DisCo
Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions

Synthesis, characterization and preliminary dissolution assessment of Cr-doped UO_2

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NucleUS Immobilisation Science Laboratory
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NGNCDT

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Gent (BE)

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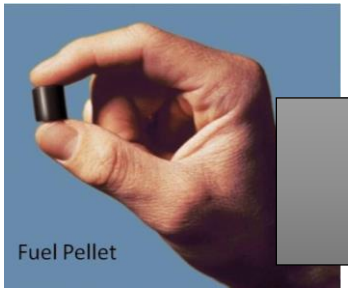
Cr- doped UO_2 fuels



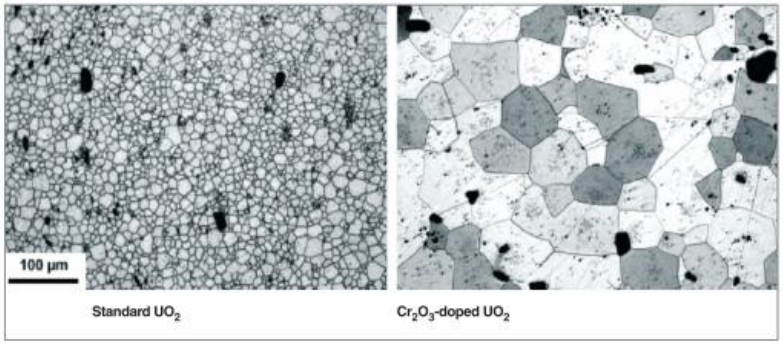
UO_2

Drivers for fuel improvement

- Increased burn up
- Longer dwell times
- Flexible operation

+ Additives e.g. Cr_2O_3 and Al_2O_3 [1-3]

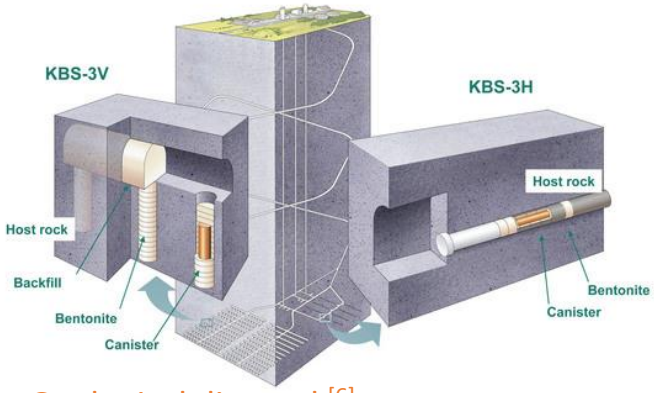
Doped UO_2 fuels



Alternative microstructure

Storage and disposal

How will spent doped fuel fare in storage conditions compared to UO_2?



Geological disposal [6]

[1] Ph. Dehaudt et al, 1996; [2] L.Bourgeois et al, 2001; [3] S.Valin et al, 2003; [4] world-nuclear.org; [5] nuclear.duke-energy.com; *[6]* posiva.fi/en/final_disposal

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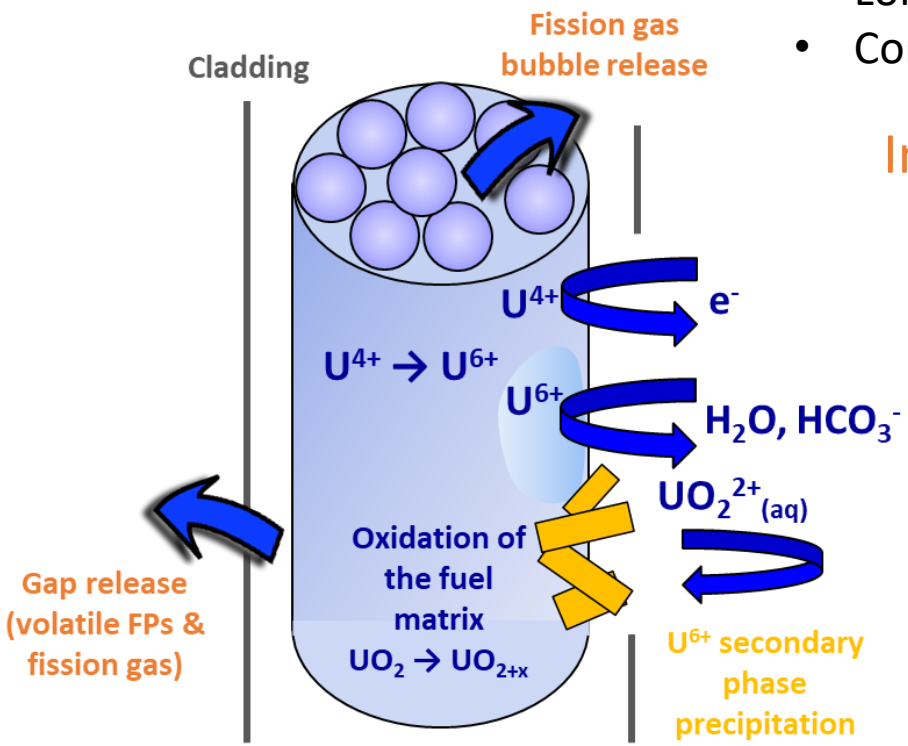
Literature

Mechanisms of UO_2 dissolution

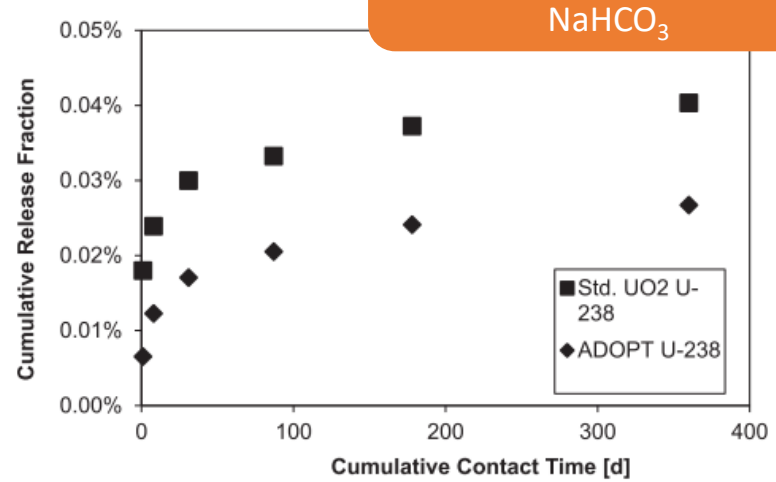


Source: Adapted from Long-term storage of spent nuclear fuel, R.C Ewing 2015.

