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Literature Review of Intrinsic Actinide Colloids Related to Spent Fuel Waste Package Release Rates

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Contents

1. Introduction

The existence of actinide colloids provides an important concentration enhancing mechanism in the migration of radionuclides and will be important in the performance of a geologic repository for high-level nuclear waste. Actinide colloid formation during long-term unsaturated dissolution of spent fuel by groundwater has been observed in ongoing laboratory experiments [Finn and Buck 1994]. In order to predict the radionuclide release in repositories under various conditions, the chemistry of actinide colloids should be understood. This article summarizes a literature search of "actinide colloids". Two types of actinide colloids have been identified in groundwaters [Kim 1985, 1989, 1991, 1994, Silva and Nitsche 1995]: (1) intrinsic or real colloids, mostly generated by the products of actinide hydrolysis through oxo and/or hydroxyl bridge formation; (2) pseudocolloids, formed by sorption of actinide ions or intrisic colloids onto aquatic colloids, which are composed of inorganic or organic water constituents. This report emphasizes the formation of intrinsic actinide colloids, because they would have the opportunity to form soon after groundwater contact with the spent fuel and before actinide-bearing groundwater reaches the surrounding geologic formations. Formation of intrinsic actinide colloids in the waste package may allow apparent actinide concentrations to considerably exceed their solubility limits, increasing the actinide source term from the waste package significantly. These apparent actinide concentrations would control all downstream actinide concentrations. Actinide pseudocolloids are referenced when appropriate. Because colloid formation is an inherent part of waste glass dissolution, it is a separate subject with a different genesis and is not included here.

The migration behavior of colloids in groundwater can be very different from either soluble species and precipitates [Silva and Nitsche 1995, McCarthy and Zachara 1989]. The role of colloids in transportation of contaminants in groundwater is not well understood. However, the observed evidence demonstrates that the presence of colloids can increase the total concentrations of actinides above the equilibrium thermodynamic solubility limits, and thereby increase the mass amount of actinides transportable to the environment. Actinide colloids have attracted significant attention in the last two decades and several review articles have been published [Kim 1985, 1989, 1991, 1994; Silva and Nitsche 1995, Avogadro and Marsily 1984, Ramsay 1988, Lieser 1995, Lieser et al. 1986, Kepák 1971, McCarthy and Zachara 1989, Remius 1995]. Perhaps the most recent review on the subject is given by Silva and Nitsche in 1995. A review by Lieser in 1995 focuses on the pseudocolloids. Kim has reviewed the results of studies on actinides colloids several times [Kim 1985, 1989, 1991, 1994] in the last decade. Kim has been focusing also on the groundwater colloids, with an emphasis on pseudocolloids.

2. *Characterization of Colloids*

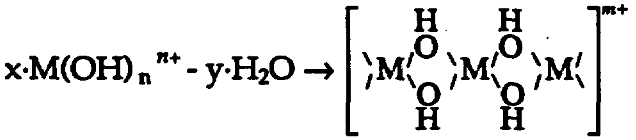
A colloidal system consists of particles permanently dispersed in a liquid medium typically with particle diameters smaller than one micrometer [Sheludko 1966a; Hunter 1987, 1993]. The particles are collectively known as the disperse phase and the liquid is called dispersing medium. The actinide colloidal systems discussed in this report contain actinide elements in fine particle forms with water as the dispersing media. Depending upon the formation mechanisms, actinide colloids in groundwaters are classified as intrinsic colloids or pseudocolloids. References [Kim 1985, 1989, 1991, 1994; Silva and Nitsche 1995, Avogadro and Marsily 1984] describe intrinsic colloids as those composed primarily of an actinide and formed by condensation of actinide molecules or ions by a hydrolitic or precipitation process. The chemical properties of intrinsic colloids are expected to be similar to their original compounds in macroamounts. Intrinsic colloids are also called "real", "pure", "eigen", "primary", and "true" colloids. The pseudocolloids, on the other hand, are the products of actinide elements (colloids or ions) adsorbed onto groundwater colloids due to their affinity to these colloids or hydrophobic properties of the dispersing medium. The chemical properties of pseudocolloids are expected to be similar to the groundwater colloids to which they are attached. Other terms such as "associative" or "fremd" may be used for pseudocolloids as well. Experience shows that groundwater colloids larger than 0.45 µm will not be stable [Kim 1991], so it is likely pseudocolloids are less than 0.45 µm in diameter.

