Development of inactive analogues for Fukushima nuclear debris: an initial assessment of corrosion behaviour

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Context

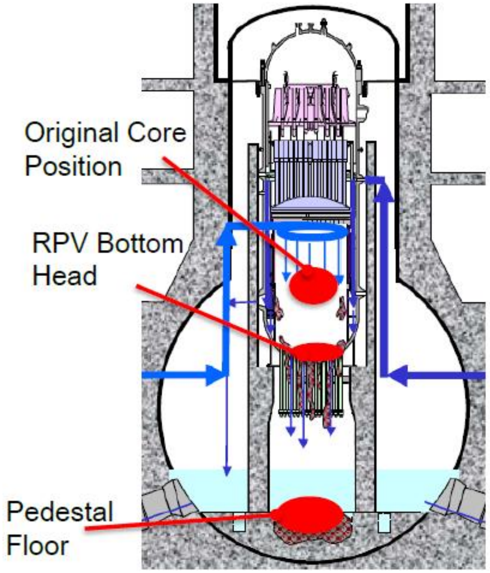
- ✓ On March 2011 at the Fukushima Daiichi NPP:
  - ↠ Loss of coolant accident
  - ↠ Partial meltdown of boiling water reactor Units 1 to 3
    - ↳ *Increase of the temperature in the reactors up to 2000°C*
    - ↳ *Melting & reaction of UO_2 with zircaloy fuel cladding*

$U_{1-x}Zr_xO_2$ solid solution

Nuclear Fuel Debris (NFD)

NFD + Concrete + Stainless steel

Corium



- ✓ Cooling NFD and corium by water injection since the accident
  - ↠ Seawater
  - ↠ Fukushima NPP groundwater
  - ↠ Filtered water

↳ *Temperature reduced < 100°C*

Technical strategy plan for decommissioning Fukushima (2016)
Washiya, Management of Severely Damaged Spent Fuel and Corium conference, 2019

Objectives

Need for an **understanding of their behaviour** in contact with solutions relevant to Fukushima molten core cooling

Synthesise **realistic simulant of NFD** and **Corium**

- ✓ Syntheses and Characterisation
  - ↠ $Ce_{1-x}Zr_xO_2$ solid solutions ($0 < x < 0.9$)
  - ↠ Corium
- ✓ Degradation of realistic simulant fuel debris and corium
  - ↠ Different dissolution media (nitric acid, groundwater, filtered water)
  - ↠ One temperature (60°C)

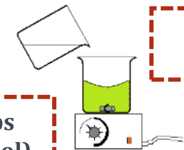
Anderson, Radiochim Acta, 1993

Synthesis of $Ce_{(1-x)}Zr_xO_2$

Room Temperature

5 M NH_4OH – pH = 9

Zr(IV) ; Ce(III)



Drying

T : 90°C

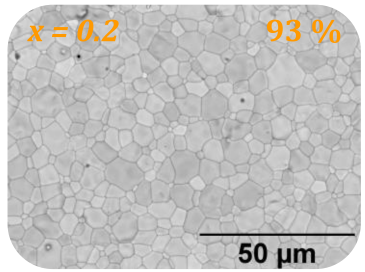
Washing steps

(water + ethanol)