- Long term dissolution is matrix controlled
- Combined oxidation $U^{4+} \rightarrow U^{6+}$ and dissolution of U^{6+}

Investigation of doped UO_2 dissolution[7]

Reactor irradiated
10 mM NaCl + 2 mM $NaHCO_3$



What is the dopant effect on matrix dissolution?

- Little or no effect on matrix dissolution
- Highlight reactive surface area importance

[7] K. Nilsson et al, 2017

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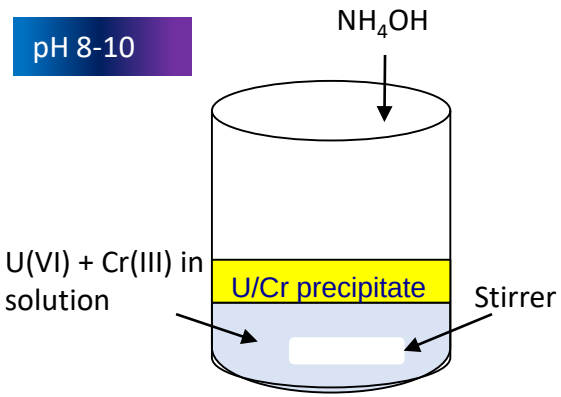
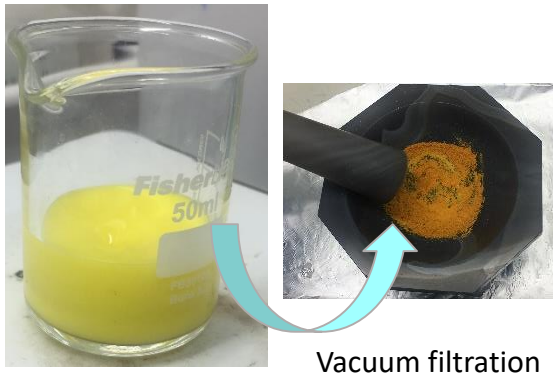
Synthesis route

Nitrate Precipitation

pH 8-10

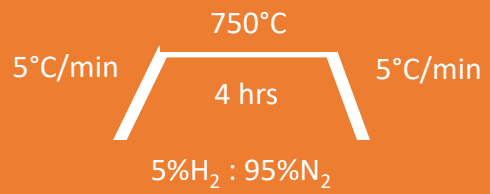




Vacuum filtration and dried at 50°C

ICP-OES of supernatants >99.86% Cr incorporation

Calcination

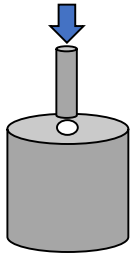


Precursor

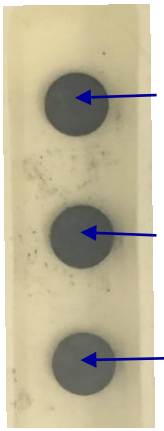
UO_2

Heat treatment in fully reducing atmosphere

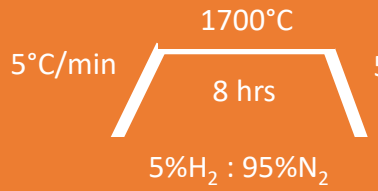
Homogenisation pellet pressing



35 Hz for 15 mins



Sintering



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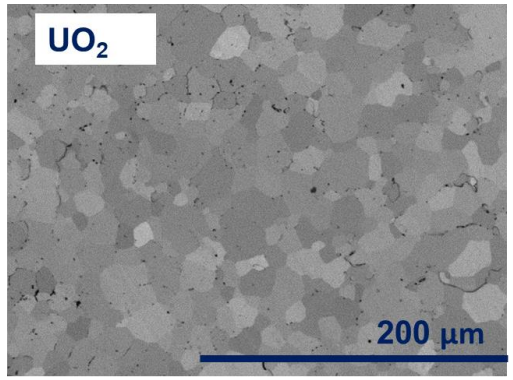
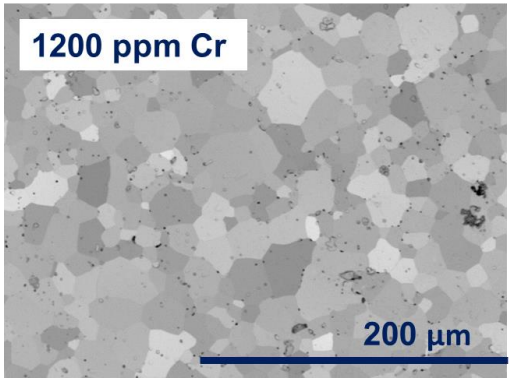
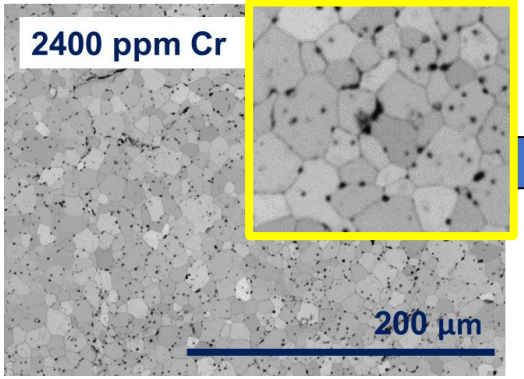
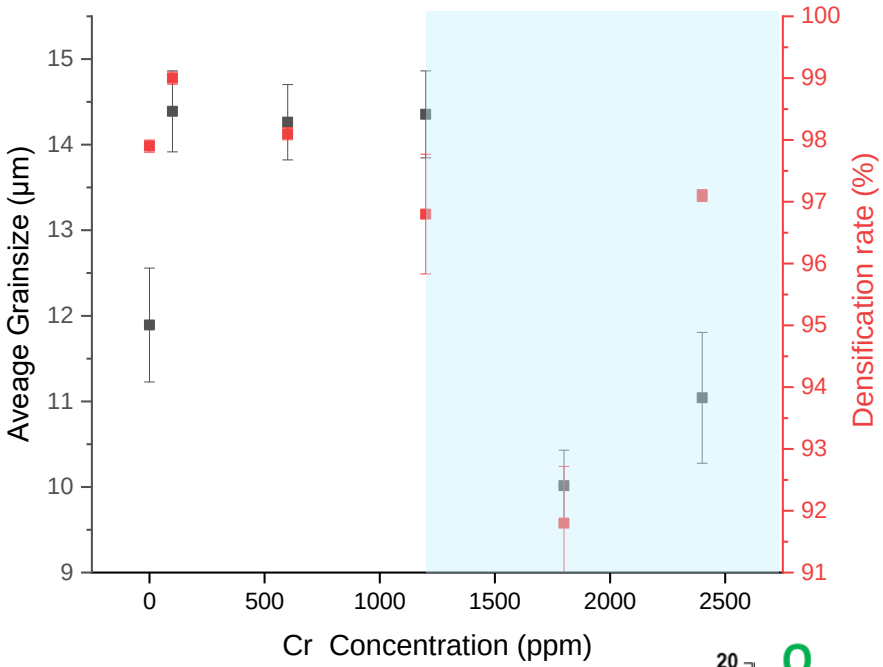
Sample characterisation