Generally, the stability of a colloidal system mainly depends on the electric charge on the surface of the colloid [Sheludko 1966a; Hunter 1987, 1993]. The greater the net surface charge, the more stable is a colloid system, because the surface charges generate repulsion between colloidal particles and prevent them from coagulating and settling out of the solution. Perhaps the most important factors which can affect the surface charges are the pH and ionic strength of a dispersing medium. Most intrinsic actinide colloids are hydroxide or oxide related. They tend to adsorb H_3O^+ and OH^-, in acidic and basic solutions respectively, and gradually develop either highly positive, neutral or highly negative surface charges. The pH value at which the colloids have zero surface charge is termed as pH_{pzc}. Obviously, the further the pH of colloidal system is from its pH_{pzc}, the larger the surface charge and the more stable the colloid system. Each colloidal system is characterized by its pH_{pzc}, so that the pH can be adjusted to stabilize or destabilize a colloidal system. The effect of ionic strength on the surface charge, on the other hand, is due to the "salt effect" in a colloidal system. If electrolytes are present in a colloidal solution, the cations tend to adhere on a negatively charged colloid to compensate the excess local charges of opposite sign and vice versa for anions. This will reduce the double layer potential of the colloid and enhance the coagulation process in that colloidal system.

3. Formation of Colloids

Extensive studies [Kim 1985, 1989, 1991, 1994; Silva and Nitsche 1995, Avogadro and Marsily 1984, Ramsay 1988, Lieser et al. 1986] demonstrate that hydrolysis is a primary step to polymerization of aqueous ions and thus generation of actinide colloids. Therefore, the tendency of formation of actinide colloid is parallel to their hydrolysis order: $M^{+4} > MO_2^{2+} > M^{3+} > MO_2^{+}$ [Kim 1985, Silva and Nitsche 1995, Choppin 1983]. Ions decrease their effective charges on the central atoms in this order. The explanation for ion MO_2^{2+} having a greater tendency than that of M^{3+} is that the linear geometry of MO_2^{2+} gives a relative high charge density at its equatorial directions. Ramsay in 1988 suggested that the tendency of hydrolysis of cations is indicated by their first hydrolysis constant K_1, which is correlated with the ratio of the charge on central atom to the metal-oxygen (M-O) bond length (z/d). Actinide hydroxides and oxides usually have very small solubilities in natural water, making them the common source of intrinsic colloids. Because formation of intrinsic colloids is related to their hydrolysis, thermodynamic studies and hydrolysis data [Choppin and Mathur 1991, Fuger 1992, Kraus 1956] are primary references to colloid studies. Some stability constants of various hydrolysis reactions of different actinide ions are summarized in the literature [Kraus 1956].

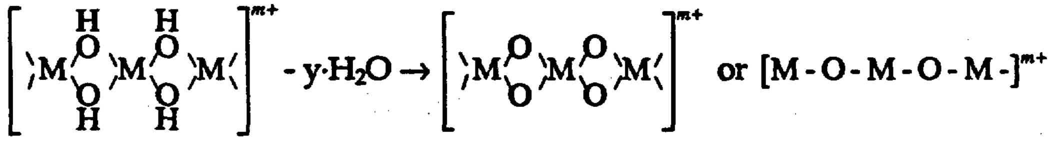
A possible model for a product of hydrolysis undergoing polymerization may involve formation of aggregates with hydroxy bridges [Choppin 1983]:



$$x\cdot M(OH)_n^{\,n+} - y\cdot H_2O \rightarrow \left[\ \rangle M\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\ }}\rangle M\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\ }}\rangle M\langle\ \right]^{m+}$$

(1)

Aging or further dehydration may occur by changing the hydroxy bridges to oxo bridges:



$$\left[\ \rangle M\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\ }}\rangle M\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\ }}\rangle M\langle\ \right]^{m+} - y\cdot H_2O \rightarrow \left[\ \rangle M\overset{O}{\underset{O}{\ }}\rangle M\overset{O}{\underset{O}{\ }}\rangle M\langle\ \right]^{m+} \text{ or } [M-O-M-O-M-]^{m+}$$

