in many countries at the sub-surface under surveillance.

Radiation exposure of a power reactor is extremely small, as compared to different kinds of radiation exposures

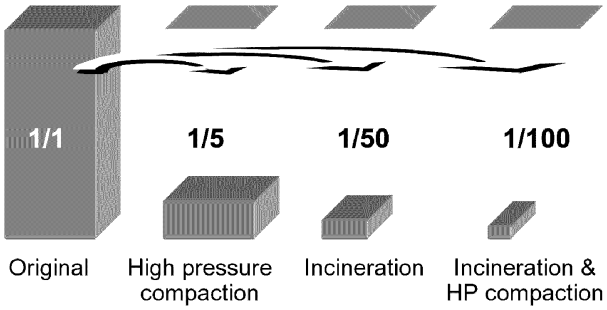


Fig. 10. A Typical Volume Reduction Procedure of Operation Waste from Power Reactors in Germany

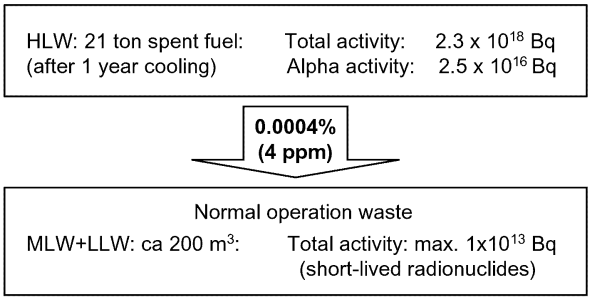


Fig. 11. A Comparison of the Radioactivity of Yearly Discharged Spent Fuel with that of Operation Waste from a Power Reactor of 1,300 MWe Capacity in Germany

shown in Fig. 12 [24]. For the equivalent energy generation, a coal power plant has the same radiation exposure as a nuclear power reactor. This figure illustrates that the radiation exposure from both types of energy generation is on average 1000 times lower than natural and other radiation exposures we are surrounded.

3.2 A Multi-barrier System for the Disposal Safety

The major radioactivity inventory from nuclear energy generation belongs to HLW, which is divided into two categories: spent fuel optioned for direct disposal and vitrified mainstream waste from fuel reprocessing which contains MA and FP+AP, including a minor amount of Pu ($\leq$ 1% of total). Both types of HLW contain actinides, which persist in the primary radioactivity inventory for permanent disposal (cf. Fig. 7). Accordingly, the long-term safety assessment entails fundamental knowledge on the aquatic actinide chemistry, since, in the case of unrehearsed water permeation into a repository, the migration of actinides probably takes place in the course of time elapsing.

The final disposal of nuclear waste shall be undertaken in the geologic formation of non-water permeation or of least permeation, to which belong clay formation [32] and salt dome [33]. A hard-rock formation enhanced by a geo-engineered barrier can also be taken into consideration [34]. Whatever the repository site is favored; a multi-barrier concept is generally optioned, which comprises engineered, geo-engineered and geological barriers [35]. A conceptual sketch of multi-barriers is shown in Fig. 13. Nuclear waste is contained at the onset in an engineered barrier, which as a host matrix (e.g. cement) immobilizes radionuclides chemically for the case of MLW and LLW, or which encases conditioned HLW (either vitrified HLW from reprocessing or compacted spent fuel) physically in massive metal containers. The engineered barrier is so conceived that, even in the case of accidental water permeation, the self-sustained barrier prevents the release of radionuclides for many hundreds or more years. The engineered barrier shall be surrounded by geo-engineered barrier (e.g. Bentonite), which then functions for preventing water permeation as well as for immobilizing dissolved radionuclides by sorption. Such a barrier is particularly favored for the hard-rock formation, where fracture channels may conduct water penetration. Any geologic formation overlying the core part of a repository performs as a geological barrier against the possible radionuclide migration; for obvious reasons, one formation is more effective than another.

Supposing that all barrier-systems could function effectively, as envisaged, for upholding the immobilization of all radioactive elements for a desired time period, only appropriate engineering enterprise would be sufficient enough for preserving the long-term safety of nuclear waste disposal. Such an expectant view has been the accepted wisdom in the nuclear community. However, various uncertainties involved in any possible forecast for the geologic evolution of a given repository site are not minimal and hence cannot be underestimated, particularly where the heat generating radioactive materials are disposed. Major uncertainties are concerned with not the macroscopic material behavior but the nanoscopic chemical behavior of individual radioactive elements in nuclear waste, once they become in contact with accidentally permeated water and thus exposed to geochemical reactions that develop possible migration. Therefore, a deep insight into such nanoscopic geochemical behavior of radioactive elements, particularly long-lived actinides, shall facilitate the proper appraisal of the long-

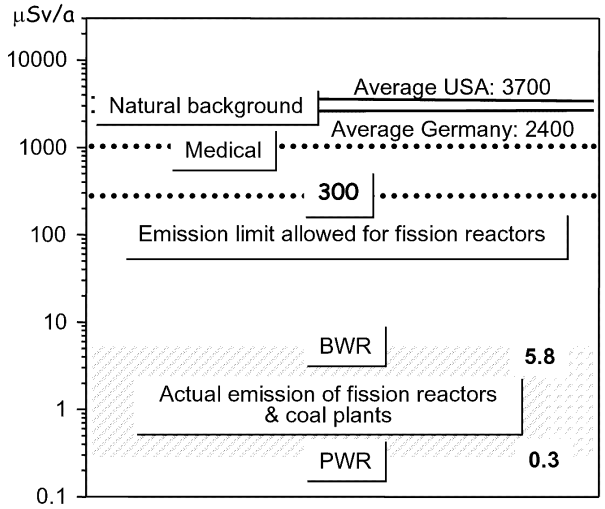


Fig. 12. Relative Illustration of Natural and Anthropogenic Radiation Exposures per Year

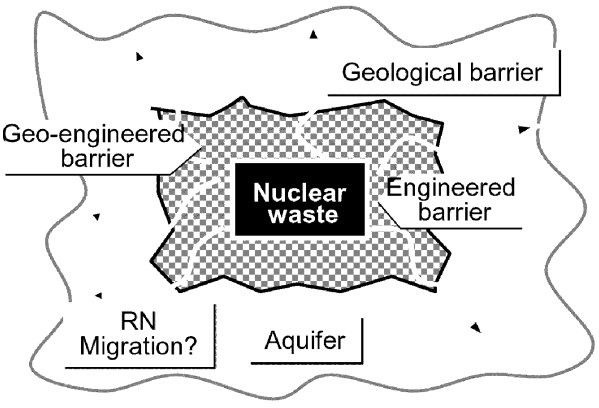


Fig. 13. Conceptual Illustration of a Multi-barrier System: Engineered, Geo-engineered and Geological Barriers

term safety of nuclear waste disposal. Essential exploitation of the aquatic actinide chemistry indispensable for this purpose is briefly discussed below.

4. ACTINIDE CHEMISTRY IN NATURAL AQUATIC SYSTEM

4.1 Fundamental Chemical Properties of Actinides

A commercial power reactor generates in its fuel, either UO_2 or $U(Pu)O_2$ (MOX), transuranic elements: Np, Pu, Am and Cm by neutron capture reactions (cf. Fig.4). Actinides (An) beyond Cm are produced only a negligible amount. Aquatic chemistry of actinides pertinent to the waste disposal safety is therefore restricted to aforementioned five elements. Chemical states of these actinides, together with elements associated with their decay chains, are given in Fig. 14 as a simplified form. Chemical feature of primary importance is the probable oxidation state of each element, which varies from trivalent to heptavalent. Under normal aquatic conditions, the oxidation state varies up to hexavalent only, as indicated with gray background. The heptavalent state of either Np or Pu can only be stable in highly alkaline media. Charges of various oxidation states in aqueous medium are as follows [4,5]:

$$An^{3+}(III),\ An^{4+}(IV),\ AnO_2^{+}(V),\ AnO_2^{2+}(VI) \qquad (1)$$

The aquatic chemical properties of actinide ions are largely governed by their effective charge states, which are somewhat different from the above-given nominal charge state. For example, the hydrolysis and complexation undergoes the following order:

$$An^{4+}(IV) > AnO_2^{2+}(VI) > An^{3+}(III),\ > AnO_2^{+}(V), \qquad (2)$$

The fact that the AnO_2^{2+} has an effective charge greater than the An^{3+} ion may be ex-plained by a linear bonding structure of the O-An-O^{2+} ion, in which the charge at the equatorial side becomes exposed. Such a structure results in the effective charge of AnO_2^{2+} and AnO_2^{+} corresponding to 3.3±0.1 and 2.3±0.2, respectively [36]. The effective charge state can be directly appraised from the hydrolysis behavior of different oxidation state. A typical example is shown below by comparing thermodynamic constants of primary hydrolysis reactions [5]:

An(III)	$Am(OH)^{2+}$	$\log\beta_{11} = 6.3 \pm 0.3$
An(IV)	$Pu(OH)^{3+}$	$\log\beta_{11} = 12.3 \pm 0.3$
An(V)	$Np(OH)^{o}$	$\log\beta_{11} = 2.7 \pm 0.2$
An(VI)	$Pu(OH)^{+}$	$\log\beta_{11} = 8.3 \pm 0.3$

The given constants reflect the hydrolysis tendency of each actinide oxidation state, which is the primary parameter for understanding aquatic chemical reactions of actinides, i.e. the higher is the hydrolysis tendency, the lower is the solubility.

The electronic state of actinides is distinguished by *5f* shells (Fig. 14), which with uniquely resolved energy levels present the distinctive spectroscopic properties [37]. Applying such properties, the spectroscopic chemical speciation of some actinides in trace concentrations is possible, especially with laser as a light source [10,11]. The spectroscopic speciation is only the possibility for the moment to appraise nanoscopic chemical reactions of actinides straightforwardly in aquatic systems.