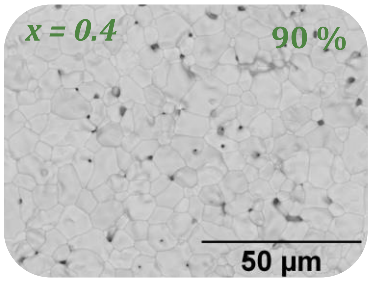
Sintering

1500°C

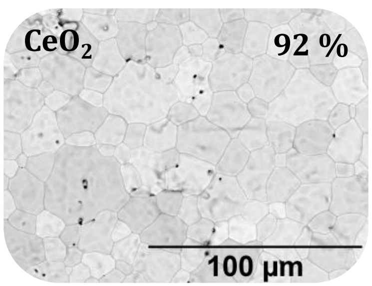
8 h – air



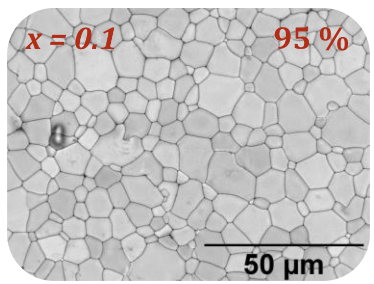
5.9 ± 1.0 µm



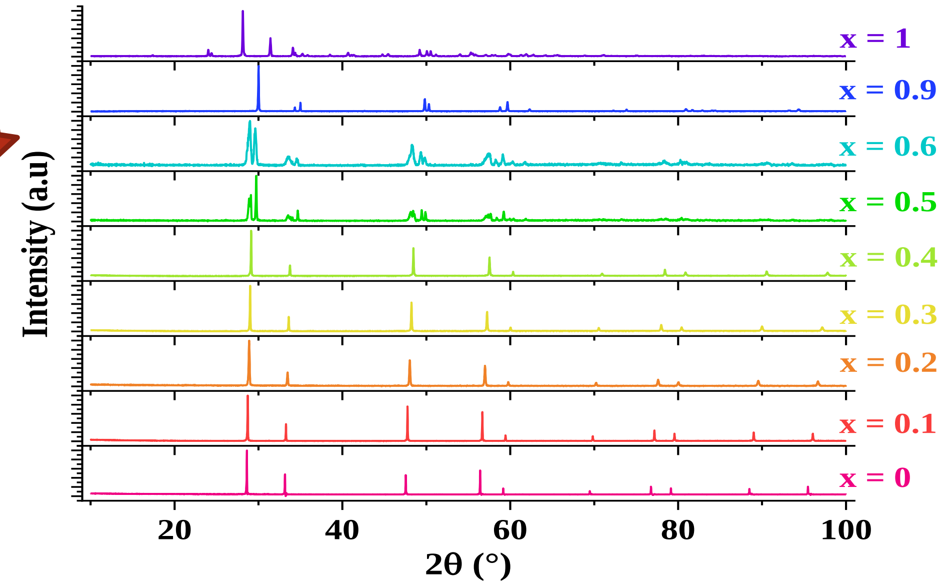
4.1 ± 1.0 µm



14.6 ± 0.9 µm



6.9 ± 0.8 µm



Composition	Lattice parameter (Å)	Literature
CeO_2	5.4041 ± 0.0021	5.453(7)
$Ce_{0.90}Zr_{0.10}O_{2\pm y}$	5.3813 ± 0.0013	–
$Ce_{0.80}Zr_{0.2}O_{2+y}$	5.3531 ± 0.0016	–
$Ce_{0.75}Zr_{0.25}O_2$	–	5.3621
$Ce_{0.60}Zr_{0.40}O_{2\pm y}$	5.3085 ± 0.0011	–

✓ Incorporation of Zr into fluorite structure

↠ Lattice contraction due to the incorporation of smaller size Zr^{4+} in CeO_2

Ce^{4+} (VIII): 0.97 Å Zr^{4+}(VIII): 0.84 Å

Neto, App. Cata., 2013

Norris, J. Nucl. Mater., 1983

Dissolution test: Methodology

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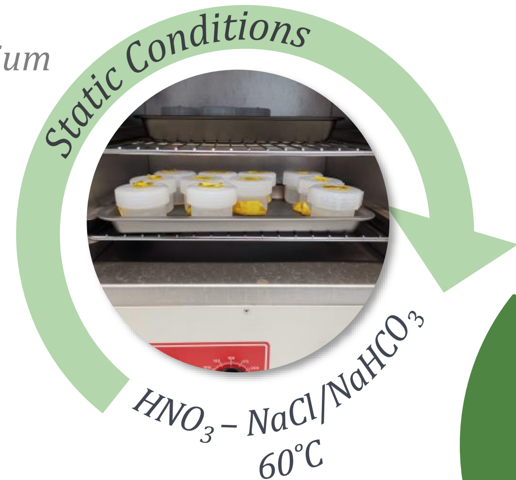
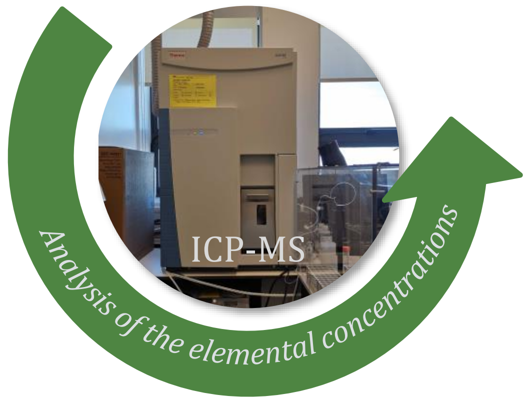
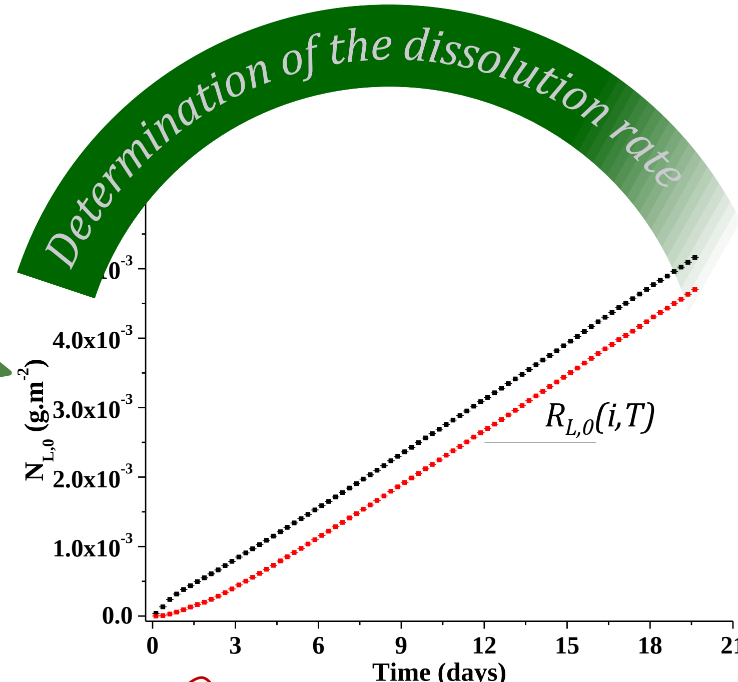
$$R_L(i,T) = k \times e^{-E_a/RT} \times g(I) \times \prod_i (a_i)^{n_i} \times f(\Delta_R G)$$

Close to equilibrium







↠ Study of the effect of the dissolution media and saturation on the normalized dissolution rate

$$R_{L,0}(i,T) = \frac{dN_L(i)}{dt} = \frac{1}{f_i} \times \frac{d}{dt}\left(\frac{C_i \times V}{S}\right)$$

