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Overview of actinides (Np, Pu, Am) and Tc release from waste glasses: influence of solution composition

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Abstract

Studies on the release of actinides from nuclear waste glasses are numerous and essentially focus on the retention of actinides in the surface layer, their mobility, solubility and speciation in the medium of interest. Even if the chemical properties of the actinides, such as solubility and speciation in groundwaters, have been studied by many researchers, everything is not yet understood. Indeed, the radionuclide behaviour during glass alteration depends on many parameters like the nature of the solution in contact with the glass (pH, E_h, complexing agents, colloids). Several radionuclides are redox sensitive and their mobility is linked to the local redox conditions, expected to be reducing in deep repository environments. Their chemical species and solubilities will be greatly influenced by the redox conditions. Laboratory tests on glass corrosion in pure water under oxic or anoxic conditions show Tc and Np to be released to a greater extent than Pu or Am. Most of the Np and Tc are found in a dissolved form whereas Pu and Am are present as colloidal material with a mobility varying according to the nature of the solutions. The presence of carbonates increases more significantly the mobility of the actinides compared to phosphate and sulfate ions. Most of the released radionuclides will also adsorb on environmental materials or form colloids like Pu and Am, often associated with colloids attributed to the spallation from the alteration layer of the active glass. Parameters affecting the actinide speciation and release (redox conditions, complexation effects, colloid formation) are overviewed through a survey of literature data on active leaching tests. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

During the last decades, corrosion tests on actinide-doped glasses were performed and the release of actinides investigated. The experimental studies were essentially focused on actinides such as Am, Pu, Np and on Tc, potentially the most critical radionuclides because of their contribution to the radioactivity in the long term [1].

In models predicting the long-term behaviour of HLW, radionuclides may be assumed to be released at the same rate as other soluble glass elements like boron (B), providing a conservative limit for radionuclide release. However, glass dissolution is not congruent and insoluble elements, like actinides, will incorporate or sorb on glass alteration products. Consequently, the release of some radionuclides could be some orders of magnitude lower than predicted by conservative models.

Due to the complexity of the waste disposal system, many other parameters and mechanisms have to be taken into account when evaluating the release of actinides, such as the solubility limits of the individual radionuclides, the composition of the solution in contact with the glass including the pH, the redox potential, the presence of complexing agents or natural colloids, their sorption behaviour onto the glass or onto environmental materials. The objective of this paper is to briefly review the present status of knowledge on actinide and Tc behaviour in solution in contact with glasses like the French R7T7 glass, the German PAMELA glass and to discuss the main factors affecting their mobilisation and transport away for the waste form.

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2. Effects of the redox conditions on the release of the main radionuclides

2.1. Release of the radionuclides in aqueous solutions

In most of the corrosion tests reported in the literature, Np and Tc are released into solution to a greater extent than Pu and Am during glass corrosion of several glass compositions in oxic or anoxic conditions at the basic pH values expected in most repositories [2–8]. The release behaviour of the actinides is essentially linked to the redox conditions in the tests, which affects the observed concentration of the released radionuclides as well as their chemical behaviour in solution.

Static and dynamic corrosion tests with borosilicate glass doped with Np, Pu and Am were conducted under oxic and anoxic conditions. The release of Np, Pu, Am from R7T7 glasses into distilled water was measured by Vernaz and Godon [9] under oxic conditions. After ultrafiltration through a membrane with a pore size of 1.8 nm, Np was found to be dissolved in the leachates with a concentration of 1.5×10^{-6} M while most of the Pu and Am were present as suspended material (Fig. 1). The Np concentration in the leachate increased with the glass dissolution and did not appear to be controlled by any solubility limit. Grambow [10] showed that the release of Np from a glass, even under anoxic conditions, proceeded almost at the same rate as some other glass soluble elements and was thus controlled by the kinetics of glass dissolution. The Pu concentrations after 1 year dropped after ultrafiltration to a concentration of 4×10^{-8} M indicating that 90% of the released Pu is in a colloidal form while 99% of the released Am was found in particle form giving a final concentration of 5×10^{-10} M. They estimated the fractional release rate of individual radionuclides from the corroding glass using an actinide retention factor (RF) in the alteration film, defined as the ratio between the normalised B mass loss and the normalised actinide mass loss [9]. All the actinides are retained to some extent in the gel layers, particularly Pu and Am and only about 10% of Np, 3% of Pu and 0.3% of Am were finally released into the solution. Dynamic tests with Pu-doped glass [9] show that as long as the water is renewed daily, Pu was released at the same rate as other glass soluble elements. When the water renewal was interrupted, the Pu release rate dropped significantly, an amorphous gel layer being able to form on the glass surface and retain Pu. The results suggest that with solution renewal, the actinides are released at the same rate as the other glass elements whereas with the interruption of the water renewal, the activity in solution quickly reaches a steady-state value implying that the actinide release kinetics are controlled by the solubility of an actinide compound.

