

Review

The pentavalent actinide solution chemistry in the environment

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ABSTRACT

With regard to environmental monitoring of certain nuclear facilities, pentavalent actinides, in particular neptunium and plutonium, play a key role, as the chief soluble, mobile forms of actinides. In the past five years, investigations carried out by hyphenating capillary electrophoresis to ICP–MS (CE–ICP–MS) have allowed a number of hitherto unknown thermodynamic data to be determined for Np(V) and Pu(V) interactions with the chief environmentally abundant anions. For the first time, data were provided for Pu(V) interactions with carbonate, sulfate, oxalate, chloride, and nitrate ions, allowing the Np(V)/Pu(V) analogy to be verified experimentally. Knowledge of Np(V) chemistry, especially in carbonate, and sulfate media, was also refined. These CE–ICP–MS studies, combined with some earlier findings, have brought about a renewal in the knowledge of An(V) chemistry in solution.

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1. Introduction

Actinides may be found in the environment in four different

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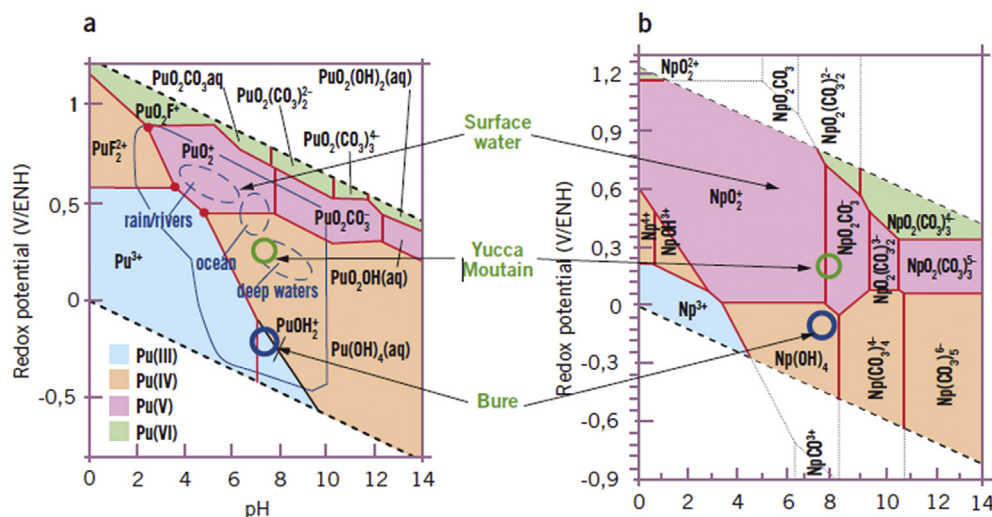


Fig. 1. Speciation diagram for Pu (left) (Heckert, 2000), and Np (right) (Vitorge and Poinssot, 2005), as a function of redox potential, pH, and complexing species (hydroxide, carbonate, and fluoride ions). The surface water (rain/river and ocean), the Bure and Yucca Mountain repository project are pointed out by a circles.

oxidation states: the trivalent and tetravalent forms (An^{3+} , An^{4+}), and pentavalent and hexavalent forms (AnO_2^+ , AnO_2^{2+}), also known as actinyl forms. The chemistry of pentavalent actinides is of special interest with regard to environmental monitoring, and nuclear waste management. Indeed, the stabilization of actinides in this oxidation state may be promoted by a variety of environmental conditions, especially in oxidizing conditions (see Fig. 1).

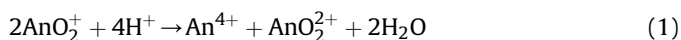
This is mainly the case for two major actinide products yielded by U nuclear fuel, Pu and Np; and for Pa, one of the main products of Th fuel. The protactinium behavior is much less studied than that of Np, and Pu, even if several data exist for organic and inorganic interactions (Morss et al., 2006; Mendes et al., 2010). The protactinium interactions will not be covered in this review. The + V oxidation state of Np and Pu is predicted to play a key role under the conditions prevailing in the environment, especially in surface waters (seawater, lakes). The AnO_2^+ monocation ($An = Np, Pu$) stands as the least reactive form of An aqua ion ($AnO_2^+ < AnO_2^{2+} \approx An^{3+} < An^{4+}$), this resulting in high mobility and solubility, and emphasizing the importance of ascertaining the behavior of this ion in the environment.

A number of difficulties arise, as regards investigation of Np(V) and Pu(V) chemistry. Oxidation state ratios vary rapidly with small variations in the medium. The disproportionation equilibrium entails that An(V) is stable only at trace levels, and at $pH > 3$ (especially as regards Pu(V)). Interactions with environmental species (carbonate, chloride, sulfate ions) are weak (Guillaumont, 2003; Morss et al., 2006). Recent investigations of An(V) interactions with the major environmental ligands have made it possible to enhance, substantially, knowledge of An(V) chemistry in the environment (Topin et al., 2009a, 2009b, 2010; Brunel et al., 2015). These experiments were carried out through the hyphenation of capillary electrophoresis (CE) to inductively-coupled plasma mass spectrometry (ICP–MS), allowing measurements to be made at ultra-trace level, close to environmental levels. Data were determined for the first time as regards Pu(V) interactions with carbonate (Topin et al., 2009a), sulfate and chloride (Topin et al., 2009b), nitrate (Topin et al., 2010), and oxalate ions (Brunel et al., 2015). Data were likewise acquired concurrently, for Np(V), making it possible to reassess the chemistry of this species. These experiments have made it possible to investigate experimentally, for the first time, the analogy between species exhibiting a similar charge-to-size ratio: Np(V) and Pu(V). Recently, the aqueous

actinide chemistry was widely investigated and reviewed by Altmaier et al. (2013). The purpose of this paper is to review more specifically knowledge of An(V) chemistry in the environment, especially as regards interactions with the chief environmental ligands. The state of knowledge as to An(V) behavior in the environment is presented first, including a section describing speciation tools. An(V) interactions with environmental ligands are then detailed, and discussed, with the recent CE–ICP–MS investigations, along with earlier data, being considered.

1.1. An(V) stability in the environment

The chemistry of pentavalent actinides is chiefly governed by the disproportionation reaction. The An(V) species disproportionates chiefly in the environment into An(IV) and An(VI), in accordance with the overall reaction (Clark et al., 2006):



Disproportionation is promoted by acidic conditions and high actinide concentrations (Eq. (1)). Consequently, pentavalent actinides are not stable under the conditions prevailing in spent fuel reprocessing chemistry, which usually operates at low pH and high actinide levels, promoting stability of Np and Pu in their + IV oxidation states. Conversely, An(V) disproportionation is considerably slower under the conditions present in the environment (neutral pH, trace actinide levels). The An(VI) species tend to be reduced to An(V) species in natural water conditions (Neck et al., 2007). To sum up, under the conditions found in the environment, Np and Pu species may be stabilized in their + V oxidation states. The stabilization of An(V) species in the environment is also dependent on oxygen concentration. Indeed, oxic conditions (especially in surface waters) promote stabilization of the *trans*-dioxo bond in An(V) and An(VI) aqua ions (see Fig. 1). These species are less liable to be present under anoxic conditions (subsurface media), which promote the An(III) and An(IV) actinide forms. This is of particular interest for the purposes of nuclear waste management (see Fig. 1). Of actinide species, An(V) species are the most soluble, and are almost exclusively stabilized in aqueous solutions. Consequently, An(V) species exhibit high mobility in the environment, emphasizing the importance of gaining a good understanding of their behavior. The Pu(V) concentration is dependent on the

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