Amount of (E_i) in solution ($g.L^{-1}$)

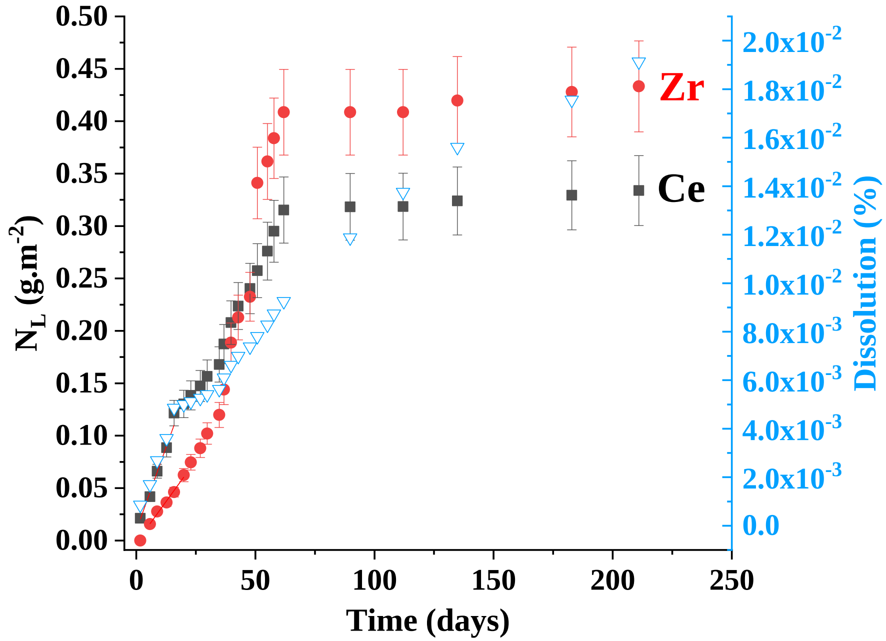
Effective surface area (m^2)

Mass ratio of (E_i) in the solid

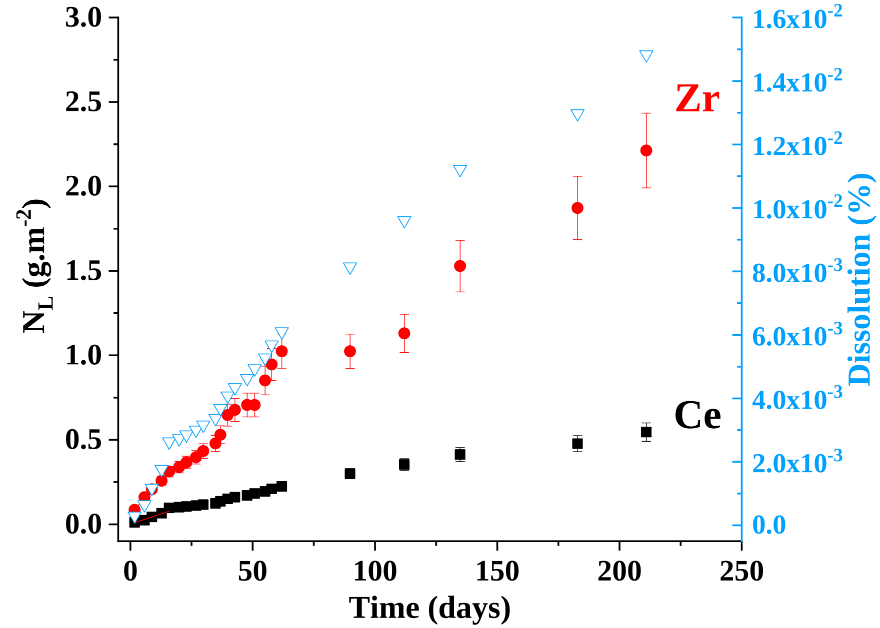
$R_L(i) \approx R_L(j)$	*Congruent dissolution*
$R_L(i) \neq R_L(j)$	*Incongruent dissolution*

Dissolution test: 9 M HNO_3 – 60°C

✓ $Ce_{0.6}Zr_{0.4}O_2$



✓ $Ce_{0.8}Zr_{0.2}O_2$



$$R_{L,0}(Ce) = (6.34 \pm 0.44) \times 10^{-3}\ g.m^{-2}.d^{-1}$$

$$R_{L,0}(Zr) = (3.14 \pm 0.19) \times 10^{-3}\ g.m^{-2}.d^{-1}$$

$$R_{L,0}(Ce) = (2.63 \pm 0.16) \times 10^{-3}\ g.m^{-2}.d^{-1}$$

$$R_{L,0}(Zr) = (1.38 \pm 0.09) \times 10^{-2}\ g.m^{-2}.d^{-1}$$

↠ Slight increase of the $R_{L,0}$ when increasing the amount of Zr in the oxide

- *Potential presence of Ce^{3+} (sintering in air)*
- *Presence of oxygen vacancies*