As shown in Fig. 14, some actinides are redox-sensitive, e.g. U, Np and Pu, meaning that different oxidation states can be present depending on the redox-potential of a given aquatic system [5]. The redox-behavior of each element is governed by its pH dependent redox-potential, as can be appreciated from Fig. 15. At near neutral pH, Np is stabilized normally as a pentavalent state, if the medium is not strongly reducing. Under the same condition, Pu is expected to prevail as a tetravalent state but Pu(IV) undergoes a disproportion reaction: $2Pu(IV) \Leftrightarrow Pu(III) + Pu(V)$, which further proceeds $2Pu(V) \Leftrightarrow Pu(IV) + Pu(VI)$ and $Pu(III) \Rightarrow Pu(IV)$. The fact indicates that under certain

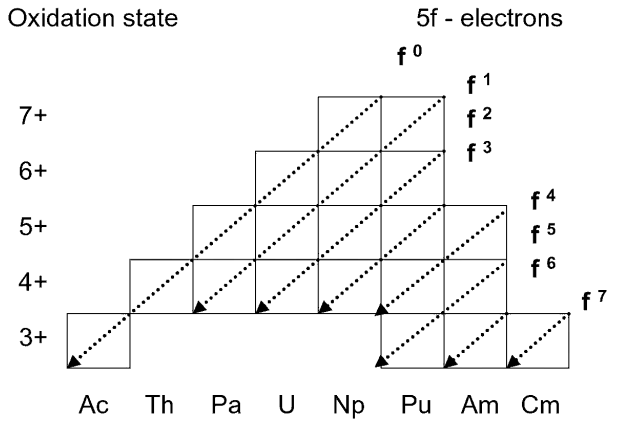


Fig. 14. Primary Chemical Properties of Actinides Involved in Nuclear Waste: Oxidation State Related to *5f* Electronic State

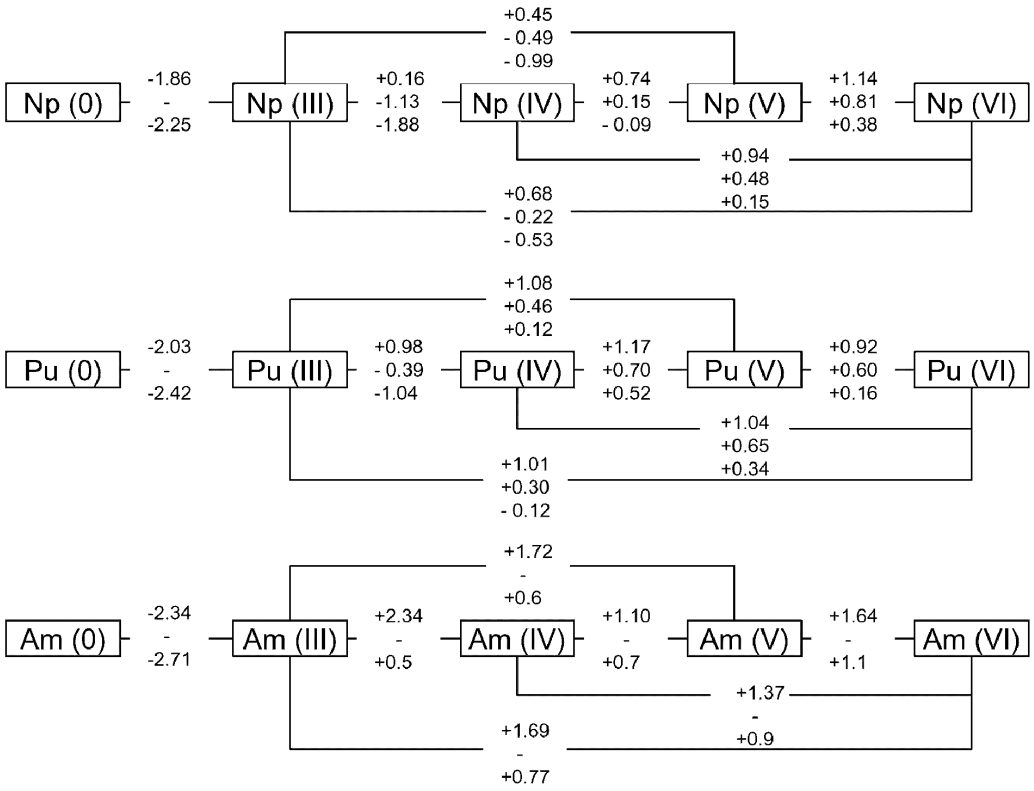


Fig. 15. Redox-potentials of Transuranic Actinides of Different Oxidation States at 1 M $HClO_4$ (upper), pH 8 (middle) and 1 M NaOH (down)

conditions, Pu may be present in solution in four different oxidation states [38]. Am is present always as a trivalent state, besides in a strong oxidizing medium, where Am(V) prevails then [39]. Under deep groundwater conditions with a low redox-potential, tetravalent is a dominating oxidation state for U, Np and Pu, while Am and Cm are stable as a trivalent state. According to the hydrolysis tendency discussed above, actinides of tetravalent are least soluble, followed by those of trivalent [40,41]. This fact implies that the disposal safety of actinide bearing waste can be best main-tained under reducing conditions of a deep geologic formation.

4.2 Aquatic Chemical Behavior of Actinides

Natural water contains a large number of metal ions as well as counter part anions, mostly in trace concentrations. Among the natural aquatic anions, some are predisposed to complex with actinides and thus stabilize them as aqueous ions [42]. Complexation increases the actinide solubility as opposed to the hydrolysis reaction. The primary complexation constants (β_{11}) for actinides of different oxidation states are comparatively illustrated in Fig. 16, which shows

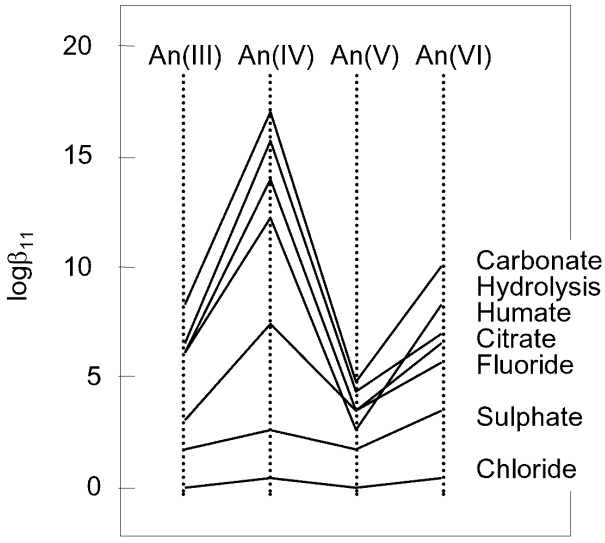


Fig. 16. The Primary Complexation Behavior (β_{11}) of Actinides of Different Oxidation States with Common Aquatic Ligands. Distinction Follows: An(IV) > An(VI) ≥ An(III) > An(V)

a general overview of the actinide behavior in aquatic systems, as characterized by each oxidation state [5]. The complexation tendency follows closely the relation depicted by Eq. 2. This figure points out the most important aquatic reactions of actinides: complexation with carbonate ion and humic acid that competes with the hydrolysis reaction. The last one controls the actinide solubility, facilitates at the same time colloid formation via oxo-bridging and/or leads to sorption onto mineral surfaces also by oxo-bridging [43]. At the same time, the hydrolysis reaction is counterbalanced by complexation, as an example, with carbonate anion [41] or with humic acid [44]. As a result, ternary complexation and colloid formation are the dominant aquatic chemical reactions of actinides.

All natural water contains aquatic colloids made of inorganic or organic-inorganic composition [45]. They are formed either by nucleation of metal ions via oxo-bridging [46], some being additionally complexed with organic ligands, e.g. humic acid [47], or by dispersion from the mineral surfaces via weathering effects [48]. Actinide ions exposed to natural water are prone to interact with ubiquitous aquatic colloids and hence become colloid-borne species [46-48]. Therefore, the appraisal of the actinide behavior in natural aquatic systems calls for the comprehension of interactions in a three-phase system: ionic, colloidal and mineral matrix phases. Potential chemical interactions of actinides in such a relationship are illustrated in Fig. 17, which makes up a distinction of mobile and immobile states:

Mobile state:

Complexed ionic state (prefigured anions)
Colloidal state

Immobile state:

Precipitate, Co-precipitate (solid solution)
Surface sorbed state

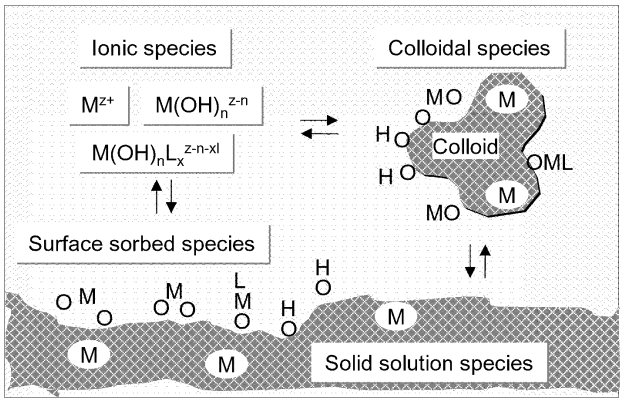


Fig. 17. Conceptual Illustration for Chemical Interactions of Actinides in Natural Aquifer Systems: Immobilization into Geomatrices and Mobilization by Ionic and Colloidal Species

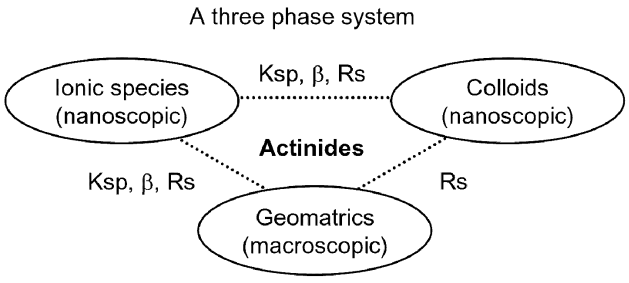


Fig. 18. Quantification of Reaction Parameters (equilibrium constants) Necessary for the Actinide Distribution in a Three Phase System of Natural Aquifers (Ksp: Solubility Product, β: Complexa-tion Constant and Rs: Distribution Ratio)

Quantification of the probable distribution of actinides in either mobile or immobile state in aquifer systems of the given repository environment is the primary task for the long-term safety assessment of nuclear waste disposal [49]. Evaluation of dynamic equilibrations can be assisted by an illustration given in Fig. 18. For quantifying the three phase interactions of actinides, it is necessary to determine the solubility product (Ksp), complexation constants (β) and surface distribution coefficients (Rs) of each actinide ion, in addition to evaluating the aquatic colloid formation. Direct in-situ determination of these parameters for each actinide ion is practically impossible. Therefore, laboratory experiments under simulated conditions are generally practiced [8,9], starting from the appraisal of solubility, distribution of solid-water interface and generation of colloid-borne actinides. Recent developments in these subject fields are briefly sketched in the following with some notable examples.

