The Development of Glass-Ceramic Wasteforms by Hot Isostatic Pressing for Actinide Immobilisation.

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DISTINCTIVE Annual Conference
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Contents

Introduction

Pu-residues

Have higher Pu content than Intermediate level PCM waste and complex compositions and physical forms:

- Low or high PuO_2 content, MOx fuel
- Powders, sludges, solid lumps, pellets, fuel pins etc.

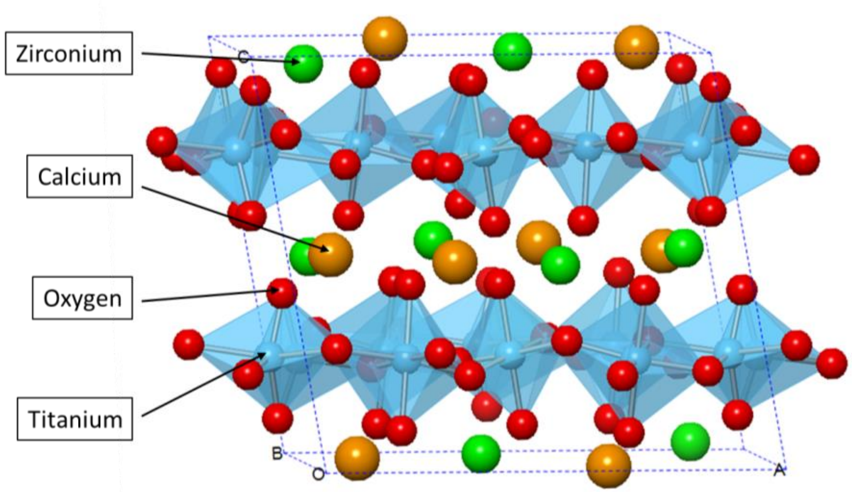
Low Pu residues	High Pu residues	MOx residues	Metal encapsulation
Contain glass-formers	Impure PuO_2 streams	Pure/high actinide streams	Other waste
Zirconolite Glass-ceramics	Zirconolite full ceramic	Pyrochlore full ceramic	Copper/ stainless steel

High-fraction zirconolite glass-ceramics

Small ceramic crystalline phase(s) homogeneously distributed throughout an amorphous glass matrix.

Double barrier system partitions actinides into the crystalline phase(s) and retains miscellaneous material in the glass phase.

Zirconolite-2M, $CaZrTi_2O_7$ is a monoclinic cubic structure derived from the pyrochlore structure, $A_2B_2O_7$.



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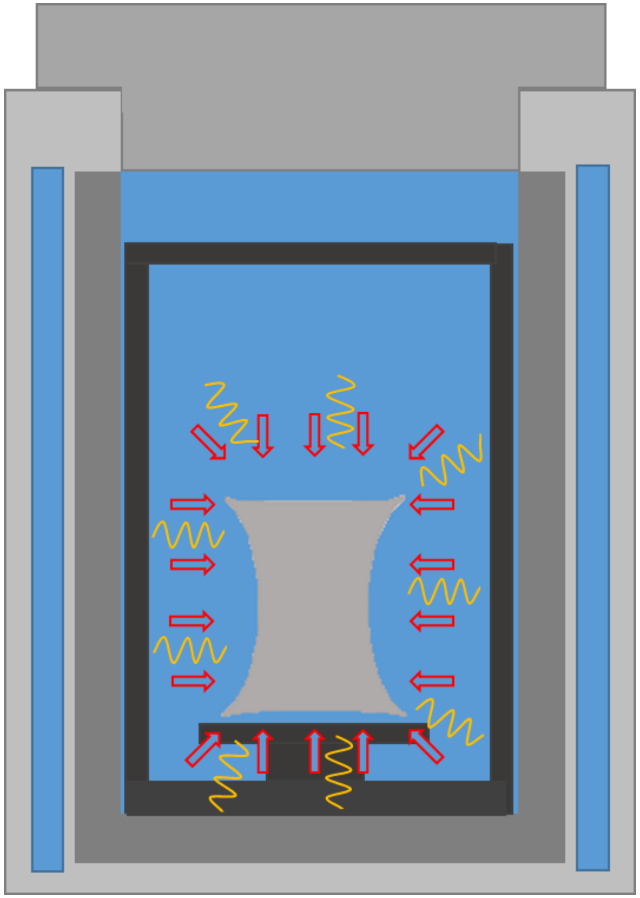
Hot Isostatic Pressing

Simultaneous application of heat and pressure to form dense, durable wasteforms with radionuclides homogeneously incorporated into the structure.

