Investigating the effects of surfaces during dissolution of materials with a fluorite structure – the REDUPP project

M.C. Stennett\textsuperscript{1}, C.L. Corkhill\textsuperscript{1}, D. Bailey\textsuperscript{1}, S. Thornber\textsuperscript{1}, N.C. Hyatt\textsuperscript{1}, P. Maldonado\textsuperscript{2}, P.M. Oppeneer\textsuperscript{2}, E. Myllykylä\textsuperscript{3}, K. Ollila\textsuperscript{3}, M. Vähänen\textsuperscript{4}, V. Salo\textsuperscript{4} and L. Z. Evins\textsuperscript{5}

1. University of Sheffield (UK)
2. Uppsala University (SE)
3. VTT (FI)
4. Posiva (FI)
5. SKB (SE)

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Project start: 1 April 2011
Project end: 31 March 2014
Background (1)

• Remaining uncertainties related to understanding of dissolution mechanism

• Studies to approach expected repository conditions
  – laboratory to natural setting

• Processes near the solid-liquid interface

Two main uncertainties addressed:

1) Effect of surface changes during dissolution on long-term dissolution rates

2) Effect of natural groundwater on dissolution rates

Methods to address these issues:

1) Combine experimental work with modelling of solids with fluorite structure. Experimental data from both solution and surface

2) Dissolution experiments using alpha-doped UO2 and natural groundwater of varying ionic strengths
Background (2)

• The laboratory approximation:

1) The ratio of solid to liquid (SA/V)
   * In the repository the space is filled by solids and there is very little space for liquid
2) The rate of “flow” of the liquid
   * Diffusion if the bentonite is present; otherwise controlled by fracture flow
   * In the laboratory: simulate flow by flow-through tests or by replacing the solution in a sequential sampling scheme.
3) The type of solid analogue:
   * Ceramic UO₂, ~5% porosity, crushed to 2-4 mm
   * Spent fuel much more complex solid with variable grain size and surface area
4) The type of fluid:
   * Chemistry of natural groundwater versus synthetic solution
   * Natural gw changes CO₂ content when brought to surface
   * Equilibration with glove box atmosphere
• Do laboratory measurements overestimate?
  From Ollila and Oversby (2005):

  • “.. the dissolution rate appeared to decrease as the samples were exposed to sequential testing periods. This indicates that the results are still influenced by transient effects such as high-energy surface sites, which implies that the dissolution rates measured are upper limits.”

• Why does the dissolution rate decrease with sequential exposure to solution?
  • Noted by geochemists studying mineral weathering (eg White and Brantley, 2003)
  • Freshly prepared mineral fragments, short experimental duration; given time - in nature - the surface will mature – by a decrease of reactive surface area & effects of secondary precipitates
Effect of surface changes during dissolution on long-term dissolution rates

Energetically reactive surfaces decrease during dissolution → rates decrease with time; laboratory measurements overestimate the long-term dissolution rate.

Dissolution of solid surfaces: Corners, edges and crystal faces have different energies. High energy sites & defects on crystal surfaces should be the first to go.

Collaboration with José Godinho (PhD student Stockholm Uni) in the Delta-Min Network (Mechanisms of Mineral Replacement Reactions)

The effect of crystallographic orientation (different crystal faces in contact with solution) on dissolution rate.
REDUPP set-up

Work divided in 8 work packages
WP1 : Prepare and characterise samples : CaF2, CeO2, ThO2 (USFD)
WP2 : Dissolution of CeO2 & CaF2 (USFD)
WP3 : Dissolution of ThO2 (VTT)
WP4 : Dissolution of UO2 in natural groundwaters (VTT)
WP5 : Post-test examination of solid surfaces (VTT, USFD)
WP6 : Modelling of surface development (UU)
WP7 & 8 : Coordination and Management (SKB, Posiva)
Sample preparation

- Samples made at Sheffield: CaF2, CeO2, ThO2
- Goal: samples with similar microstructure to UO2 fuel and SIMFUEL.
- Ce powders from oxalate, thermal decomposition at different T. Commercial CaF2 and ThO2 powder.
- Powders were uniaxially pressed, then sintered at high T
- Methods described in publications:
  


