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# Spent fuel dissolution results from completed project REDUPP and ongoing project Disco

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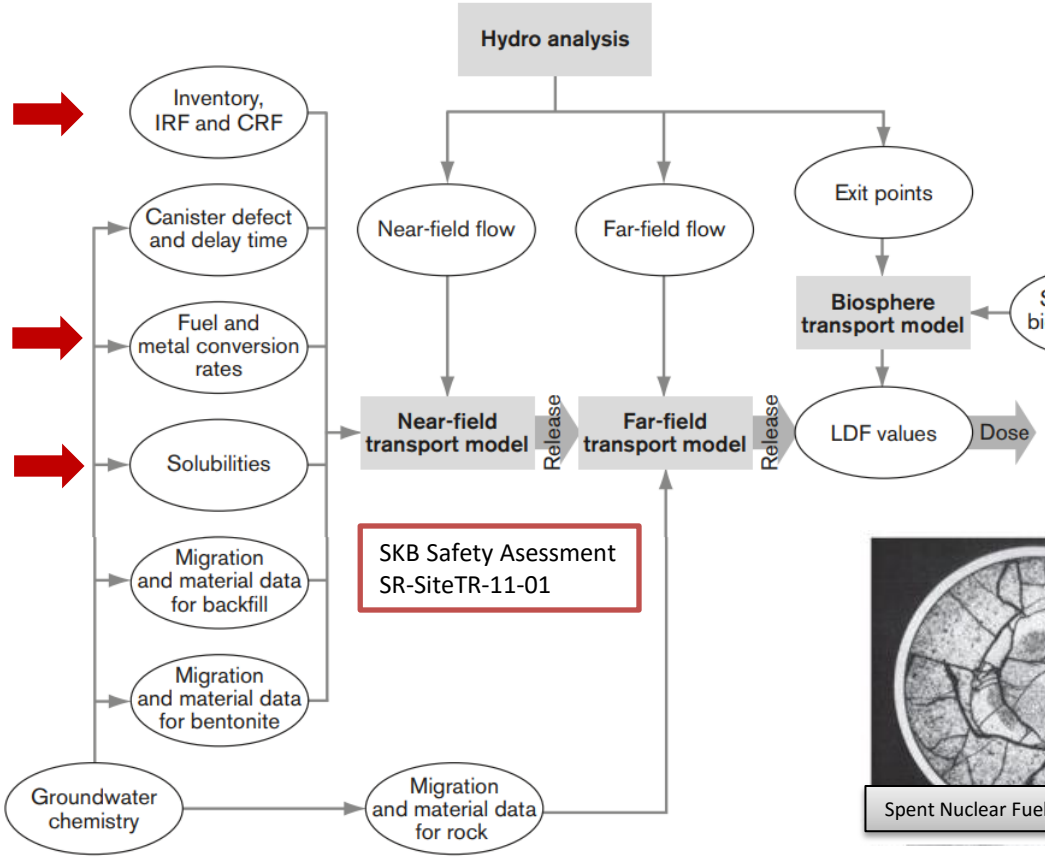
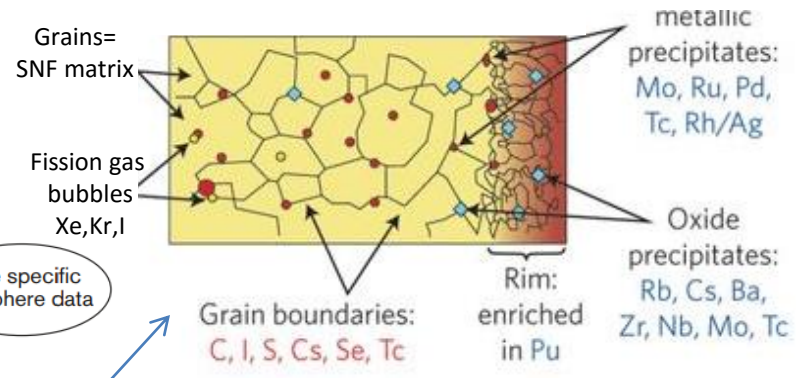
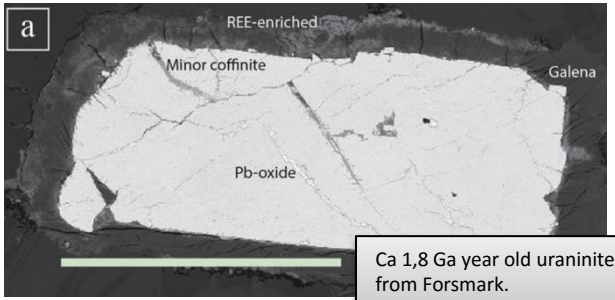
# Introduction Spent Nuclear Fuel dissolution