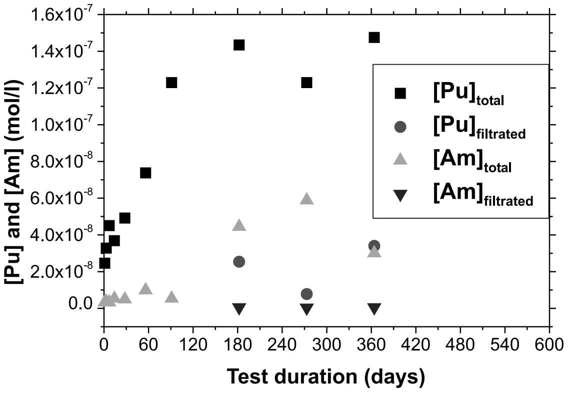

Fig. 1. [Pu] and [Am] before and after ultrafiltration for static leach tests of R7T7 glass into distilled water [8].

Bates et al. [11] and Ebert [6] reported also that Pu and Am were retained mainly in the gel layers whereas Np was found in solution with a release rate close to B. The ability of the reaction layer to retain the actinides varies from glass to glass as reported by Van Iseghem et al. [12].

Such observations on dissolved Np, colloidal Pu and Am in the leachates were also done by Advocat with experiments on aqueous silicate solutions under oxidising conditions [13] and by Grambow et al. [14] in saline solutions.

Inagaki et al. [15] evaluated the effects of the redox conditions and the presence of iron corrosion products on the release of Pu and Np in deionised water from R7T7 glasses. The presence of magnetite under both oxidising and reducing conditions had no remarkable influence on the Pu concentrations equal to 10^{-9} M. From thermodynamic data and conditions applied for the tests, Pu(IV) is expected to be the dominant oxidation state under both redox conditions. However, it should be pointed out also that in the case of a closed system, magnetite is not stable under 'oxidising' conditions and whatever initial oxygen was available, it should have been consumed by oxidation of magnetite explaining also the Pu concentration. In the absence of magnetite, the redox conditions had no remarkable influence on Np behaviour and Np dissolved species were dominant in the leachates whereas in the presence of magnetite under reducing conditions, the Np concentration decreased from 10^{-6} to 10^{-7} M. Other corrosion experiments [10] performed with highly active R7T7 glass with and without iron powder showed that the concentrations of Tc, Np, Am decreased by a factor of 100 in the presence of iron. The observed decrease of Np and Tc concentrations in the presence of iron may be explained either by sorption or by reduction of Np(V) and Tc(VII) to sparingly soluble Np(IV) and Tc(IV) or a combination of the two possibilities.

The same kind of behaviour is observed with tests performed in synthetic claywater with glasses doped with Np, Tc, Pu, Am in anoxic conditions [16]. The Tc and Np concentrations were found to be stable with time at 10^{-6} M after ultrafiltration while the Am concentration was equal to 10^{-11} M. The difference found between the ultrafiltered and non-filtered leachates proved that most of the Am forms colloids as well as Pu, present with a concentration of 10^{-8} M. When solids like clay or corrosion products were added to the clay water, lower Np and Tc concentrations were found in the clay leachates caused probably by the reducing capacity of the clay and some sorption and/or precipitation phenomena (Fig. 2). Adding clay does not decrease the Pu and Am concentration to a lower level than that in synthetic claywater. Having well-controlled reducing conditions and a high Boom Clay content, Lemmens et al. [17] with Np- and Tc-doped glasses showed that the Np and Tc concentrations tend to strongly decrease with time reaching values of 10^{-9} M for Np and between 6×10^{-7} and 6×10^{-8} M for Tc depending on the temperature. All these experiments indicate the Np and Tc behaviour depend strongly on the redox conditions compared to Pu and Am which are less sensitive. Using the thermodynamic data, Np(V) and Tc(VII) should dominate under oxidising conditions while under reducing conditions, lower Np and Tc concentrations are expected in agreement with the solubility of Np(IV) and Tc(IV). The high Np and Tc concentrations found in the leachates in most of the leaching experiments reported in the literature indicate that Np(V) is still the dominant oxidation state even under anoxic or well-controlled redox conditions. Np(V) is released as neptunyl which remains stable even under reducing conditions, due to an extremely low rate of reduction to Np(IV). The redox potentials of various groundwater systems are established by the presence of redox pairs such as Fe(II)/Fe(III). The presence of magnetite, iron corrosion products or other iron(II) bearing minerals like clay facilitates the reduction of these elements through the reducing capacity of these minerals and their catalytic effect by surface complexation.

