

DU COMBUSTIBLE NUCLÉAIRE AUX DÉCHETS : RECHERCHES ACTUELLES

FROM NUCLEAR FUELS TO WASTE: CURRENT RESEARCH

Confinement and migration of radionuclides in a nuclear waste deep repository

Pierre Toulhoat

CEA, centre de Saclay, Direction de l'énergie nucléaire, bâtiment 125, 91191 Gif sur Yvette cedex, France

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Abstract

The safety of the geological disposal of nuclear waste is evaluated, among other factors, through the ability of radionuclides to be confined, first by waste packages then by engineered barriers and host rocks. Deep underground conditions favour the immobilisation of most radionuclides by sorption or precipitation, which means that mobile radionuclides, such as ^{129}I or ^{36}Cl , may contribute to most of the ultimate dose release during up to a million years. However, degraded evolution scenarios must be taken into account (oxygen intrusion, faults, . . .) to assess earlier dose releases. *To cite this article: P. Toulhoat, C. R. Physique 3 (2002) 975–986.*

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radionuclide / migration / solubility / sorption / isotopic exchange / performance assessment

Confinement et migration de radionucléides dans l'environnement d'un stockage de déchets nucléaires

Résumé

Pour évaluer la sûreté d'un stockage géologique de déchets nucléaires, il est primordial d'évaluer la capacité du système colis/barrière ouvrage/milieu géologique à confiner à très long terme certains éléments. Il s'agit de ceux qui, initialement présents dans les combustibles nucléaires usés ont des isotopes radioactifs à vie longue et des descendants de ces radionucléides. Les conditions physico-chimiques régnant dans les milieux actuellement envisagés, confèrent à la plupart des radionucléides une très faible mobilité due aux phénomènes de sorption et précipitation, seuls les plus mobiles comme ^{129}I ou ^{36}Cl pourraient contribuer à la dose annuelle à l'exutoire du stockage après quelques dizaines ou centaines de milliers d'années. Cependant, certains scénarios dégradés doivent être examinés (intrusion d'oxygène, failles) pour s'assurer de la valeur de la dose dans ces cas. *Pour citer cet article: P. Toulhoat, C. R. Physique 3 (2002) 975–986.*

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E-mail address: pierre.toulhoat@cea.fr (P. Toulhoat).

1. Introduction

In France, the Fundamental Safety Rule RFS-III-2 f, ‘Guideline for the conception of deep underground disposal’, emphasises the necessity of a confinement by waste packages up to 10 000 years. Thus, engineered barriers and natural barriers (host rock) must contribute to the confinement of radionuclides. Considering existing or future waste packages, present disposal concepts, and possible repository sites, scientists have to evaluate the radiological impact due to the release of radionuclides into the biosphere. Such evaluations are first conducted considering a normal succession of events (normal scenario). Degraded scenarios, with a very low probability of occurrence, including human or societal factors (human intrusion) and natural events (major climate changes or tectonic events) have also to be considered. The multi-barrier confinement system is conceived to be efficient in normal scenarios, but is mostly dedicated to minimize the consequences of degraded scenarios. In order to accurately estimate the confinement performance of this multi-barrier system, the chemical properties of the elements to which radionuclides belong have to be determined as functions of environmental conditions. Fortunately, most elements are retarded or immobilised in deep, chemically reducing environments, but their behaviour can change if the medium undergoes physical or chemical perturbations, such as an oxidation, consecutive to the opening of a major fault, or worse to a human intrusion.

2. Description of a multi-barrier system

Most geological disposal concepts are based on a ‘multi-barrier’ system, which is composed of the following elements:

- the waste package, in which the first barrier may be either a matrix (borosilicate glass, for instance) or a container wall (concrete or metal), or both;
- in some cases, an overpack (which is present in some concepts such as those used in Switzerland and Japan), generally in carbon steel with or without a cover made in noble metals (titanium, copper), or in stainless steel, can act as an additional barrier;
- the engineered barrier, which is emplaced to protect the waste packages from water, to stabilise the environment of the packages and to retard sorbing radionuclides. This second barrier is often made of compacted swelling clay (montmorillonite) or concrete;
- the geological barrier, generally chosen as a stable and/or impervious rock formation (granite, clay, tuff, etc . . .) is considered as the third barrier.

All these barriers are supposed to play a complementary role, in order to optimise the confinement performance even in degraded scenarios.

3. Inventories of radionuclides

High activity wastes such as vitrified wastes from reprocessing contain:

- fission products, among them some having very long half lives;
- minor actinides, Np, Am, Cm.

Spent fuel contains in addition:

- major actinides, U and Pu;
- some activation products from fuel impurities or structural materials of fuel assemblies (cladding, end-pieces).