See also our First Annual Report: Posiva Working Report 2012-28
Methods for characterisation

Density measurements by gas picnometer

- Densities in excess of 93% (ThO2), and 96% (CeO2), sintering pressed pellets at 1750 °C and 1700 °C, respectively.
- Densities of CaF2 ~95% on pellets sintered at 1000-1240 °C

Phase identification with X-ray diffraction (XRD)

Microstructure imaging and characterization by ESEM with EBSD,

Surface topography by profilometer using confocal lens

X-ray photoelectron spectroscopy (XPS) on crushed CeO2 pellet confirmed that cerium was present only as Ce(IV)
CeO$_2$ studies

- Synthesis and characterisation of CeO$_2$

CeO$_2$ pellet sintered at 1700 °C (SEM). Grain size 8 - 20 μm, & lowest porosity (~96% theoretical density)

Representative crystal orientations CeO2. Pole figures show the random orientation of grains in the (111), (110) and (100) crystal planes.
CeO$_2$ Dissolution experiments

Stennett et al (2013): Size fractions: 75–150 um, 0.1 g of powder in 40 ml of 0.01 M HNO$_3$ solution, giving a surface area to volume ratio of 200 m$^{-1}$. Placed in 90 °C oven and removed at 0, 1, 3, 7, 14, 21, 28 and 35 days. Solutions analysed with ICP-MS.

(a) Normalised leaching NL(Ce), crushed CeO$_2$ in 0.01 M HNO$_3$ at 90 °C
(b) confocal profilometer image of CeO$_2$ monolith after 9 days of reaction (same conditions)
CeO$_2$ studies

Further studies:

* Different sized crushed powders -> different densities of high energy sites on the exposed surfaces

* Single pass flow through and the micro-channel flow through experiments are planned

* Flow-through method for in situ AFM will enable further studies on the monolith sample (Collaboration w University of Edinburgh).
ThO$_2$ studies

- Synthesis and characterisation of ThO$_2$

ThO$_2$ pellet sintered at 1750 °C.

~93% theoretical density
Grain size 10 - 20 µm in diameter
ThO$_2$ Dissolution experiments

*2 -4 mm fragments
*Solution: 0.1 M NaCl and 0.01 M NaCl + 2 mM NaHCO$_3$
*25 °C.
*Triplicates + blank

Ultrafiltered samples: Initial increasing trend in both test solutions

The solubility and the dissolution rate increased in the solution containing carbonate due to the formation of carbonate/hydroxide complexes

Lena Z Evins
Euradiss, Montpellier
25-26 October 2012
ThO₂ studies

Further studies:

* Artificial isotope ²²⁹Th in tracer study
  - Dissolution-precipitation phenomena could occur during the dissolution.
  - avoid problems with detection limit of HR-ICP-MS (close to the solubility of ThO₂ in basic conditions)

* Dissolution studies with different particle sizes.
  75 to 150 um particles
  10 to 40 um particles.
Conducted partly under glove box conditions (under Ar)
**UO₂ studies**

- **Samples used previously**

  Dissolution rates of U (mol m⁻² yr⁻¹) (fraction/yr) in the presence of corroding iron (NF-PRO, IN-CAN projects)