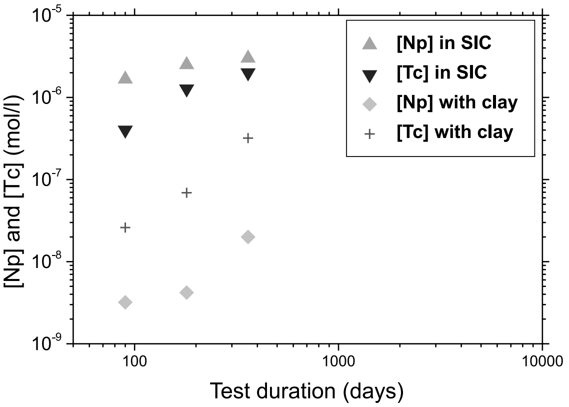

Fig. 2. Influence of solids like clay or corrosion products on [Np] and [Tc] [15].

2.2. *Release of actinides in contact with solids*

Most of the radionuclides released from the glass will sorb onto environmental materials. When solids are added to the leaching experiments, the mobile radionuclide concentrations are usually some orders of magnitude lower than those for tests with pure waters or natural groundwaters. This is attributed either to very high sorption factors on the environmental materials or to precipitation of very low solubility compounds. Furthermore, the environmental materials present in the vicinity of the corroding glass can influence the retention of the actinides in the gel layer to a considerable extent. Static tests with R7T7 glass showed that the amounts of Np and Pu retained in surface layers varied when other materials including sand, granite, bentonite, smectite, illite and Boom Clay were included in the test vessel, the presence of these materials also affecting the solution chemistry and the glass corrosion rate [9]. Smectite, illite and Boom Clay sorbed Np weakly and Pu strongly. The Pu fraction retained in the gel surface and the Pu fraction fixed by the materials were much greater than for Np. Most of the leached activity not fixed on the materials was in particle form and was removed by filtration. Moderate alteration was found in the presence of sand, bentonite and granite while alteration was severe with smectite, illite and Boom Clay. It was also found by Bates [18], Ebert [6], Vernaz and Godon [9], that Pu and Am have very low concentrations (10^{-10}–10^{-12} M) in basic pH systems and sorb strongly onto metal components in laboratory tests.

The enhancing effect of the presence of clay on waste glass corrosion and its influence on the mobile radionuclide concentrations have been demonstrated by various authors [9,12,16,17,19–23]. The enhancement is the function of the type and the amount of clay [12]. Laboratory experiments studying the influence of Boom Clay have shown that Pu and Am are strongly sorbed onto the clay such that only a minor fraction remains mobile with average concentrations of 10^{-9} M for Pu-239 and 10^{-11} M for Am-241. The Pu and Am concentrations in a mobile form were found to be independent of duration while increasing concentrations were found for Np and Tc. After 4 years, maximum 0.2% of the total released Pu and Am inventory, 5% for Np and 4% for Tc were in a mobile form with Np and Tc concentrations, respectively, 10^{-7} and 10^{-6} M. These concentrations decrease further when adding Fe_2O_3 corrosion products [24,25]. The Pu, Am and Np concentrations were comparable to the concentrations found in a granite containing medium after filtration through a 0.45 μm filter [26]. The results for Pu confirm the