After 10 000 years in spent fuel (Fig. 1) the following radionuclides remain at a significant level of activity:

Actinides: ^{223}Pa , ^{234}U , ^{236}U , ^{237}Np , ^{239}Np , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , ^{243}Am , ^{245}Cm ;

Fission products: ^{99}Tc , $^{93\text{M}}\text{Nb}$, ^{93}Zr , ^{126}Sb , ^{126}Sn , ^{135}Cs , ^{107}Pd , ^{129}I , ^{79}Se ;

Activation products from impurities: ^{14}C , ^{59}Ni , ^{36}Cl , ^{94}Nb , ^{41}Ca , ^{93}Mo , ^{99}Tc ;

Activation products from structure materials: ^{59}Ni , $^{93\text{M}}\text{Nb}$, ^{93}Zr , ^{95}Zr , ^{94}Nb , ^{14}C and ^{36}Cl .

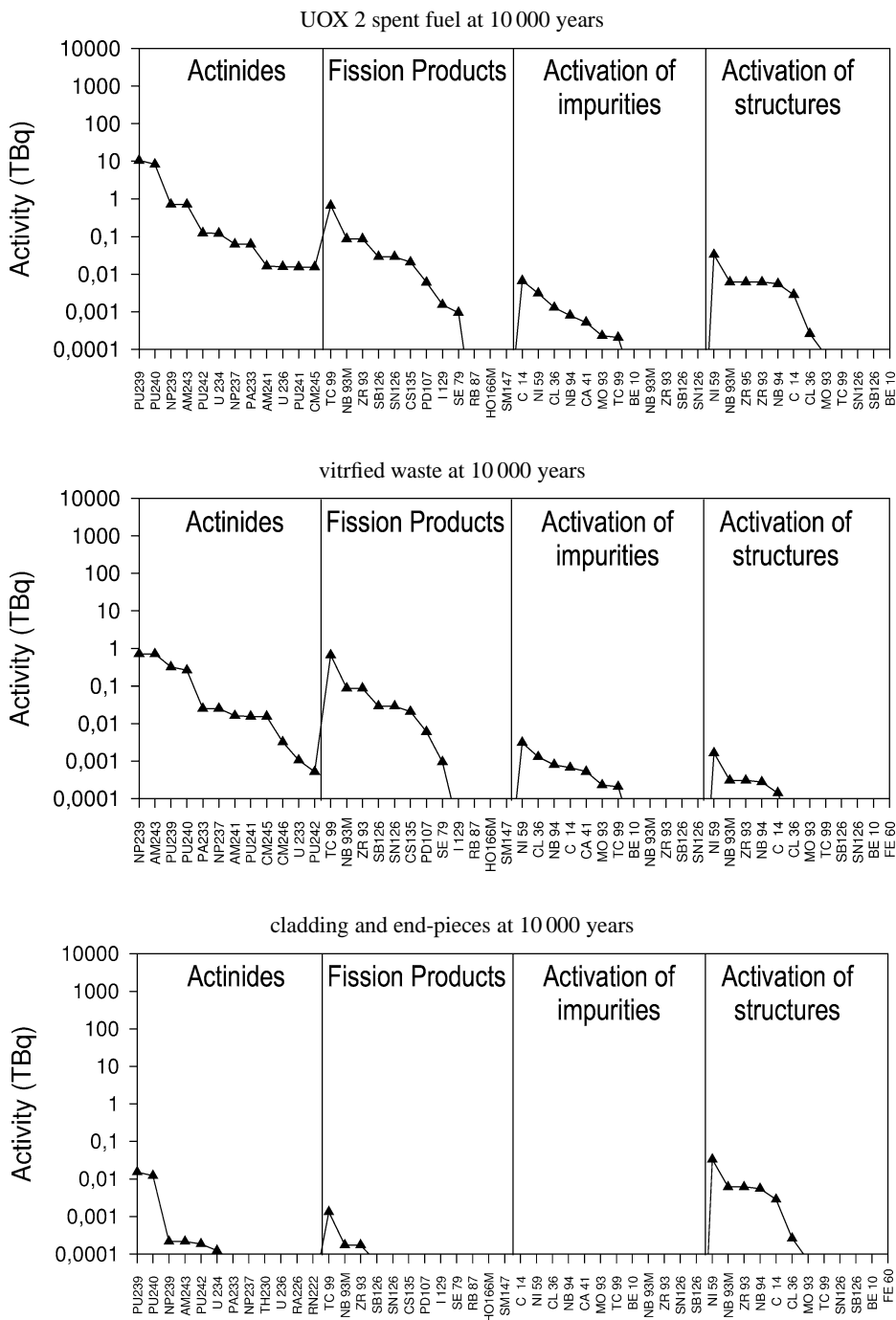


Figure 1. Residual activities after 10 000 years in Spent Fuel (UOX2), Vitrified wastes (CSDV) and Cladding and End-pieces (CSDC) (CEA—Commissariat à l'Énergie Atomique Internal Report, NT SPRC/LECy 00/310, 2000). Computed activities per tonne of heavy irradiated metal with the CESAR code. PWR assembly UOX2-AFA 2GE CPY (45 GWd/t).