<table>
<thead>
<tr>
<th>UO₂ solid doping level</th>
<th>0.01 M NaCl</th>
<th>0.5 M NaCl</th>
<th>1 M NaCl</th>
<th>modified synthetic groundwater (Allard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 % ²³³U (1)</td>
<td>2.1 x 10⁻⁶ (1x10⁻⁷)</td>
<td>2.7 x 10⁻⁶ (1x10⁻⁷)</td>
<td>6 x 10⁻⁷ (3x10⁻⁸)</td>
<td>2.7 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
<tr>
<td>0 % ²³³U (2)</td>
<td>4.2 x 10⁻⁶ (2x10⁻⁷)</td>
<td>2.5 x 10⁻⁶ (1x10⁻⁷)</td>
<td>1.1 x 10⁻⁶ (5x10⁻⁸)</td>
<td>2.9 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
<tr>
<td>5 % ²³³U (1)</td>
<td>2.1 x 10⁻⁶ (1x10⁻⁷)</td>
<td>2.3 x 10⁻⁶ (1x10⁻⁷)</td>
<td>4 x 10⁻⁷ (2x10⁻⁸)</td>
<td>2.1 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
<tr>
<td>5 % ²³³U (2)</td>
<td>8 x 10⁻⁷ (4x10⁻⁸)</td>
<td>1.2 x 10⁻⁶ (5x10⁻⁸)</td>
<td>6 x 10⁻⁷ (3x10⁻⁸)</td>
<td>2.7 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
<tr>
<td>10 % ²³³U (1)</td>
<td>8 x 10⁻⁷ (4x10⁻⁸)</td>
<td>1.3 x 10⁻⁶ (6x10⁻⁸)</td>
<td>4 x 10⁻⁷ (2x10⁻⁸)</td>
<td>2.7 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
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<td>10 % ²³³U (2)</td>
<td>8 x 10⁻⁷ (4x10⁻⁸)</td>
<td>1.3 x 10⁻⁶ (6x10⁻⁸)</td>
<td>4 x 10⁻⁷ (2x10⁻⁸)</td>
<td>2.7 x 10⁻⁶ (1x10⁻⁷)</td>
</tr>
</tbody>
</table>

*No indication of an effect of alpha radiolysis*

*The UO₂ solid samples have experienced many years of dissolution time;*

-> dissolve rates **slowly decreasing** with each subsequent exposure to synthetic groundwater.
Olkiluoto natural groundwater

-Moderately saline
-100 days stabilization
-No precipitates
-Escape of CO₂
-Fe decreased (0.35 to 0.15 mg/l)

<table>
<thead>
<tr>
<th></th>
<th>nonfiltered</th>
<th>filtered</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Total alkalinity, mmol/l</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Na⁺, mg/l</td>
<td>1520</td>
<td>1520</td>
</tr>
<tr>
<td>Ca²⁺, mg/l</td>
<td>520</td>
<td>530</td>
</tr>
<tr>
<td>Mg²⁺, mg/l</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>K⁺, mg/l</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Si⁴⁺, mg/l</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>S total, mg/l</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>Fe total, mg/l</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Br⁻, mg/l</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Cl⁻, mg/l</td>
<td>3300</td>
<td>3300</td>
</tr>
<tr>
<td>SO₄²⁻, mg/l</td>
<td>419</td>
<td>430</td>
</tr>
</tbody>
</table>
UO$_2$ dissolution in natural groundwater

In 0.01 M NaCl solution (Ollila 2008) under reducing conditions (Fe). Parallel dissolution tests with 5 % 233U-doped UO2 fragments

Measured $[^{238}\text{U}]$ and $[^{238}\text{U}]$ calculated from the isotopic ratio changes in natural OL-KR6 groundwater (on the left)

SA/V = 5 m$^{-1}$
Additional solid samples (3 g) from Chalmers University of Technology. Higher surface area to volume ratio (SA/V=15 m⁻¹) -> higher release of U from 10 % alpha-doped UO₂ sample is observed, compared with 0 and 5 %-doped UO₂ samples.
Further studies:

* Isotope dilution tests with 1g samples (SA/V = 5 m⁻¹) will be finished, and potential sorbed or precipitated U on vessel surfaces and on iron strips will be analysed.

* Calculation of dissolution rates per surface area unit.

* Continued test series with higher SA/V.

* Isotope dilution tests will be performed in a second natural groundwater: saline Olkiluoto groundwater, OL-KR5 (457.2 - 476.2 m)
Ab initio modelling: Aims

- Setting up of structure for surface reaction calculations

- Testing surface convergence, reconstruction at surfaces

- Model set-up for describing surface formation energies

- Chemical reactions at surfaces: Vacancies formation, Molecular adsorption & Molecular dissociation on surfaces

- Material’s aspects of the various surfaces ThO₂, UO₂, CeO₂, CaF₂, ...

- Effect of dopants at surfaces
Computational details

- CaF$_2$: Exchange correlation potential: GGA (PBE) Generalized Gradient Approximation
- CeO$_2$: Exchange correlation potential: Dudarev LDA+U approach with $U_{\text{eff}}=5.5$ eV, LDA = Local Density Approximation;

GGA & LDA: functionals which describe the electron in the mean field of all other electrons.