Spent Nuclear Fuel in cladding




Krall et al (2019)

Ca 1,8 Ga year old uraninite from Forsmark.
Scale bar 200 µm

# Introduction REDUPP

- April 2011 – April 2014
- FP7 Collaborative Project
- Reduce remaining uncertainty 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 structure : $CaF_2$, $CeO_2$, $ThO_2$, $UO_2$

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

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

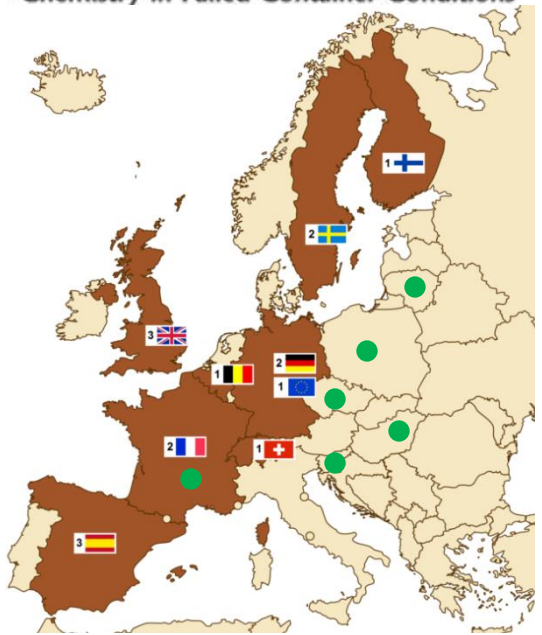
Experiments & Ab Initio modelling

# Introduction DisCo

- June 2017 – May 2021
- Horizon 2020 Collaborative Project
- Improve understanding of spent fuel matrix dissolution in repository conditions
- Test modern nuclear fuel types (doped & MOX) for comparison with conventional fuels:
  - *Both real spent fuel and synthesized model materials*
- 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)

DisCo

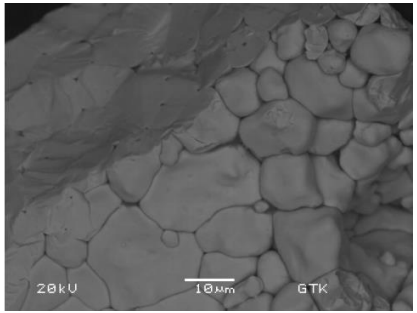
Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions



# Methods REDUPP

## Experimental

- Synthesis of spent nuclear fuel analogues: fluorite structure, grain size, porosity, defects …
- Dissolution in various conditions & aqueous phases 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