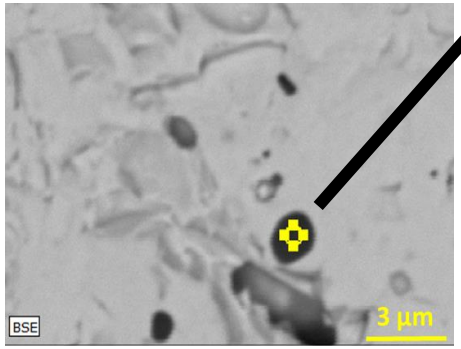


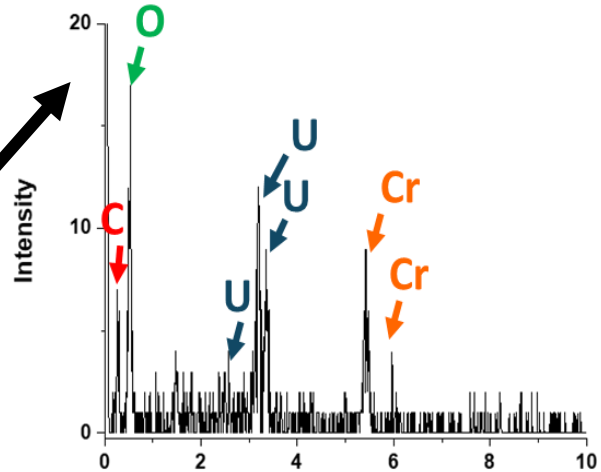
SEM Images



- Grain size increase up to 1000 ppm
- Solubility limit of Cr reached > 1200 ppm grainsize decrease
- Cr agglomerates in matrix

EDX Analysis





Dissolution experiment set up

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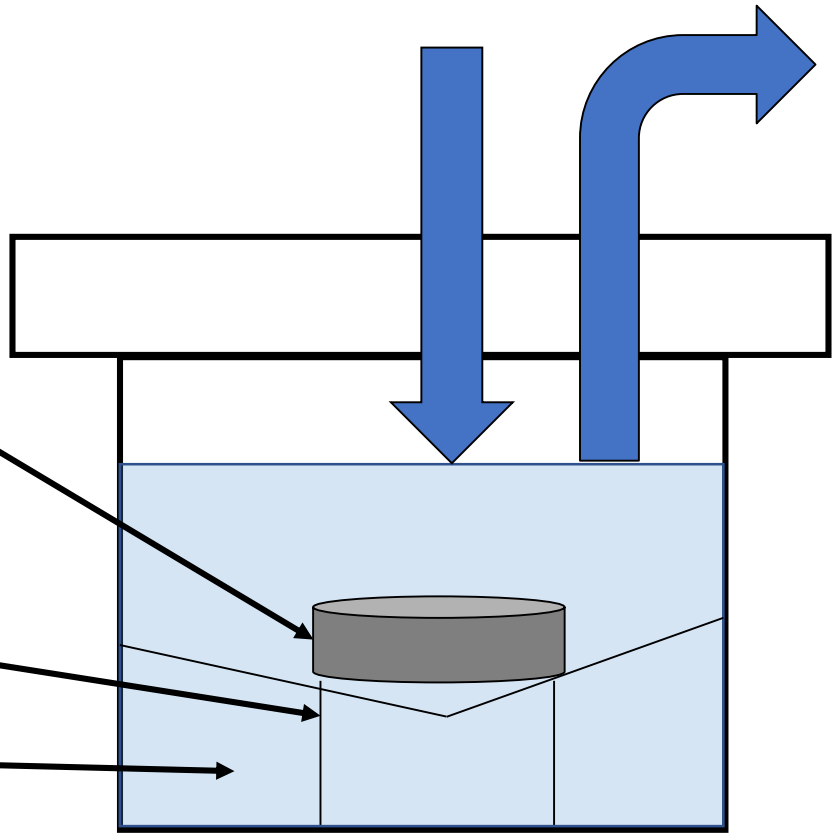
Remove and replace aliquot of solution for analysis via ICP-MS



Doped and un-doped UO_2 samples

Suspension basket

50 ml solute solution

Dopant range (ppm Cr)
0
100
300
600
1200
1800
2400

Solutions	Composition	Time line
Simulant ground water	19mM NaCl + 1mM $NaHCO_3$	120 days +..
Strong acid	2M HNO_3	12 hours

25°C

60°C

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Normalised mass loss (U)