(2)

Knowledge of the size of colloidal particles is important, because it is related to colloid stability in the dispersing media, which may affect the mechanism of actinide migration in surrounding geologoc media. In principle, the size of colloids depends on two competitive processes: the formation rate of new nuclei and the growth rate of aggregates. A slow rate of formation of new nuclei and rapid aggregation gives rise to a small number of large particles. On the other hand, a high rate of formation of new nuclei and a slow rate of growth of aggregates forms a large number of small particles. The mechanisms for the nucleation and growth in particle size of colloids are similar to those of precipitation [Sheludko 1966a]. Hence, the concentration of an actinide exceeding its solubility limit in a solution with certain limits in the growth of particle size is essential for formation of a colloid.

In 1984, Avogadro and De Marsily discussed the potential sources of colloid formation relevant to nuclear waste forms. Two sources are responsible for the formation of intrinsic colloids: (1) Leaching of the waste form with groundwaters.-- The possibility of colloid formation depends on the leaching rate and the solubilities of a given actinide in groundwater; (2) Precipitation processes. --The effect of radiation and elevated temperatures may convert some of actinide elements into their higher oxidation states, thereby enhancing the dissolution of these actinides into the surrounding waters. As such, soluble species migrate from the disposal repository toward more natural environments. Reduction, hydrolysis and precipitation processes may occur and form a disperse phase. These phenomena induce the formation of intrinsic and pseudocolloids.

4. Methods for the Study of Actinide Colloids

Numerous methods have been used to observe and measure the properties of actinide colloids. A review article [Kepák 1971] summarized some of these methods and their results. Filtration and centrifugation are the most common and effective techniques used in the literature. Various spectroscopic methods, such as UV/VIS, laser-induced photoacustic, light scattering, as well as scanning and transmission electron microscopies, have been used in actinide colloids studies.

4.1. Centrifugation, Ultracentrifugation, Filtration and Ultrafiltration

These methods are used to separate the colloids from their dispersing media and the percentage of material retained and passed through the filter membrane can be obtained. Filtration and ultrafiltration with pore-sized filters have been used to obtain the size distribution of colloids in the studied systems. Ultracentrafugation was used to determine the density [Rundberg 1988] and relative particle size distribution [Ichikawa and Sato 1984] of Pu(IV) colloids. The influence of various factors such as: aging time of the colloid, change of pH in solution, the presence of electrolytes of different type and concentrations, and the effect of temperature, were extensively studied.

4.2. Electrophoresis

The sign of the colloid charge can be determined by electrophoresis. Electromigration experiments were conducted [Kepák 1971] as a function of pH of the investigated solutions to study the change of sign of charges on the colloids. In general, a large fraction of colloidal particles carry a positive charge at lower pH, negative charge at higher pH and zero charge at pH_{pzc}. In most cases the pH_{pzc}'s are near neutral pH, but some times pH_{pzc} can vary significantly from pH 7. For instance, the pH_{pzc} for Am(III) was determined to be 5 to 8 [Olofsson et al 1982a, 1982b]. For Pu(IV) the pH_{pzc} was about 7 to 8 if the plutonium concentration is higher than 10^{-6} M about 3.5 at a [Pu(IV)] concentration of 10^{-7} M [Kepák 1971. The measurement of electrophoretic mobilities of colloidal particles allows the calculation of the colloid zeta potential, which may be the best parameter to describe the behavior of colloids in a medium [Sheludko 1966b, Fourest et al 1994].

4.3. Ion Exchange and Adsorption

These two techniques can be conducted by batch, column and/or field experiments [Lieser et al. 1990]. Ion exchange techniques have been used to study the adsorption behavior of actinide colloids on the exchanger. Experimental results showed that electrolytes either increase adsorption of radiocolloids or do not influence adsorption at all.

The adsorption studies of radiocolloids onto different materials, such as glass, polyethylene and various metals have been reported, in order to investigate the adsorption mechanism and the state of the microcomponent in the different solutions. The adsorption of radionuclides on glass, for example, was used to differenciate between intrisic and pseudocolloids [Kepák 1971]. It is generally assumed that primary impurities in solutions are colloidal silicic acid, which shows a particular adsorption profile on glass within a certain pH range. If the adsorption properties of the colloid under investigation does not fit a profile of the carrier-colloids, then the colloid is more to be likely an intrinsic one than a pseudocolloid.