4.3 Solubility of Actinides and Thermodynamics

Once actinide-bearing waste (spent fuel or any conditioned solid-phase) becomes in contact with water, various physical and chemical processes take place in the course of time. Corrosion of surfaces leads to leaching of matrices at first, which are then followed by dispersion and dissolution of actinides. Subsequent progresses are redox-reaction, hydrolysis, complexation and colloid formation of actinides [49]. Fig. 19 presents a schematic illustration of such processes, which are anticipated as a near-field chemical progression. The entire geochemical reactions shall convert all the way through the original solid waste into various sec-ondary solid-phases as consolidated in the new environment. Under given geochemical conditions, new dynamic equilibrations

of actinides shall be established between the secondary solid-phases and solution. The solution phase contains ionic and colloidal species of actinides that may migrate in given aquifer systems. The formation of secondary phases, structuring into different minerals, is demonstrated in Fig. 20, as an example, for the HLW-glass dissolution [49,50]. The original vitrified-phase becomes converted to different mineral segments as secondary solid-phases. Therefore, the investigation on the secondary phase formation that immobilizes actinides effectively appears to be an important issue. Results may facilitate the development of a so-called intelligent engineered barrier for promoting the permanent immobilization of actinides within a given repository.

The mobile solution phase in dynamic equilibration with secondary solid phases contains ionic and colloidal species. Knowledge on the generation of such a new mobile phase is essential for the appraisal of the actinide migration probability in the near-field aquifer system (cf. Fig. 19). An example is shown in Fig. 21 for the dissolution of spent fuel in granite water [49], in which the original oxide form of spent fuel is converted to hydroxide in contact with water and hence dissolution is enhanced (cf. Fig. 23). Columns with stripes show dissolution rates of elements accounted for 200 days in leaching solution at room temperature. Dark columns belong to those in filtrate after separation of colloidal species. This figure thus demonstrates the formation of colloid-borne species in accordance with the oxidation state of each element. Monovalent Cs(I) is not incorporated into colloids, whereas divalent Sr(II) is colloidal only to a small extent. Trivalent and tetravalent actinides and trivalent lanthanides (REE) are found to be predominantly colloidal in leachate, followed in a gradual decrease by hexavalent U(VI) and then by pentavalent Np(V). Hepta-

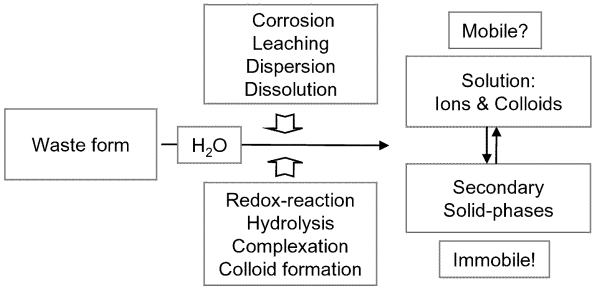


Fig. 19. Physical and Chemical Reactions of Nuclear Waste Anticipated in the Near-field Repository for a Long-term Period: Conversion of Primary Waste Form to Secondary Solid Phases and Generation of a New Mobile Phase (ionic and colloidal species)

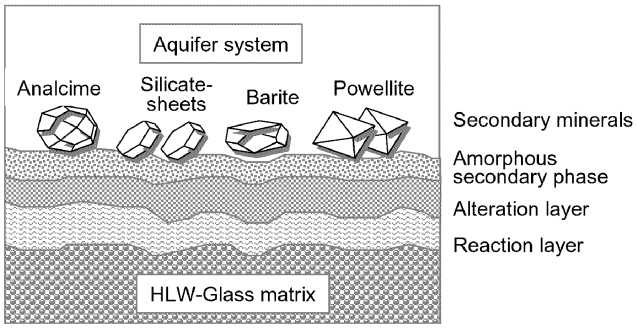


Fig. 20. Chemical Conversion of a HLW-glass Matrix to Secondary Mineral Phases in Contact with Water at the Surface (an example)

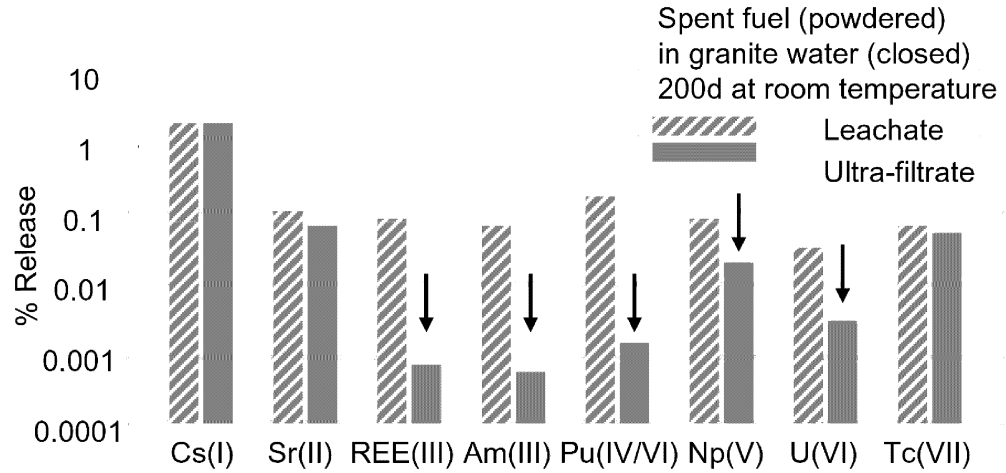


Fig. 21. Colloid Formation in Dissolution of Spent Fuel in Granite Water: Relative Released Amounts of Individual Elements after 200d in Leachate (ionic and colloidal species) and in Filtrate (ionic species)

valent Tc(VII), stable as a TcO_4^- anion, is affected little by colloid formation. In the course of conversion from oxide to hydroxide, the elements present in spent fuel are released as ionic and colloidal species.

Dissolved concentrations of Pu from spent fuel are particularly chosen for demonstration in Fig. 22 as a function of pH [51,52]. For comparison, thermodynamic solubilities of Pu(IV) and Pu(VI) hydroxides with and without the presence of carbonate ions are also presented [6]. Since the predominant Pu species in solution is colloidal, the concentration varies widely in different batches of experiment. Variation ranges three orders of magnitude and is not visibly dependent on pH. Fig. 22 demonstrates that a thermodynamic approach fails for estimating the apparent Pu(IV) solubility from spent fuel, as a consequence of colloid generation.

Further details on the dissolution of tetravalent actinides can be comprehended by the illustration presented in Fig. 23. Thermodynamic solubilities of tetravalent actinides are shown in the left side for their oxides and hydroxides [40]. The oxides, present in spent fuel or in other conditioned waste, are extremely insoluble at neutral pH, but a conversion to hydroxides by contact with water increases the solubility six orders of magnitude. At pH $\leq$ 3, An(IV) oxides in solid phase become converted in water to oxo-hydroxides, which are then modified to amorphous hydroxides at pH > 3. Accordingly the solubility increases. This process is spontaneous, if an external effect, e.g. temperature, is not experi-

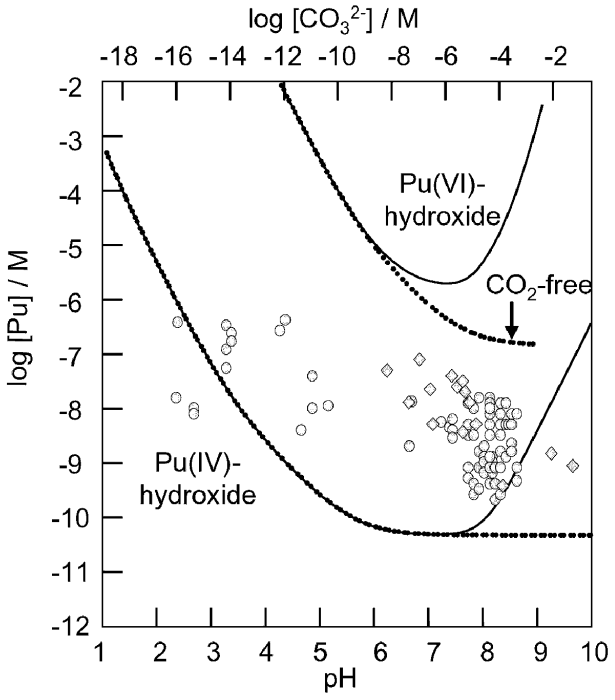


Fig. 22. Dissolution of Pu from Spent Fuel in Saline and Non-saline Groundwater as a Function of pH. A Comparison is Made to Thermodynamic Solubilities (dark and dotted lines) of Pu(IV) and Pu(VI) Hydroxides. The Prevailing Species is Found to be Colloid-borne-Pu(IV) (cf. Fig. 21)