} Increase of the structural defects

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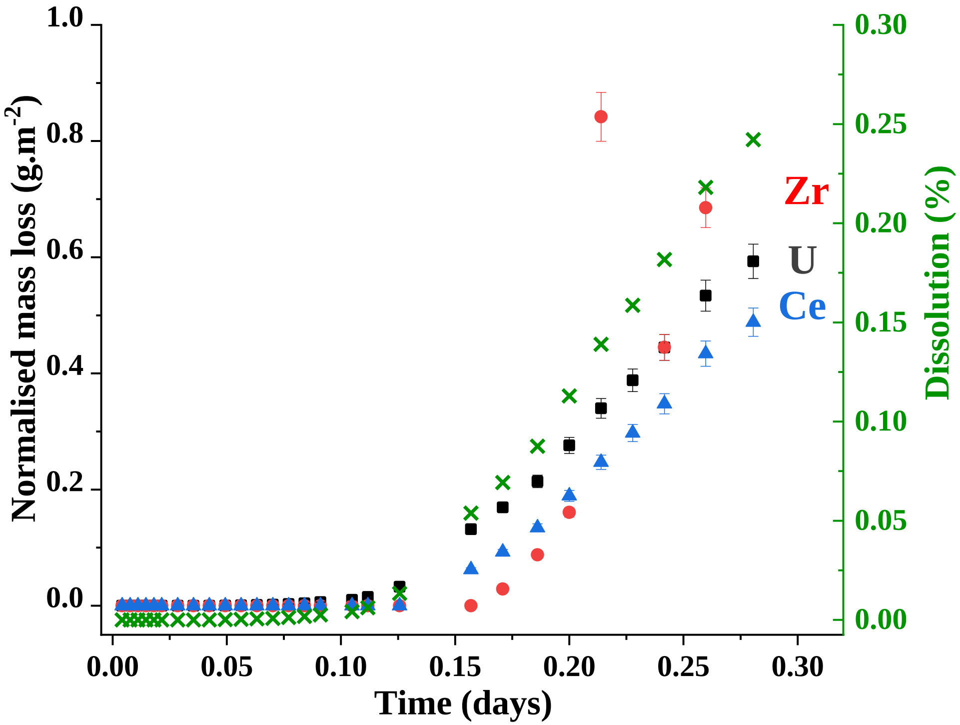
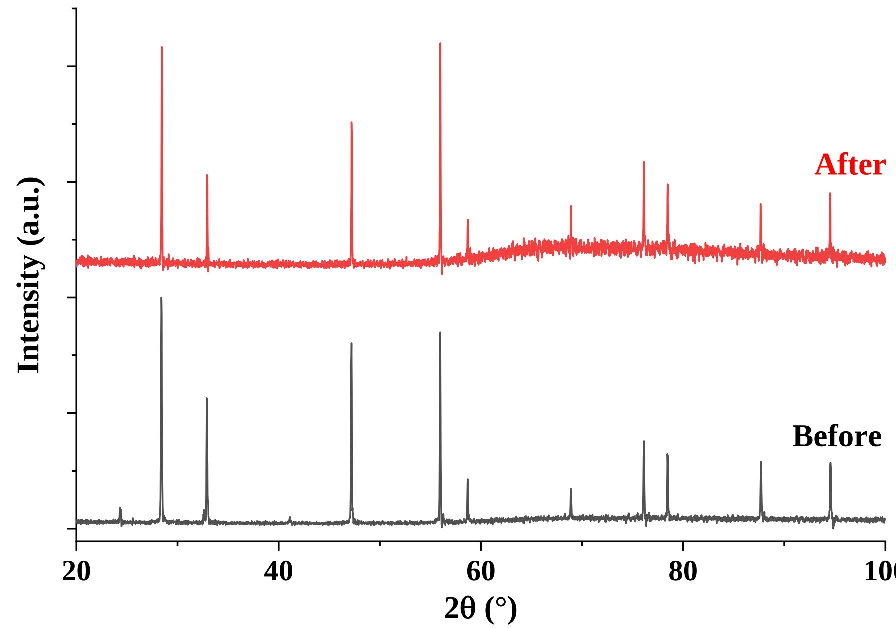
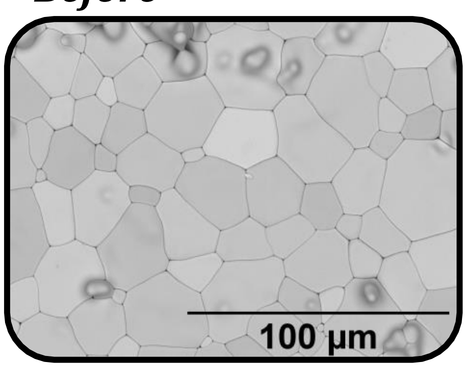
Dissolution test: 2 M HNO_3 – 60°C

