REDUPP - IGDTP Evaluation at EF6

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Reducing Uncertainty in Performance Prediction

1 April 2011 - 31 March 2014

CONSORTIUM

SKB, Coordinator: Lena Z Evins

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Uppsala University: Peter Oppeneer, Pablo Maldonado

University of Sheffield: Neil Hyatt, Claire Corkhill, Martin Stennett

Objectives

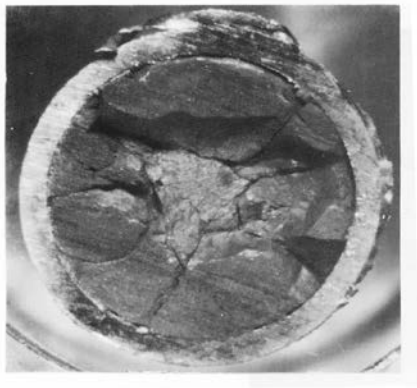
1) Increase understanding of the processes that control spent fuel dissolution in the long term. The overall purpose is to reduce the remaining uncertainties concerning dissolution rate in the safety case.

Focus: surface properties of spent nuclear fuel affecting dissolution in realistic repository conditions

2) Provide training opportunities for young researchers and contribute to the knowledge transfer

Approach

Dissolving fluorite materials:
in experiment and from first-principles



Rates changing with time? Slowing down?

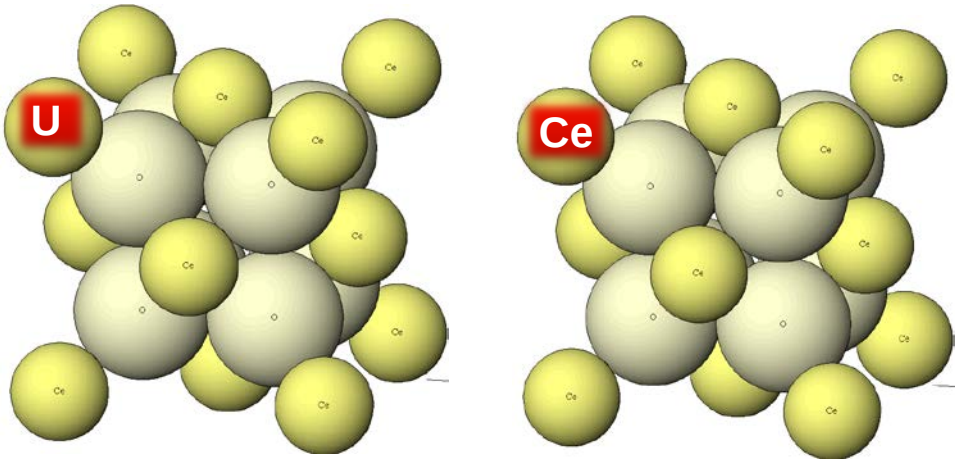
The influence of “high-energy sites”

Rates affected by trace elements in groundwater?

- For example, does Br^- impair the hydrogen effect?

Uranium dioxide,
UO_2: fluorite structure

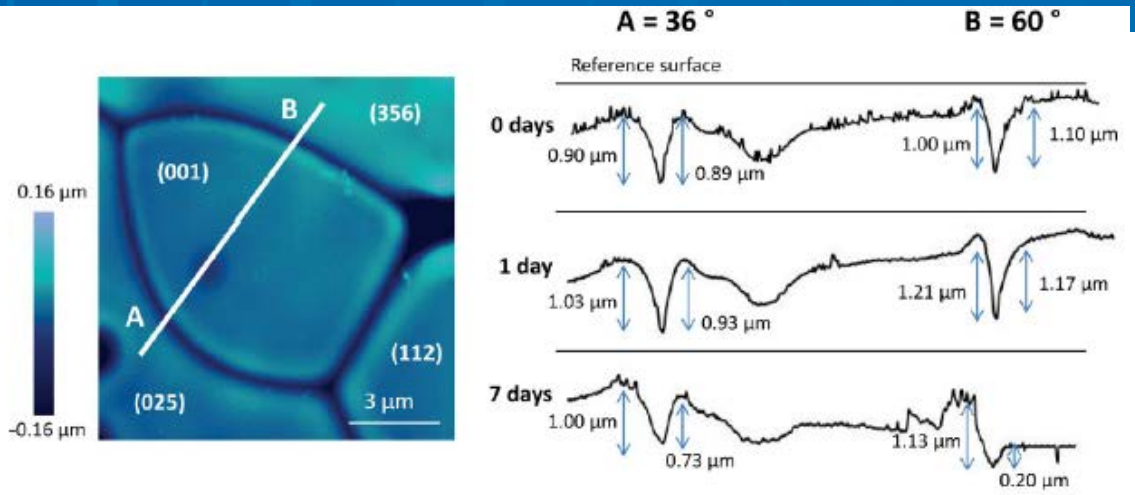
- Same as ThO_2, CeO_2 , and CaF_2
  - Avoiding complications from redox-sensitive U