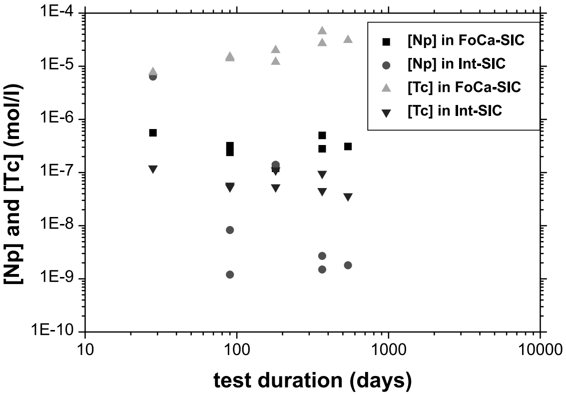

Fig. 3. [Np] and [Tc] in the FoCa and Int-SIC leachates for tests at 90°C after ultrafiltration over 100.000 molecular weight cut-off filters [16].

observation by Vernaz and Godon [27] (see also [25]) that the presence of clay reduces the retention of Pu in the glass surface layers of SON68. Previous work on R7T7 glass [28] has shown that in pure water typical RF are 5–10 for Np, 50–100 for Pu and 500–1000 for Am while actinide retention was lower in Boom Clay with values of 3 for Np and Tc, 10 for Pu and 40 for Am. The release of Pu and Am is characterised by their considerable sorption on the clay, typically 99.8% of the actinide inventory released.

Tests with Np- and Tc-doped glasses were performed by Lemmens et al. [17] in two different clay media (an oxidised clay and a mixture composed of Boom Clay containing reducing components namely pyrite, Fe_3O_4 powder and stainless steel powder added to simulate canister corrosion products). As expected from the characteristics of the two media, the Np and Tc concentrations were higher in the oxidised clay than in the reducing medium for which a very low redox potential was measured (Fig. 3). At the positive redox potential found in the oxidised clay, the Tc concentrations reached values up to 10^{-4} M. Tc is present in the highly soluble TcO_4^- form for which no sorption on clay is expected. In the second medium, the Tc concentrations are not higher than 3×10^{-7} M. Under reducing conditions, Np(V) and Tc(VII), leached from the glass, are reduced to the very insoluble Np(IV) and Tc(IV) which are sorbed or precipitated into the clay.

3. Effects of complexation on the leaching behaviour of the main radionuclides

Most of the complexation studies have focused on radionuclide-complexation reactions in solution in the absence of nuclear waste glasses. In this section, we will first give a brief overview of the chemistry and expected species of the radionuclides of interest in solution for studies performed without any glass and second, an overview of the observed behaviour of these nuclides in systems involving the interaction of glass with various aqueous solutions.

3.1. Radionuclide chemistry in solution expected in most repositories

It is well known that Am, Pu, Np and Tc readily undergo hydrolysis as the solution pH increases, with the ease of hydrolysis increasing with the atomic number.

Am(III) is stable under both reducing and oxic conditions. Trivalent carbonate complexes such as $AmCO_3^+$, $Am(CO_3)_2^-$, $Am(CO_3)_3^{3-}$ are the dominant species in solution under basic conditions when carbonate is present [29,30] while uncomplexed Am^{3+} and hydroxo species such as $AmOH^{2+}$, $Am(OH)_2^+$, $Am(OH)_3$ dominate in solutions with low carbonate content [29]. Even if the high stabilities of carbonate complexes with Am(III) are similar to those of humic acid complexes, in groundwater rich of humic acids, Am is usually found to be associated with organic matter.

Tetravalent and hexavalent Pu are also expected to be strongly complexed by humic acids. However, $Pu(OH)_4$ is usually admitted to be the dominant solution species at neutral pH values under slightly oxidising conditions. At higher pH values, in the presence of small amounts of carbonates, species such as $PuCO_3^{2+}$, $Pu(CO_3)_2$, $Pu(CO_3)_4^{4-}$, $Pu(CO_3)_5^{6-}$, and $Pu(OH)CO_3^+$ are expected [31] while under strongly reducing conditions, Pu(III) species such as $Pu(CO_3)_2^-$ and $Pu(CO_3)_3^{3-}$ are stable at increasing pH. The Np behaviour is expected to be controlled by the chemistry of Np(V) under mildly oxidising conditions or by $Np(OH)_4$ under reducing conditions. Because of its low electric charge, Np(V) in the form NpO_2^+ is more soluble and less strongly hydrolysed and complexed than Np(IV) [32]. Under oxidising conditions, it will dominate at low to neutral pH values while carbonate complexes of Np(V) like $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ become important above pH 8 at high carbonate content [33–36]. $Np(OH)_2(CO_3)_2^{2-}$ and $Np(OH)_4(CO_3)_2^{4-}$ are also stable at high carbonate concentrations [32]. Np(V) is only weakly complexed by humic acids whereas Np(IV) should give strong interactions with humic acids even if this was not demonstrated until now due to the difficulty to study systems involving tetravalent actinides with humic substances.