In glass, due to reprocessing, the remaining activity of Pu and U is considerably lower, but minor actinides still contribute to a significant activity level. In cladding and end-piece waste packages, a small activity of radionuclides resulting from the activation of metallic structural elements remains, together with a very small activity of actinides and fission products.

These results indicate that a rather large variety of elements has to be considered after 10 000 years, in order to evaluate their chemical and geochemical behaviour in the confinement system. Some short half-life nuclides are to be considered because they are in secular equilibrium with their long-life parents, for example ^{239}Np with ^{243}Am , $^{93\text{M}}\text{Nb}$ with ^{93}Zr , etc.

4. Release and transport mechanisms

The first step in the release of radionuclides is the dissolution of the confinement matrix (if any) or the corrosion or degradation of the container/overpack, if the wastes are not stabilised or confined in a matrix. In the case of a confinement matrix such as borosilicate glass, the dissolution rate of the matrix is very slow, typically around $10^{-2} \text{ g}\cdot\text{m}^{-2}\cdot\text{day}$ in an open aqueous system, and in confined conditions, below $10^{-5} \text{ g}\cdot\text{m}^{-2}\cdot\text{day}$. The release of radionuclides is generally considered as congruent [1]. Some waste packages may release a certain percentage of their inventory as soon as water degrades the last effective barrier. As soon as a given radionuclide is in the presence of the underground aqueous fluid, it adapts its speciation to the ambient chemical conditions (Eh, pH, ligand complexation), and if chemical conditions are favourable (high pH, chemically reducing conditions) it precipitates, at least if the concentration of the corresponding element is high enough. The remaining fraction in solution is then transported by diffusion or advection through corrosion or alteration products, or more or less degraded engineered barrier materials. After having migrated in the near-field, it can be transported in the far-field, which is the unperturbed portion of the geological host formation. During the transport, radionuclides may be retained by sorption on highly reactive and divided materials such as clay minerals, or transported as dissolved ions or complexes, or in some cases as colloids [2].

5. Chemical factors controlling radionuclide mobility

The mobility of radionuclides is influenced by the following factors:

- solution chemistry (pH, ligand concentrations, Eh);
- solubility limiting mineral phases (K_S);
- availability and capacity of sorbing phases;
- co-precipitation with major-element bearing phases in the case of reaction fronts coupled with the radionuclide migration;
- mobility induced by colloid migration.

Under normal circumstances, colloids should be filtered in clay barriers or retained on fracture walls. Most deep underground waters tend to be alkaline (pH = 7 to 9) and chemically reducing (Eh < $-250 \text{ mV}_{\text{SHE}}$). This is due to water-rock interaction processes [3] and to a progressive consumption of oxygen, first by organisms, then through the oxidation of Fe^{2+} or Mn^{2+} bearing reduced minerals. They are also enriched in dissolved salts, up to more than $10 \text{ g}\cdot\text{l}^{-1}$. As shown further on, such conditions favour the precipitation of many cations. Specific ligands may be encountered in some areas: a high concentration of bicarbonates, known to increase by complexation the solubility of metals, or humic substances, sometimes present as colloids. Other ligands such as HS^- may also decrease the solubility of transition metals through the precipitation of solids [4].

6. General consideration of environmental properties of radionuclides

Goldschmidt [5] produced pioneering guidelines to account for the geochemical behaviour of elements, based on so called ionic potentials, i.e., Z/R ratios (Z = ionic charge, R = ionic radius). In Fig. 2, the

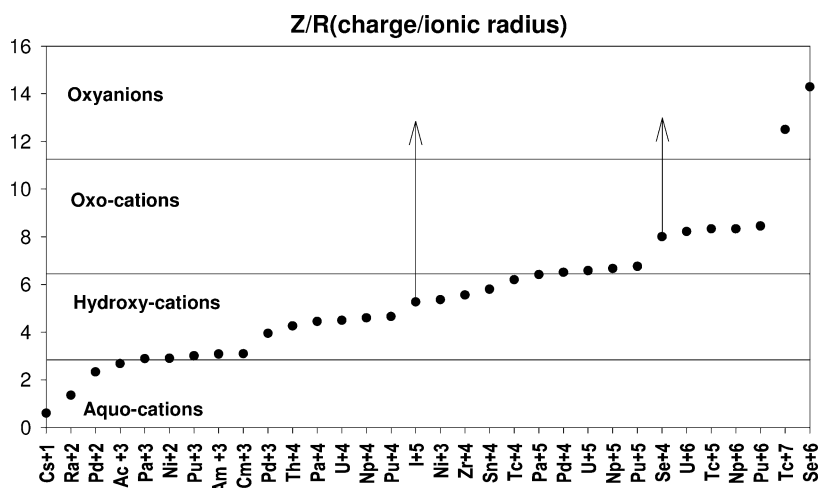


Figure 2. Z/R (charge/ionic radius) for several radionuclides (generally in 6-fold coordination), extracted from [7]. According to their oxidation state, common actinide or fission products ions plot into different domains (for instance: Tc(IV) in the hydroxycation domain, and Tc(VII) in the oxyanion domain). This graph applies for aqueous solutions near pH 7.