Simulant groundwater dissolution @ 25°C

ICP-MS will measure concentration of U and Cr in solution

$$C(i) = \frac{m(i)}{V}$$

Mass element in solution

Volume of solution

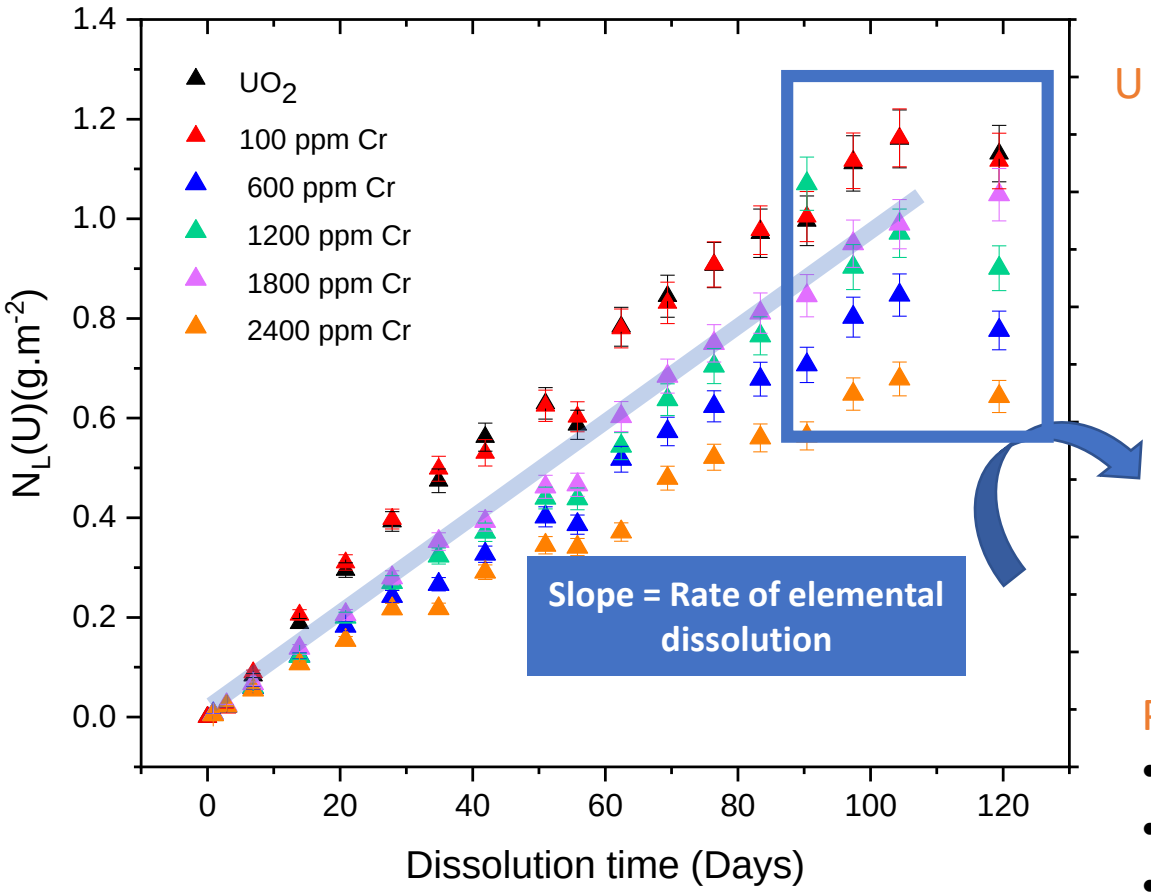
Normalised mass loss

$$N_{L(i)} = \frac{M(i)}{f(i) \times S}$$

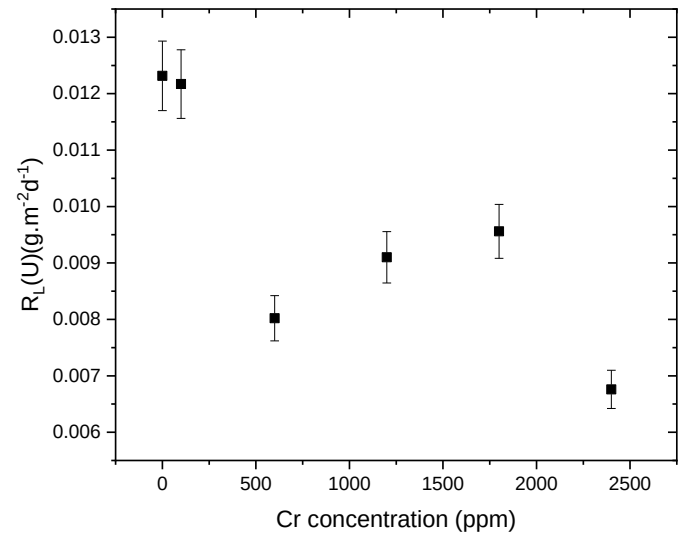
Mass fraction of element

Geometric specific surface area

Normalised U mass loss



U dissolution rate



Potential influencing factors

- Grainsize
- Doping induced defects
- Cr oxidation state

- Decreased N_L (U) with increased Cr content

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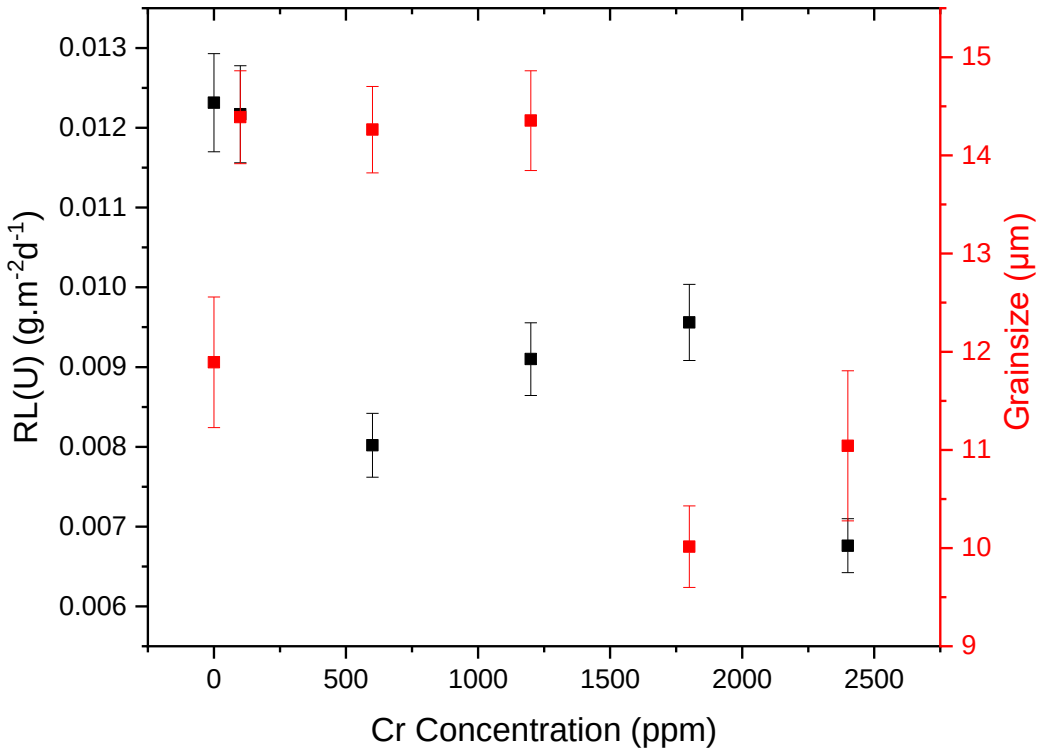
Grain size effects

