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## **Evidences about the contribution of Pu(IV) oxo-hydroxo cluster [Pu 6 (OH)<sub>4</sub>O<sub>4</sub>]<sup>12+</sup> during the formation of Pu(IV) intrinsic colloids**

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## EVIDENCES ABOUT THE CONTRIBUTION OF Pu(IV) OXO-HYDROXO CLUSTER $[\text{Pu}_6(\text{OH})_4\text{O}_4]^{12+}$ DURING THE FORMATION OF Pu(IV) INTRINSIC COLLOIDS

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Because of nuclear testing, space exploration or industrial development, anthropogenic activities significantly contributed in the release of radioactive particles in the environment. Both pseudo- and intrinsic colloids of the element plutonium have been considered as potential sources of radioactivity migration in aquifers.[1,2] While the former deals with natural colloids where Pu has been incorporated or adsorbed, the latter rather rely on the exceptional property of Pu to form its own colloid as a result of hydrolysis and condensation reactions, even under strongly acidic conditions. Such a property was already discussed by Kraus during the Manhattan project who reported the formation of an opalescent green solution when ammonia or sodium hydroxide aqueous solutions were contacted with acidic solutions of Pu(IV).[3] Through the years, these suspensions were rather prevented in industrial processing by using strongly acidic conditions thus resulting in a knowledge gap regarding the formation, properties and reactivity of these species. Nevertheless, much insights have been reached during the last decade about the structural properties of Pu(IV) intrinsic colloidal phases which are now described as *ca.* 2 nm spherical particles exhibiting a PuO<sub>2</sub>-like local structure and a local disorder attributed to a surface effect mostly resulting from the nanometric size of the particle.[4] It has been reported that the formation conditions of intrinsic Pu colloids may significantly impact their structural properties and intensify their environmental migration relevance.[5,6]

A better knowledge about the formation conditions and stability of PuO<sub>2</sub> nanoparticles in geochemical conditions thus appear of particular interest for the clarification of the environmental fate of this long-lived radioactive element. Nevertheless, tetravalent Pu exhibits a complex chemistry in aqueous solution particularly expressed by hydrolysis, complexation, redox and disproportionation reactions.[7] While hydrolysis leads to the accumulation of PuO<sub>2</sub> nanoparticles, disproportionation reactions may lead to the additional observation of Pu(III), Pu(V) and Pu(VI) species. Furthermore, the additional contribution of polynuclear Pu nanostructures during the formation of the colloids has been interrogated. Indeed, the recent examination of oxo-hydroxo clusters containing 16, 22 and 38 atoms of tetravalent Pu revealed related PuO<sub>2</sub> core structures and suggested that bigger entities could result from the assembly of smaller units.[8,9] The gradual loss of hydroxo-bridges in aid of oxo-ligands in the Pu<sub>38</sub> structures, which shows some striking structural properties with Pu(IV) colloids, suggested that the latter might be formed by a succession of olation and oxolation reactions.

In this work, the formation kinetics of intrinsic Pu(IV) colloids was studied in different aqueous solutions including light (H<sub>2</sub>O) and heavy water (D<sub>2</sub>O) but also electrolyte model systems encountered in natural aquifers rich in alkaline or alkaline-earth elements (LiCl, NaCl, LiNO<sub>3</sub>, MgCl<sub>2</sub>, etc.). Time-dependent measurements were carried out with UV-Vis absorption spectroscopy and coupled with deconvolution studies. The colloidal particles formed in these systems were characterized with synchrotron radiation using X-ray scattering and absorption techniques. New insights were established about the formation mechanism of Pu(IV) intrinsic colloids with the transient observation of

$[\text{Pu}_6(\text{OH})_4\text{O}_4]^{12+}$  oxohydroxo cluster (Fig. 1). Furthermore, the reaction medium were interrogated about their effect on the structural characteristics of the final  $\text{PuO}_2$  nanoparticles.

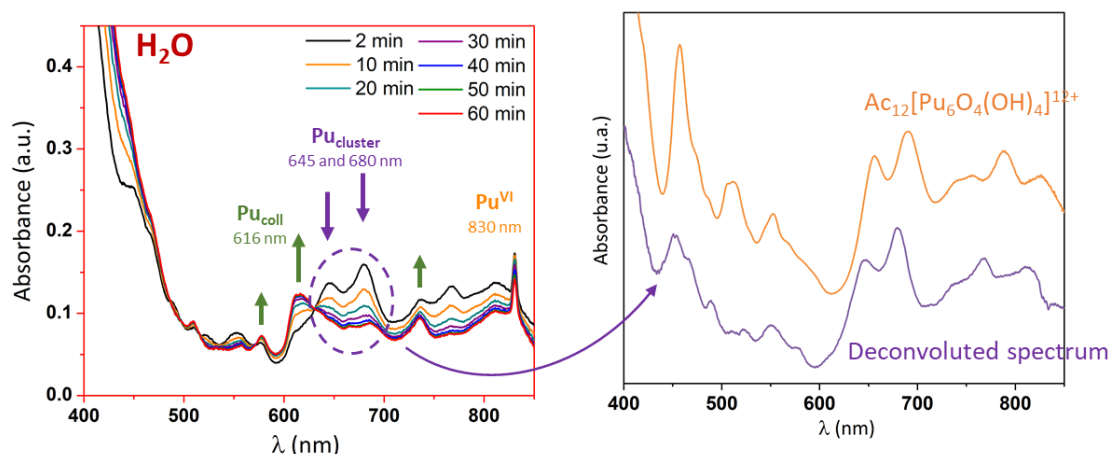


Fig. 1: Formation kinetics of Pu(IV) intrinsic colloids in pure water. UV-vis absorption spectra acquired during synthesis were deconvoluted and revealed the appearance of  $[\text{Pu}_6(\text{OH})_4\text{O}_4]^{12+}$  cluster.

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