Columns can be filled with different materials, such as backfill [Nowak 1984], sediments from near- or far-fields [Lieser et al. 1990] and/or a particular oxide depending on the experiment [Olofsson et al. 1983]. The mobilities of Am(III), Pu(IV) and Np(V) colloids were studied by α-Al_2O_3 packed columns [Olofsson et al. 1983]. The results showed that the colloids tend to be retained on the column at lower pH and mobilized at higher pH. Am(III) colloids were adsorbed at pH's of 6 to 8, and become mobilized at pH's of 12 to 13. A particle fraction of plutonium colloid was observed at pH's above 8, and it dominated at pH's greater than 12. The authors concluded that the high-pH particle fractions may represent true hydroxy colloids, while the particle fraction of Am(III) collected at pH 6 may be pseudocolloids related to impurities in the system.

4.4. Spectroscopy

Various spectroscopic techniques have been reported in studies of actinide colloids. These techniques can provide information at micro or molecular levels for characterization of colloids. Aqueous plutonium ions at all four oxidation states are easily distinguished from Pu(IV) colloids by their absorption spectra [Costanzo et al. 1973]. Since conventional absorption spectrometers have relatively low sensitivity, laser-based techniques have been used for measurement of very weak absorbances.

Laser-induced photoacoustic spectroscopy was employed to detect the presence of Am(III) colloid in $NaClO_4$ (pH 6.5) solution by Kim et al [Kim 1985, Buckau et al. 1986]. The absorption band of Am(III) at 503 nm increased and became better resolved in solutions filtered through smaller pores (220, 2 and 1 nm), while the total concentration of Am(III) kept decreasing as the the filter pore sizes decreased.

Light-scattering spectroscopy is well-known for the measurement of size of small particles in solutions [Shaw 1992]. Particle size of colloids were determined using autocorrelation photon spectroscopy [Triay et al. 1991, Ramsay et al. 1988], which is a laser based light-scattering techniques. Scanning electron microscopy [Shaw 1992, Ramsay et al. 1988, Feng et al. 1994], energy dispersive X-ray spectroscopy and transmission electron microscopy [Ramsay et al. 1988, Feng et al. 1994] can be used to obtain insight into the mechanisms of formation and sorption behavior of colloids.

5. Summary of Some Actinide Colloid Studies

5.1 Plutonium Colloids

The solution chemistry of plutonium can be very complex because of the unique disproportionation reactions of plutonium, which make it possible for all four common oxidation states of plutonium to co-exist in the same solution. In general, the lower oxidation states, such as Pu(III) and Pu(IV), tend to be more stable in acidic solutions, and the higher oxidation states, like Pu(V) and Pu(VI), become stabilized when alkalinity of solutions has increased. Plutonium hydrolysis, as described elsewhere [Kim 1989, Silva and Nitsche 1995, Choppin 1983], has the following pattern: $Pu^{4+} > PuO_2^{2+} > Pu^{3+} > PuO_2^{+}$, in which $Pu(OH)_4$ has an extremely small solubility product of about 10^{-56} [Cleveland 1979, Rai 1984, Kim and Kanellakopulos 1989] in comparison with $PuO_2(OH)_2$, which has a value of $3x10^{-18}$ [Pashalidis et al. 1993a]. Pu(IV) colloids were once thought to be due to polymer formation from hydrolysis products [Cleveland 1970], but Lloyd and Haire [1978] have shown that the colloid consists of very discrete particles of hydrated plutonium dioxide, which can be amorphous or crystalline. Because of the insolubility, Pu(IV) intrinsic colloids readily form in a solution at a pH of 2 [Cleveland 1979], and remain stable in acidic solutions for years [Rundberg et al. 1988]. Colloidal Pu(IV) has a light green color, completely different from the dark brown color that Pu(IV) ions exhibit. Thus the characterization of Pu(IV) colloids can be easily carried out using absorption spectroscopy [Costanzo et al. 1973].