Fluorite structure

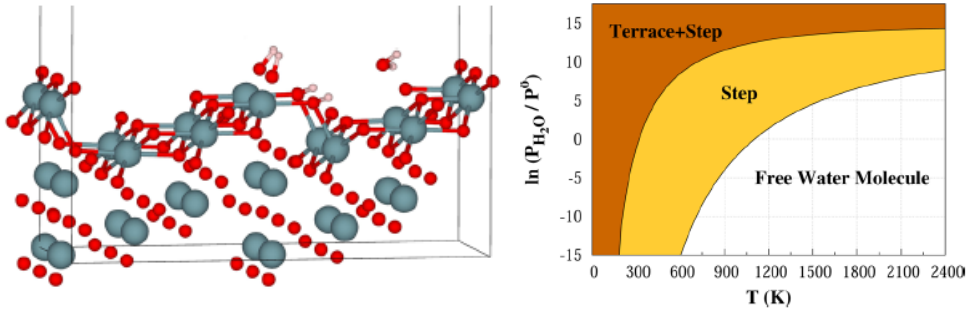
Scientific Results

- Importance of surface defects in initial stages of dissolution: Vacancies, grain boundaries. Crystallographic control: Etch pits and lattice mismatch in grain boundaries. Rates become lower as dissolution proceeds on a laboratory time scale.



Corkhill et al 2014, ACS Applied Materials and Interfaces

- Stability & dissolution rate vary with crystallographic orientation & atomic scale surface structure. Experimental retreat rates & computed surface stabilities follow same trends. H_2O dissociation on the (111) UO_2 surface is virtually barrierless. Dissociative adsorption of water at a step edge will occur at all relevant pressures and temperatures & lead to modification of surface morphology.

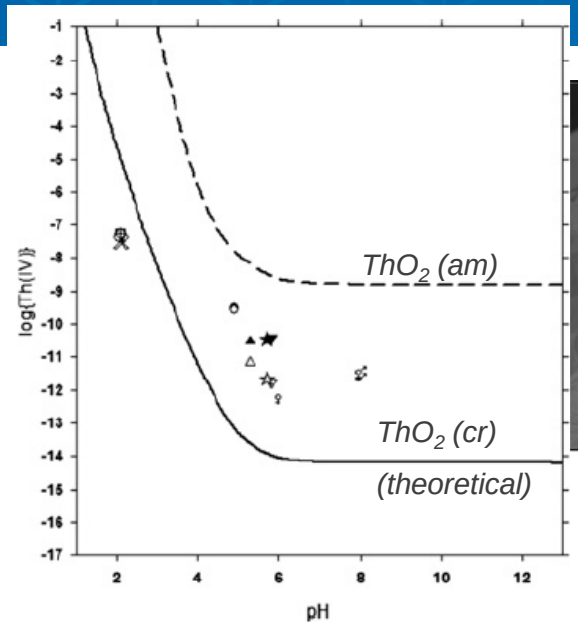


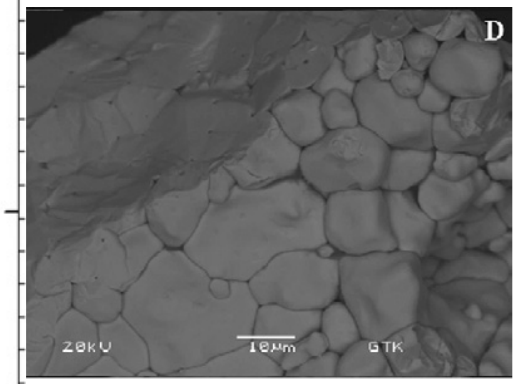
Maldonado et al 2014, Journal of Physical Chemistry C