Z/R ratio of several ions is plotted, according to ionic radii published in [6]. The main tendencies in aqueous solutions appear in a quite simple way: low Z/R ions remain as simple aqueous cations, with a rather weak reactivity towards hydrolysis. When hydrolysis becomes dominant, hydroxycations in solution (e.g., $\text{Am}(\text{OH})_3^0$) appear and they generally tend to precipitate as insoluble hydroxides. If Z/R increases, oxocations appear (e.g., UO_2^{2+}), and the concentration of the element could be quite high in neutral solutions. Highly charged ions such as Tc^{7+} are only stable in solution as oxoanions (TcO_4^-), which gives the element a very high solubility. Se and I ions tend to form oxoanions at higher degree of oxidation (iodates, selenites and seleniates). The influence of pH and Eh of the solution is of course essential in the control of hydrolysis/oxidation reactions. Complexation by other anions than OH^- may occur. In this case the solubility of a given element can significantly increase. The ability of ions to form outer-sphere or inner-sphere complexes is determined by the ionic or covalent character of the bonds. Covalent bonds are established between highly polarisable so called ‘soft acids’ and ‘soft bases’ according to Pearson’s HSAB theory [7]. Among soft bases are found HS^- , I^- , CN^- and most organic anions. Hard acids form electrostatic bonds with hard bases (F^- , H_2O , OH^-), but bonds tend to become more covalent when Z/R increases. Organic anions generally exhibit a stronger affinity towards ‘soft acids’ (so-called Irving Williams Series). For most elements, databanks has been established, containing relevant and consistent thermodynamical data (complexations constants, solubility products). For actinide and fission products, the databanks are less comprehensive and data are still lacking, either relative to inorganic anions, or more frequently to organic anions. Gathering such data on alpha-emitters such as Pu, Am or Np is a difficult task requiring specific facilities [2]. Heterogeneous systems, including reactions between dissolved species and mineral surfaces are generally documented by rather empirical datasets, generally site or system specific, which cannot be generalised in terms of prediction. The quest for a satisfactory representation of such heterogeneous reactions is an important challenge for environmental chemists. When predicting the speciation of radionuclides in solution or on mineral surfaces, it is generally assumed that thermodynamical equilibrium conditions are achieved. Considering the time needed for radionuclide migration, this assumption is generally acceptable, although kinetics may play a role in surface systems, or biologically mediated redox reactions.

7. Isotopic effects

Isotopic effects have to be considered, when using solubility limits. As the solubility is the maximum concentration at equilibrium with a given limiting mineral phase, the dissolved concentration of a given isotope may be lowered if there is a significant contribution of natural (non-radioactive isotopes) in the system. In addition, if a given isotope migrates through the geological medium, it may be sorbed and simultaneously exposed to isotopic exchange if the corresponding stable isotope is present and accessible to exchange in the solid phase, or in a stagnant portion of the interstitial fluid. However, such phenomena are generally difficult to account for, as they require a precise description of the location and accessibility of stable corresponding isotopes. The effect of ‘isotopic dilution’ on solubility limits is easier to predict, as it only requires an estimation or measurement of the corresponding stable isotope concentration in the groundwater. In most safety assessment studies, isotopic effects have been omitted, and conservative solubility values have been selected, as for a mono-isotopic element. For radionuclides which are considered as mobile, such as ^{129}I , ^{36}Cl and ^{14}C , and not ‘solubility limited’, but which are minor in terms of isotopic composition compared to stable isotopes ^{127}I , ^{35}Cl and ^{37}Cl , ^{12}C , isotopic exchange with immobile stable isotopes would contribute to considerably decrease their impact. This is extremely important to consider, as in most safety cases these mobile radionuclides dominate in terms of impact [8].

8. Behaviour of actinides

A short overview is reported here, more details are given in [2]. In chemically reducing conditions and slightly alkaline conditions, U, Np and Pu are tetravalent and rather insoluble (10^{-10} to 10^{-8} M), their solubility is generally assumed to be controlled by amorphous oxy-hydroxides in the upper portion of the pH range, and by crystalline oxides in the lower pH range. Trivalent Am and Cm estimated solubilities are in the same range, also controlled by their oxides or hydroxides. The presence of carbonate/bicarbonate ions in large concentration could increase their solubility through the formation of hydroxy-carbonate complexes.

