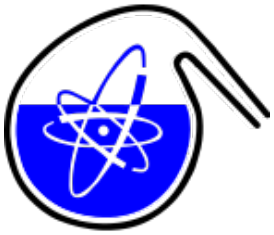

Contribution ID: **597** Type: **Verbal**

Thermal decomposition and structural changes of lanthanide-doped uranium dioxide particles prepared by internal gelation

Thursday, May 17, 2018 2:15 PM (15 minutes)

In any advanced nuclear fuel cycle, partitioning and transmutation (P&T) is a key strategy to reduce spent nuclear fuel's radiotoxicity and heat generation: Long-lived minor actinides (MA) are partitioned from spent nuclear fuel and subsequently converted to fuel pins or targets. These are used as nuclear fuel in fast reactor systems where the actinides are fissioned to short-lived radionuclides.
An essential link between the partitioning and the transmutation is the conversion of the separated minor actinides into solid precursors to fabricate fresh fuel suitable for minor actinide recycling. Among transmutation fuels, particle fuel offers certain advantages compared to pellet fuel. Particles can be prepared without any formation of dust via an aqueous synthesis pathway. Moreover, the fuel-manufacturing process offers advantages in terms of automation up to and including the rod filling step. Strategies to fulfil this task are sol-gel processes, where a stable solution containing the desired metals, the sol, is converted into a solid gel.
Within this study, the feasibility of the sol-gel route via internal gelation was investigated for the fabrication of neodymium- and cerium-doped UO_2 microspheres. Nd^{3+} was used as simulant for the minor actinide Am^{3+}. Cerium was used in the tetravalent and trivalent state to simulate plutonium and to investigate the influence of the metal's oxidation state on the synthesis process and final product. Depending on the chosen preparation conditions, stable microspheres with lanthanide contents ranging from 5 % to 40 % could be prepared. Additionally, non-doped reference particles were fabricated using the same synthesis parameter and conditions.
A method to convert the gelled microspheres into a dioxide form was investigated in detail. The thermal decomposition pathway under oxidizing conditions was first investigated by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), coupled with evolved gas analysis via mass spectrometry (MS). The calcined particles were then sintered for 10 h at 1600 ℃ under reducing conditions. The study also focussed on assessing the crystal structure evolution in the intermediate products via powder X-ray diffraction (XRD).
Single phase solid solutions according to the formula $U_{1-y}Ln_yO_{2\pm x}$ were found in case of the sintered particles. A cubic fluorite structure with a lattice parameter linearly decreasing with increasing lanthanide content according to Vegard's law was observed via XRD. In case of the intermediate products after calcination a more complex, mixed-phase behaviour was found. The non-doped particles contained a single orthorhombic phase, whereas the doped particles contained the orthorhombic phase and an additional fluorite phase. Interestingly, the relative amounts of fluorite phase depended on the amount of dopant and maximum temperature applied during the calcination. For compositions with *Ln* contents of 30 % calcined at 1300 ℃ only the fluorite phase and no orthorhombic phase was found. The implications of these results on the conversion strategy will be further discussed.

Primary author: Mr SCHREINEMACHERS, Christian (Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science)

Co-authors: Dr LEINDERS, Gregory (Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science); Prof. MODOLO, Giuseppe (Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-6)); Dr VERWERFT, Marc (Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science); Prof. BINNEMANS, Koen (KU Leuven, Department of Chemistry); Prof. CARDINAELS, Thomas (Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science)

Presenter: Mr SCHREINEMACHERS, Christian (Belgian Nuclear Research Centre (SCK•CEN), Institute for Nuclear Materials Science)

Session Classification: NFC 5

Track Classification: Chemistry of Nuclear Fuel Cycle, Radiochemical Problems in Nuclear Waste Management