Scientific Results

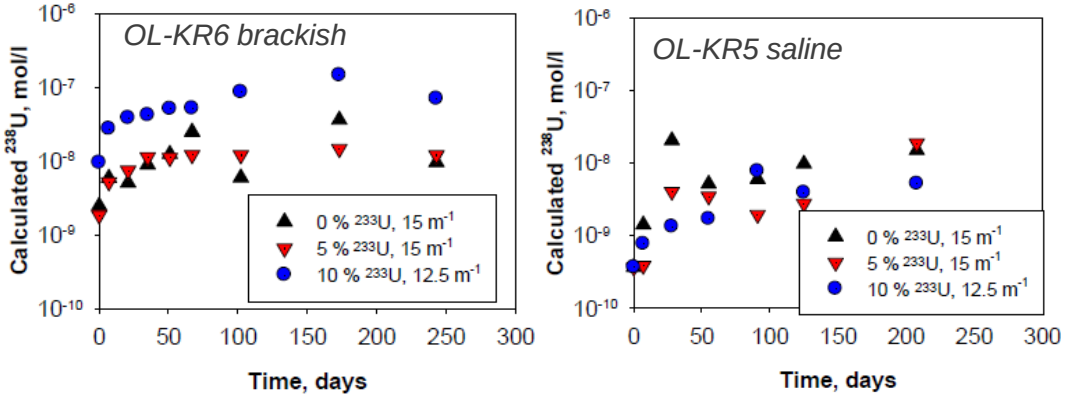
- Low ThO_2 solubility, concentrations down to 10^{-12} mol/L at pH >4, with HR-ICP-MS.
  Repository conditions: higher pH and complexing ligands → colloid formation. Influence of particle size: Initial surface characteristics, local micro-chemical environment.
  Both dissolution & precipitation in the vessel.

- Alpha-doped UO_2 in real groundwater using U isotopes:
  U dissolution followed by precipitation. Increased surface area/ fluid volume: better precision, some effect seen for 10% alpha-doped material in brackish water
  - *No observed effect of higher salinity groundwater*





Myllykylä et al 2015, Radiochimica Acta



Ollila et al 2013, Journal of Nuclear Materials & REDUPP Final Report Posiva WR 2014-12

Scientific journal publications

Godinho, J.R.A., Piazolo, S., Stennett, M.C. and Hyatt, N.C. (2011). Sintering of CaF_2 pellets as nuclear fuel analogue for surface stability experiments. **Journal of Nuclear Materials**, 419, 46-51. (SU & USFD)

Stennett M.C., Corkhill C.L., Marshall, L.A. and Hyatt, N.C. (2013). Preparation, characterisation and dissolution of a CeO2 analogue for UO2 nuclear fuel. **Journal of Nuclear Materials** 432, 182–188. (USFD)

Corkhill, C.L, Bailey, D. J., Thornber, S.M., Stennett, M. C. and Hyatt, N. C. (2013). Reducing the uncertainty of nuclear fuel dissolution: an investigation of UO2 analogue CeO2. **Mater. Res. Soc. Symp. Proc**. Vol. 1518, DOI: 1 1557/op2013.90 (USFD)

Maldonado, P., Godinho, J. R. A., Evins, L. Z., and Oppeneer, P. M. (2013). Ab Initio Prediction of Surface Stability of Fluorite Materials and Experimental Verification. **Journal of Physical Chemistry C**, 117, 6639−6650. (SU, UU & SKB)

Ollila K., Myllykylä, E., Tanhua-Tyrkkö, M. and Lavonen. T. (2013). Dissolution rate of alpha-doped UO2 in natural groundwater. **Journal of Nuclear Materials** 442, 320–325. (VTT)

Maldonado et al. (2014) Ab Initio Atomistic Thermodynamics of Water Reacting with Uranium Dioxide Surfaces. **Journal of Physical Chemistry C**, 118, 8491−8500 (UU & SKB)

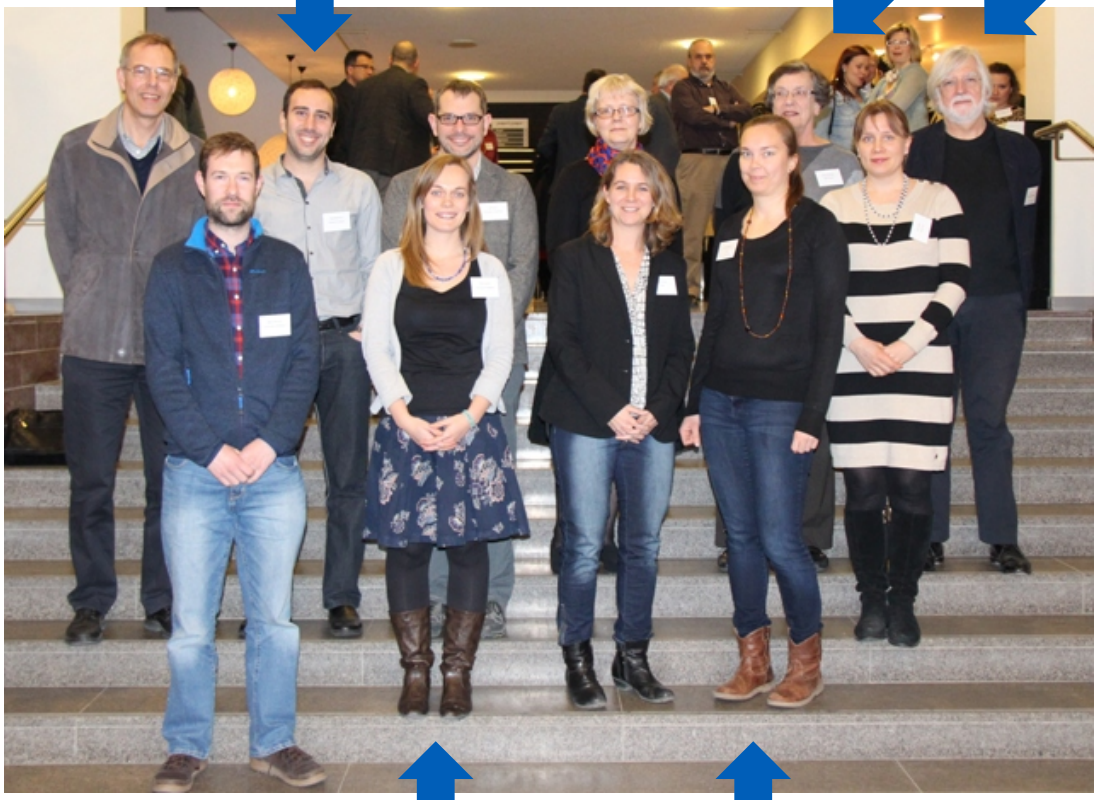
Corkhill et al (2014) Contribution of Energetically Reactive Surface Features to the Dissolution of CeO2 and ThO2 Analogues for Spent Nuclear Fuel Microstructures. **ACS Applied Materials & Interfaces** 6, 12279−12289. (USFD, UU, VTT & Univ. Edinburgh)