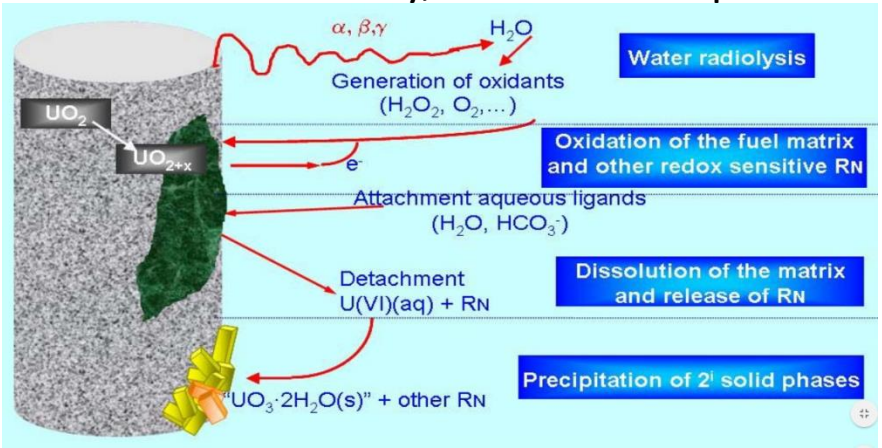
# Methods DisCo

## 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

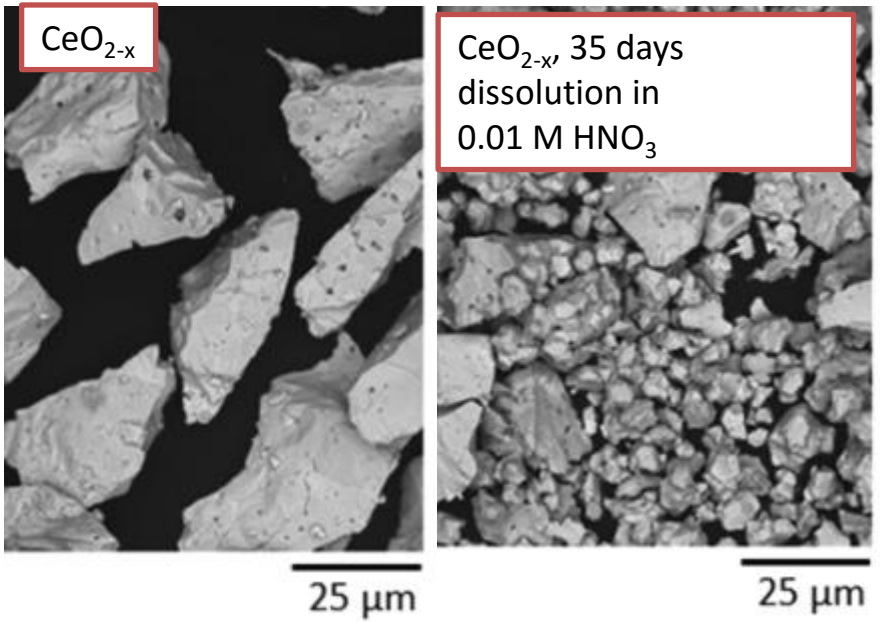
- Improve existing models through inclusion of Fe corrosion, hydrogen effect & metallic particles
- Thermodynamics, chemical kinetics, electrochemistry, reactive transport…



# Results 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, resulted in the 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

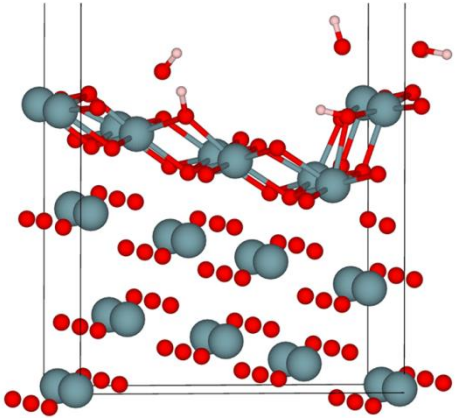
Corkhill et al, 2016. Role of Microstructure and Surface Defects on the Dissolution Kinetics of CeO2, a UO2 Fuel Analogue. ACS Applied materials &Interfaces 8, 16, 10562-10571