✓ $U_{0.9}Ce_{0.05}Zr_{0.05}O_2$

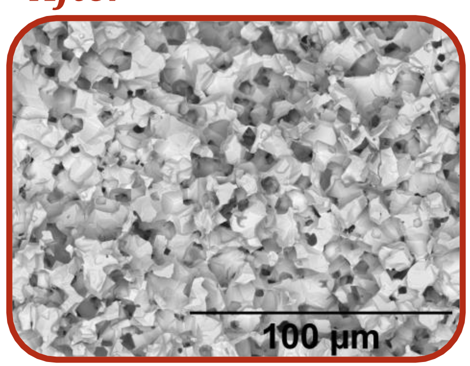




Before



After



$$\boldsymbol{R_L(U) = 3.726 \pm 0.131\ g.m^{-2}.d^{-1}}$$

$$\boldsymbol{R_L(Ce) = 3.297 \pm 0.163\ g.m^{-2}.d^{-1}}$$

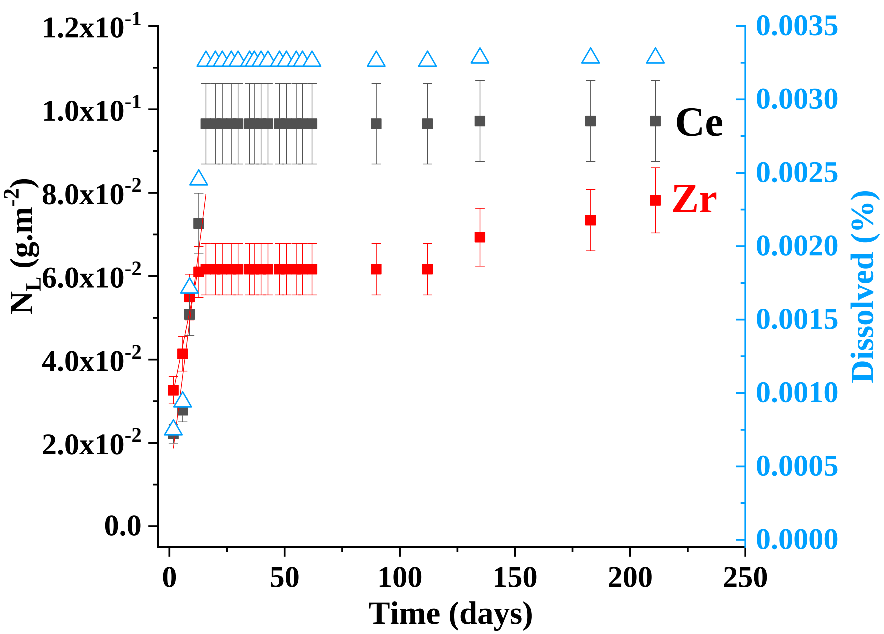
↠ Decrease of the R_L in presence of Zr in the oxide

- $R_L(U) = 22 \pm 2\ g.m^{-2}.d^{-1*}$
- $R_L(Zr - 90°C) = 8.64 \times 10^{-4}\ g.m^{-2}.d^{-1*}$

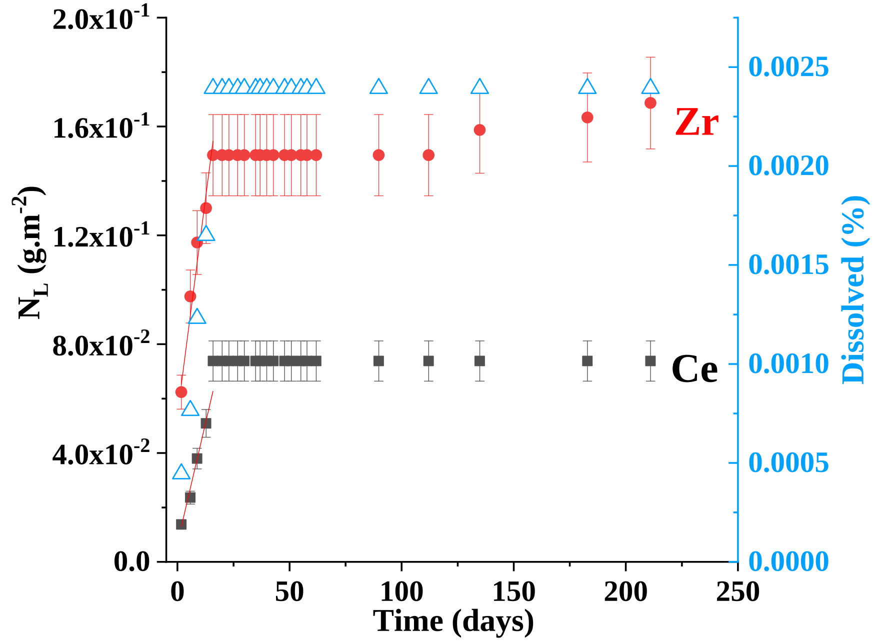
**Prajapati R.R., Des. Water, 2013*
Cordara, J. Nucl. Mater., 2017

Dissolution test: 19 mM NaCl & 1 mM $NaHCO_3$ – 60°C

✓ $Ce_{0.6}Zr_{0.4}O_2$



✓ $Ce_{0.8}Zr_{0.2}O_2$



$$R_{L,0}(Ce) = (4.31 \pm 0.99) \times 10^{-3}\ g.m^{-2}.d^{-1}$$

$$R_{L,0}(Zr) = (2.71 \pm 0.33) \times 10^{-3} g.m^{-2}.d^{-1}$$

$$R_{L,0}(Ce) = (3.53 \pm 0.40) \times 10^{-3} g.m^{-2}.d^{-1}$$

$$R_{L,0}(Zr) = (6.34 \pm 0.61) \times 10^{-3} g.m^{-2}.d^{-1}$$

↠ Release of the elements at the beginning of the dissolution

↠ Observation of a plateau (no more dissolution ?): formation of $Ce_2(CO_3)_3{\cdot}nH_2O$?