Plutonium intrinsic colloids, particularly the Pu(IV) colloid, have been studied extensively. Several reviews [Kim 1989 and 1985, Silva and Nitsche 1995, Cleveland 1979, Choppin 1988] discuss the results in great detail. In the pH range of 4 to 9 the solubilities of colloidal Pu(IV) will fall between those of crystalline $PuO_2(c)$ and amorphous $Pu(OH)_4(a)$ [Rai et al. 1980a, Rai and Swanson 1981]. Therefore, the solubility curves of $PuO_2(c)$ and $Pu(OH)_4(a)$ [Rai and Swanson 1981] can be used to estimate the concentration of Pu(IV), at which colloidal plutonium may form. The stability of Pu(IV) colloids depends on their size, and the pH and ionic strength of the dispersing media. At lower pH values, the lower the ionic strength, the more stable would be the colloids in solution [Rai and Swanson 1981, Sheludko 1966]. However, in solutions with a higher pH (7 to 11, for example), stable Pu(IV) colloids are more likely to be found in solutions of higher ionic strength [Zhao, in press]. These phenomena must be related to the particle size of Pu(IV) colloids, charges on the plutonium colloids, and interactions between colloidal particles and electrolyte ions in solutions.

Kosiewicz in 1984 has reviewed the techniques used for the determination of size of plutonium colloids including: filtration and ultrafiltration, gel permeation chromatography, high performance liquid chromatography, and diffusion. Other methods, such as ultracentrifugation [Ichikawa and Sato 1984], and autocorrelation photon spectroscopy (APS) [Triay et al. 1991, Rundberg et al. 1988] have also been used to obtain size information of plutonium colloids. The size range was determined to be 1 nm to 1 µm [Ichikawa and Sato 1984], depending on how the colloids were generated and effects of α-radiation [Rundberg 1988]. The density of ^{242}Pu(IV) colloids was determined using ultracentrifugation in conjunction with APS. The results showed that the density of ^{242}Pu(IV) was slightly lower than the estimated density of crystalline PuO_2.[Rundberg 1988].

Other studies [Rai et al. 1980b, Rai and Serne 1979] showed that "Pu(III) would be expected to be the predominant species under relative reducing environmental conditions and that Pu(V) would be the expected predominant species under relative oxidizing conditions". Nevertheless, Pu(IV) colloids can form in aqueous solutions of Pu(V) and Pu(VI) mixtures with [Newton et al. 1986] or without [Bell et al. 1973, Costanzo et al. 1973] the effect of α-particle self-irradiation [Silver 1988], and equilibrate with Pu(V) aqua ions to form a stable system [Rai and Serne 1979, Silver 1989].

Kinetic studies on plutonium polymerization in HNO_3 solutions as functions of acidity (0.04 - 0.1 M) and temperature (25 - 75 °C) were conducted in solutions of relatively high concentration of Pu(IV) [Costanzo et al. 1973, Bell et al. 1973]. At 25 °C, the fraction of polymerized Pu(IV) went from 0% in 0.1 M HNO_3 to almost 100% in 0.04 M HNO_3. "The effect of an increasing temperature is to increase the rate of polymerization at the expense of the ionic plutonium species." The distribution of Pu(III), Pu(IV), Pu(V), Pu(VI) and Pu(IV) polymer was analyzed using absorption spectroscopic data [Costanzo et al. 1973] and the rates of Pu(IV) polymerization under various conditions were calculated [Bell et al. 1973]. Hobart et al. [1989] also reported on the acidic agglomeration of Pu(IV) ions and that the colloid is electrochemically reactive.