Convergence
Relaxation

Instabilities avoided by moving out 50% of O atoms from upper surface to lower surface.

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Euradiss, Montpellier  
25-26 October 2012
Surface Model

• Fluorite structure: most stable surfaces = lowest Miller index, (111), (110) and (100) surfaces.
• = reference planes from which one can build any other higher Miller indexed surface (Godinho et al, 2012).

• Any surface viewed as a stepped surface made of terraces and steps oriented in the directions of the reference planes.

<table>
<thead>
<tr>
<th>Terrace/Step</th>
<th>Miller Indices</th>
<th>Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>111/100</td>
<td>(p,p-1,p-1)</td>
<td>(211), (322), (433),...</td>
</tr>
<tr>
<td>111/110</td>
<td>(p,p,p-1)</td>
<td>(221), (332), (443),...</td>
</tr>
<tr>
<td>100/111</td>
<td>(2p-1,1,1)</td>
<td>(311), (511), (711),...</td>
</tr>
<tr>
<td>100/110</td>
<td>(p,1,0)</td>
<td>(210), (310), (410),...</td>
</tr>
<tr>
<td>110/111</td>
<td>(2p-1,2p-1,1)</td>
<td>(331), (551), (771),...</td>
</tr>
<tr>
<td>110/100</td>
<td>(p,p-1,0)</td>
<td>(210), (320), (430),...</td>
</tr>
</tbody>
</table>

From Godinho et al (2012)
(116) surface; mainly composed by the (001) type surface. Reference surfaces: dashed line (001), solid line (110) and dotted line (111)
Surface Model

Surface formation energy depending on the geometry of the planes involved.

CaF$_2$ and CeO$_2$ surface formation energies ($E^{(hkl)}_\sigma$):

\[
E^{(hkl)}_\sigma = \frac{1}{2} \left( E_n^{(hkl)} - nE_B \right)
\]

\[
E^{(hkl)}_\sigma = (p - 1 + f)E^{ref}_\sigma + \frac{\cos \alpha}{|A|^{2} |B|^{2}}
\]

$p$ is number of atomic rows of the terrace

$f$ is a constant that depends exclusively on the structure of the surface

Surface formation energy of any stepped surface calculated from:
- the surface formation energy of the reference plane,
- the size of the reference plane
- step direction

$E_n^{(hkl)}$ is total energy of the n-layer slab, $E_B$ is total energy of the bulk. Factor $1/2$ accounts for the presence of two surfaces.

Lines are given by the second function. Dots are calculated surface formation energies.
CaF$_2$ & CeO$_2$

A proportionality relation between the surface formation energies in CeO$_2$ and CaF$_2$:

Extension of the model to CeO$_2$ by using a proportionality constant ($r$):

$$E_{\sigma}^{(hkl)}(CeO_2) = rE_{\sigma}^{(hkl)}(CaF_2)$$

Consequently, in this way we can easily describe the surface formation energy of any stepped surface of a fluorite material.

• Example of chemical reactions on the surface: dissociation reaction of a H$_2$ molecule on the (111) surface of CeO$_2$:

H$_2$
dissociation
on CeO$_2$
(111) surface
Ab initio modelling

Future modelling work:

*the dissolution process; need to describe binding energies of atoms “sticking out” from the step edge.

*Ab initio investigations of dissociation energies of other molecules such as H2O.

*Modeling UO2 surface in similar fashion as CaF2 & CeO2
Final points

- REDUPP looks at surface changes during dissolution & extrapolation from short term laboratory experiment to long-term dissolution in a natural setting.
- Effect of disappearing high-energy sites: are laboratory results overestimating the dissolution rate?
- First-principles calculations combined with experimental studies: can a model be set-up which describes the long-term surface evolution of a dissolving fluorite-type solid?
- Polycrystalline materials: the effect of crystallographic orientations, grain boundaries and pores
- Importance of characterizing solid before and after experiment
- Project is on-going and progressing. 2nd annual meeting coming up in Sheffield April 2013.