Dissolution of spent nuclear fuel – Results from completed EU –project REDUPP and ongoing project DISCO

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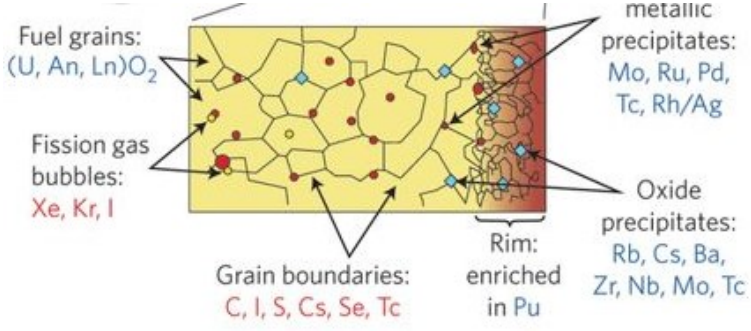
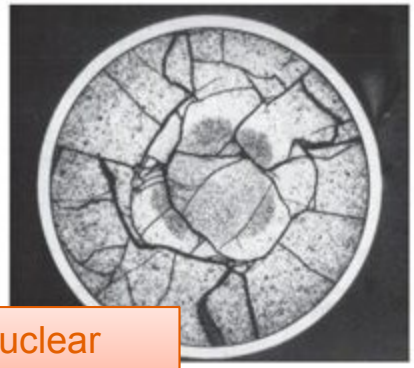
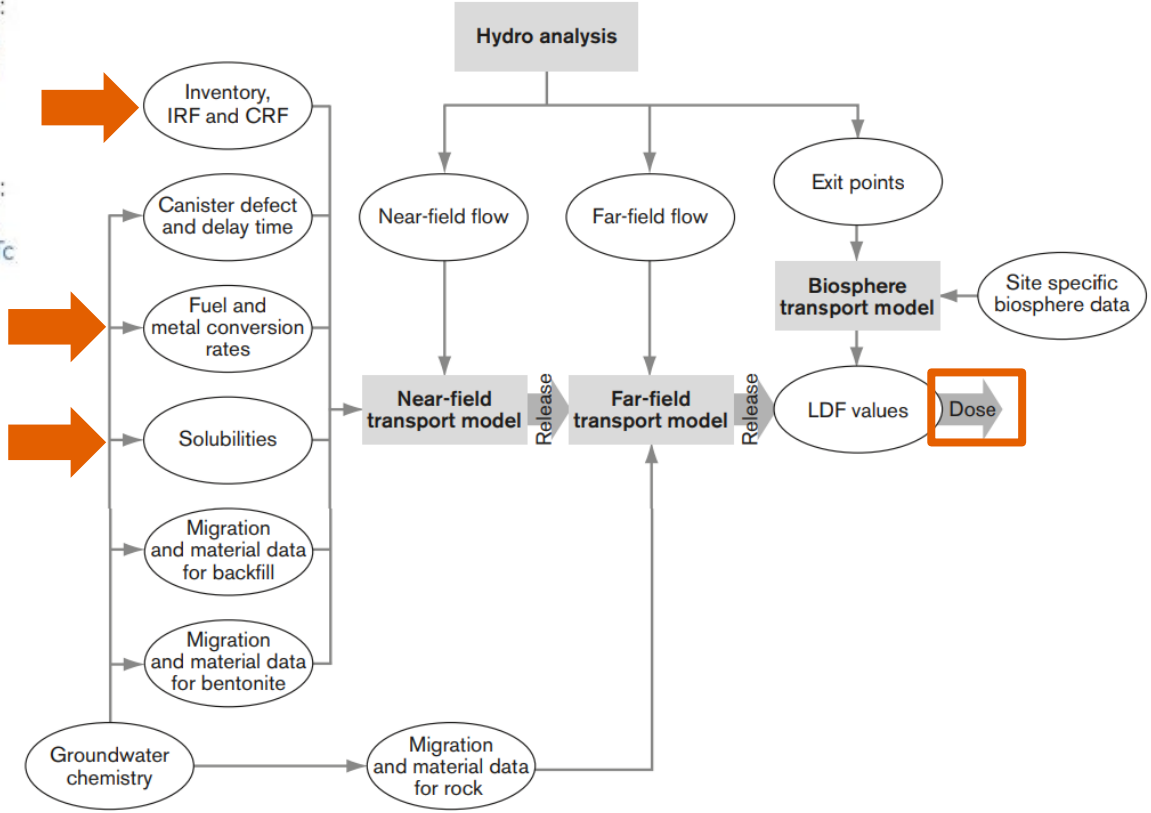
Introduction Spent Nuclear Fuel dissolution