Simulant groundwater dissolution @ 25°C



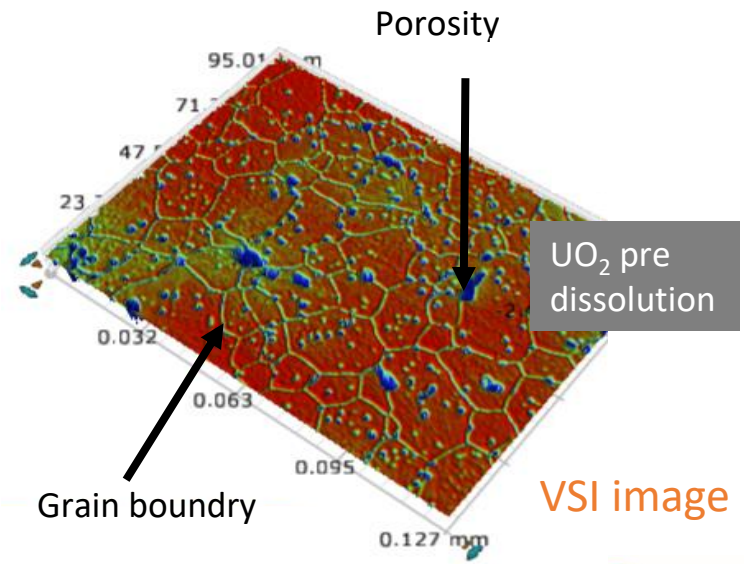
- We expect large grainsize to give the lowest rate of dissolution
- Small differences in the average grainsize don't allow this observation

Greater control of grainsize

- Sintering atmosphere and H_2O control

Systematic mapping of microstructure

- Map evolution of grains and grain boundaries with dissolution
- Allow better understanding of the reactive surface

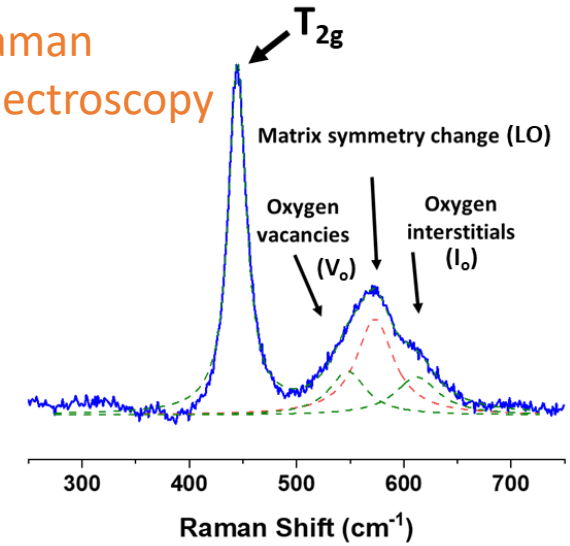


VSI image

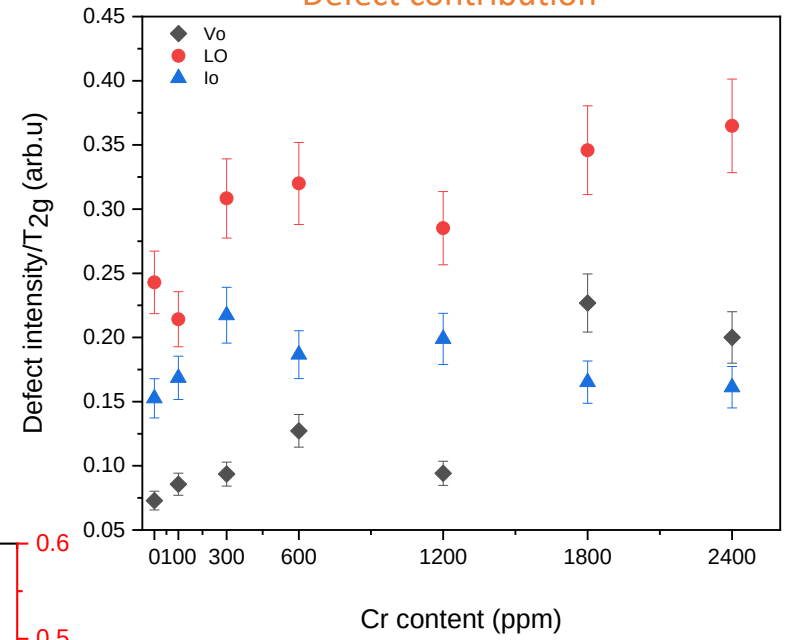
Defect concentrations

Simulant groundwater dissolution @ 25°C

Raman spectroscopy

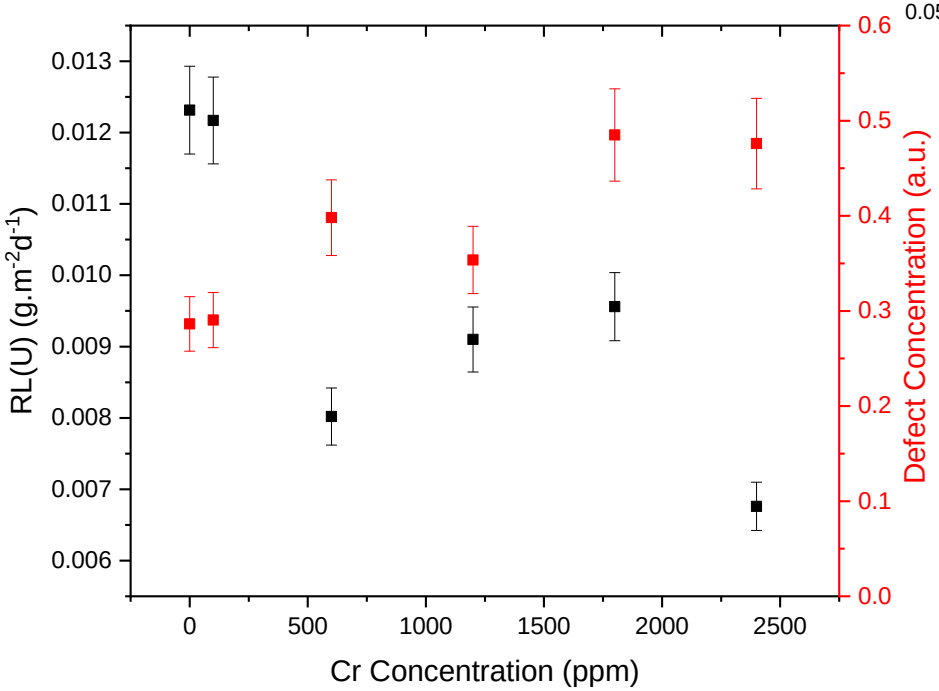


Defect contribution



I_o = Hyperstoicio metric UO_{2+x}

V_o = Charge compensation in Cr^{3+} doping



- Defect concentration increases with increasing Cr content
- Expect with increased V_o the reactivity would increase [5]
- Decreased dissolution rate is observed
- Future work U M-edge to determine U oxidation state