Except in highly reducing solutions, Tc exists as pertechnetate ion which is not easily complexed in solution, does not sorb or form pseudocolloids and does not hydrolyse even at very high pH values. Tc exists as $TcO(OH)_2$ under reducing conditions which can sorb to a greater extent. Tetravalent Tc has been observed to be complexed by carbonate and sulfate.

3.2. Release of radionuclides in the presence of complexing agents

If the distribution of the radionuclides between the mobile and immobile phases as glass corrodes is influenced by the presence of sorbing materials, the presence of complexants can increase the actinide solubility and mobility in solution and stabilise some of the oxidation states. The actinides form strong complexes with many ligands commonly present in groundwaters like carbonates, sulfate, phosphate and halides. Because of its high complexing strength and natural occurrence in most groundwaters, carbonate is one of the dominant ligands for actinides, its concentration depending on pH. Other important complexing agents are the humic substances which are naturally occurring polyelectrolytes containing a large number of functional groups. The stabilities of organic complexes are generally similar to those of hydrolysis and carbonate complexes. So, competition will occur in natural waters unless the concentration of one ligand predominates.

As shown by Advocat et al. [13], the mobility of the actinides is linked to the nature of the anions present in the solutions. In oxic conditions, they found Pu was mainly in particle form with its mobility increasing according to the nature of the solution in contact with the glass (carbonate > sulfate > phosphate) (Fig. 4). Pu release rates were about 60 times (in carbonate media) and 180 times (in phosphate media) lower than the glass dissolution rate. The mobility of Np, found in a dissolved form in the different leachates, varied also in the same order. Leaching of Np-doped glasses by 5×10^{-3} M carbonate solutions results in 45% Np retention in the alteration film while in phosphate and sulfate solutions, Np retention was, respectively, 94% and 67%. In the presence of carbonate ions, Np will form stable $NpO_2(CO_3)_n^{1-2n}$ complexes (n ranging from 1 to 3) whereas in a sulfate solution, $NpO_2(OH)_n^{1-n}$ complexes (n varying from 1 to 2) are dominant. The presence of carbonate ions increases more significantly the mobility of actinides than sulfate or phosphate ions in oxic conditions and tends to limit the Np incorporation in the gel. Under reducing conditions, the same soluble concentrations were found for Pu with values of 2×10^{-8} M in carbonate media, 2×10^{-10} M in phosphate medium and 5×10^{-9} M in water [13]. On the basis of the thermodynamic data, only a few phases are stable under the experimental conditions. However, the Pu concentrations are two orders of magnitude higher than the theoritical concentrations near saturation meaning that the retention of Pu is not controlled by the precipitation of simple phases like PuO_2 or $Pu(OH)_4$. The same remark can be made for Np for which the concentrations are lower (10^{-6} M) than the stability limits of well-known phases like $NpO_2(OH)am$ or $NaNpO_2CO_3 \cdot 3.5H_2O$. In a tuff groundwater (reference water for the Yucca Mountain formation Site in Nevada), Nitsche [37] reported also that complexation with carbonates probably increased the solubilities of oxidised form of Np and Pu. However, in real reducing conditions expected in most repositories, Pu and Np are predicted to be in a tetravalent oxidation state but until now, experimental data on the dependence of Np(IV) and Pu(IV) on carbonate concentration are rather limited [38,39].

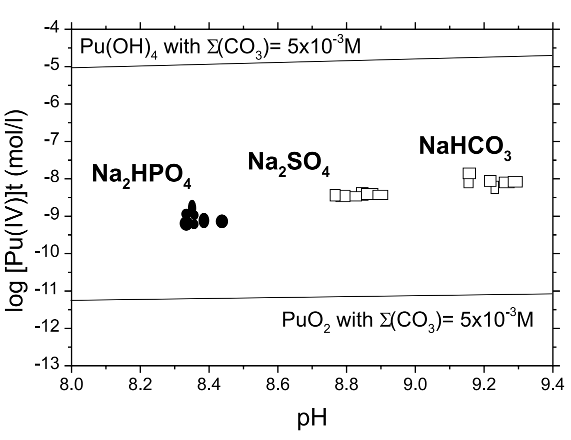

Fig. 4. Influence of various complexing agents on the Pu mobility under oxidising conditions (carbonate > sulfate > phosphate) [12].