↠ $R_{L,0}$ higher than in UHQ

Synthesis of Simulant Fukushima Corium through thermal route

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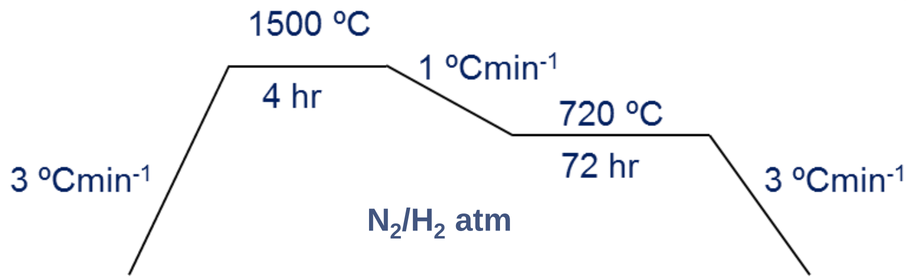
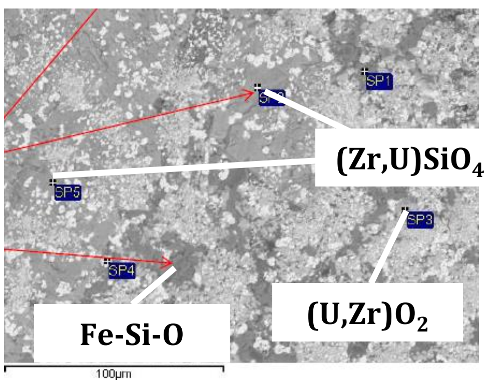
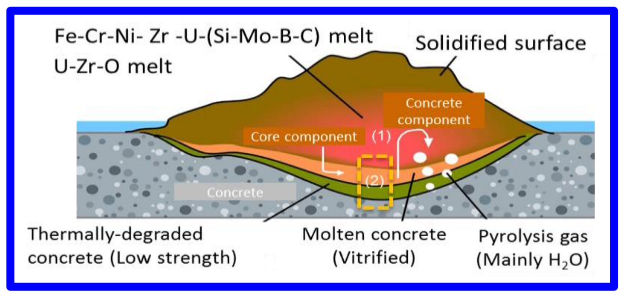


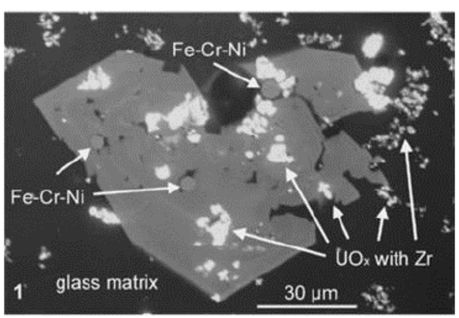
Fukushima – Vulcano MCCI samples



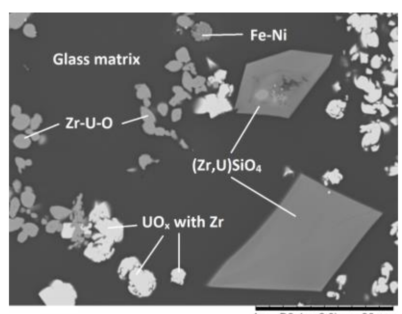


Component	C1 Wt.%	C2 Wt. %	C3 Wt. %
SiO_2	43.6	43.6	43.6
CaO	8.85	8.85	8.85
ZrO_2	**4.56**	**4.56**	**4.56**
Al_2O_3	10.78	10.78	10.78
Stainless Steel	2	2	2
$Ce_{0.8}Zr_{0.2}O_2$	–	10.87	–
CeO_2	10.87	–	–
$Ce_{0.6}Zr_{0.4}O_2$	–	–	10.87

Chernobyl – LFCM



Simulant – LFCM



Tanabe, J. Nucl. Sci. Technol., 2011
Washiya, Management of Severely Damaged Spent Fuel and Corium conference, 2019
Anderson, Radiochim Acta, 1993

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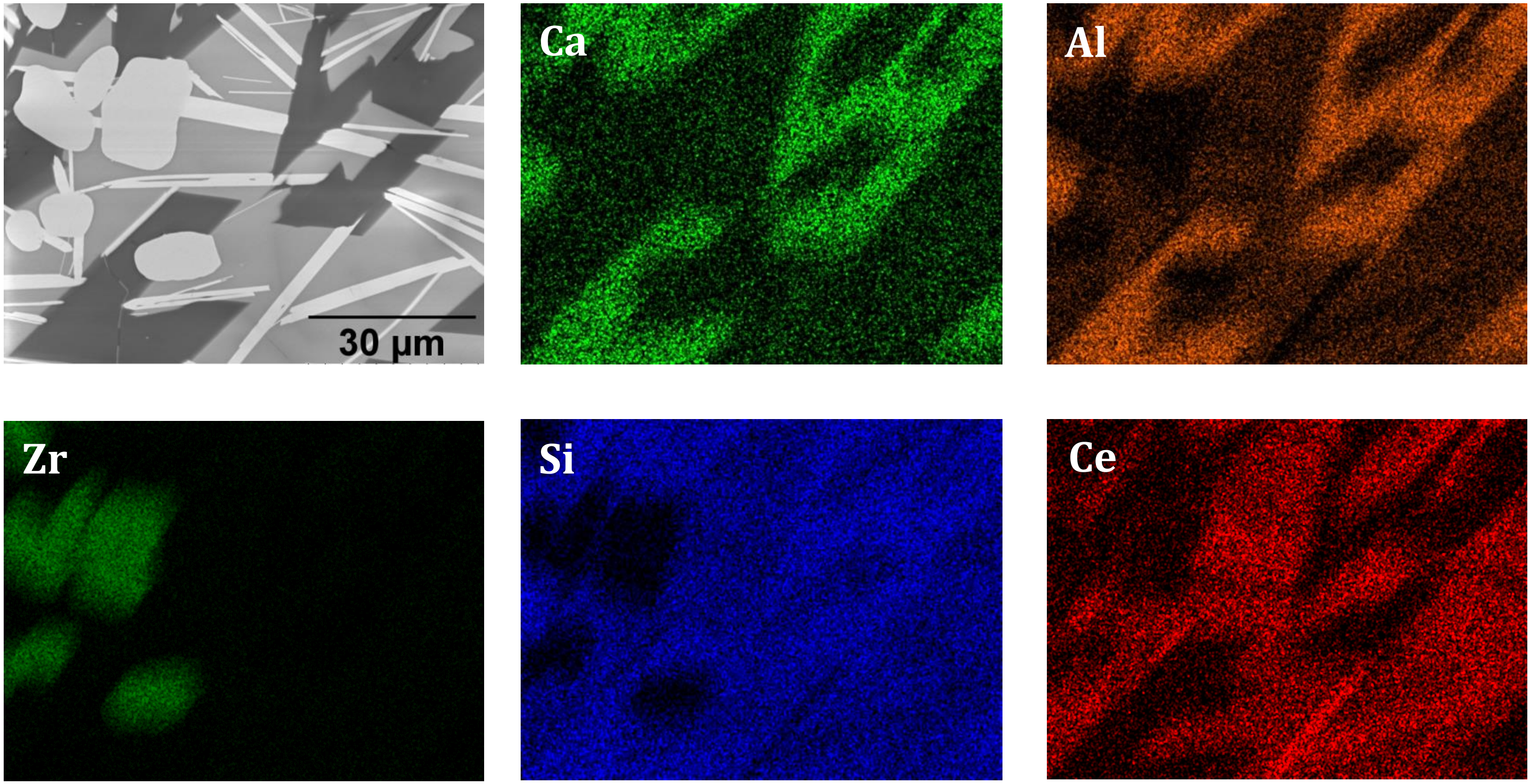
Characterisation of Simulant Fukushima Corium