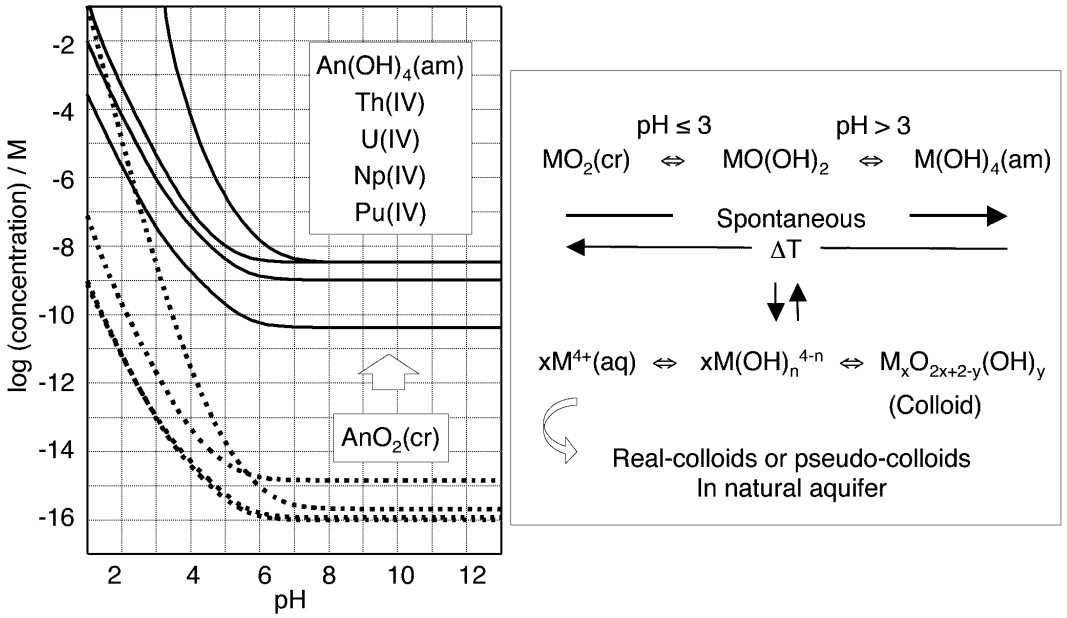


Fig. 23. Thermodynamic Solubilities of Tetravalent Actinides as Oxides (dotted lines) and Hydroxides (dark lines). Conversion of Oxide to Hydroxide takes Place in Contact with Water as Illustrated in the Right Side. The Apparent Solubility Increases with Colloid Generation

enced. In the case of $^{239}Pu(IV)$, the microscopic heat generated by alpha decay may convert its hydroxide to oxide, if a bulk solid phase is present to mount up the resulting heat. The dissolved An(IV) ion undergoes nucleation via oxo-bridging and further to colloid formation, either "real-colloid" by nucleation of identical elements or "pseudo-colloid" by aggregation of different elements [47,48]. Generation of pseudo-colloids is always expected from the waste dissolution [49,53]. The formation of colloidal species is illustrated in the right side of Fig. 23.

Different from the solubility experiment for individual actinides in laboratory systems, the dissolution of actinides from spent fuel containing various elements instigates colloid formation as is apparent from Figs. 21 and 22. The process is attributed to the aggregation via oxo-bridging among actinides (also other elements) of different oxidation states [49]. Particles composed of elements of mixed oxidation states are polarized on the surface that favors hydration and thus prevents precipitation in the trace concentration range [54]. Therefore, the colloid generation of actinides is distinctively enhanced in dissolution of waste.

As can be explained by Fig. 24, the apparent solubility of individual actinides in waste dissolution is always greater than the value available from a thermodynamic approach [53]. While quantification of ionic species of individual actinides can be made on the basis of known thermodynamic data [6], there is no possibility to assess the generation of colloid-borne actinides. As a result, the apparent solubility (including colloid-borne species) of individual actinides in waste dissolution remains as an uncertain quantity that varies directly in proportion to the amount of colloids generated [49,53]. On the other hand, the concentration level of stable aquatic colloids is constrained under given geochemical conditions. By knowing the colloid generation process, the upper level of individual actinide dissolution in a given aquifer system can be estimated as a relevant source-term for the safety assessment.

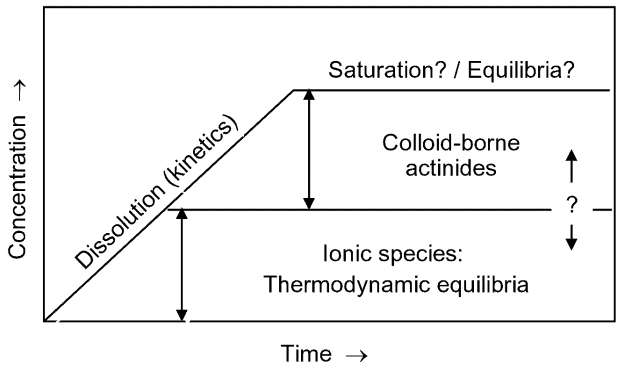


Fig. 24. Conceptual Illustration of the Actinide Dissolution in Groundwater: Formation of Ionic and Colloidal Species. Quantification Entails a Three-phase Equilibration System as Shown in Fig. 18

4.4 Source-term Assessment

Source terms for individual actinides are the essential parameters for the long-term safety assessment of a repository [55]. However, the evaluation of source terms involves large uncertainties for the reason discussed above. A thermodynamic approach hitherto practiced is therefore not satisfactory for natural aquatic systems [53]. As pointed out already in Fig. 19, knowledge on the formation of secondary solid-phases is essential for the appraisal of the new solution phase in equilibration, which comprises generation of colloid-borne actindes. Quantification of actinide concentrations in such equilibration leads in the end to the reliable source-term estimation, including both ionic and colloidal species. The long-term safety assessment (or performance assessment (PA)) practiced worldwide till now [55] has regrettably not taken into account the geochemical processes given in Fig. 19. As actinides are dissolved always as colloidal species in natural aquatic systems, definitely under near-field geochemical conditions (cf. Figs. 21-24), the source-term evaluation entails obviously the basic knowledge on the aquatic colloid formation.

4.5 Migration Behavior of Actinides

As is apparent from the above discussion, the dissolution of solid-waste delivers both ionic and colloidal species of actinides. Under normal geochemical conditions, the prevailing species are pseudo-colloids built-up by incorporation of actinides into aquatic colloids [4,5,45,47,48]. In the near-field, aquatic colloids are expected to be originated either from waste matrix dissolution as well as from dispersion of mineral surfaces. As a result, a significant amount of aquatic colloids is anticipated in the near-field, which incorporate actinides easily either by sorption onto the surface or by oxo-bridging into colloidal structure.

Apart from the colloid formation, the ionic species present in aquatic systems are predominantly hydrolyzed or complexed, thus emerging as positive or negative ions. Regardless of the charge state, they are prone to sorption onto mineral surfaces by the following process:

$$\begin{aligned} &An(OH)_nL_m^{(z-n-m)-} \Leftrightarrow An^{z+} + nOH^- + mL^{-} \text{ and} \\ &(Surface)\text{-}O^- + An^{z+} \Leftrightarrow (Surface)\text{-}O\text{-}An^{(z-1)+} \end{aligned} \quad (3)$$

As various mineral surfaces are abundant with all negatively charged oxygen at neutral pH in natural aquifer systems, the above reaction tends to proceed ultimately to the surface sorption of actinide ions following the process given by Eq. (3). Accordingly, all ionic actinide species

shall be sorbed onto mineral surfaces with fast or slow kinetics depending on the available concentration of complexing ligands (L). For this reason, the ionic actinide species are of no great consequence for the long-term safety assessment, unless they become sorbed onto aquatic colloids.

On the other hand, the colloid-borne actinides may migrate in aquifer systems without hindrance, i.e. little sorption onto mineral surfaces, since aquatic colloids, in which actinides are incorporated by stable oxo-bridging, are negatively charged,. The possible migration of colloid-borne actinides is visualized in Fig. 25. Stable and preponderant aquatic colloids are normally in the size range of < 100nm in diameter [46,56], which is much smaller than the pore dimension of aquifer systems in most cases. The formation of aquatic colloids as well as of colloid-borne actinides is therefore an important issue for the rational assessment of the actinide migration behavior. In view of that the issue is of cardinal importance for the long-term safety assessment.