Organic matter (small organic molecules, humic acids,...) is also well known to be able to complex the actinides. The effect of humic substances on the leaching behaviour of metals from several glasses has been studied [40]. These specific tests have shown trivalent metal ions to be strongly complexed in the presence of humic materials while the hydrolysis of tetravalent ions seems to be the most important mechanism. The humic acids, present at high concentrations in the Boom Clay medium have been shown by Gin [41] to have very limited influence on the glass dissolution itself. The importance of humic acid complexation is expected to decrease at pH values greater than about 8 [42].

4. Influence of colloid formation of the mobility of the main radionuclides

In addition to the complexation effects, the generation of actinide colloidal species may be of importance for the actinide transport processes. Such colloidal particles have a considerable adsorption capacity for ions of high charge like actinides and create great difficulties for the theoritical prediction of 'real' actinide soluble concentration in natural water [43]. Colloids may form from hydrolysis of dissolved metal ions in solution and polymerisation (real colloids), by adsorption of radionuclides onto existing natural groundwater colloids (size: 1 nm–1 μm) or onto glass alteration products. These both adsorption processes generate pseudocolloids. Groundwater colloids are composed of inorganic and organic molecular constituents including mineral products (clay minerals, polysilicic acid, $CaCO_3$, FeOOH), hydrolysed precipitates of mixed metal ions, macromolecular components of dissolved organic carbon (DOC), biocolloids composed of microorganisms [43]. The tendency to generate real colloids of actinide ions follows their hydrolysis properties leading to hydroxide colloids and polynuclear species. With few exceptions, the following trend is observed for tendency of colloid formation: $\mathrm{Np(V)} < \mathrm{U(VI)} < \mathrm{Am} < \mathrm{Th(IV)}$, Pu(IV), tetravalent ions being the most unstable in solution. Kim [44] described the formation of actinide real colloids leading to high concentrations of Pu and Am hydroxide or oxide in solution.

Glass may be also a source of colloidal material, the radioactivity associated to this last kind of colloids being usually very high. The processes which cause the formation of colloids during glass reaction have been defined in terms of spallation of surface layer of the waste glass (primary colloids) and precipitation reactions in the leachates by Ahn [45]. At high ratios of surface area to the solution volume, high colloid concentration fractions can be detected because high S/V tests generate supersaturated solutions which naturally tend to precipitate a larger quantity of solid alteration phases, some of which are colloidal [46]. Bates et al. [47] reported the formation of Pu and Am containing colloids in simulated groundwater mainly attributed to the formation of fragments of the alteration layer which were spalled from the active glass surface. Their results show that 70% of the Np passed through all filter sizes and can be considered truly dissolved in solution.

The presence of colloids bearing radionuclides may lead to aqueous concentrations which exceed the solubility limits of pure phases. Most of the colloidal studies have been concentrated on the colloids already present in groundwater and on colloid generation in the absence of nuclear waste form [43]. However, the dissolution of HLW glasses in the presence of groundwater results generally in actinide pseudocolloid formation. Actinide pseudocolloids were confirmed by many experiments and sizes as small as 1 nm were found [43,44]. For obvious reasons, laboratory experiments with nuclear glasses require a long time to form actinide colloids in the leachates. It is crucial to filter correctly the solutions to separate the dissolved and colloidal fraction. However, it must be pointed out that most of the colloid studies have been done on solutions that have been allowed to cool down to room temperature before filtration. This can produce artifacts as the colloids could have formed during the cooldown and might not have been present at test temperature. Cooling could also have changed the size distribution.