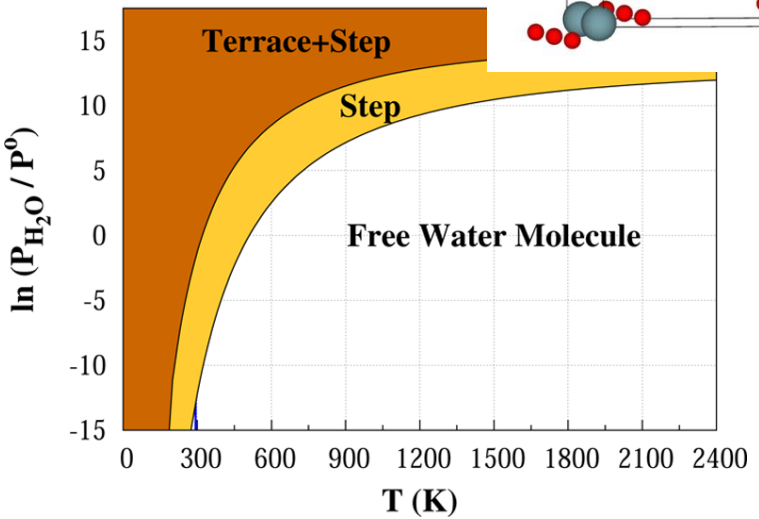
# Results REDUPP Ab Initio

## Water on $UO_2$ surfaces

- Ab Initio Molecular Dynamics combined with atomistic thermodynamics
- Dissociative adsorption: hydroxylated surface stable at environmental conditions
- More reactive surfaces with steps and terraces: reaction accompanied by a modification of the step morphology.

3 molecule water adsorption on the (221) surface of $UO_2$.






Maldonado et al , 2014. Ab initio atomistic thermodynamics of water reacting with uranium dioxide surfaces.
The Journal of Physical Chemisty C 118, 8491−8500.

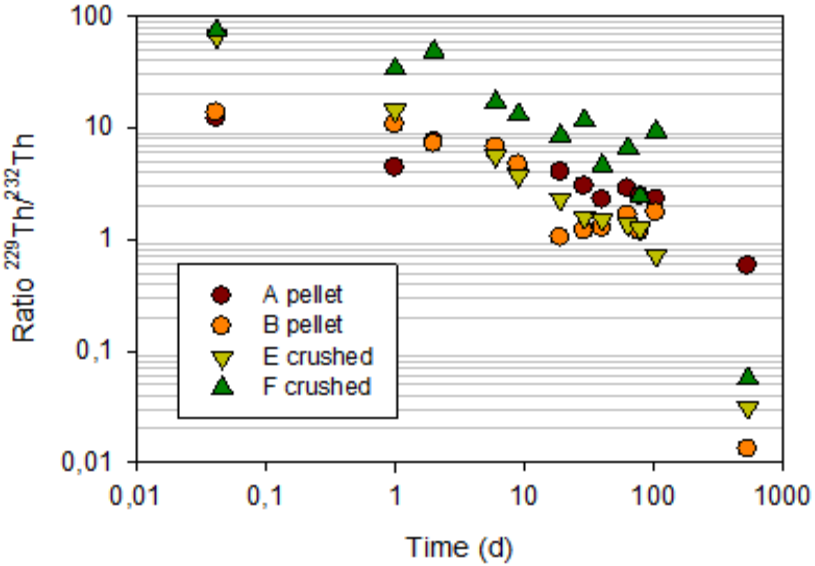
# Results REDUPP $ThO_2$

## Insight from isotope exchange

- Isotopic tracer ($^{229}Th$) to track surface processes: Continued isotopic exchange in spite of apparent chemical equilibrium
- Continuous change of isotopic ratio $^{229}Th/^{232}Th$ : precipitation/dissolution reactions are still ongoing at the interface despite apparent chemical equilibrium
- Alpha-spectrometry: surface layer, maximum 0,1 µm thick containing $^{229}Th$ and daughter nuclides of $^{229}Th$ and $^{232}Th$ decay series.

Myllykylä et al 2017 Dissolution of $ThO_2$: study of dissolution process with initial $^{229}Th$ spike. Journal of Radioanalytical and Nuclear Chemistry 311, 225-235.