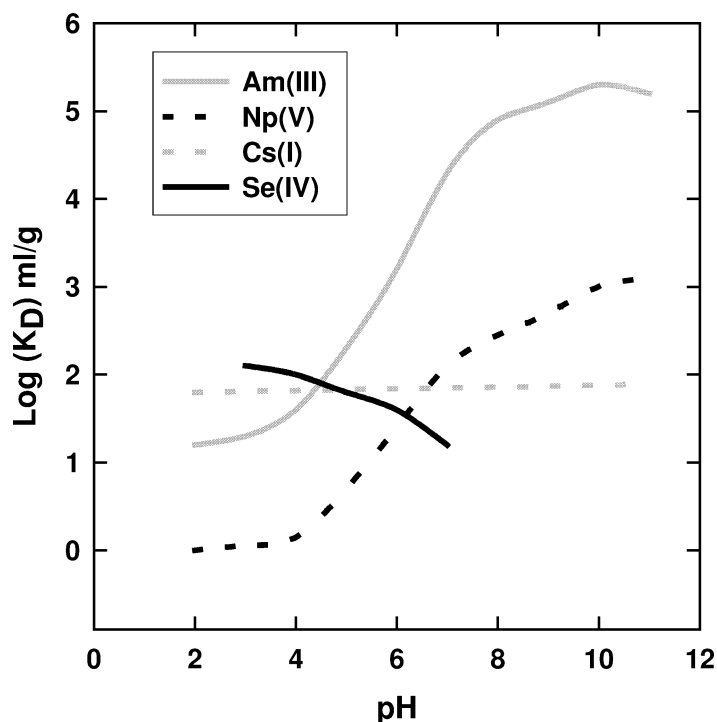


Figure 3. Retention of some elements on a smectite type clay mineral [23]. Above pH 7, Np(V) and Am(III) are significantly retained, whereas the distribution coefficient of Cs is almost constant. Se(IV) sorption decreases with increasing pH, due to its anionic character.

Alkaline conditions may favour the formation of anionic hydroxocomplexes, which increase the solubility of tetravalent actinides, but experiments are still necessary to check existing data, as it is a real challenge to perform solubility experiments on such compounds, and maintaining real anoxic or reducing conditions. Dissolved organic matter and namely humic or fulvic acids are also known to increase the solubility of tri and tetravalent actinides. In oxidising conditions, U Np and Pu tend to be oxidised as UO_2^{2+} , NpO_2^+ , PuO_2^+ or PuO_2^{2+} , whose solubility is generally controlled above 10^{-5} M by hydroxides or carbonate compounds. In heterogeneous systems, the most reactive trivalent and tetravalent cations are very efficiently sorbed on solid phases such as oxides, clays or other silicates. The compared behaviour of Am and Np can be seen in Fig. 3. Above a ‘pH edge’, in near neutral conditions, organic (humics) and inorganic complexants can compete with the solid phase. In addition, tetravalent or trivalent actinides may be mobilised as colloids or pseudo colloids [2,4], when they form partially polymerised hydroxides or when they are adsorbed onto inorganic oxide or aluminosilicate colloids, released during the alteration of wastefoms or primary host minerals, or when they are complexed by high molecular weight humic substances. The mobility of such colloids may be significant in highly porous systems or in largely open fracture systems. In very small fractures or in nanoporous media, such as compacted clays, the mobility of such colloids has been proven to be considerably reduced [9].

9. Behaviour of fission products

In Table 1, the solubility features of long-lived fission products are reported. Some of them are immobile in chemically reducing conditions. This is probably the case of Tc, which is stabilised under valence IV in reducing conditions. An average solubility of 10^{-8} M is reached [10,11], but technetium chemistry

Table 1. Simplified solubility data in near neutral aqueous solutions of some long-lived fission products. When species are not explicitly mentioned, this means that there are still uncertainties or a certain degree of variability, according to the composition of the aqueous phase

Element	Reducing	Oxidising
Zr (^{93}Zr)	Zr^{4+} strongly hydrolysable: insoluble: $< 10^{-8}$ M	Zr^{4+} strongly hydrolysable: insoluble: $< 10^{-8}$ M
Tc (^{99}Tc)	Tc^{4+} : hydrolysable ($\text{Tc}(\text{OH})_4^0$?) insoluble ($\sim 10^{-8}$ M?)	TcO_4^- : soluble
Se (^{79}Se)	Se_0 , Se_{-II} ? Insoluble (sulfides/selenides) $\sim 3 \times 10^{-9}$ M	$\text{Se}_{IV} \text{SeO}_3^{2-}$, $\text{Se}_{VI} \text{SeO}_4^{2-}$ soluble
Pd (^{107}Pd)	$\text{Pd}_{<IV}$ (Pd^{2+} or Pd_0)? Insoluble ?	Pd_{IV} or $\text{Pd}_{>IV}$?
Nb (^{94}Nb)	Nb_V moderately soluble? 10^{-5} to 10^{-4} M	Nb_V moderately soluble? 10^{-5} to 10^{-4} M
Cs (^{135}Cs)	Cs^+ soluble sorption, coprecipitation	Cs^+ , soluble sorption, coprecipitation
I (^{129}I)	soluble sorption on organic matter	soluble