✓ C1 – CeO_2



- ↠ All 3 samples present a Ca and Al rich glassy phase
- ↠ Zr rich phase and Ce rich phase

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Characterisation of Simulant Fukushima Corium

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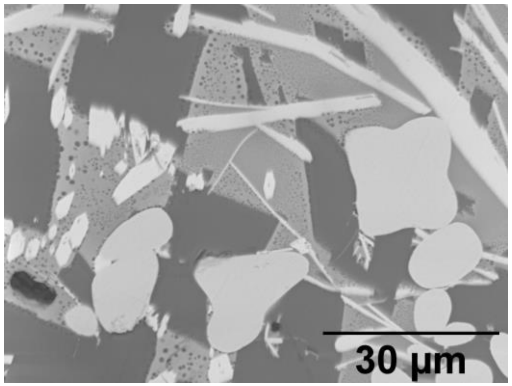
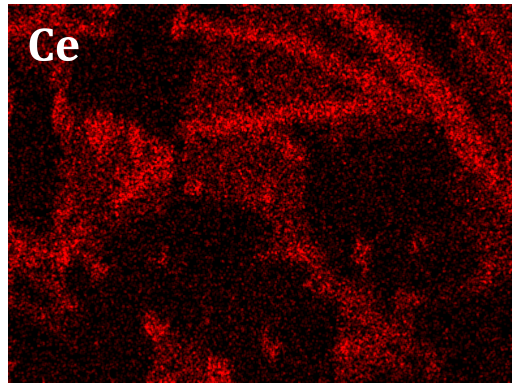
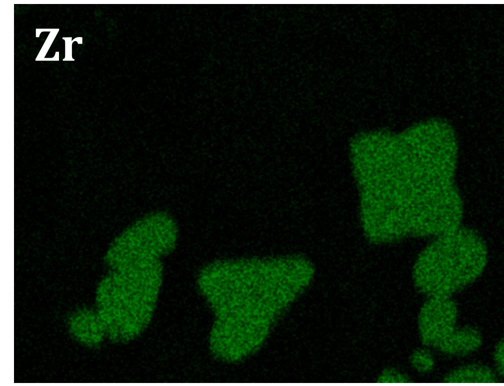
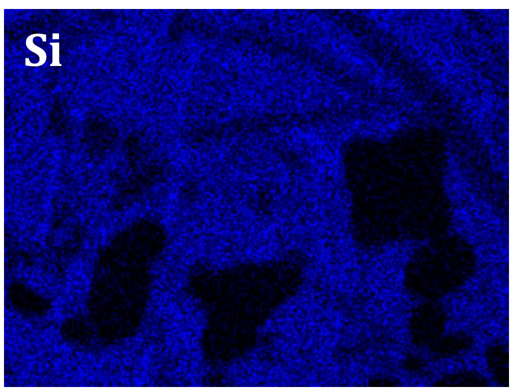
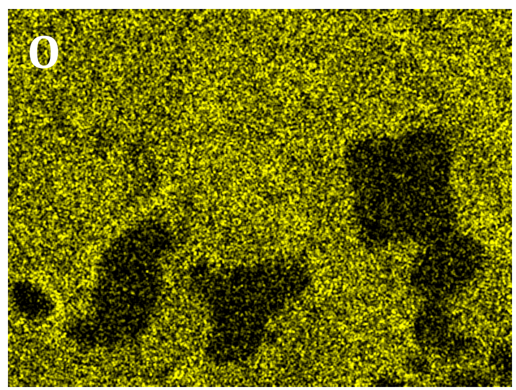
✓ C2 – $Ce_{0.8}Zr_{0.2}O_2$











- ↠ Ce rich phase : Ce_2O_3 or CeO_2
  - ↳ *Reducing atmosphere process*
- ↠ Si and Ce rich phase: part of Ce in a glass matrix
- ↠ Zr rich phase : Zr metal?

