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Synthesis of uranium and plutonium oxides by peroxide precipitation and hydrothermal treatment

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With the development of Fast Neutrons Reactors (FNR) and of Mixed Oxide (MOx) fuel multi-recycling policy, opportunities are opening to move toward a closed nuclear fuel cycle. Within this framework, some modifications of the different industrial steps are required. In particular, the MOx fuel synthesis has to be reconsidered as the oxide properties will have to meet different specifications. More specifically, the homogeneity of the cation distribution will have to be improved to allow the use of higher Pu content and subsequently, the further reprocessing of spent MOx fuel.

In this context, new innovative ways of converting uranium and plutonium in nitric solution into actinide oxides (UO₂, PuO₂ and mixed (U,Pu)O₂) are studied. On the one hand, the plutonium peroxide precipitation is known as an interesting way since the Manhattan project [1] and its thermal decomposition into PuO₂ has also been studied [2]. On the other hand, uranium dioxide synthesis by peroxide pathway is currently developed at an industrial scale. Moreover, uranium and plutonium co-precipitation by hydrogen peroxide is possible [3], however, its development has been hampered by the impact of the particle morphology on the separation step and the risks associated with handling dry peroxide phases. One of the potential innovative pathway to rule out these difficulties consists of hydrothermal conversion with hydrogen peroxide as a precipitating agent. The first stage of the process involves the direct and simultaneous precipitation of both uranium (VI) and plutonium (IV) by H₂O₂ in nitric acid (in their most stable oxidation state in this medium), as uranium (VI) peroxide and plutonium peroxide. Then, actinide peroxide decomposition is achieved under mild hydrothermal conditions (100 < T < 250°C and self-generated pressures of 1 to 50 bars) instead of conventional heat treatment. This step allows to safely manage the peroxide decomposition reaction without handling powdered materials. Moreover, the oxides obtained exhibit a very low carbon content, as only carbon-free reagents are used.

During actinide peroxide precipitation, the effect of the initial acidity or the initial peroxide concentration on the yield and nature of the precipitate were investigated. Although the influence of these parameters is different for uranium and plutonium, quantitative precipitation conditions have been determined for both actinides. Moreover, the impact of initial chemicals conditions on morphologies were investigated and as far as plutonium peroxide phases are concerned, new structural characterizations using synchrotron radiation, allowed a deeper understanding of the synthesized peroxy-nitrate phase.

The second part focuses on the hydrothermal conversion of these peroxy-phases to form the corresponding oxide. For the first time, plutonium oxide has been synthesized by this original and novel conversion route. For the conversion of uranium (VI) peroxide, a U(VI) oxo-hydroxo phase commonly called “dehydrated schoepite” was obtained. Its formula was calculated to be (UO₂)O_{0.17±0.01}(OH)_{1.66±0.01}. For both actinides, the effect of initial acidity, treatment temperature and time on the yield and nature of the powder was investigated. These results provided the first key insights into the mechanisms involved in the hydrothermal conversion of peroxy-phases. These results were compared to those obtained for uranium/plutonium mixtures.

[1] Hamaker, J. W. et al. *Paper 6.02*. The transuranium Elements - Research papers. Seaborg, G. T., Katz, J. J., Manning, W. M., Eds. 1949. Vol. 14B-part I, 666–681.

[2] Hibert, N. PhD. Thesis, Université de Lille, 2020.

[3] Hibert, N. et al. Dalton Trans. 2022, **51** (34), 12928–12942.