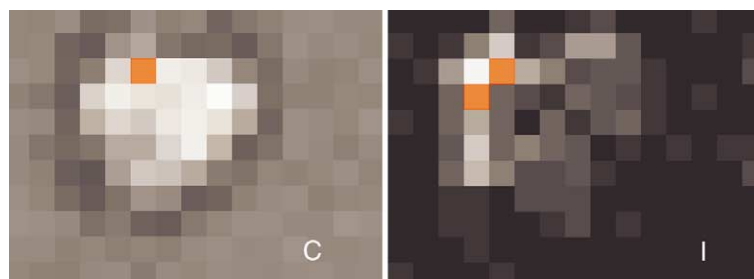


Figure 4. Correlated analysis of elemental carbon and iodine in organic matter particles sampled in groundwaters obtained by nuclear microprobe techniques [15].

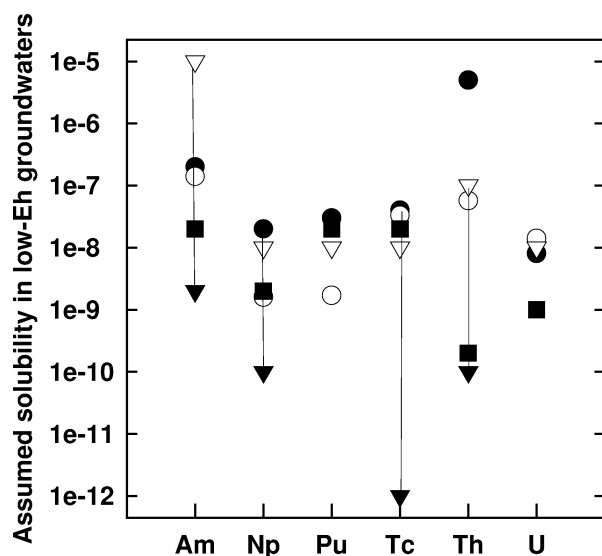


Figure 5. Estimated solubilities of long lived radioelements in low Eh near neutral or slightly alkaline groundwaters according to: [18] black dots; [19] maximum: hollow triangles, minimum: black triangles; [20] hollow circles; [21] black squares. Although some variability can be noted, an average solubility of 10^{-8} M can be assessed, for Am and Th, carbonate and bicarbonate ions may change the solubilities (complexation, and/or appearance of hydroxycarbonates limiting solids).

is really difficult to handle. In oxidising conditions, Tc^{7+} dominates, and is—as all elements giving oxoanions—highly soluble and therefore mobile. Zr is stable in most conditions as Zr^{4+} , which is a strongly hydrolysable insoluble cation (solubility around 10^{-8} M in neutral pH conditions). Nb is found in solution as Nb(V), which is moderately soluble in alkaline conditions [12]. Pd has been reported to be stable as metallic Pd in reducing conditions [13] but also as Pd^{2+} or Pd^{4+} in oxidising conditions. Concerning these two elements, experimental data are scarce. I and Cs are generally considered to be mobile elements, although Cs may be significantly retained by sorption onto clay minerals [14,15], Fig. 3; or by coprecipitation with alkali bearing aluminosilicates appearing in reactions fronts which occur in presence of concrete based materials, or during the reprecipitation of aluminosilicates during groundwater re-equilibration after any kind of thermal or chemical near-field perturbation [4]. Iodine has been reported to be mobile as I^- in deep groundwaters. However, recent results report a tendency of organic matter (humic materials and/or kerogens) to have a great affinity for iodine [16], Fig. 4. As mentioned above, the mobility of iodine would be significantly decreased through isotopic dilution phenomena with natural stable iodine that would be fixed on organic matter. The chemical behaviour of selenium chemistry is very close to sulphur: $Se_{(IV)}$ and $Se_{(VI)}$ form respectively soluble selenite SeO_3^{2-} and selenate SeO_4^{2-} anions, whereas in reducing conditions, selenide Se^{2-} is rather insoluble as iron selenide if Fe^{2+} is available in the system. Selenite ions are moderately retained, especially at low pH on oxides and clays, as shown on Fig. 3, whereas selenate ions are not retained. ^{36}Cl is known to be unreactive and therefore very mobile, as the solubility of chloride salts is almost never reached in natural waters, excepted concentrated brines after evaporation. ^{14}C

behaviour is more complex to decipher. Carbonate ions are the major dissolved ions, but are also frequently precipitated as calcite or dolomite. ^{14}C can be removed from solutions by precipitation, but is also expected to be isotopically exchanged with immobile carbonate bearing compounds. Such processes have not been extensively studied, but would deserve more attention. The solubility of ^{59}Ni is expected to be limited at low concentration, by hydroxides or carbonates, and especially in presence of dissolved hydrogen sulphide by nickel sulphides.