5.2 Americium Colloids

The solubility products ($\log_{10}K_{sp}$) for both amorphous and crystalline $Am(OH)_3$ at 25°C and zero ionic strength were reported to be -21.0 and -24.3 respectively [Silva 1982]. The estimated maximum solubility of $Am(OH)_3$ in neutral aqueous solution could be as high as 10^{-4} M. However, the formation of intrinsic Am(III) colloids have been reported at concentrations which are much lower than the calculated maximum solubility using existing thermodynamic data [Nagasaki et al. 1994a, Olofsson et al. 1982a, Buckau et al. 1986]. In 1994, Nagasaki and co-workers investigated colloid formation and adsorption of Am(III) in a water/carbonate/bentonite system, in a pH range from 3 to 10 with initial concentrations of Am(III) at 10^{-9} and 10^{-10} M. Their results showed that in a solution of 0.1 M $NaClO_4$ and 1.4×10^{-4} M CO_3^{2-} the formation of Am(III) colloids started at a pH of 3 and the colloidal fraction reached its maximum around a pH of 7. The colloidal fraction gradually decreased when the pH was greater than 8 due to the significant formation of Am(III)-CO_3^{2-} complex species. Colloid formation was greatly influenced by Am(III) hydrolysis, and, therefore, the authors believed that the colloid was an intrinsic Am(III) colloid. In a water/bentonite system, there was always a greater fraction of americium colloid detected in comparison with similar experiments carried out in water. Batch experiments showed that the sorption ratio of americium in this system was linear, proportional to the ratio of water volume to bentonite mass (V/m). This phenomenon was explained as the formation of pseudocolloids, in addition to the formation of intrinsic colloids in the system.

Quite extensive studies of colloidal americium were conducted by Olofsson and co-workers [Olofsson et al 1982a, 1982b, 1983]. The formation and sorption properties of colloidal americium(III) in aqueous solutions were studied with variations of pH (2-12), ionic strength (0.01-1.0 $NaClO_4$ M), initial concentration of Am(III) (10^{-7} -10^{-11} M), storage time (6 hours-6 months) and centrifugation speed (0-17000 rpm). According to the authors, at lower pH the pseudocolloid, which absorbs strongly onto Al_2O_3, dominated the disperse phase, while at pH's greater than 12, the intrisic colloid, which had high mobility in the Al_2O_3 column, was the major portion in the particle fraction. The pH_{pzc} of the americium colloid was determined to be near 5 to 8.

The presence of intrinsic and pseudo Am(III) colloids were confirmed with laser-induced photoacoustic spectroscopy [Kim 1985, Buckau et al. 1986]. Am(III) aqua ions have a sharp absorption band with maximum at 503 nm. The band becomes less distinguishable at higher pH and becomes sharp again when Am(III) is released from the colloids by acidification of the solution.

5.3. *Thorium colloids*

Thorium(IV) has a relative large hydrolysis constant ($K_{sp} \sim 10^{-39}$) [Kraus 1956] in comparison with other tetravalent actinides, and its hydrolysis behavior has been studied extensively [Fuger 1992]. Although polymeric hydroxide species of Th(IV) exist in solutions of various electrolytes, such as perchlorate, chloride and nitrate, there are few studies on colloidal behavior of Th(IV) relevant to the environment. Lieser and Hill [1992a, 1992b] have studied colloid formation in both pure water and groundwater. Filterable (pore size of 0.45 and 1.2 μm) and ultrafilterable (pore size of 2 nm) fractions of thorium were obtained in pure water experiments with initial concentrations of Th(IV) of 10^{-6} and 10^{-9} M in a pH range from 1-3.5. Authors assigned these fractions as intrinsic thorium colloids since there was very little opportunity to form other colloids. On the other hand, thorium is also easily adsorbed onto aquatic colloids to form pseudocolloids in groundwaters. The interesting part of their study is that thorium pseudocolloids can form even in ultrafiltered groundwaters. The formation mechanism of those pseudocolloids is not clear yet. However, the authors believe it is "due to the interaction of the hydroxo complexes of thorium with molecular forms of silicic acid" [Lieser and Hill 1992b].

5.4. *Uranium Colloids*

Although substantial efforts have been devoted to the investigations of the thermodynamic behavior of uranium, a major radionuclide constituent in waste forms, no systematic study on the formation of uranium colloids was found in the literature. The formation of colloids has been observed in leachates from tests of dissolution and corrosion of nuclear spent fuel [Feng et al. 1994], nuclear waste glasses [Bates et al. 1992, Fortner and Bates 1995], and cements [Ramsay et al. 1988]. However, the role uranium plays in the formation of those colloids is far from clear. Solid phases of shoepite ($UO_3 \cdot 2H_2O$, particle size of 20-50 nm) and soddyite ($(UO_2)_2 \cdot SiO_4 \cdot 3H_2O$, particle size of 50-100 nm) were identified in colloids collected from leachates of spent fuel by transmission electron microscopy [Finn et al. 1994]. The authors concluded that the results "indicate that the uranium in the spent fuel matrix can dissolve in a manner similar to that found in a natural analogue."