## Continuous change in isotopic ratio

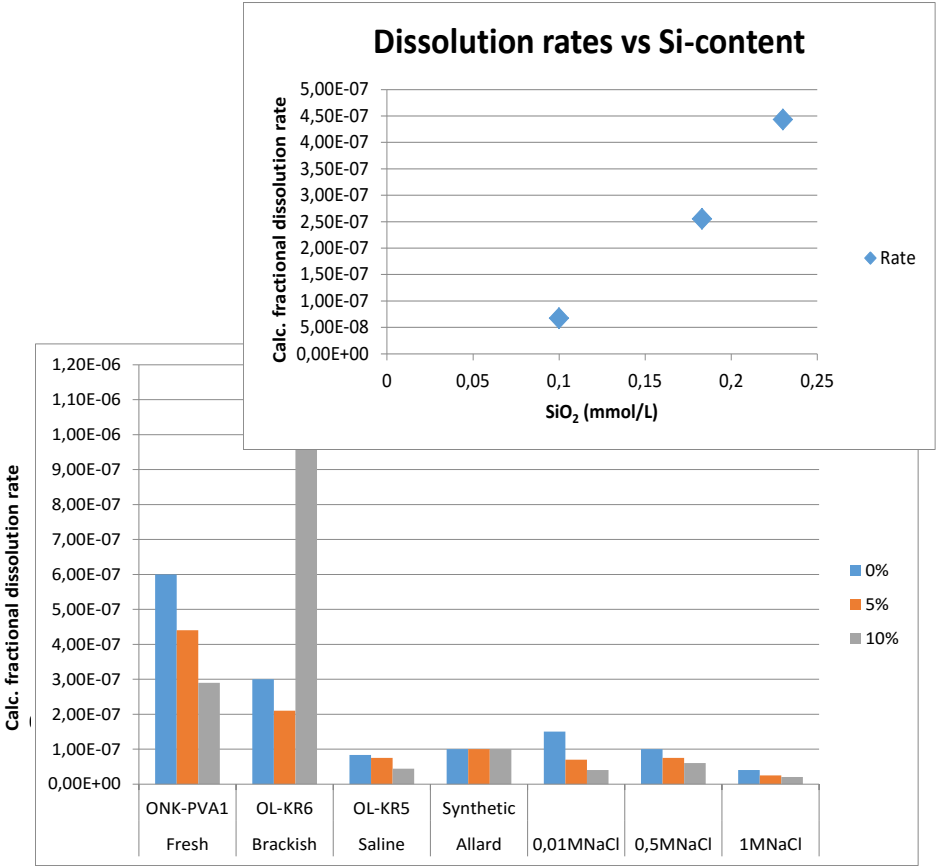



Myllykylä et al 2017, Direct alpha spectrometry for analysing leached $ThO_2$ pellets. Journal of Nuclear Materials, 493,2017, 69-76. doi.org/10.1016/j.jnucmat.2017.06.003

# Results REDUPP $UO_2$ in natural groundwater

## Effects of natural groundwater

- 3 ground waters with different salinity
- Experiments used isotopic exchange: Rates are calculated using change in isotopic ratio
- Calculated dissolution rates highest in fresh groundwater
- This has highest silica and carbonate content
- Precipitates were found with U and Si





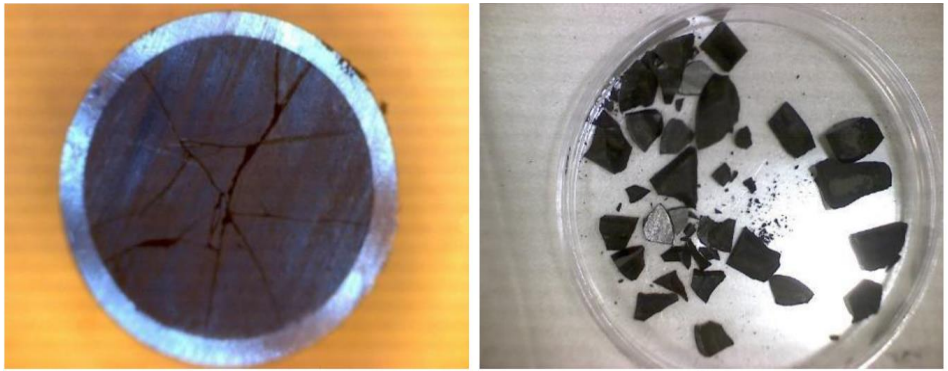
Ollila et al 2013. Dissolution rate of alpha-doped $UO_2$ in natural groundwater. Journal of NuclearMaterials 442 (2013) 320–325