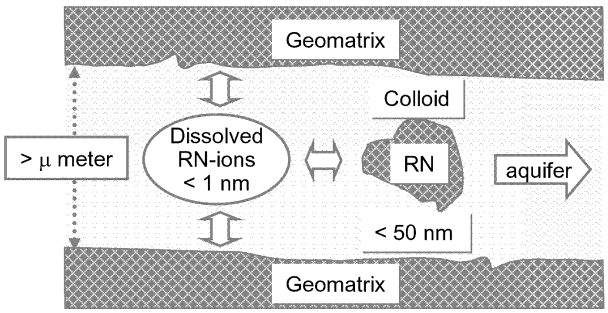


Fig. 25. An Example of the Actinide Migration Phenomenon in Porous or Fracture Aquifer Systems

For illustrating the colloid facilitated migration of actinides, a proportional sketch is drawn in Fig. 26 for the migration processes of both ionic and colloidal species. Ionic species migrate in a given aquifer slowly as compared to the water flow velocity by reason of their intense interaction with mineral surfaces (cf. Fig. 25). Therefore, the retardation coefficient (R_f) of ionic species is always larger than one. The larger is the coefficient, the higher is the benefit for the long-term safety. For all ionic actinides, the retardation coefficient appears to be very large as corroborated by most laboratory experiments [57,58]. This fact is in accordance with Eq. 3. On the other hand, once actinides become colloidal, as anticipated from waste dissolution (cf. Fig. 19), their migration is found to be faster than, or at least equal to, the water flow velocity. The process results in $R_f \leq 1$, because aquatic colloids undergo little interaction with mineral surfaces and in addition their advection promotes migration. A number of laboratory [59-62] and field [63,64] experiments have confirmed such colloid facilitated actinide migration

As a demonstration to the point, the in-situ experiment performed in the Grimsel field laboratory is shown in Fig. 27. A 5m fracture located to the granite tunnel was taken as a migration path for trivalent and tetravalent actinide homologues: Th(IV), Hf(IV) and Tb(III) in trace concentrations. Bentonite colloids of < 200nm size (composed of smectite type) were dispersed together with the tracers in

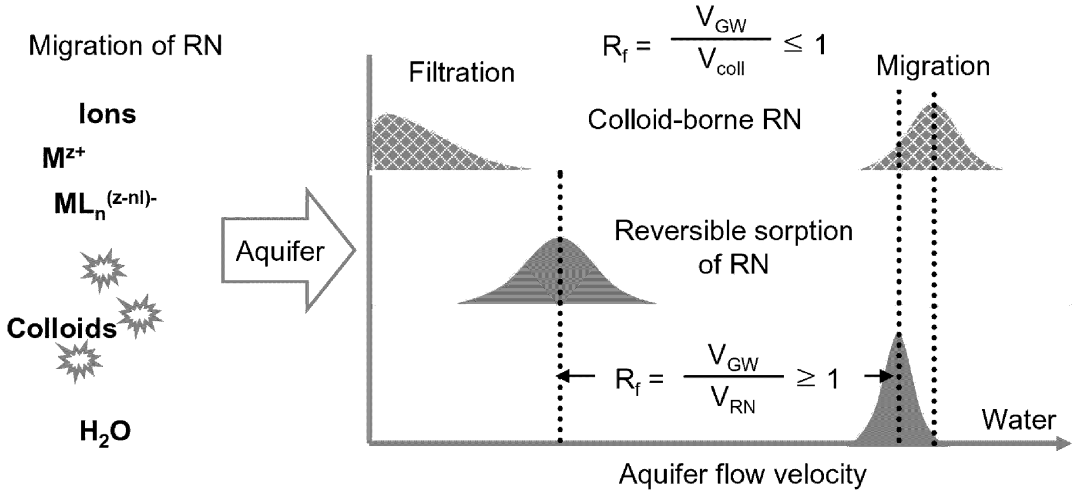


Fig. 26. Migration Phenomena of Actinides in Aquifer Systems: Retardation of Actinides as Ionic Species ($Rf > 1$: slower than water) and as Stable Colloid-borne Species ($Rf \leq 1$: equal to or faster than water)

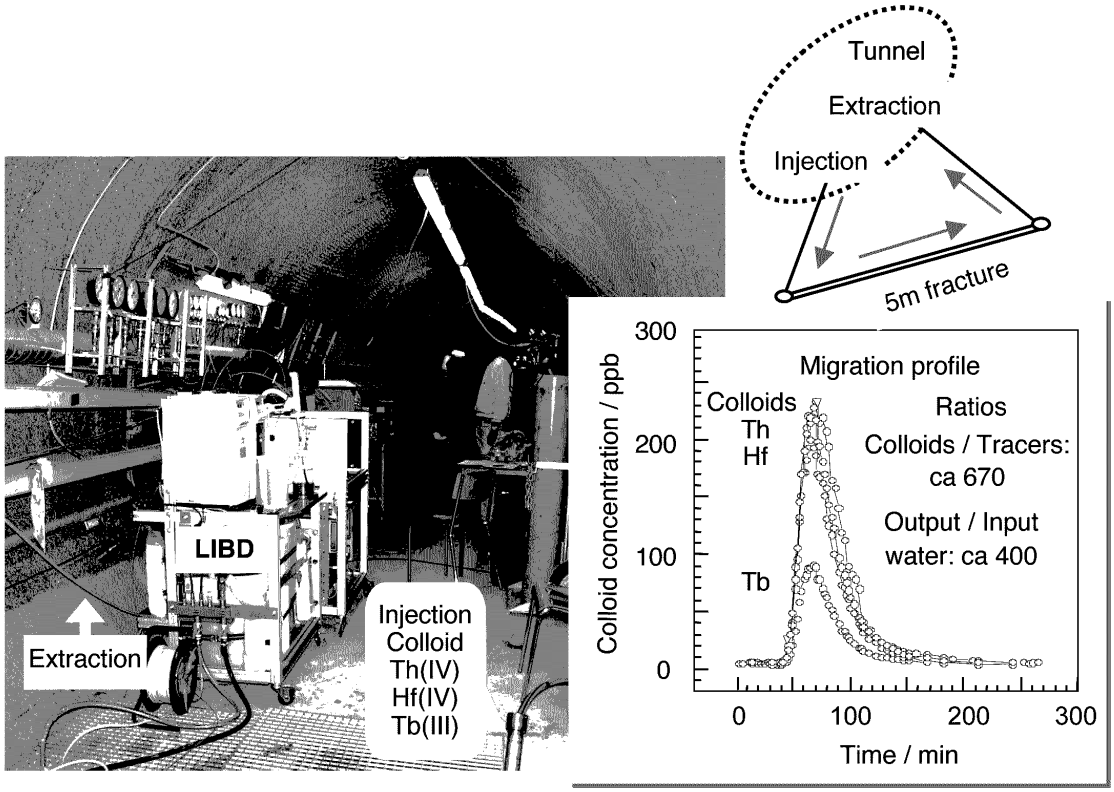


Fig. 27. A Field Experiment of the Colloid (bentonite) Facilitated Migration of Actinide Homologues: Th(IV), Hf(IV) and Tb(III) at a 5m Granite Fracture Distance in the Grimsel Field Laboratory, Switzerland

in-situ groundwater for conditioning as an input sample. Injection was made by air-pressure into one end of the fracture and extracted from another end at a 5m-distance. About 80% colloids were recovered together with tetravalent Th and Hf, while the recovery of trivalent Tb remained at about 40% [63]. A further refined experiment with longtime careful conditioning of tracers with bentonite colloids results in about quantitative recovery of actinides [64]. The field experiments, together with laboratory experiments [59-62], manifest that the actinide migration may primarily be facilitated by aquatic colloids in aquifer systems.

4.6 Actinide Chemistry Pertinent to the Long-term Disposal Safety

The present practice of once through recycling of spent fuel in some countries does not diminish the worldwide actinide inventory noticeably. A so-called ADS cycle anticipated for reducing the TRU inventory and at the same time generating energy thereby [27-30] shall produce inevitably actinide-bearing waste as well. Since nature of nuclear reactions is governed physically by cross sections of elements concerned and a neutron flux available, the secure burn-up rate can never reach over 20% at one cycle. This means that any form of nuclear burn-ups entails the fuel recycling and accompanying waste disposal (cf. Fig. 5). A process of multiple recycling, though theoretically possible [24], shall never be able to burn-up all TRU actinides as can be desired wistfully. At the same time, such a recycling augments inevitably the amount of waste comprising TRU actinides. Therefore, the development of the long-term safe disposal of long-lived TRU actinides is at any time indispensable.

Whatever the fuel cycle each country options, the achievement of the long-term disposal safety is an unavoidable technical and scientific mission, which demands naturally the research on the actinide chemistry, in particular, in the geochemical environment. One of the distinguished global forums for promoting such research developments is the MIGRATION conference [8,9], which was established 20 years ago by a group of international experts. In the European union, the network of excellence for actinide sciences (ACTINET) is recently created for promoting actinide research. The ACTINET-network is now promoting the joint research projects using pooled facilities, the mobility of young scientists among the member laboratories, and the workshops and summer schools for dissemination of advanced knowledge [65]. The major scientific scope of ACTINET comprises the basic and applied actinide

chemistry pertinent to the long-term disposal safety as well as to the fuel cycle. For obvious reasons, the long-term disposal safety is of global interest and hence the development of actinide sciences needs a joint promotion.

5. APPROACHES TO ACTINIDE RESEARCH (NOTABLE EXAMPLES)

The chemical behavior of actinides related to the long-term safety disposal can only be comprehended by appropriate speciation potentials for nanoscopic geochemical reactions, since the apparent solubility of actinides is in general very low (< 10^{-6} M) and their chemical reactions are submerged in aquatic multi-component tracer-interactions [4,5,53]. Although actual aquatic actinide concentrations are expected to be thus low, their radiological impact can be long lasting. Many efforts have been attended to developing various possibilities of speciating such nanoscopic geochemical reactions of actinides. As a result, knowledge on the aquatic actinide behavior has been advanced significantly in the last two decades [8,9]. Some notable examples are selected for the purpose of demonstrating how the subject field is developing at present.

As mentioned already, the 5*f*-electron configuration of actinides provides the possibility of speciating their chemical reactions sensitively by means of various optical methods with laser as a light source. A typical example of various optical methods associated with the actinide speciation can be appreciated from Fig. 28. A fine-tuned modulation of the incident light source, as modern laser, enables a specific excitation of aquatic trace actinides and the resulting relaxation processes can be monitored by different sensor-techniques.

