ASGARD 5th Project Meeting
July 1st – July 3th 2014 (Lancaster, England)

Progress Report of Beneficiary No 5: Jülich

Domain 2:

WP 2.1 Inert Matrix Fuels
WP 2.3 Conversion from solution to oxide pre-cursors
  Task 2.3.1 Co-conversion by sol-gel routes
  Task 2.3.2 Co-conversion by impregnation of solid matrixes

Christian Schreinemachers, Ronald Middendorp, Elena Ebert, Andrey A. Bukaemskiy, Stefan Neumeier, Giuseppe Modolo

Institut für Energie- und Klimaforschung (IEK-6)
– Nukleare Entsorgung und Reaktorsicherheit
Co-conversion by sol-gel routes

Particles fabrication by internal gelation

1. **sol preparation**
   - UO$_2$(NO$_3$)$_2$
   - Nd(NO$_3$)$_3$
   - HMTA
   - urea
   - ice bath

2. **gelation**
   - silicone oil (ϑ = 87°C)

3. **washing**
   - petroleum ether (2x)
   - ammonia, w(NH$_4$OH) = 12.5 %, (3x)

4. **drying at air**

5. **thermal treatment**
## Introduction

### Particle characterization

#### ICP-MS Data

<table>
<thead>
<tr>
<th>( \chi(\text{Nd})_{\text{ICP-MS}} )</th>
<th>%</th>
<th>0</th>
<th>5.80</th>
<th>11.99</th>
<th>17.40</th>
<th>22.62</th>
<th>27.59</th>
<th>33.49</th>
<th>37.68</th>
<th>42.63</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c(\text{U+Nd})_{\text{sol}} )</td>
<td>mol/L</td>
<td>2.50</td>
<td>2.60</td>
<td>2.62</td>
<td>2.56</td>
<td>2.58</td>
<td>2.60</td>
<td>2.62</td>
<td>2.65</td>
<td>2.67</td>
</tr>
</tbody>
</table>

#### Particle Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{m}(\text{particle}) )</td>
<td>mg</td>
<td>5.38</td>
<td>5.23</td>
<td>4.96</td>
<td>5.24</td>
<td>4.83</td>
<td>5.00</td>
<td>5.34</td>
<td>5.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \bar{d}(\text{particle}) )</td>
<td>mm</td>
<td>1.35</td>
<td>1.35</td>
<td>1.33</td>
<td>1.38</td>
<td>1.34</td>
<td>1.35</td>
<td>1.38</td>
<td>1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \bar{\rho}(\text{particle}) )</td>
<td>g/cm³</td>
<td>4.15</td>
<td>4.04</td>
<td>3.99</td>
<td>3.85</td>
<td>3.87</td>
<td>3.86</td>
<td>3.85</td>
<td>3.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\chi(\text{Nd}) = \frac{n(\text{Nd})}{n(\text{Nd + U})}
\]

\[
R(\text{urea}) = \frac{n(\text{urea})}{n(M^{n+})} = 1.80
\]

\[
R(\text{HMTA}) = \frac{n(\text{HMTA})}{n(M^{n+})} = 1.35
\]

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ASGARD 5th Project Meeting, (Lancaster, England)
c.schreinemachers@fz-juelich.de

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Characterization of U/Nd microspheres
XRD analyses of particles treated in air

Presence of orthorhombic and cubic crystal lattice structure

\[ I_C = \frac{I(111)_C}{I(111)_O + I(001)_C}, \quad I_O = \frac{I(001)_O}{I(001)_O + I(111)_C} \]

Lattice parameter determination:
1. Gaussian function \( \rightarrow 2\theta \)
2. Bragg’s law \( \rightarrow a_i \)
3. Nelson & Riley method \( \rightarrow a \)
Characterization of U/Nd microspheres

XRD analyses of particles treated in air

- Constant $a$ for mixed phase region (5.4374 Å)
- Linear increase for single phases

Vegard’s rule

$$a_{AB} = a_A (1 - \chi_B) + a_B \chi_B$$

**Thermal treatment of microspheres**

*Optimization of sintering conditions*

- **Treatment 1**
  - $\bar{m} = 4.17 \text{ mg}$
  - $\bar{d} = 919.1 \text{ µm}$
  - $\bar{\rho} = 10.25 \text{ g/cm}^3$

- **Treatment 2**
  - $\bar{m} = 3.96 \text{ mg}$
  - $\bar{d} = 899.7 \text{ µm}$
  - $\bar{\rho} = 10.13 \text{ g/cm}^3$

- **Treatment 3**
  - $\bar{m} = 3.96 \text{ mg}$
  - $\bar{d} = 922.3 \text{ µm}$
  - $\bar{\rho} = 9.56 \text{ g/cm}^3$

$\chi(\text{Nd}) = 42.63 \%$

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c.schreinemachers@fz-juelich.de
Thermal treatment of microspheres

XRD analyses - comparison with literature data

→ lattice formation depends on synthesis route

Sintering time not sufficient => increase of plateau to 10 h
Determination of gelation temperature

Viscosity measurements

- Measurements with given geometry
  \( V = 9 \text{ mL} \) (Ethylenglycol)
- Verification with self-made geometry
  \( V = 2 \text{ mL} \) (Ethylenglycol)

![Graph showing viscosity measurements](image)

- Measurements at different heating rates:
  - 0.25 °C/min
  - 0.25 °C/min
  - 0.25 °C/min
  - 1.17 °C/min
  - 1.20 °C/min

Data sources:
- Viswanath et. al, 2007
- Haynes, 2013
Determination of gelation temperature
Viscosity measurements

- Zr/Y/Ce (76:14:10); RHMTA = 0.56, R_urea = 0.75
  - influence of the heating rate
  - the reproducibility of the system

\[ \bar{\vartheta}_{gelation} = 43.55 \pm 0.14 \, ^\circ C \]
\[ \vartheta_{gelation} = 39.73 \, ^\circ C \]

Calculation of 1st derivation to determine \( \vartheta_{gelation} \)
The vibrating nozzle system

Change of synthesis strategy: 2 feed solutions

System modification: Replacement of syringe pump by peristaltic pump.

Batch experiments with $\chi(\text{Nd}) = 40\%$.

→ precipitation
The vibrating nozzle system

Precipitation (*XRD*): UO$_3$NH$_3$ · H$_2$O; UO$_3$ · 2 H$_2$O; Nd$_2$O$_3$

→ suspension transformed into a gel
Outlook

- Characterization of the precursor solution: Influence of the U/Nd ratio on the gelation system by potentiometric titrations.
- Characterization of the sol: Determination of pH-values (initial and during process, time dependent).
- Temperature depending viscosity measurements to determine the gelation temperature of the sol.
- Preparation of a large amount of particles of each composition by the use of the “vibrating nozzle” system.
- Thermal treatment with increased sintering time of existing particles.
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Thank you for your attention!