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

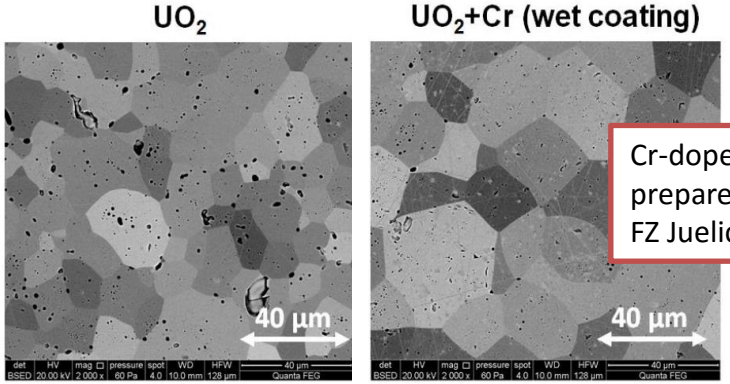


Spent nuclear fuel (MOX) prepared at KIT INE

## 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




<D> = 12.1 µm

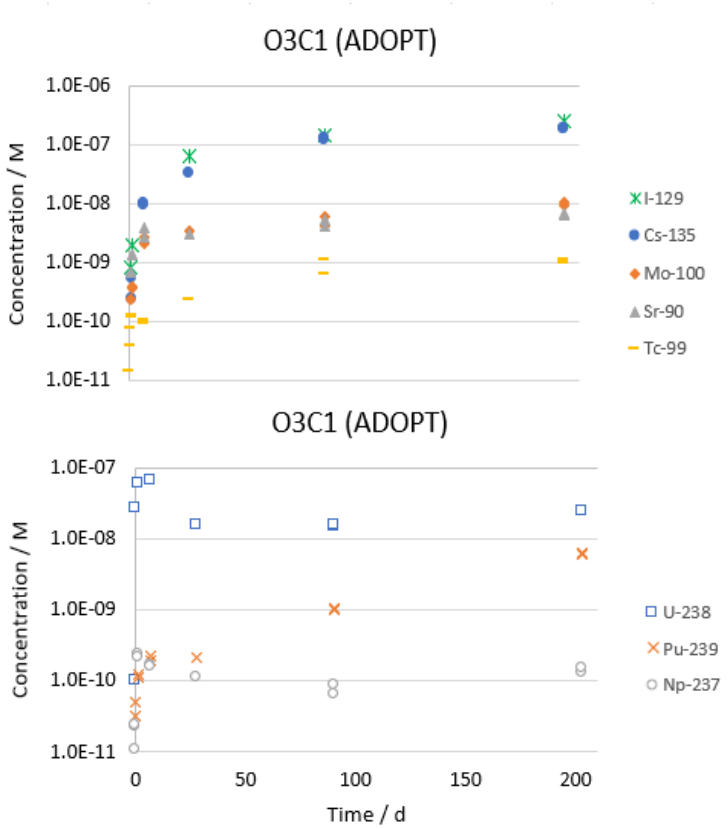
<D> = 19.4 µm

Cr-doped $UO_2$ prepared at FZ Juelich

# Results DisCo WP3: Spent fuel dissolution

## 1st leaching results available

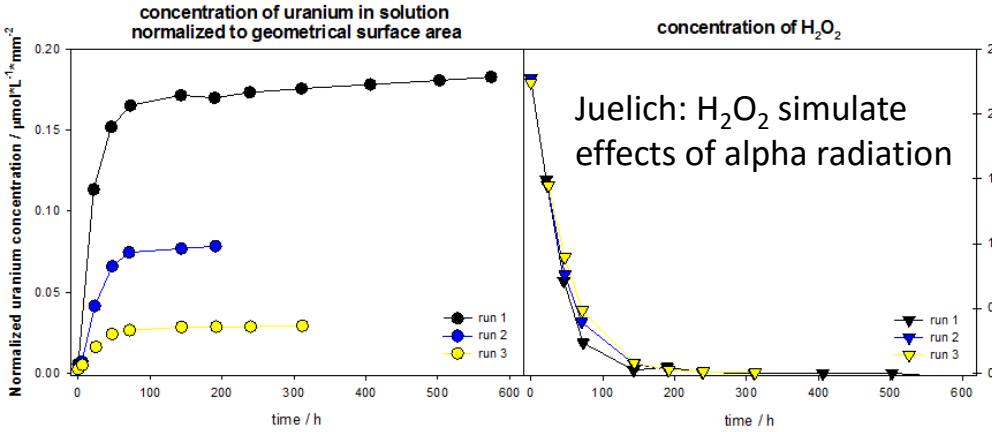
- Next year data will be available for inclusion in the chemical models (WP5)
- Tests run in reducing conditions: $H_2$ or Mix of Ar/$H_2$ , plus reference test in air
- Studsvik Example given here



