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## Electrochemical Behavior of Plutonium in Nitric Acid and n-Tributyl Phosphate

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The redox behavior of actinides is particularly complex because these elements have both many degrees of oxidation and many disproportionation reactions. In the case of plutonium, the most common oxidation states in the aqueous phase are +3 to +6. For the +3 and +4 oxidation states the solution ions are in the aquo hydrate form whereas the +5 and +6 oxidation states are in the “yle” form, ie in the trans-dioxo form. These differences in chemical forms of the ions in solution is the source of slow kinetics between the aquo and “yles” ions, whereas in the same family the kinetics of the redox reactions is fast. Moreover, it is now well known that under certain conditions Pu(IV) and Pu(V) is disproportionate. The coupling of these two phenomena leads to complex chemical reactions with mechanisms that are not yet perfectly established.

Since the treatment / recycling of irradiated fuels is carried out industrially in aqueous nitric acid (HNO<sub>3</sub>) and organic phase n-tributyl phosphate (TBP) for extraction cycles, it is useful to better understand and control the redox equilibria of plutonium in these processes. Electrochemical techniques therefore seem perfectly suitable for studying the redox behavior of plutonium.

This presentation concerns the electrochemical behavior of plutonium in HNO<sub>3</sub> medium as well as in TBP. The two redox couples Pu(IV)/Pu(III) and Pu(VI)/Pu(V) will be described more from a thermodynamic point of view. The redox mechanism of the Pu(IV)/Pu(III) pair in a nitric medium will also be discussed following the use of the coupling of electrochemical and spectroscopic techniques.

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