Spent Nuclear Fuel in cladding



Introduction REDUPP

- April 2011 –April 2014
- FP7 Collaborative Project
- Reduce remaining uncertainty in the dissolution in the dissolution rate of spent uranium oxide fuel + train young scientists for future needs in our field

REDUPP
Reducing Uncertainty in Performance Prediction

Fluorite structures : CaF_2, CeO_2, ThO_2, UO_2

Sample surface changes during dissolution, effects of ”high-energy sites”

Effects of natural ground water on dissolution of alpha-doped UO_2

Experiments & Ab Initio modelling

Introduction DisCo

DisCo
Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions

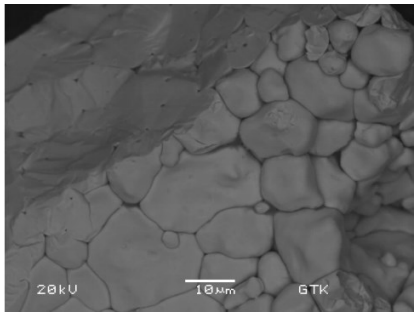
- June 2017 – May 2021
- Collaborative Project under Horizon 2020
- Enhance spent fuel matrix dissolution understanding in repository conditions
- To test modern nuclear fuel types (doped & MOX) for comparison with conventional fuels:
  - *Both real spent fuel and synthesized model materials*
- To disseminate the new knowledge : reach a wider community through training and mobility measures
- Associated Group: CV Rez (CH), LEI (LT), MTA EK (HU), ICHTJ (PL), EIMV (SI), Subatech(FR)

Methods

Methods REDUPP

Experimental

- Synthesis of spent nuclear fuel analogues: fluorite structure, grain size, porosity, defects …
- Dissolution in various conditions & aqueous phase analyses
- Post-dissolution analyses of the solid phases



Back-Scattered Electron (BSE) image of ThO_2 fragment, 4 weeks leaching

Modelling

- Density Functional Theory in first-principles (Ab Initio) modelling (L(S)DA & DFT+U)
- Modelling a surface: 6-8 layers
- Stepped surfaces on fluorite materials: terraces and steps
- Ab initio molecular dynamics (AIMD) and atomistic thermodynamics simulations for different temperatures & water reactions on UO_2 surfaces