Myllykylä et al (2015) Solution composition and particle size effects on the dissolution and solubility of a ThO2 microstructural analogue for UO2 matrix of nuclear fuel. **Radiochimica Acta** 2015; 103(8): 565–576 (VTT & USFD)

2nd objective

Post doc, Uppsala

SAB



Post doc, Sheffield

PhD, VTT

Lecture Series, open for external audience (students etc) = 9 lectures by international experts and leaders in the field

Fruitful Collaboration, example Corkhill et al 2014: USFD, UU, VTT & Univ. Edinburgh

Knowledge transfer through interaction with Scientific Advisory Board (SAB)

Research coordination & communication

- 3 project meetings, 2 informal workshops, 3 Annual reports,
  5 Newsletters, web site, press release, 3 publications for a wider audience…

REDUPP Final Conference in Stockholm, February 2014

Main conclusions

Overall, measured dissolution rates are affected both by surface properties and by fluid composition.

Notably, the crystallographic structure of the exposed surface also influences the interfacial reactions.

These parameters should be carefully considered when measuring dissolution rates in the laboratory, and when extrapolating these rates far into the future.

Training and outreach have been successfully implemented through various means.

All deliverables have been submitted, and the project members have published the results in peer-reviewed journals. Various dissemination activities have been carried out, including a final open conference at the end of the project.

Evaluation

Full budget: € 1 596 802: EC contribution: € 929 304

Impact on Safety Case

- Defects and grain boundaries increasing initial dissolution rate in laboratory:
  rate for spent fuel in the long term should be overestimated. Evolution of grain boundaries over time - The time scale is still an issue.
- Improved thermodynamic data base through new and improved Th solubility data
- Natural saline (high Br^-) groundwater does not increase dissolution rate in laboratory
- New way of modelling the surface using DFT+U: method developement. The surface and surface stability and hydroxylation is described, but dissolution process requires further efforts.

Impact on Training/Developement and Knowledge transfer

- Post docs in Sheffield & Uppsala turned into academic staff posititions
- REDUPP results taken forward in Fellowship application (Claire Corkhill)

CC position at USFD:
Vice Chancellor's Fellow in Geological Disposal of Nuclear Waste

- Increased successful collaboration between experimenters and modellers in the field: joint publications
- Outreach & Knowledge transfer - Scientific Advisory Board provided peer review.
  The project spread awareness of spent fuel issues to a wider audience

Meeting the objectives?

- 1) Increase understanding of the processes that control spent fuel dissolution in the long term. The overall purpose is to reduce the remaining uncertainties concerning dissolution rate in the safety case
  - "*measured dissolution rates are affected both by surface properties and by fluid composition ….these parameters should be carefully considered when measuring*"
  - Increased understanding – yes, REDUPP has equipped us with the tools to approach the problem of changing surface characteristics experimentally and theoretically, for the purpose of reducing the remaining uncertainties.
    Qualitative rather than quantitative impact on uncertainties in dissolution rate
- 2) Provide training opportunities for young researchers and contribute to the knowledge transfer
  - Yes, successfully

Where to go forward

- Remaining issues to fulfil the IGD-TP vision
- What part of the dissolution process requires further investigations? Is there a need to deepen the general understanding in this area?

  - We need to make sure we meet the demands from authorities

- Focus should now be on how to finding a way for an efficient European cooperation and obtain more data which will strengthen our case.