(i) *Non-radiative relaxation*, producing heat on the probe, can be measured by acoustic detection or optical deflection of a probe laser for the chemical speciation of oxidation and complex states at trace level. The sensitivity of such methods for actinides is superior by 100 times or over to conventional absorption spectroscopy. One of the methods, named laser-induced photo-acoustic spectroscopy (LPAS) [10] demonstrates its sensitivity as follows:

An(III) (Am^{3+}): $5x10^{-9}$ M

An(IV) (Pu^{4+}): $5x10^{-8}$

An(V) (NpO_2^+): $5x10^{-8}$ M

An(IV) (PuO_2^{2+}): $2x10^{-8}$ M

The sensitivity limitation arises from the light scattering and sorption by a probe medium, in this case, water. LPAS is broadly applicable, as it functions like a conventional absorption spectroscopy but with a better sensitivity.

(ii) *Radiative relaxation* proceeds with emission of fluorescence via different discrete energy levels at each specific lifetime. A combination of both energy selective excitation and monitoring of definite relaxation, together with lifetime differentiation, gives rise to a high spectroscopic sensitivity for fluorescing actinides, e.g. Am(III), Cm(III), U(VI) etc. A typical example is time-resolved laser fluorescence spectroscopy (TRLFS) [11], which

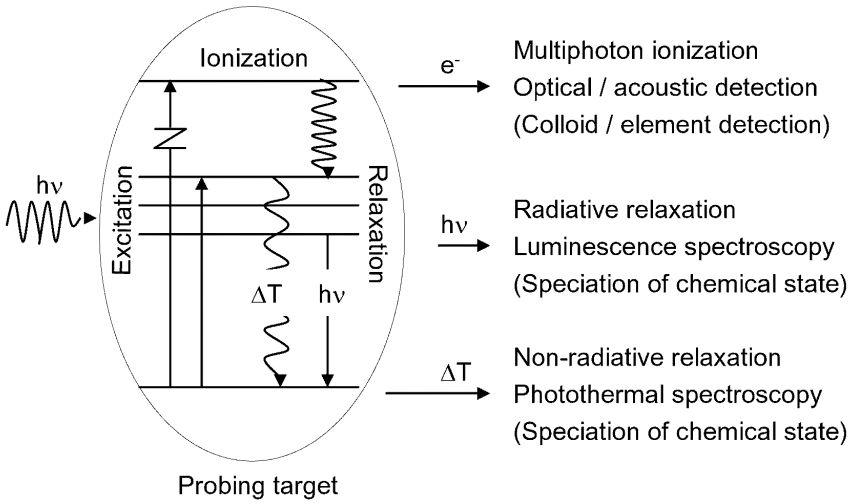


Fig. 28. A Simplified General Scheme of the Laser-induced Optical Spectroscopy Applied for Investigating Nanoscopic Actinide Geochemical Reactions

provides the speciation sensitivity for Cm(III) at about 10^{-10} M, as an example. The method enables a sensitized excitation via ligands as well and is thus applicable for appraising the complexation state in detail [66].

(iii) *Multiphoton ionization* by a modulated intense light source facilitates selective characterization of aquatic colloids. A typical application is known as laser-induced breakdown detection (LIBD) [12,13]. The principle is based on the distinctive threshold irradiance necessary for each probe phase in a series of $I_{solid} < I_{liquid} < I_{gas}$. Physical nature of LIBD incites a breakdown event preferentially on colloids (solid phase) in water at an irradiance level lower than the threshold value of water. Generation of plasma at a breakdown event can be monitored optically or acoustically [12,67]. A spatial distribution of breakdown events along with the irradiance gradient within a laser focus volume can be correlated to the average size of preponderant colloidal particles. The LIBD method is superior to a conventional light scattering technique by a factor of $10^4 - 10^7$ for particles of < 100nm size, which corresponds to the natural size range of ubiquitous aquatic colloids [67].

Some selected examples of the aforementioned spectroscopic speciation are briefly illustrated in the following for the purpose of demonstrating how advanced methods are being applied to appraise the aquatic behavior of actinides at trace level.

5.1 Thermodynamic Study

A typical example is shown here for demonstrating how the spectroscopic speciation allows the precise determination of solubility products of tetravalent actinides. Submitting the Np^{4+} ion at different concentrations to a pH titration from 1 to 3.5, the LPAS measurement of the prominent Np(IV) absorption peak at 723nm is carried out as shown in the upper part of Fig. 29 [68]. The Np(IV) concentration decreased at certain pH suggests the species conversion to colloid formation or precipitation due to solubility constraints. A slope of –2 observed for various conversion pH vs. different Np(IV) concentrations indicates that the converting species is attributed to $Np(OH)_2^{2+}$. A complimentary experiment with LIBD, as shown in the lower part of Fig. 29, for a fixed Np^{4+} concentration at 3.2×10^{-5} M shows the formation of colloidal species at pH 2.2. The equilibration pH in LIBD is matching to the conversion pH in LPAS for the equal Np(IV) concentration. A combination of the two different approaches thus enables formulating the reaction process as follows:

$$n(Np(OH)_2^{2+}) - (2n\text{-}x)H^+ \Leftrightarrow Np_nO_{2n-x}(OH)_x^{\delta x-}\,(colloids) \quad K_{sp} \tag{4}$$

The reaction constant of Eq. 4 corresponds closely to the solubility product (K_{sp}) of Np(IV) oxo-hydroxide (either

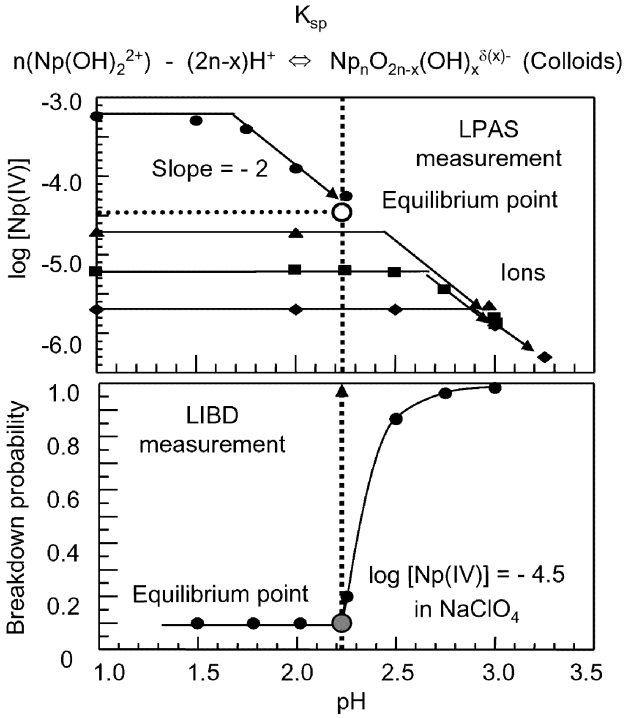


Fig. 29. A Combination of Laser-induced Photo-acoustic Spectroscopy (LPAS) and Laser-induced Breakdown Detection (LIBD) for the Thermodynamic Study of Np(IV) in Equilibration of Ionic Species with Colloids

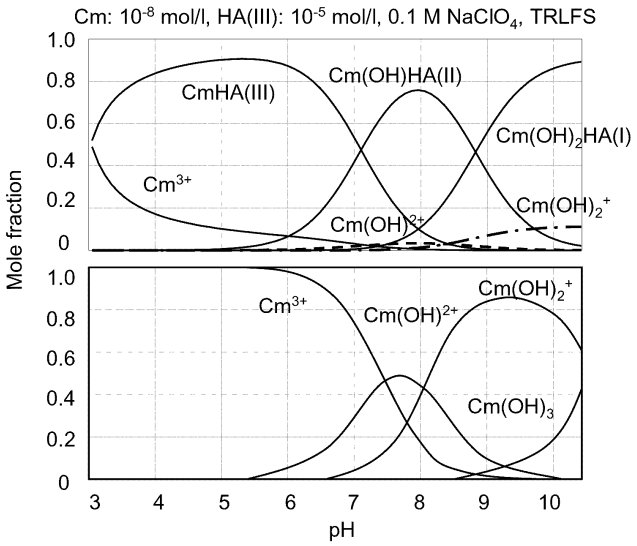


Fig. 30. Speciation of Binary and Ternary Complexation of Trivalent Actinides (example of Cm(III)) Carried Out by Time-resolved Laser Fluorescence Spectroscopy (TRLFS) with and Without the Presence of Humic Acid

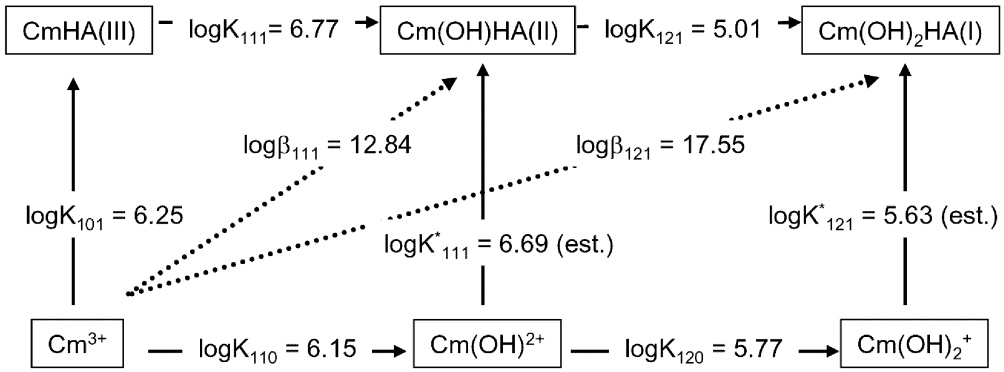


Fig. 31. Thermodynamic Constants Derived from the Nanoscopic Speciation of Cm(III) by TRLFS for Binary Hydrolysis Reactions and Ternary Hydroxo-humate Complexation

colloids or precipitate). This is a noble approach applicable for the thermodynamic study of actinides and homologues, as manifested for tetravalent Th(IV) [69], U(IV) [70], Pu(IV) [71] and trivalent Eu(III) [72].