10. Solubility predictions versus in situ observations

In order to verify the solubility predictions concerning actinides and fission products in deep groundwaters, systematic measurements of trace element concentrations have been carried out. Indeed, as confined waters have a very long residence time in deep aquifers, it is expected that chemical equilibrium conditions are reached, either for major elements or for insoluble trace elements. Such studies were conducted by Alaux Negrel et al. [4], Toulhoat et al. [3] in thermal waters from the Pyrenees and Corsica, whose composition is very close to the expected composition of confined waters surrounding a deep geological repository in granitic environments. Uranium and some transition elements have been established to be controlled by the precipitation of secondary phases (oxide for U, sulphides for transition metals). Th and rare earth elements (REE) are mostly present associated to small particles or colloids (in the range 0.01 to 0.45 μm) and, however, lower in concentration than expected solubilities in granitic groundwaters. On Table 2, it is possible to check that the solubility of several radionuclides in deep granitic groundwaters is generally very conservatively estimated. Several reviews have recommended solubility limits in low Eh ‘granitic’ groundwaters [18–21]. In Table 3, one can see that the discrepancy between solubility predictions is rather limited, and generally in the range of associated uncertainties. In some cases, very conservative assumptions can extend the ranges mentioned in Table 3. Reported Th

Table 2. Observed trace element concentrations in deep granitic groundwaters versus recommended solubility values by different sources. Observed ‘dissolved’ concentrations, i.e., after 0.01 μm filtration, for Zr, and Th are very low, but a significant contribution of colloids (particle size between 0.01 and 0.45 μm) may be observed. The observed concentration is in the range of recommended solubilities for Zr and far below for U Th and Zr

Element	Filtered at 0.45 μm ($\text{mol}\cdot\text{kg}^{-1}$) [4]	Filtered at 0.01 μm ($\text{mol}\cdot\text{kg}^{-1}$) [4]	Recommended solubility [17] ($\text{mol}\cdot\text{kg}^{-1}$)	Recommended solubility [20] ($\text{mol}\cdot\text{kg}^{-1}$)
Zr	6.5×10^{-7}	6.2×10^{-8}	1.0×10^{-6}	2.0×10^{-10}
Th	5.5×10^{-10}	4.3×10^{-12}	5.0×10^{-6}	2.0×10^{-10}
U	1.0×10^{-10}	1.0×10^{-10}	8.0×10^{-9}	1.0×10^{-9}

Table 3. Recommended solubility limits for some radioelements in low Eh granitic waters (in $\text{mol}\cdot\text{kg}^{-1}$), pH ranges between 7 and 9. Some explanations for the differences are mentioned in the text (possibility of carbonates complexes and/or limiting solids for Am). An average maximum solubility of 10^{-8} M is generally assessed in low Eh neutral groundwaters

Element	H12 [17]	SKI90 [19]	Review 1 [18]	Review 2 [20]
Am	2.0×10^{-7}	1.4×10^{-7}	2×10^{-9} to 10^{-5}	2.0×10^{-8}
Np	2.0×10^{-8}	1.6×10^{-9}	10^{-10} to 10^{-8}	2×10^{-9}
Pu	3.0×10^{-8}	1.7×10^{-9}	$\sim 10^{-8}$	2×10^{-8}
Tc	4.0×10^{-8}	3.3×10^{-8}	10^{-12} to 10^{-7}	2×10^{-8}
Th	5.0×10^{-6}	5.7×10^{-8}	$\sim 10^{-10}$	2×10^{-10}
U	8.0×10^{-9}	1.4×10^{-8}	$\sim 10^{-8}$	1×10^{-9}

solubilities correspond to situations in which the concentration in carbonate is high enough to allow the formation of a $\text{Th}(\text{OH})_3\text{CO}_3^-$ complex, a similar behaviour being also expected for Am. Indeed, most granitic groundwaters are considered to be buffered by calcite/calcium aluminosilicate associations; in such conditions, the carbonate or bicarbonate concentration is very low, which explains the lower values generally estimated for Th solubility in most of the low temperature granitic groundwaters. In higher Eh environments, the situation may be quite different. The Total System Performance Assessment for the Yucca Mountain Site recommends higher solubilities corresponding to $\text{Np}_{(\text{V})}$ and $\text{U}_{(\text{VI})}$ bearing solids Np_2O_5 and UO_3 (Schoepite), typically around 10^{-5} M for neutral pH groundwaters [17]. Some authors have also reported a possible mobility of actinides as colloids in the context of Yucca Mountain [22].