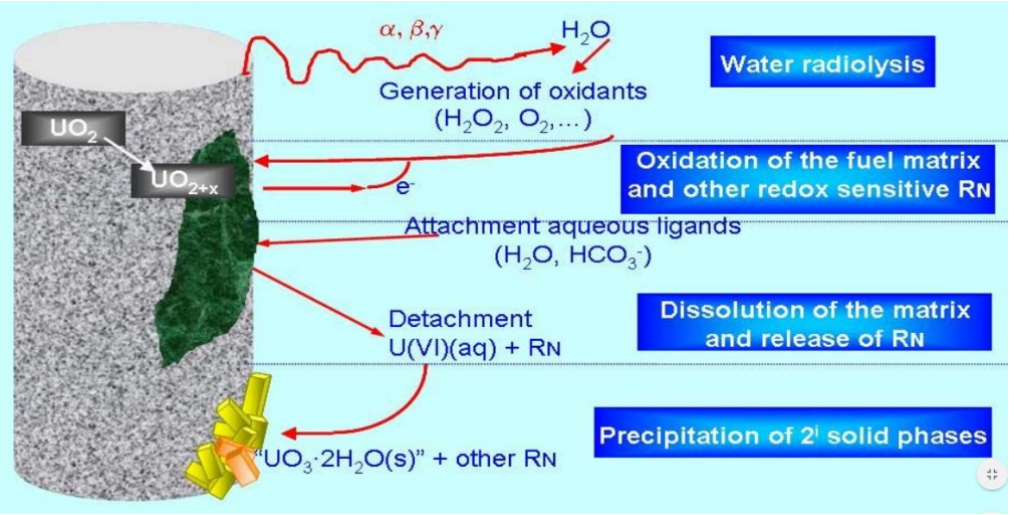
Methods DisCo

Experimental

- Real Spent Fuel dissolution experiments: used MOX, Cr-doped, Cr/Al-doped, and standard fuel.
- Model materials: UO_2 with and without dopants (Cr, Al, Gd), with and without alpha-emitter (^{233}U, ^{238}Pu)
- Dissolution experiments
  - 1) oxidizing, SNF & air (as reference, SNF & Ar, Model materials & H_2O_2)
  - 2) inert atmosphere & Fe (reducing)
  - 3) under Hydrogen (reducing)
- Post-dissolution analyses

Modelling

- Improve existing models through inclusion of Fe corrosion, hydrogen effect & metallic particles
- Thermodynamics, chemical kinetics, electrochemistry, reactive transport…



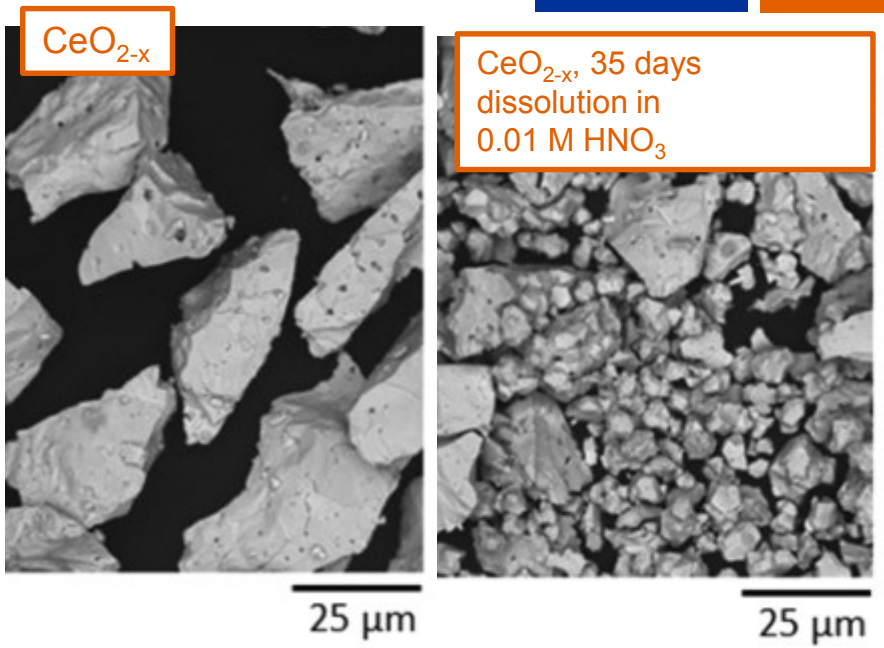
Results

Results REDUPP CeO_2

Role of defects and grain boundaries

- Initial fast dissolution is focused on grain boundaries: misorientation angles & crystallographic control.
- Intrinsic defects: oxygen vacancies replaced by oxygen during dissolution, Ce^{3+} in CeO_{2-x} rapidly oxidized to Ce^{4+}
- Lattice strain and enhanced oxygen mobility, created by the removal of oxygen vacancies

→ disintegration of particles, preferentially along grain boundaries



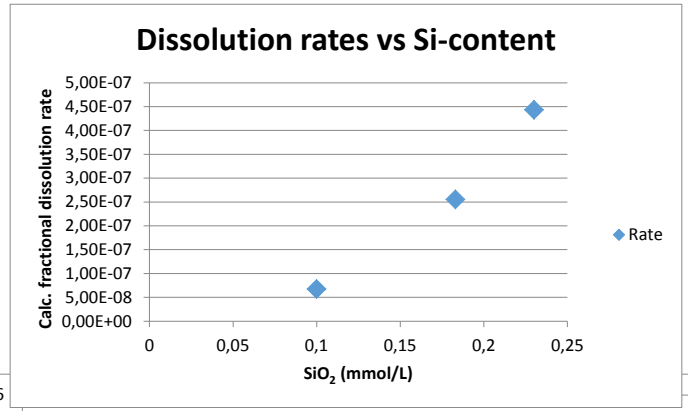
Corkhill et al 2014. Contribution of Energetically Reactive Surface Features to the Dissolution of CeO2 and ThO2 Analogues for Spent Nuclear Fuel Microstructures ACS Appl. Mater. Interfaces, 6, 15, 12279-12289