A thermodynamic study of trivalent actinides can be conveniently carried out by taking Cm(III) as a representative element. Both the high spectroscopic sensitivity of Cm by TRLFS and its precise quantification possibility in trace concentrations by radiometry provides an opportunity to investigate various geochemical reactions of trivalent actinides. As a typical example, Fig. 30 [44,73] shows the spectroscopic speciation of Cm as a function of pH for its hydrolysis reactions as well as its complexation with humic acid present at a normal level (2 ppm) in natural water. Similar investigations for various aquatic complex reactions have been carried out for establishing thermodynamic database [74,75]. Thermodynamic constants evaluated based on the spectroscopic speciation of multiple reaction species (Fig. 30) are shown in Fig. 31, as an example. Such thermodynamic data are fundamental for the geochemical modeling of possible actinide reactions in a given aquifer system, unless the colloidal effect is superseding.

5.2 Quantification of Aquatic Colloids

Advent of the LIBD instrumentation has made it possible to determine for the first time aquatic colloids ubiquitous in natural water [67], including our daily potable water [76]. The sensitivity of LIBD can be appreciated from Fig. 32, together with that of conventional light scattering methods [67]. In the concentration range and the particle size region of aquatic colloids (< 10^{14} particle per liter; < 100 nm diameter), the conventional method fails to detect them. Amounts of aquatic colloids monitored by LIBD in various potable waters in Germany are illustrated in Fig. 33 [76]. The number density varies from 10^{11} to 10^{14} particles per liter water. This indicates that everyone drinks so many

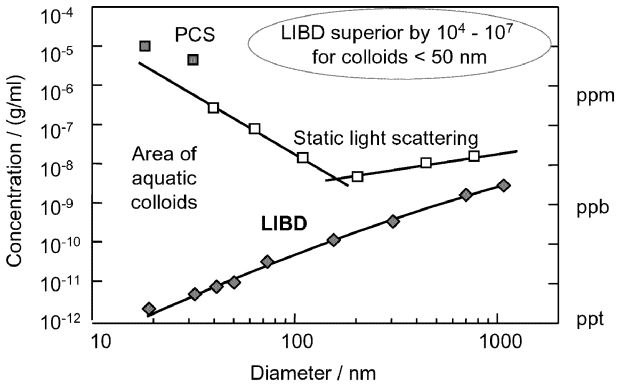


Fig. 32. The Colloid Detection Sensitivity of LIBD as a Function of the Particle Diameter, Compared with that of Light Scattering Methods. The Particle Size Range of Aquatic Colloids is Indicated by Shadow

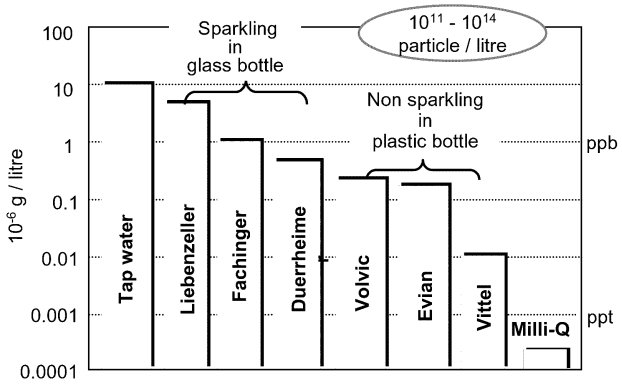


Fig. 33. Colloid Concentrations in Some Selected Potable Waters: Distinction can be Noticed Between Sparkling Water in Glass Bottles and Non-sparkling Water in Plastic Bottles

colloids via daily water consumption. In the case 100 actinides ions on average would be incorporated into each particle, the colloid-borne actinide concentration might range from 10^{-11} M to 10^{-8} M. The level may be chemically of no consequence but in the long run be significant for the radiological point of view. How such aquatic colloids can be generated and how they may facilitate actinide migration has attracted until now only sporadic attention. Hence, the subject appears as one of the key uncertainties in the assessment of the long-term disposal safety.

5.3 Generation of Aquatic Colloids and Colloid-Borne Actinides

By a combination of TRLFS and radiometry, the formation of both aquatic colloids and colloid-borne actinides has been investigated recently [46,56,77]. Hydroxy-alumi-nosilicates (HAS) are known to be kernels of aquatic colloids, since Al and Si are omnipres-ent in natural aquatic systems. The formation process of HAS-colloids, which may be anticipated in the near-field chemistry of a repository, incorporates actinides and thus results in colloid-borne actinides. As a result, the colloid-facilitated migration of actinides becomes probable in aquifer systems [63,64].

A study of HAS-colloid-borne Cm as a function of pH shows, as given in Fig. 34 [77], the formation of three different kinds of colloids: Cm-HAS(I), Cm-HAS(II) and Cm-HAS(III), which can be unambiguously quantified by TRLFS. The last one is found to be most stable at normal aquatic pH, as it incorporates trivalent actinides firmly within its structure of oxo-bridging. Fig. 35 illustrates under what geochemical conditions the formation of each HAS-colloid-borne Cm species can be favored [77]. In this figure contour lines indicate each 10% increment of the colloidal fraction towards darker color. Such HAS-colloids are found to be in the size range of < 50nm diameter, as confirmed by LIBD [46,56]. Conversion of Cm-HAS(I) and Cm-HAS(II) to Cm-HAS(III) takes place with time and the colloidal species Cm-HAS(III) prevails in the end at neutral pH. The formation process of HAS-colloid-borne Cm shown here can be applicable also to other An(III) and further to An(IV). As a result, the colloid-facilitated migration of actinides can be anticipated as exemplified by the field experiment illustrated in Fig. 27 [63].

The HAS-colloid-borne actinides thus formed may undergo further geochemical interaction with humic acid and hence become more stable HAS-humic colloids [78], which may migrate without hindrance in porous or fractured aquifer systems (cf. Fig. 27). The speciation of Cm in HAS-humic colloids by a sensitized modus of TRLFS explains the chemical binding structure as given in Fig. 36 [78]. The mixed structure stabilizes colloid-borne Cm, which remains resistant to dissociation. A thermodynamic approach is not yet available to describe the formation of such complex colloidal species. They can however be found in nature as shown below.

Aquatic colloids of inorganic-organic composition are found abundant in the deep Gorleben aquifer system, overlying the salt dome envisaged once as a final repository site in Germany [5]. In this aquifer rich in humic substances, trivalent and tetravalent elements, analogous to actinides, are present mainly as colloid-borne species. As shown in Fig. 37, the concentration of each element varies in proportion to the amount of combined humic and fulvic acids available (concentration given by dissolved organic carbon (DOC in mgC/L)). For the reason of humic substances

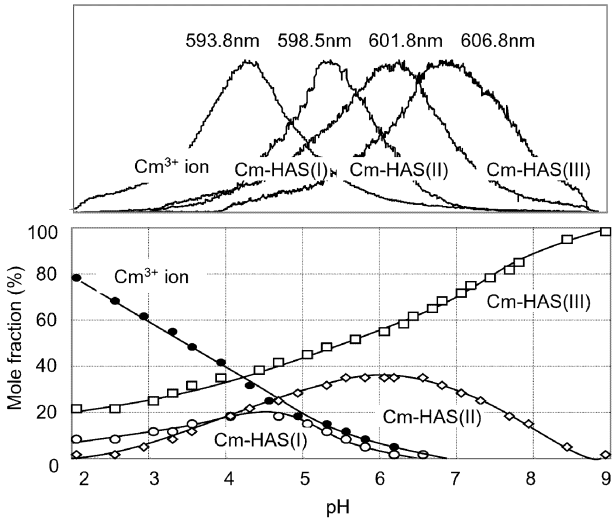


Fig. 34. Speciation of Aquatic Colloid-borne Cm(III) as a Function of pH by TRLFS: Different Types of Incorporation of Cm During the Formation of Aluminosilicate Colloids (kernels of aquatic colloids)

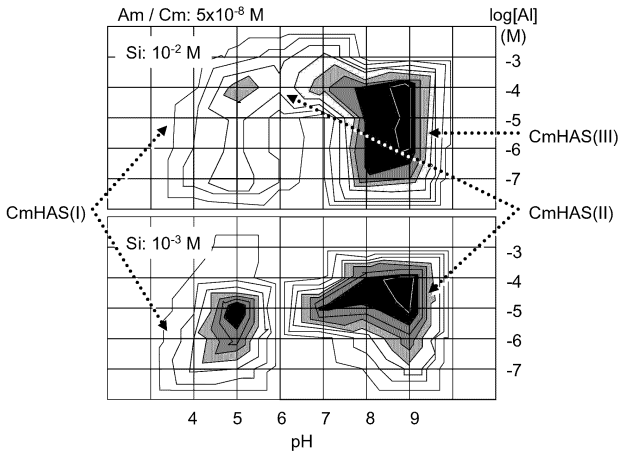


Fig. 35. An Overview for the Formation of Different Colloid-Borne Trivalent Actinides under Various Geo-chemical Conditions of Generating Aluminosilicate Colloids

involved, they are called humic colloids. Detailed experiment points out that trivalent and tetravalent elements are bound irreversibly to humic colloids [79]. The age of these humic colloids determined by ^{14}C-dating is over 20 thousands years [80]. All observations justify the long-term stability of natural aquatic colloids in the Gorleben aquifer.

In reference to the natural metal ion concentrations shown in Fig.37, the solubilities of trivalent and tetravalent actinides can be anticipated under given geochemical conditions. Considering the most abundant Ce(III) and Zr(IV), the aquatic concentrations of trivalent and tetravalent actinides may reach the maximal values of 10^{-6} M and 10^{-5} M, respectively. These data can be upper limits for the source-term estimation of actinides, which are certainly higher than thermodynamic values. Important issues become therefore apparent, i.e. how actinides in waste shall become converted into such aquatic colloids and then how colloid-borne actinides shall be mobilized in a given aquifer system. Answer can only be formulated based on the fundamental knowledge on geochemical actinide reactions, as demonstrated by aforementioned examples.

