Synthesis of Uranium-based Microspheres for Transmutation of Minor Actinides

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Abstract – Utilisation of the internal gelation process is a promising perspective for the fabrication of advanced nuclear fuels containing minor actinides (MA). The formulation of appropriate precursor solutions for this process is an important step towards a working process as the chemistry of uranium-MA systems is quite complex. In this work, actinide surrogates were utilised for basic research on their influence on the system. The ceramics obtained through thermal treatment of the gels were characterised to optimise the calcination and sintering process.

A. INTRODUCTION

An alternative to the direct disposal of long-lived radionuclides is their separation from the original waste in connection with subsequent transmutation. One promising concept after the partitioning step is embedding the minor actinides (MA: Am, Cm, Cf) in uranium-based nuclear fuel by an internal gelation process. This will allow the MAs to be destroyed by fast-neutron reactions in the upcoming generation-IV reactors.

The method for the internal gelation of uranium was developed by the KEMA laboratory in the 1960s and is based on the decomposition of hexa-methylene-tetra-amine (HMTA), after its protonation, to ammonia in heat. This causes a drastic pH increase, resulting in hydrolysis and condensation reactions. The reactions taking place are illustrated in equations (1) to (4):

\[
\text{HMTA protonation: } [(\text{CH}_2)_6\text{N}_4] + \text{H}^+ \leftrightarrow [(\text{CH}_2)_6\text{N}_4\text{H}]^+ \quad (1)
\]

\[
\text{HMTA decomposition: } [(\text{CH}_2)_6\text{N}_4\text{H}]^+ + 6 \text{H}_2\text{O} + 3 \text{H}^+ \rightarrow 4 \text{NH}_4^+ + 6 \text{CH}_2\text{O} \quad (2)
\]

\[
\text{Uranyl hydrolysis: } \text{UO}_2^{2+} + 2 \text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{OH})_2 + 2 \text{H}^+ \quad (3)
\]

\[
\text{Uranyl condensation: } \text{UO}_2(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{UO}_3 \cdot 2\text{H}_2\text{O} \quad (4)
\]

Several studies have been carried out on the whole subject and a common element for the fabrication of U(VI) gels is the need for a so-called acid-deficient uranyl-nitrate solution (ADUN) as precursor solution. This allows the use of a reduced quantity of HMTA due to the lower initial acidity. Moreover, a substoichiometric amount of nitrate improves the solubility of uranium and therefore allows higher concentrations. Understanding the influence of this step is crucial for the development of a working process. [1, 2, 3]

As the MAs, unlike uranium, are present in a trivalent oxidation state in the precursor solution, special attention has to be paid to their gelation behaviour, as well as to their distribution and structural influence in the gel. Therefore, in this work, Nd³⁺ was used as an MA surrogate to investigate the influence of such cations on the system. This is reasonable as the chemical properties of trivalent actinides and their corresponding lanthanides are very similar.

During the thermal treatment, phase transitions of the uranium matrix occur. After calcination at about 800 °C, uranium is present in the form of U₃O₈ which has a layered orthorhombic crystal structure [4]. Introducing quantitative amounts of trivalent actinides can have a certain impact on this structure’s integrity. Investigations are necessary related to phase segregation and the general integrity of the obtained products.
B. PREPARATION OF ACID-DEFICIENT URANYL-NITRATE

There are different ways of preparing ADUN. Amongst these are: dissolution of U$_3$O$_8$ in an understoichiometric amount of HNO$_3$, chemical removal of nitrate by a reducing agent like formic acid, and the extraction of HNO$_3$ from a uranyl-nitrate solution by amines. [5]

After a series of preliminary tests, we decided to focus on extractive denitrification with Primene JM-T (denoted in the following as Primene, a primary amine, M=269 g/mol, Figure 2) and this process was further investigated. Therefore, experiments concerning the appropriate molar ratio of Primene versus nitrate were undertaken: varying amounts of Primene were contacted with a uranyl-nitrate solution of which afterwards the corresponding pH and the ratio [Nitrate] / [Uranium] was determined. As seen in Figure 1, and as expected, with increasing amounts of Primene, the resulting nitrate-uranium ratio decreases after extraction in the aqueous solution while the pH increases.

![Figure 1: n(Primene) / n(Nitrate) ratio for extraction from a uranyl-nitrate solution in relation to resulting pH and [Nitrate] / [Uranium] ratio of the aqueous phase](image)

Taking the average of 0.7 moles nitrate extracted per mole Primene into account, a 1:1 extraction mechanism as shown in Figure 2 can be assumed. This leads to a simple method for estimating the required amount of Primene by assuming a linear coherence between the amount of Primene used and the amount of nitrate extracted.

![Figure 2: Nitrate extraction with Primene](image)

It was found that with a pure 2.1-molar uranyl-nitrate solution, a denitrification ratio of about 30 % can be achieved without forming precipitates. On the contrary, a typical internal-gelation stock solution (containing uranium, actinide surrogates and urea) starts to form precipitates at a ratio of more than 25 %. Therefore, the corresponding ratio of the denitrated stock solutions should be targeted to a value of not more than 20 %.
C. FABRICATION OF URANIUM-NEODYMIUM MICROSPHERES

An adapted internal gelation process as illustrated in Figure 3 was used to create uranium / neodymium microspheres [6]. A stock solution consisting of uranyl-nitrate, Nd-nitrate, urea and HMTA was created and dropped into hot silicone oil in which the gelation took place. As the spheres travelled from top to bottom in the gelation column, an increase in opacity was observed. The obtained spheres were washed in petrol ether and ammonia solution and the metal losses in the washing solutions were measured via ICP-MS to evaluate the integrity of the gels. As all metal-concentrations in the washing solutions were in the range of $10^{-7}$ M to $10^{-6}$ M, this indicates not only complete gelation but already a certain leaching resistance.

Afterwards, the microspheres were dried at room temperature before the thermal treatment took place. Drying at room temperature led predominantly to shrinkage of the microspheres without visible crack formation. Nevertheless, the usage of too less HMTA resulted in defects after drying, when no denitrated stock solution was used (Figure 4).

Calcination was carried out at 800 °C and SEM analysis was used as an initial indicator for the quality of the obtained product.

![Flow sheet for internal gelation process](image)

After calcination, the SEM analysis showed that the spheres generally remained intact without visible phase segregation, but crack formation was present in dependence on the initial precursor solution formulation. An amount of 2.5 moles HMTA per mole metal caused cracks, while a decrease to 2.2 moles HMTA per mole metal led to an integer surface (Figure 5).

![Photos of obtained U/Nd microspheres dried at RT (not true to scale):](image)

1 Extractive denitration with Primene
D. CONCLUSION

This work demonstrates the general feasibility of an internal gelation process for creating uranium / neodymium microspheres with optional usage of acid-deficient uranyl-nitrate. A method for extractive denitration with Primene of highly concentrated uranium solutions was evaluated. The experimental outcome led to a procedure allowing direct denitration of internal gelation stock solutions by extraction. Fabrication of microspheres via an adapted internal gelation process with subsequent calcination of the gels was successfully carried out. Microspheres with an integer, crack-free surface were obtained when proper formulation and treatment of the stock solutions were applied.

Acknowledgements

Financial support for this research was provided by the European Commission (project ACSEPT – No. 211267).

References