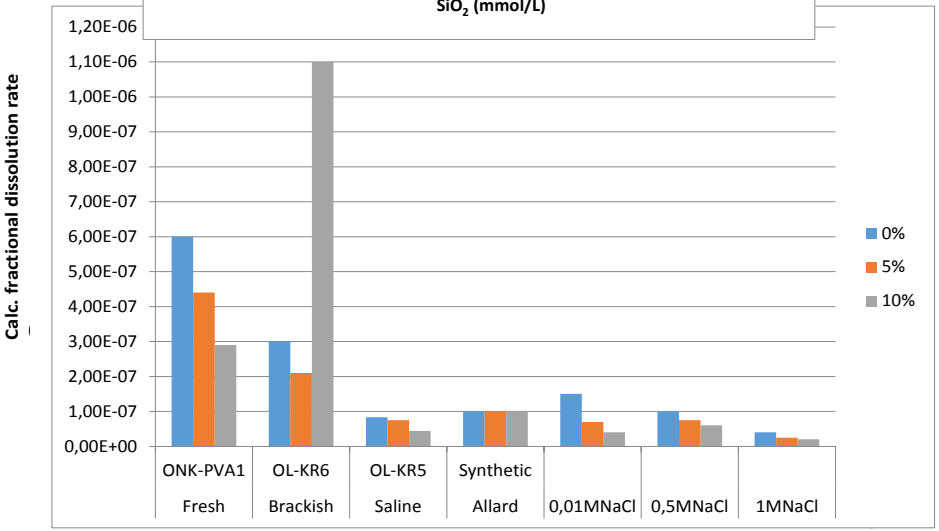
Corkhill et al, 2016. Role of Microstructure and Surface Defects on the Dissolution Kinetics of CeO2, a UO2 Fuel Analogue. ACS Applied materials &Interfaces 8, 16, 10562-10571

Results REDUPP UO_2 in natural groundwater

Effects of natural groundwater

- 3 ground waters with different salinity
- 0 %, 5%, or 10 % ^{233}U- α-doped UO_2
- Calculated dissolution rates highest in fresh groundwater
- This water has highest silica and carbonate content
- Precipitates were found with U and Si





Ollila et al 2013. Dissolution rate of alpha-doped UO_2 in natural groundwater. Journal of NuclearMaterials 442 (2013) 320–325

Evins L Z, Juhola P, Vähänen M, 2014. REDUPP. Final report. Posiva Working Report 2014-12, Posiva Oy, Finland.

Results DisCo WP2: Sample preparation

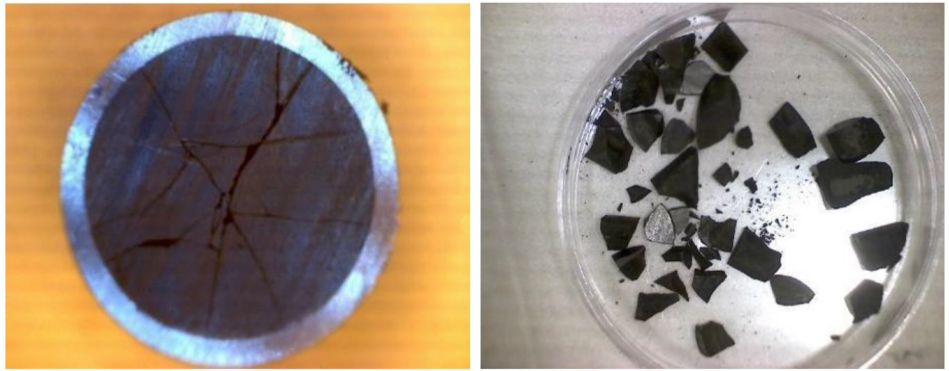
Spent nuclear fuel samples

- SNF samples prepared in Hot Cells at Studsvik , KIT INE, JRC & NNL
- Samples for dissolution prepared either as segments of a fuel rod, or as fragments with the cladding removed