[1] D. W.Shoesmith and M. Razdan, 2014

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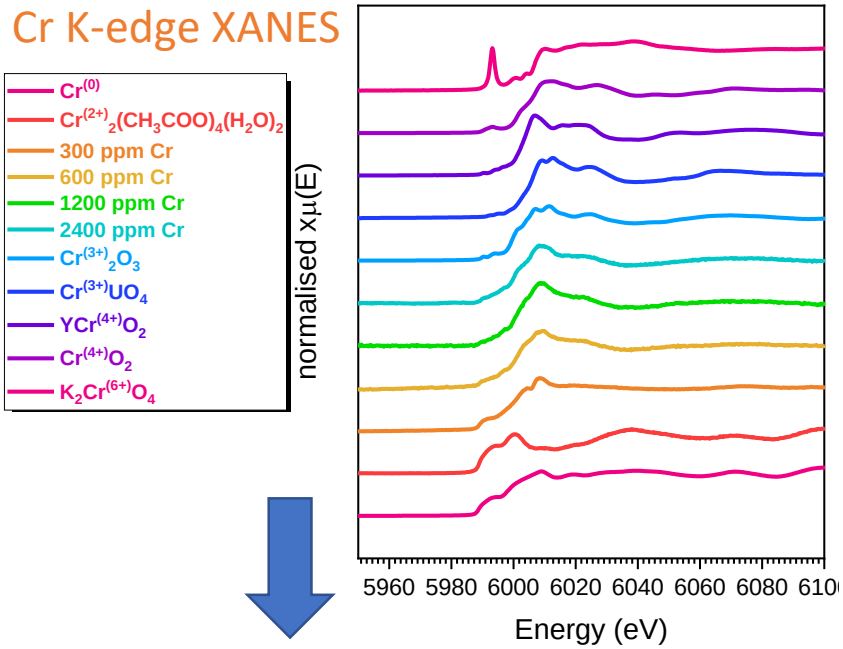
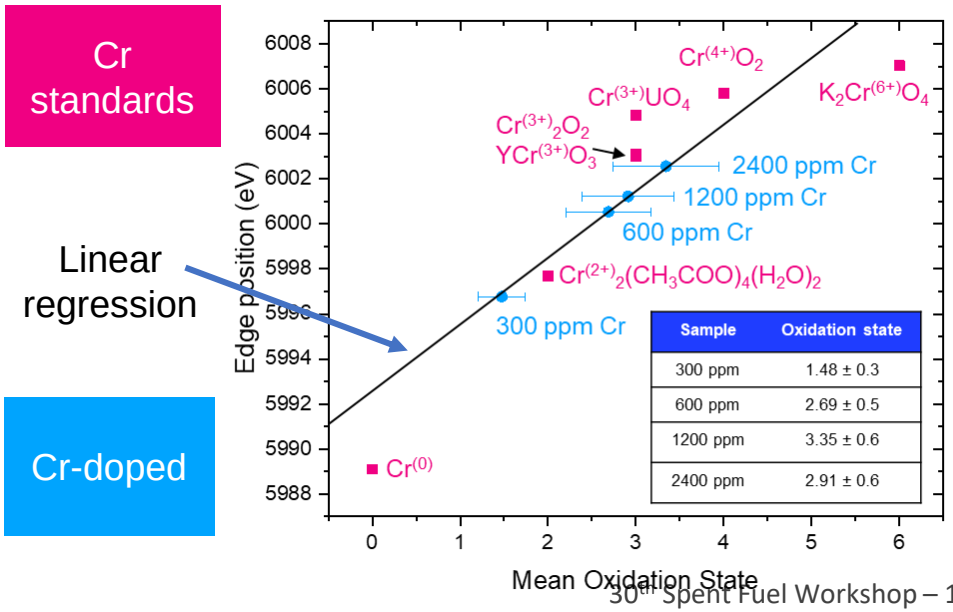
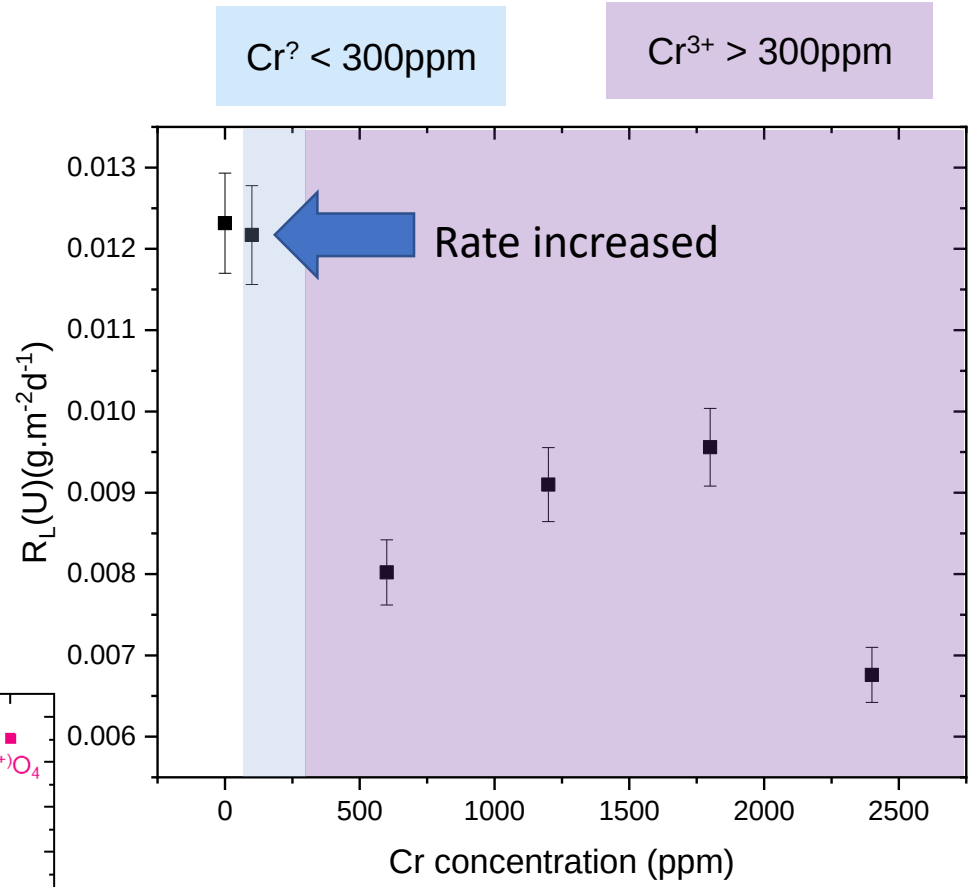
Oxidation state Cr

