Towards the Bottom of the Periodic Table

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Rossendorf Beamline (ROBL) ESRF, Grenoble

✔ Owned and operated by HZDR (Helmholtz-Zentrum Dresden-Rossendorf) since 1998

✔ Dedicated actinide beamline for the fundamental and applied science

Optics

- X-ray absorption spectroscopy
- X-ray diffraction
- X-ray emission spectroscopy
Chemistry for the bottom of periodic table

<table>
<thead>
<tr>
<th>Lanthanide Series</th>
<th>Actinide Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 Ce</td>
<td>92 U</td>
</tr>
<tr>
<td>59 Pr</td>
<td>93 Np</td>
</tr>
<tr>
<td>60 Nd</td>
<td>94 Pu</td>
</tr>
<tr>
<td>61 Pm</td>
<td></td>
</tr>
<tr>
<td>62 Sm</td>
<td></td>
</tr>
<tr>
<td>63 Eu</td>
<td></td>
</tr>
<tr>
<td>64 Gd</td>
<td></td>
</tr>
<tr>
<td>65 Tb</td>
<td></td>
</tr>
<tr>
<td>66 Dy</td>
<td></td>
</tr>
<tr>
<td>67 Ho</td>
<td></td>
</tr>
<tr>
<td>68 Er</td>
<td></td>
</tr>
<tr>
<td>69 Tm</td>
<td></td>
</tr>
<tr>
<td>70 Yb</td>
<td></td>
</tr>
<tr>
<td>71 Lu</td>
<td></td>
</tr>
<tr>
<td>90 Th</td>
<td></td>
</tr>
<tr>
<td>91 Pa</td>
<td></td>
</tr>
<tr>
<td>92 U</td>
<td></td>
</tr>
<tr>
<td>93 Np</td>
<td></td>
</tr>
<tr>
<td>94 Pu</td>
<td></td>
</tr>
<tr>
<td>95 Am</td>
<td></td>
</tr>
<tr>
<td>96 Cm</td>
<td></td>
</tr>
<tr>
<td>97 Bk</td>
<td></td>
</tr>
<tr>
<td>98 Cf</td>
<td></td>
</tr>
<tr>
<td>99 Es</td>
<td></td>
</tr>
<tr>
<td>100 Fm</td>
<td></td>
</tr>
<tr>
<td>101 Md</td>
<td></td>
</tr>
<tr>
<td>102 No</td>
<td></td>
</tr>
<tr>
<td>103 Lr</td>
<td></td>
</tr>
</tbody>
</table>

Catalysis | Medicine | Minerals | Nuclear fuel | Nuclear waste

by X-ray Spectroscopy at the Synchrotron
Why X-ray Spectroscopy?

- Electronic and Structural Information
- Element Specific
- Compatible with \textit{in-situ} and Extreme Conditions
Cerium dioxide

> 4000 publications on Web of Science since 2008 (including doped ceria)

\[
\text{CeO}_2 \leftrightarrow \text{CeO}_{2-\delta} + \delta/2 \text{O}_2
\]
CeO$_2$ Nanoparticles

Unprecedented energy resolution

Kvashnina et al, JAAS 26 1265 (2011)
Direct observation of oxidation state by high resolution X-ray Spectroscopy

Kvashnina et al, JAAS 26 1265 (2011)
Experimental setup for liquid measurements

X-rays from synchrotron
In-situ studies of the colloidal CeO$_2$ NPs

Ce(NO$_3$)$_3$·6H$_2$O

Reaction time/hr

60 seconds one scan

The Ce oxidation state in nanoparticles

CeO$_2$ NP can be chemically active without Ce$^{3+}$

Cafun et al, ASC Nano 7, 10726 (2013)
Uranium Chemistry

Oxidation and reduction conditions dominate the geochemical behavior of uranium

Insoluble  Soluble

pH 4-6  pH >6

Reduced  Oxidized

UO₂  UO₂⁺  UO₂²⁺

Theoretically possible

U(III)  U(IV)  U(V)  U(VI)  U(VII)
Improved energy resolution

Evidence of the U(V)

Ground state configuration

U(IV) – 5f^2
U(V) – 5f^1
U(VI) – 5f^0
Mixed-oxide (MOX) nuclear fuel

U(V) doped with Nd

<table>
<thead>
<tr>
<th></th>
<th>U(IV)</th>
<th>U(V)</th>
<th>U(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>93%</td>
<td>5%</td>
<td>2%</td>
</tr>
<tr>
<td>U M₄ edge</td>
<td>83%</td>
<td>14%</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>39%</td>
<td>44%</td>
<td>17%</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

U(V) is stable

Uranium on Magnetite NPs

after 10 days
after 6 days
after 3 days
after 1 day

**Pidchenko et al, ES&T 51 2217 (2017)**

Butorin et al, PNAS 113 8093 (2016)


Pu has the most complicated chemistry

Pu exists in 4 different oxidation states under environmental conditions

Pu easily changes its oxidation state

Pu has high migration rates (several km)

Novikov et al., *Science*, 2006
Ewing, *Nat. Mat.* 2015

... in progress
The European Synchrotron

- Facility for “ultimate” materials characterisation at the micro- and nano-scales •
- An international research institute funded by 19 countries •
- Based in Grenoble, France •
- 7,000 scientists use ESRF annually for public & proprietary materials research •

- Materials are characterized at more than 40 experimental stations at ESRF
  - X-ray spectroscopy allows access to chemical characterisation
  - X-ray diffraction determines crystallographic orientations
  - X-ray imaging provides information about surface morphology

The European Synchrotron
The European Synchrotron

Bulk & Surface Properties by non-destructive methods

X-rays focused to a micro-or nano-beam & Probe of big and small objects

High-speed measurements of all states of matters (liquids, solids, gases)

No structure requirements (powders, single crystals, thin films)

Chemical & Element Sensitivity

Element-specific measurements & Speciation

Probe a very dilute systems (limit is 1ppm)

High energy

In-situ measurements & wide range of sample environments

Temperature variation (from 8K to 1200K) & Pressure variations (from 5kPa to 250GPa) Variable gasses and gas flows

2D & 3D high spatial resolution Down to 100 ps time resolution
How does industry engage with ESRF?

**Feasibility access: “have a go”**
- Confidential & rapid
- >150 clients in 35 countries
- Mail-in services & a la carte

**PUBLIC ACCESS**
- 30% research involves industry, must publish
- Competitive peer review

**COLLABORATION & GRANTS**
- Industry sponsored staff
- Horizon 2020 and FP9

**TECH TRANSFER**
-Licensed >30 technologies
- In-house manufacturing
- Consultancy

**PROPRIETARY SERVICES**
- Confidential & rapid
- >150 clients in 35 countries
- Mail-in services & a la carte

**Head of business development**
Ed Mitchell
mitchell@esrf.fr  +33 (0) 476 882 664
TOP group
Looking towards the bottom of
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Thank you!

Rossendorf Beamline at ESRF