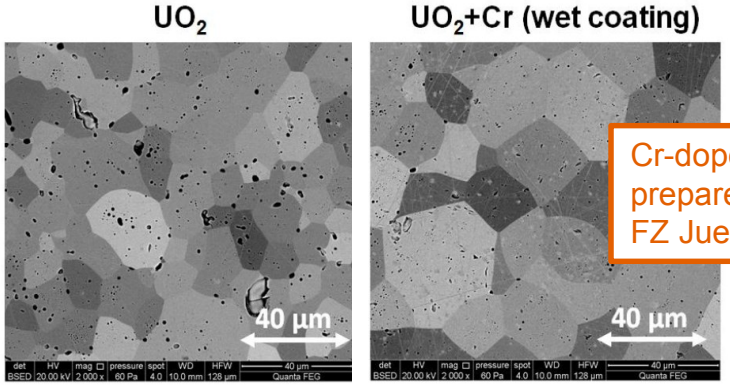
Model materials

- UO_2 (as reference), UO_2+Gd, UO_2+Cr, UO_2+Cr+Al, $(U,Th)O_2$.
- Sample synthesis procedures have been optimized and samples characterized

$+(U,Pu)O_2$ & ^{233}U-doped UO_2 already available



Spent nuclear fuel (MOX) prepared at KIT INE



<D> = 12.1 µm

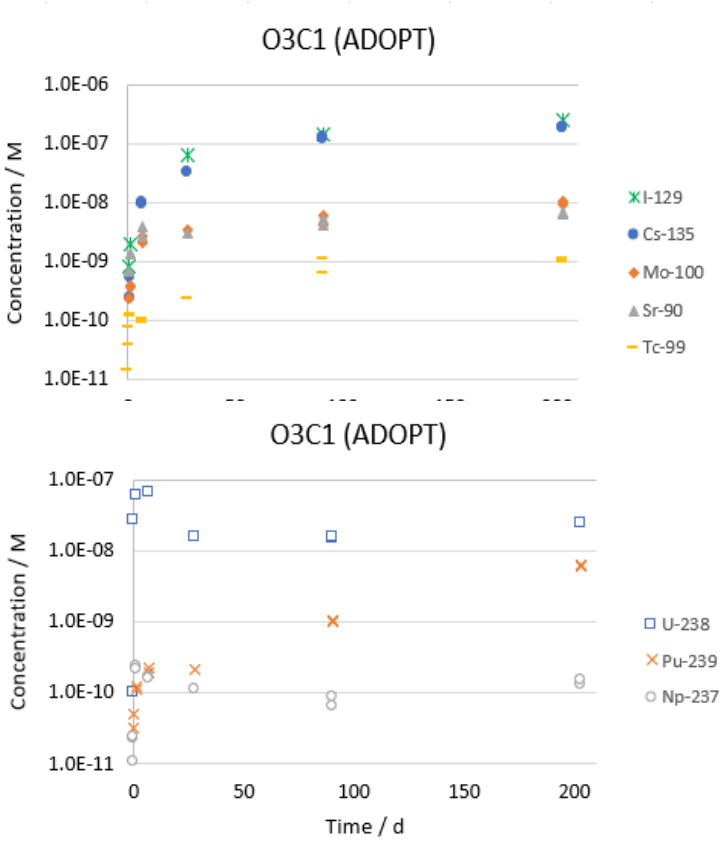
<D> = 19.4 µm

Cr-doped UO_2 prepared at FZ Juelich

Results DisCo WP3: Spent fuel dissolution

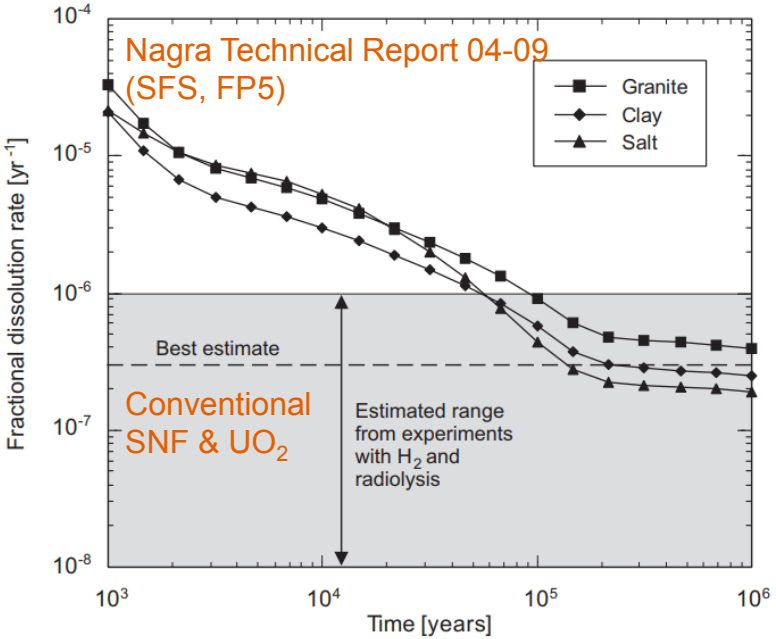
1st leaching results available

- Next year data will be available for inclusion in the chemical models (WP5)
- Tests run in reducing conditions: H_2 or Mix of Ar/H_2 , plus reference test in air
- Studsvik Example given here



Discussion

What we know



Comparison of fractional dissolution rates calculated using the MAM with the range of values estimated from experimental studies of dissolution of alpha-doped UO_2 and spent fuel in the presence of H_2

Knowledge gaps

- How do we model the "hydrogen effect" at the fuel-water interface? (DisCo)
- How do different elements in the solid affect the dissolution – eg Cr? Will they interfere with the interfacial electron transfer reactions?(DiscO)
- How do water chemistry, e.g. pH, different complexing agents, affect dissolution? (DisCo)
- Is there a "hydrogen effect" without metallic particles? Iron and Fe^{2+}(aq) is indicated to supress oxidative dissolution (DisCo) – but there is also some evidence that hydrogen is effective in this situation.
- What secondary precipitates can form (UO_2 (am), coffinite ($USiO_4$?), and how does this affect radionuclide release?

Summary

REDUPP

- Completed project (2014)
- Several papers published after project completion
- Importance of grain boundaries and defects during initial stage of dissolution