Cr K-edge XANES





Sample	Oxidation state
300 ppm	1.48 ± 0.3
600 ppm	2.69 ± 0.5
1200 ppm	3.35 ± 0.6
2400 ppm	2.91 ± 0.6

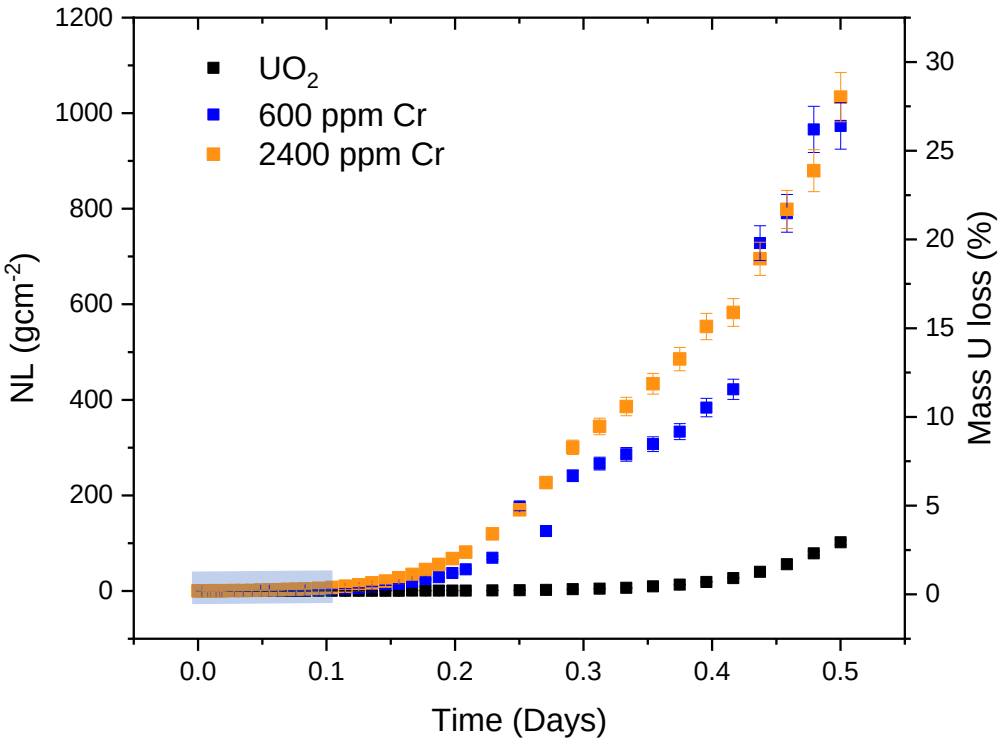


- Cr^{3+} in accordance with raman data
- Below 300ppm Cr potential mixed signal from Cr(0) and Cr^{3+}

More than one oxidation state present

Normalised mass loss (U) and (Cr)

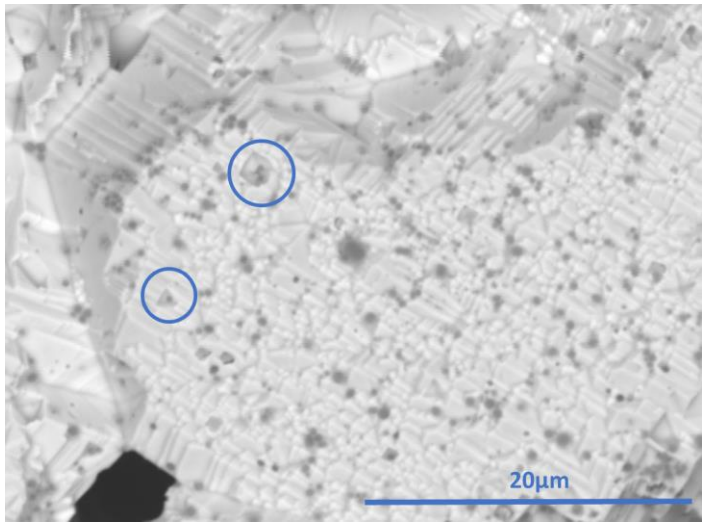
2M HNO_3dissolution @ 60°C



Cr content (ppm)	U dissolution rate ($g.m^{-2}.d^{-1}$)
0	3.6 +/- 0.2
600	27.8 +/- 1.7
2400	61.7 +/- 4.4

- Increased N_L (U) with increased Cr content
- U dissolution rate increases with increased Cr content
- Requires further investigation to be able to compare to bicarbonate solution