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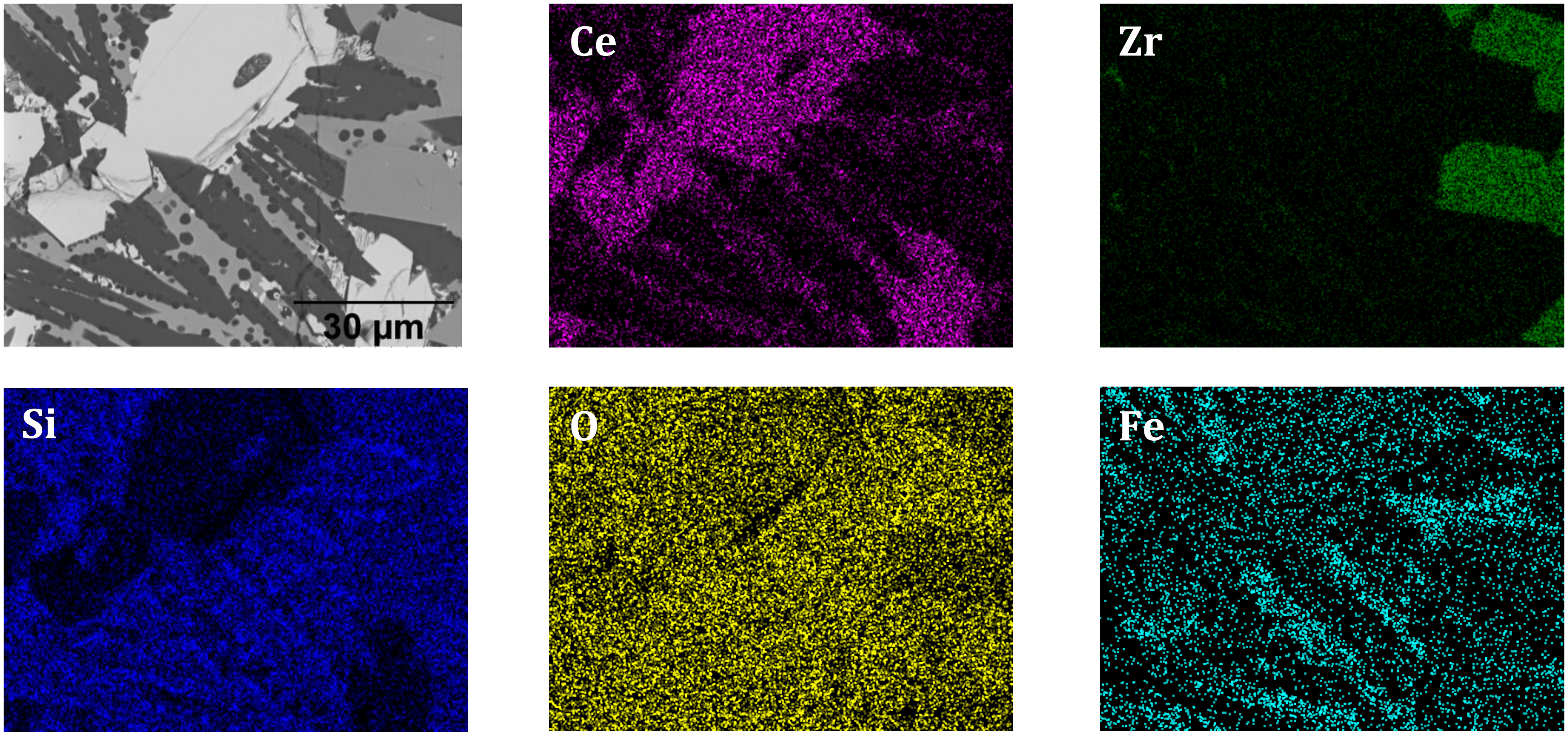
Characterisation of Simulant Fukushima Corium

✓ C3 – $Ce_{0.6}Zr_{0.4}O_2$



- Zr and Si rich phase: $ZrSiO_4$
- Si and Fe rich phase
- Ce rich phase: CeO_2 or Ce_2O_3

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Conclusion and further work

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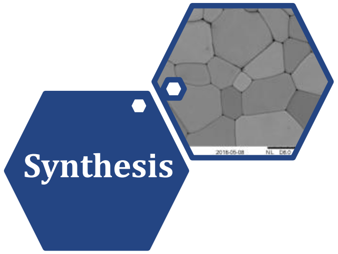

- Synthesis of $Ce_{1-x}Zr_xO_2$ through wet chemistry routes
  - *Incorporation into the fluorite CeO_2 structure (40 mol.% Zr)*
  - *Incorporation of Zr into the fluorite UO_2 structure up to 30 mol.%*

- No clear evidence of the Zr effect on the dissolution
  - *Release of the Ce slightly higher with the incorporation of Zr*
  - *Inhibition of the dissolution of U in presence of Zr*
- Difference observed between U and Ce might be due to the presence of Ce^{3+}
  - *Ce^{3+} more mobile and soluble than U^{4+}*
- Strong refractory behavior of $Ce_{1-x}Zr_xO_2$

- Similar morphology of the Fukushima corium
- Presence of Ce_2O_3 due to reducing atmosphere treatment
- Presence of Zr(m)

Need for a Raman spectroscopy study of $Ce_{1-x}Zr_xO_2$
Further investigation on the Ce-analogue Fukushima corium

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Thank you !