- Disappearing “High-Energy sites” – surface adjusts to a lower energy state
- Ab Initio model of hydroxylated stepped surface: atomic scale view of surface modification
- Calculated dissolution rates faster in fresh water with high Si and carbonate

DisCo

- Ongoing project (2017-2021)
- Spent nuclear fuel and model materials studied
- Effect of additives in nuclear fuel (Cr, Cr+Al, Gd, Th, Pu) on dissolution of spent nuclear fuel.
- Experiments are ongoing - preliminary dissolution data available
- Different modelling approaches developed
- Communication and training to include Associate Group: Knowledge transfer

The End

Thank you for listening!

Acknowledgements: all project contributors

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REDUPP:
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DisCo:
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DisCo: ongoing and planned work

Experimental matrix

Reducing (H2, Ar/N2/H2 mix, or anoxic with corroding Fe)				
Water type:	BW	YCWCa	Natural GW + Fe	synthetic Cox+Fe
Solid				
UO2 ref	**Started**	**Started**	Planned	
UO2+Gd	**Started**	**Started**		
UO2+Cr	**Started**	**Started**	Planned	
UO2+Al				
UO2+Cr+Al	**Started**	**Started**		
(U,Th)O2	Planned	Planned		Planned
UO2 ref - 238Pu/233U	**Started**	**Started**	**Started**	
UO2+Cr- 238 Pu	Planned	Planned	Planned	
(Pu,U)O2				**Started**
spent fuel UO2 (BU 57,1 &?60?)	**Started**	Planned		
spent fuel Cr&Al-UO2 (BU 59.1)	**Started**			
spent fuel Cr-UO2 (BU 58)	Planned			
MOX (BU 38)	**Started**			
Oxidizing/Anoxic(Ar), H2O2, or Air				
Water type:	BW	YCWCa	Natural GW + Fe	synthetic Cox+Fe
Solid				
UO2 ref +H2O2	**Started**	**Started**		
UO2+Cr +H2O2	**Started**	**Started**		
UOX (60 (local 73)), Air		**Started**		
MOX (BU 56&48):, Ar	Planned			