Potential microstructure effect



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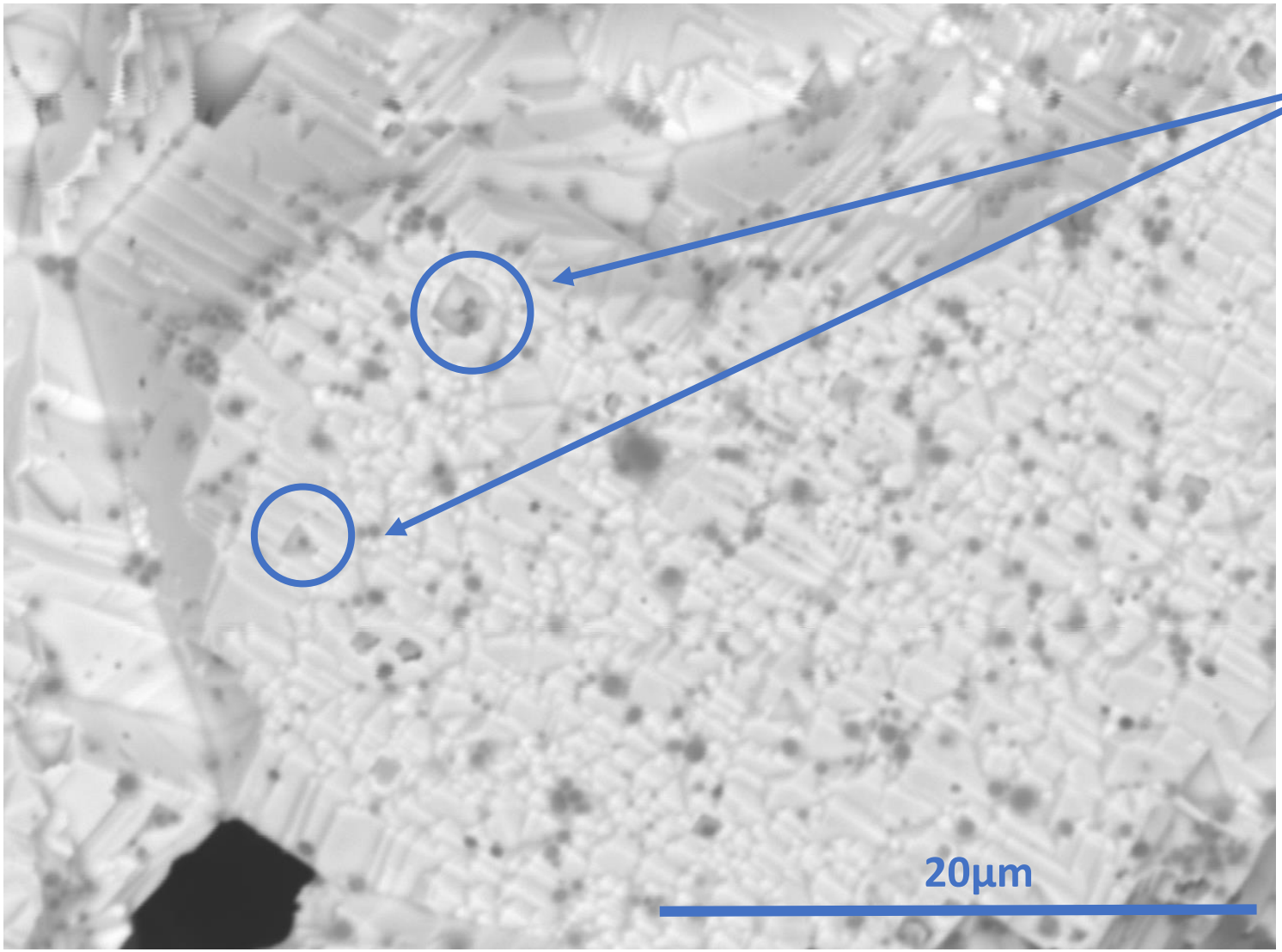
Post dissolution microstructure

2M HNO_3 dissolution @ 60°C



Dissolution pits around Cr particles

SEM Image 2400 ppm Cr doped UO_2

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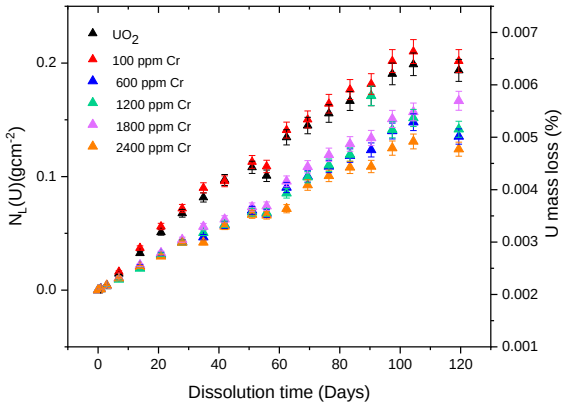
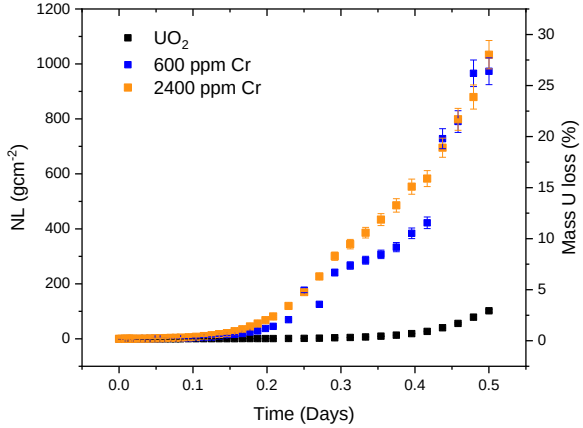
Conclusions

Dissolution in simulant ground water solution

- U dissolves slower with increase Cr content
- Difficult to investigate microstructural effects
- No relationship between defect concentration and rate
- Possible influence of Cr oxidation state





Dissolution in 2M HNO_3 solution

- U dissolves faster with increased Cr content
- Microstructural effects on dissolution rate seen – need larger grain size
- Further experiments planned to investigate more

Small changes in rates

No real microstructural change with dopant

Low dopant concentration

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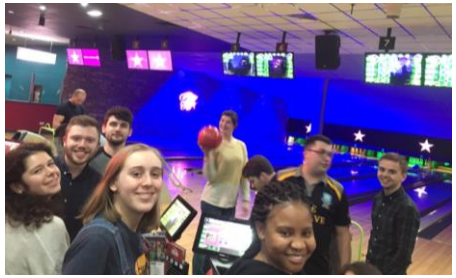
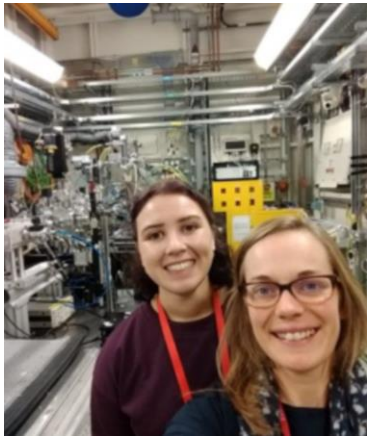
HORIZON 2020

Acknowledgements

Théo Cordara, Ritesh Mohun, Clémence Gausse, Colleen Mann, Sebastian Lawson, Martin Stennett, Claire Corkhill and ISL group @ Sheffield





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Thank you for listening

Wish to acknowledge funding for this research from Radioactive Waste Management and the European Commission Horizon 2020 Research and Training Programme, DISCO, of the European Atomic Energy Community (EURATOM), under grant agreement number 755443.