11. Safety or performance assessment evaluation

Most projects concerning nuclear waste disposal have included performance assessment exercises. Such exercises integrate a description of the disposal system (wasteforms and their inventories, containers, engineered barriers), and of the host rock. They take into account normal scenarios, in which all compartments are fulfilling the functions which they are designed for, and evolve in the long-term according to predicted thermal, chemical, hydraulic and mechanical gradients. Degraded scenarios take into account confinement failures, due to undetected initial defects, or unpredictable evolution; in some cases they account for human intrusions or major events (very low probability, but important effects). Dose rates to populations are in each case propagated towards a ‘critical group’, which represent a fictive future population in contact with aquifers (contamination and ingestion). Such biosphere models rely on various assumptions, which will not be discussed here. However, in normal evolution scenarios, in low Eh confined repository environments, most safety assessment exercises generally show that the dose which could be delivered to the critical group is generally far below recommended limits, and, as expected, due to the most mobile radionuclides such as ^{129}I , ^{36}Cl or ^{14}C , depending on the considered inventories in waste packages, [8,18]. Other fission products, such as ^{135}Cs , are sorbed on natural or artificial barriers, and therefore significantly retarded, whereas actinides are sorbed or precipitate in the near-field environment. Degraded scenarios may open the gate to more complex situations, in which the redox properties of radionuclides will be very important. An oxidising episode is a potential able to increase the solubility of U, Np and Pu by a factor of 10 000. Although actinide (V) and (VI) cations are still retained by sorption on clays and oxides, their impact in the final dose rate may become dominant compared to mobile fission products such as ^{129}I and ^{36}Cl , as their radiotoxicity is higher (dose factor). High carbonate concentrations may also increase the mobility of trivalent and tetravalent actinides. Large scale confinement failures, caused by major faults may also mobilise radionuclides, even in reducing conditions as colloids, or sorbed on colloidal detritic particles. The probabilities associated to such events is extremely low, and site selection, site characterisation, aim at reducing the risk of such scenarios. The redundancy of barriers is also an important safety requirement, in order to mitigate their consequences.

12. Conclusions

In most safety or performance assessment exercises, the long term impact is generally dominated by 2 mobile radionuclides ^{129}I and ^{36}Cl , especially if the underground fluids are chemically reducing. Due to its very small specific activity, the impact of ^{129}I is however generally very small. In addition, it has been recently shown that iodine is efficiently trapped by natural organic matter. Other mobile radionuclides such as ^{36}Cl and ^{14}C are expected to undergo isotopic exchange with stable environmental isotopes, which will also decrease their dose impact. Most actinides are insoluble in such conditions, and are expected to have a very small contribution to the total dose. In other conditions, such as those encountered in the environment of the potential repository of Yucca Mountain (Nevada, USA), chemically oxidising conditions may induce an enhanced mobility of actinides, but this site has been selected because it is expected to remain unsaturated, as it is emplaced above the water table. In such conditions, the radionuclide flux is expected to

be minimal. As a conclusion, it is possible to state that under normal circumstances, most radionuclides will be well confined, even after the failure of waste packages and containers, because their chemical properties, and the environmental conditions favour their precipitation or sorption. Their residual solubility is very small and can be predicted using published thermodynamical databases. This shows the advantage of geological repositories in deep water saturated rocks over surface facilities: deep repositories maintain stable, reducing chemical conditions over very long periods of time. Under incidental circumstances (oxidation consecutive to intrusion, creation of a high permeability zone) presumably ‘immobile’ elements may become more mobile due to oxidation or colloidal transport, but the very low probability of such events considerably lowers the associated risk.

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Discussion

Question de G. de Marsily

Est-ce que Pierre Toulhoat pourrait préciser l’état des connaissances sur les états d’oxydation de Plutonium PuO^{2+x} ?

Réponse de P. Toulhoat

Vous faites allusion aux travaux récemment publiés de chercheurs de Los Alamos faisant état d'une oxydation possible par l'eau du PuO_2 en PuO_2^{2+x} . Cette réaction a été observée à assez haute température, les mécanismes réactionnels sont encore à l'étude. En conditions de stockage profond, les éventuelles couches oxydées de PuO_2^{2+x} seraient réduites à nouveau en PuO_2 , dont la solubilité est extrêmement faible. Il n'y a donc pas à mon avis d'impact notable en conditions de stockage profond en milieu réducteur, qui correspond au cas des sites envisagés en France.

Question de J.-M. Gras

Les stockages sont conçus pour fonctionner à long terme en atmosphère réductrice, ce qui constitue, comme l'a montré l'orateur, un argument favorable vis-à-vis de la sûreté. Seul, le stockage de Yucca Mountain situé dans une roche volcanique au-dessus de la nappe phréatique, est conçu pour fonctionner en conditions oxydantes. Cela affaiblit-il la démonstration de la sûreté à long terme ?

Réponse de P. Toulhoat

Le stockage de Yucca Mountain est effectivement conçu pour fonctionner en conditions oxydantes, mais avant tout en conditions insaturées. Dans les scénarii d'évolution normale, les flux d'eau traversant le stockage sont très faibles, et garantissent ainsi un bon confinement des déchets. Dans certaines circonstances, il est envisagé que des cellules convectives puissent se mettre en place sous l'influence des gradients thermiques, pouvant localement entraîner des flux d'eau plus importants. Dans ce cas, les concepteurs doivent prévoir un conteneurage aux performances accrues, faute de pouvoir compter sur l'effet bénéfique de la géochimie en milieu réducteur.