# Results DisCo WP4 : Model materials dissolution

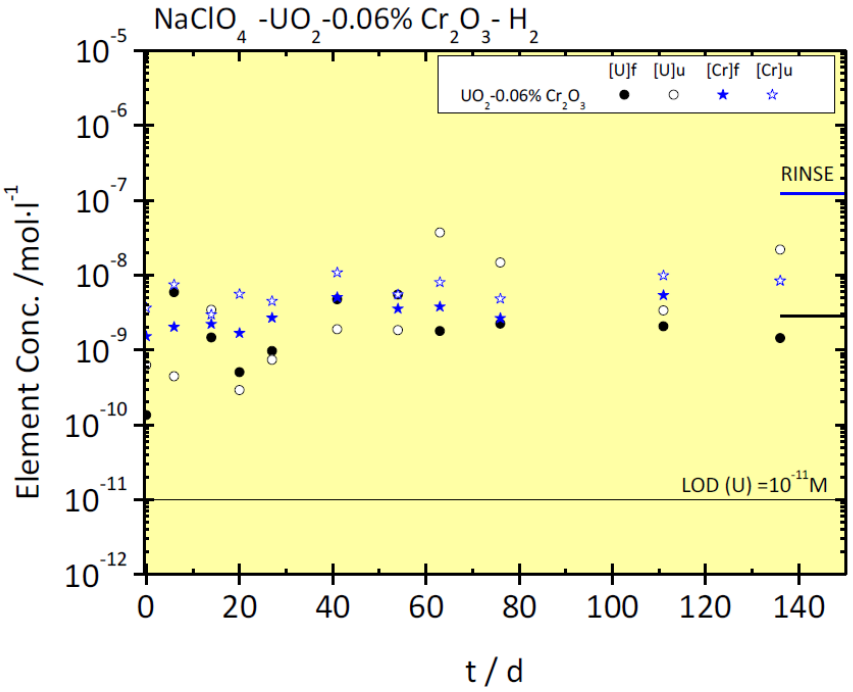
## 1st leaching results available

- Next year data will be available for inclusion in the chemical models (WP5)
- Some preliminary results given here from Juelich and Ciemat