Important valence states of uranium in nature are uranous (U(IV)) and uranyl (U(VI)) ions. U(IV) is believed to be stable in reducing environments, because of its low solubility (on the order of 10^{-9} M) in most aqueous solutions. Uranyl ions, on the other hand, are stable in oxidizing environments and have relative high solubilities. The migration behavior of colloidal uranium in the environment has been modeled [van der Lee et al. 1992]. The authors suggest the potential route to form uranium colloids is that uranium dissolves as a U(VI) species under oxidizing conditions in repositories, then it migrates with groundwater to a more reducing environment and U(VI) is reduced to U(IV). Since the solubility limit has changed drastically by several orders of magnitude, U(IV) colloids may be generated.

5.5 Neptunium Colloids

Np(V) is the stable oxidation state of neptunium in natural environments, and NpO_2OH has relatively large solubility products in various aqueous solutions [Lierse et al. 1985, Neck et al. 1995, Franghanel et al. 1995]. The colloidal behavior of Np(V) was investigated using ultrafiltration and centrifugation techniques [Itagaki 1991]. Observed trapped fractions of Np(V) implied the formation of Np(V) colloids, but the concentration of Np(V) in experiments was below its solubility limit. Further experiments may be needed to confirm their observations. The studies conducted in solutions of 0.1 M $Na_2S_2O_4$ (sodium dithionite or sodium hydrosulfite) with pH ranging from 2 to 10 showed that neptunium tends to form intrinsic colloids of amorphous $Np(OH)_4$ under reducing conditions. The Np(IV) colloids formed under these conditions had a relatively wide size distribution (3-450 nm) as determined by sequential filtration experiments [Moriyama 1989].

Sorption of Np(V) onto various materials, such as $Fe(OH)_3$, SiO_2 [Itagaki et al. 1991, Nagasaki et al. 1994b], α-Al_2O_3 [Olofsson et al. 1983], and humic colloids [Kim et al. 1994], and sorption of Np(IV) colloid on bentonite-carbonate solution [Pratopo 1993] have been investigated. These results showed that neptunium is likely to be sorbed onto these carrier-colloids. Since "conditions for Np(V) (intrinsic) colloid formation in environmental waters would usually not be achieved" [Silva and Nitsche 1995], its pseudocolloids maybe more important.

6. *Concluding Remarks*

It has been our intent to present a summary of the available literature related to the generation of intrinsic actinide colloids (radiocolloids) directly from spent fuel within the waste package of a geologic repository for high-level nuclear waste. This scenario would occur before contact with other elements of the engineered barrier system and beyond. An attempt to include all relevant publications was made. The literature on actinide-bearing colloids is large. Publications that emphasized actinide pseudocolloids were not included unless they significantly addressed issues regarding intrinsic actinide colloids. In some cases reports and journal publications were similar and only one was reported.

The observation and study of intrinsic actinide colloid formation from spent fuel in the waste package have just begun to be addressed by Bates and co-workers [Bates, Bradley et al. 1992; Finn et al. 1994 and 1995]. Because of the difficulty of such studies, detailed characterization is not yet available, although the features and quantity of such colloids will affect, perhaps significantly, the actinide source term from the waste package and subsequently affect the repository source term. Their work on colloid formation from waste glass dissolution is relevant, but involves other formation mechanisms and leads to different colloid forms that should be studied separately.

The issues related to colloid formation at Yucca Mountain have been discussed by Triay, Simmons et al. in 1995. One of the primary issues they highlighted is whether radioactive-waste-derived colloids will be present in the repository. The aqueous mass flux of actinide species, which is the actinide release rate from the waste package, is initially controlled by the intrinsic dissolution rate of the waste form and the formation and concentration of colloids, which can easily and significantly surpass the dissolved actinide concentrations that are solubility limited. These colloids will either be intrinsic or pseudocolloids coming from the high-level spent fuel or glass waste forms. Current knowledge of intrinsic actinide colloid formation by groundwater reaction with spent fuel is insufficient to conclude whether or not colloids will be the governing mode of actinide transport from the waste package. Understanding their formation, which controls the actinide source term from the waste package, and in turn bounds the radionuclide transport within and from the repository, should be studied and quantified.

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