4.1. Humic colloids

The humic substances present in natural groundwaters or leachates can behave like colloidal species readily adsorbing actinides creating pseudocolloids [48] or forming a coating on the inorganic material. The problem is then to distinguish whether the system is in true solution (metal humate complexes) or in a colloidal state because both, complexes and colloids are large in size, soluble in water and can be fractionated by ultrafiltration. However, the distinction can be made by spectroscopic investigation as demonstrated by Kim [49] who showed the difference between an Am-humate complex and the humic colloid of Am. Kim reported that the predominant amount of humic colloid is found in the size range less than 50 nm down to about 1 nm [34]. In Boom Clay, 70% of the humic acids are present in a colloidal form and strongly interact with trivalent and tetravalent ions [50]. About 90% of the humic acid colloidal particles are smaller than 15 nm whereas Kim indicated that about 94% of the DOC is smaller than 1 nm in one of the Gorleben waters [44].

Elements with oxidation states greater than +2 like trivalent and tetravalent metals (Rare Earth elements, Fe, Hf, Th, Zr) were found to be strongly associated to humic colloids [49]. In groundwater rich of humic substances like Gorleben or Boom Clay water, more than 80% of metal ions of high oxidation state were found sorbed on colloids collected on 1 nm filters. For groundwaters with DOC concentrations >1 ppm, the concentrations of elements such as Fe, Ce, Eu, Hf, Th, Zr, are found to be in a linear correlation with the DOC concentrations giving rise to a slope of one [49]. Dearlove [48] found also that the colloids concentrations in gorleben waters were directly proportional to the DOC concentration. All these elements are considered as being chemically analogous to the actinide ions.

Using Th(IV), Kim studied the interaction of a tetravalent element with groundwater humic colloids and showed the correlation, between its concentration and the DOC concentration suggesting that Th(IV) is present as being quantitatively DOC bound [34,44]. At pH 4, the Th^{4+} ion is already quantitatively sorbed on humic colloids (>99.9%) and remains on the colloids at $pH > 4$. Tetravalent Np is also expected to show strong interactions with humic colloids in water rich of humics while Np(V) is very stable against hydrolysis and will show a negligible humate complexation as well as a sorption on humic colloids [34]. Am was found also to be quantitatively sorbed on humic colloids. Over 99% of the Am was filtered with humic colloids at 1 nm pore size. In groundwaters rich of humic substances, the generation of Am pseudocolloids will dominate over the carbonate complexation.

5. Conclusion

The majority of the corrosion tests have focused on glass corrosion mechanisms rather than the release of radionuclides for some obvious reasons like difficulties in handling or monitoring radioactive materials and solutions. However, active corrosion tests were performed by different groups to determine the specific influence of different parameters, the actinide behaviour being complicated by many factors including various oxidation states, complexation reactions, colloid formation from different sources and sorption on several surrounding materials. Usually, the rate of matrix dissolution provides an upper limit for radionuclide release. The transport will then depend upon the physico-chemical characteristics of the different species as well as their interaction with the geological material. Each radionuclide has to be considered separately.

The mobile radionuclide concentrations usually reported in most of the dissolution tests are in good agreement and are interpreted in the same manner. Most of the Tc and Np are found in a dissolved form in the absence of any solid material passing through all the filter sizes whereas Pu and Am are always present as colloidal particles. Actually, the release of the radionuclides is mainly linked to the redox conditions which have no remarkable influence on Pu and Am behaviour while the redox properties have a more significant impact on Np and Tc. Pu(IV) and Am(III) are the dominant oxidation states in both mildly oxidising and reducing conditions while Np, Tc which are quite stable in their oxidised form and are expected to reach high solution concentrations in corrosion tests even under anoxic conditions. Their kinetics of reduction are indeed very low. When solids are added, lower Np, Tc concentration are observed due to their reduction to more insoluble oxidation states, and/or sorption/precipitation phenomena.

So, in most of the repositories expected to be reducing, even if the release of actinides increases in the first stage of the glass reaction, the solubilities of actinides will be very low. Unfortunately, it is difficult to determine real solubilities of individual radionuclides because usually solubility is not controlled by simple phases in corrosion tests and furthermore, colloids and complexing agents are present increasing the total radionuclide concentrations measured in solution. Among the complexing agents encountered in most groundwaters, carbonate and humic substances have been shown to increase the mobile concentration of actinides but until now, only trivalent actinides have been really proved to be strongly complexed by humic substances. The hydrolysis mechanism seems to be the most important mechanism for tetravalent actinides. Finally, even if glass alteration is followed by transfer of radionuclides in solution, fortunately, only a small fraction of them will be in a mobile form.

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