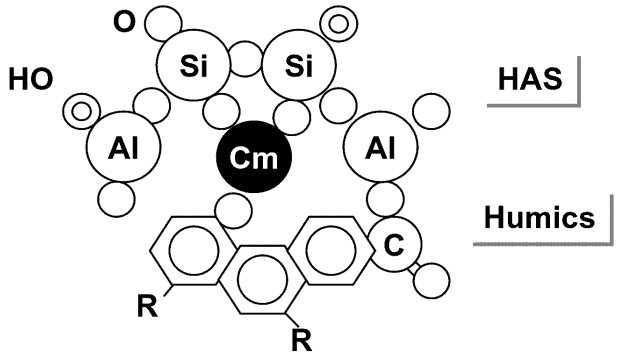


Fig. 36. A Chemical Structure of Colloid-borne Cm(III) in Mixed Inorganic-organic Aquatic Colloids, as Corroborated by a Sensitized Process of TRLFS

6. GEOCHEMICAL APPROACH TO THE LONG-TERM DISPOSAL SAFETY

As is apparent from Figs. 6 and 7, the long-term disposal safety of HLW concerns inevitably with actinides present, either in spent fuel or reprocessed waste from fuel recycling. The latter shall be originated from the future ADS fuel cycle as well. Whichever is regarded as a better option in each country, the long-term safety of nuclear waste disposal can be attained only with well-founded knowledge on the actinide chemistry in the geological environment. A simple notion retained hitherto in the nuclear community is that actinides are sparingly soluble [6] and dissolved species become readily sorbed onto mineral surfaces [57,58]. According to this hypothesis, actinides shall be "dead" locked (or permanently immobilized) chemically and physically within any repository, once a multi-barrier system is well-applied [32-35,55]. However, there is no

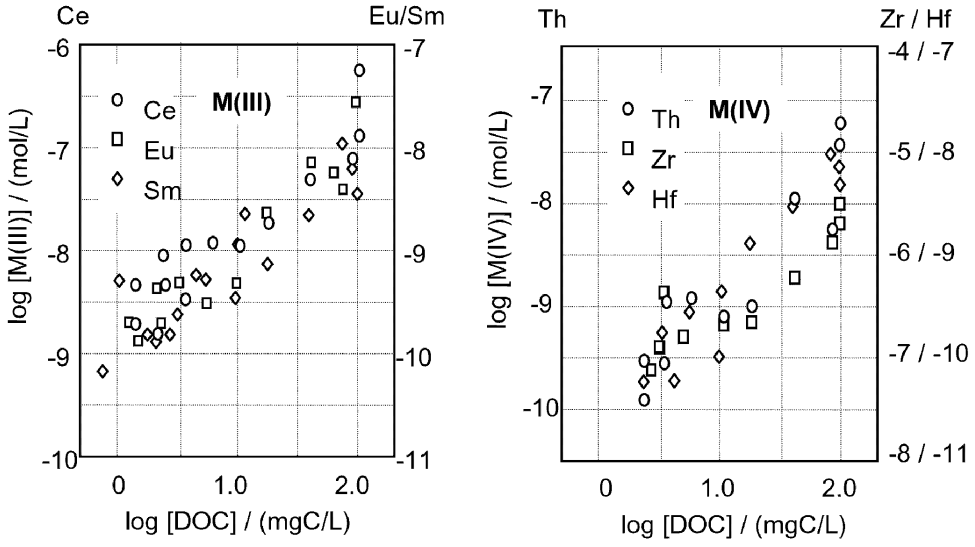


Fig. 37. Colloid-borne Elements of Trivalent and Tetravalent Oxidation States in Deep Groundwater of the Gorleben Aquifer System (Germany) as a Function of the Humic Acid Concentration (given as dissolved organic carbon (DOC) in mgC/L)

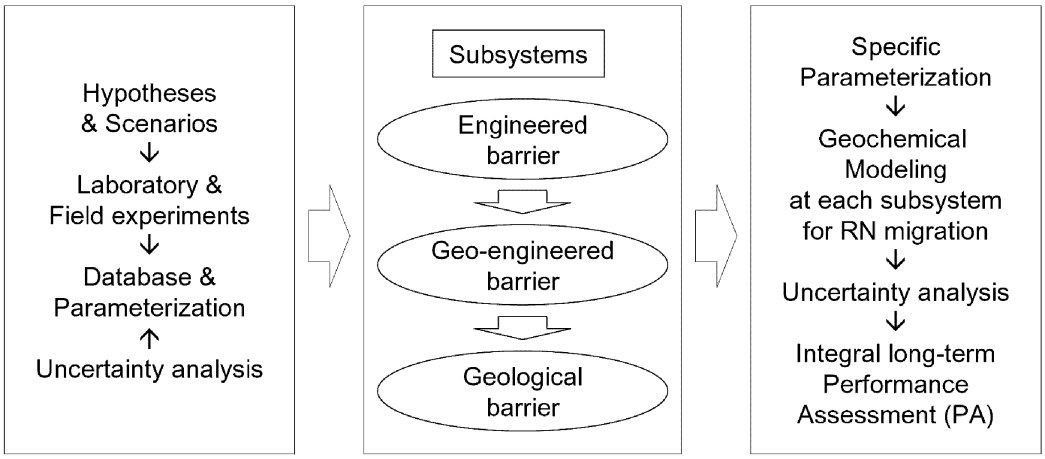


Fig. 38. An Exploratory Geochemical Approach to the Long-term Safety Assessment of Waste Disposal (also called PA)

solid foundation to validate this conjecture. The safety apprehension demands always the deliberation of unforeseeable events that may arise from various uncertainties involved in primary hypotheses.

Fundamental knowledge on the nanoscopic behavior of actinides in aquifer systems may certainly help to verify the reliability of the aforementioned common supposition. In addition, the knowledge provides a geochemical approach that can realistically improve the disposal safety. A conceptual geochemical approach is sketched in Fig. 38. All probable nanoscopic geochemical reactions involved in each barrier system can be investigated and critically assessed. In the primary assessment of each subsystem, the inherent uncertainties can be better recognized and then singled out easily for the solution. Likewise, a geochemical modeling can be applied for each barrier system based on practical knowledge exemplified in this paper. Finally the geochemical approach thus established may assist the long-term safety assessment of nuclear waste disposal.

7. EPILOGS

As a common wisdom, the energy consumption has to be increased to get the better of our life. In the Stone Age, our ancestors sustained a bare life by consuming the daily energy of about 10,000 kJ. In the relatively developed middle age, the daily energy consumption increased to a tenfold at least. Augmentation has been sustained and in the modern age we consume on average 60 to 100 folds of the daily energy necessary for a bare life. The consumption becomes more intense day by day along with technological advancement. Superfluous is a long discussion on the availability of future energy resources, since there are not many options. Nuclear energy is inevitably one of the important future energy assets.

The recorded history of human civilization can be traced back to about 10 thousands years, whereas the beginning of the extensive exploitation of fossil energy resources dates back to merely 200 years. The common understanding acknowledges the limitation of time left for taking advantage of fossil resources. The high density of molecular binding energy nature presents in fossil resources has rendered its exploitation possible only with a relatively small portion of the input energy (< 30%). That makes it so-called "cheap" energy. Nuclear binding energy is on the other hand million

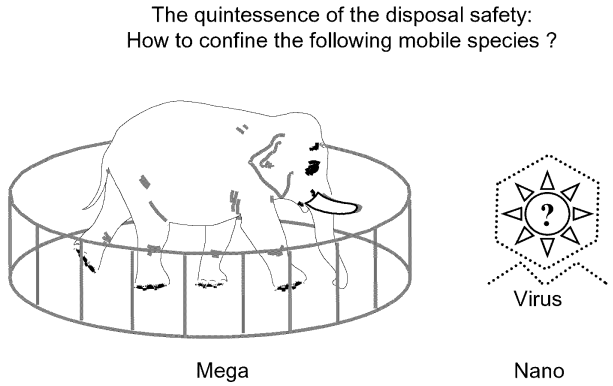


Fig. 39. A Doodle Expression for two Different Aspects: the Geologic Confinement of Waste Packages (engineering) and the Geochemical Immobilization of Mobile Actinides as Colloidal Species (nanoscopic investigation)

times greater than the molecular binding energy. Accordingly, nature has presented us how to make use of the nuclear binding energy by applying much less input energy (about 7%, for the present NPP). As far as the energy balance is concerned, no energy source can compete with the nuclear energy, as measure by a ratio of energy output to energy input [1]. Production of the regenerative energy has inherently a poor energy balance, which means, the high input energy is necessary.

For well-known reasons, the pounding consequence resulting from exploiting nuclear energy is the generation of radioactive waste that radiates for over millions years. The persistent radiation is attributed to long-lived actinides. The long-term safe disposal of nuclear waste is feasible, once accompanied by well-founded geochemical knowledge on actinides. Whereas the permanent isolation of waste from hydrosphere is an engineering challenge, the long-term safety is immediately related to the nanoscopic geochemical behavior of actinides confined in or released from waste. The two aspects are exemplified in Fig. 39. Confining the molecular level actinide behavior within a repository entails knowledge on all potential nanoscopic geochemical reactions as discussed in this paper with notable examples. Based on such practical foundations, an intelligent engineering can be promoted to confine safely the mega-size waste for the required time period. Both aspects are therefore interrelated, as was demonstrated at the advent of nuclear energy, i.e. the test-tube nano-scale chemistry made mega-scale nuclear technology available [25,81].

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