Juelich: $H_2O_2$ simulate effects of alpha radiation

Ciemat example: Cr-doped $UO_2$ in $H_2$ autoclave. [U] ~solubility limit



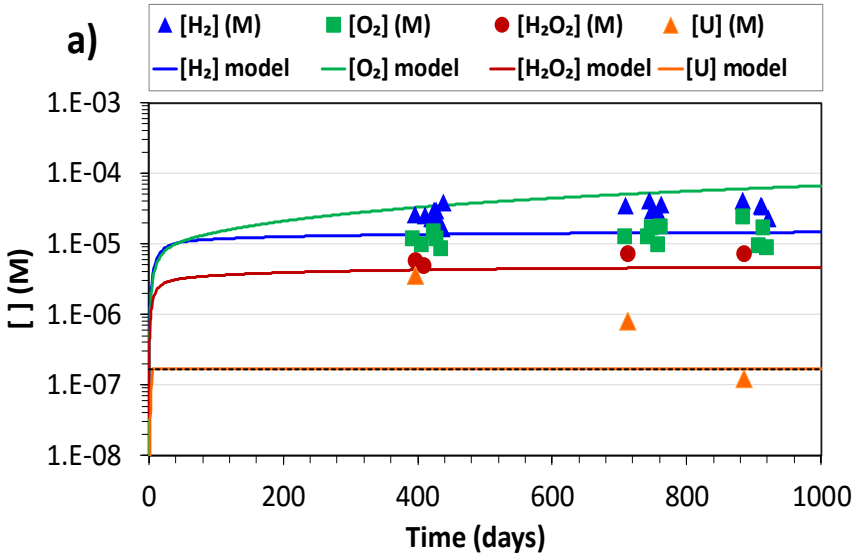
# Results DisCo WP5: Chemical Modelling

**4 modelling approaches :** Initial models available - further development ongoing

- Thermodynamic calculations of ideal solid solution : Cr (III) in SNF
- iCP: interface coupling COMSOL Multiphysics and PhreeqC. Chemical kinetics and reactive transport
- Unirradiated MOX in Fe-containing Callovo-Oxfordian water using CHESS-HYTEC : kinetics of reactions at pellet surface
- Electrochemical, mixed-potential modelling developed to address oxidative dissolution in storage ponds

Example Amphos 21:

*Reactions involving $O_2$ , $H_2$ and $H_2O_2$ occurring at the spent fuel surface*



# DisCo: ongoing and planned work

## Experimental matrix (May 2019)

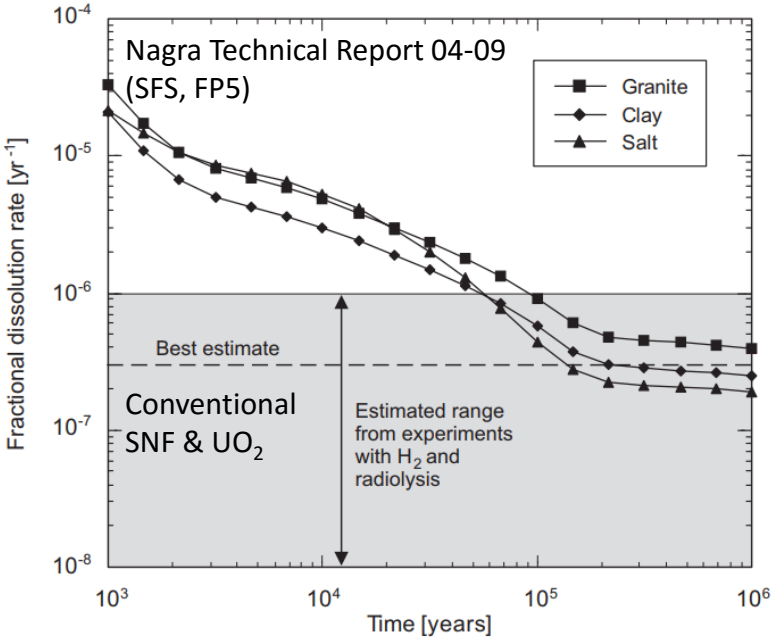
| Reducing (H2, Ar/N2/H2 mix, or anoxic with corroding Fe) | | | | |
|---|---|---|---|---|
| **Water type:** | BW | YCWCa | Natural GW + Fe | synthetic Cox+Fe |
| **Solid** | | | | |
| UO2 ref | **Started** | **Started** | Planned | |
| UO2+Gd | **Started** | **Started** | | |
| UO2+Cr | **Started** | **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 | | | |

## Model developments

- Thermodynamics of calibrated non-ideal solid solution for Cr-doped $UO_{2+y}$ : inclusion of metallic particles, “grey phase”, lanthanides, Pu and the minor actinides .
- Including heterogeneity & porosity of spent fuel matrix; Including changes in porosity due to secondary phase precipitation
- MOX model adjustment to schematic disposal cell configuration : assess the effect of near-field environment (steel canister embedded in the COx host-rock.)
- Developments to address uncertainties in Mixed-Potential model regarding assumed irreversibility of surface reactions (and more)
- **DisCo data** reported no later than May 2020 will be **included in all modelling activities**

# 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 is the driving force and mechanism behind the observed continued recrystallization and isotope exchange at apparent chemical equilibrium?
- 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

# Thank you for listening!


## Acknowledgements: all project contributors

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*REDUPP:*

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*DisCo:*

*This project has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 755443*