HIP facility at The University of Sheffield



Lab-scale HIP cans

10L HIP can[1]

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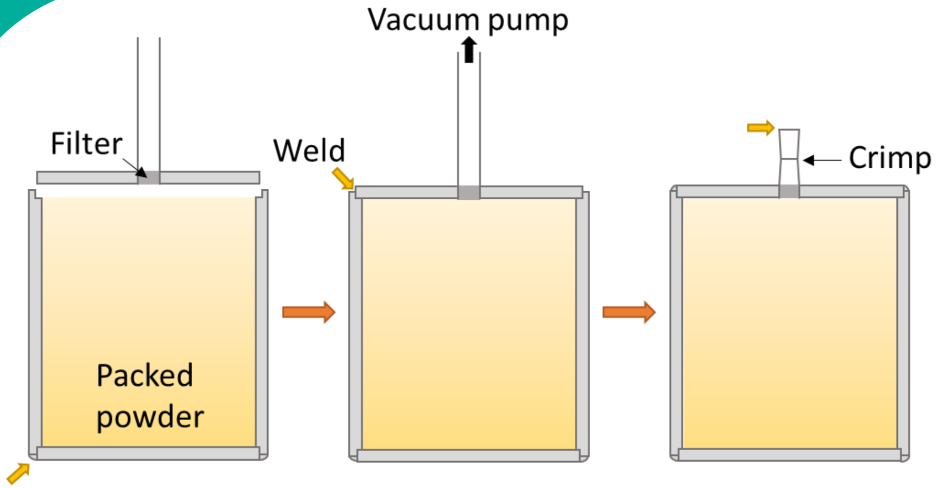
[1]Progress at ANSTO, E. R. Vance et al. 2014

Aims

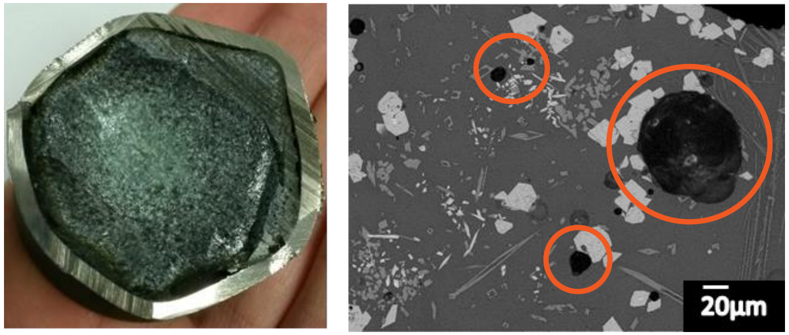
Optimise the processing route and parameters whilst maintaining ease of production.

Understand and control the crystalline phase assemblage and stability.

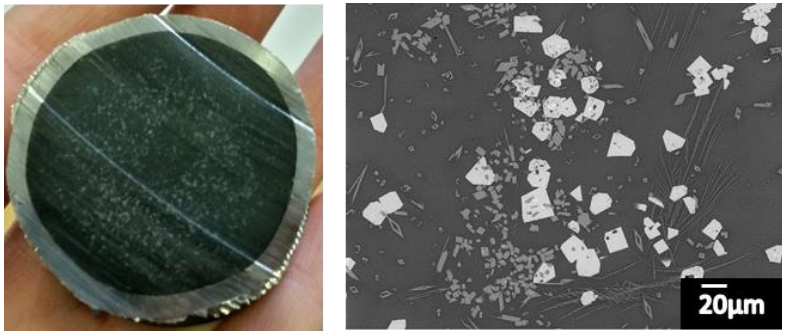
The Problem



- HIPed materials expected to have <97% theoretical density.
- Successful cans were still producing porous samples.
- A high temperature bake out eliminated the issue of porosity but slowed sample throughput.



300 °C bake out



600 °C bake out

Can a "pre-can" calcination step be an alternative to the high temperature bake out?

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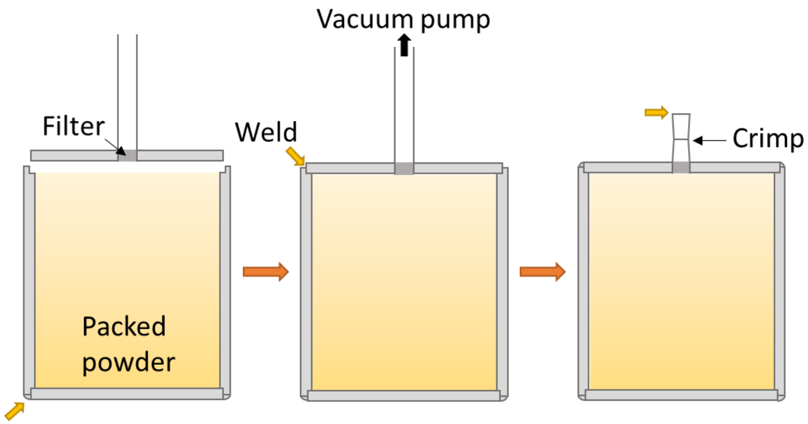
Experimental Procedure

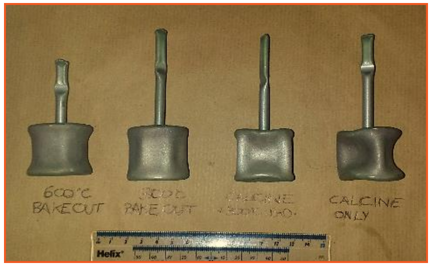


1) Powders batched to a 70:30 wt% glass:ceramic, target glass phase $Na_2Al_{0.5}B_{1.5}Si_6O_{16}$.
2) Batches were calcined according to Table 1.
3) Powder was packed into HIP can.
4) HIP can was evacuated.
5) HIP can undertook bake out step according to Table 1.
6) HIP can was crimped and sealed.

Sample	Heat Treatment	
	Calcine (°C)	Bake out (°C)
A	0	300 °C
B	0	600 °C
C	600 °C	300 °C
D	600 °C	0

HIPed at 1250 °C, 100 MPa with a 4 hr dwell.

Before HIP



After HIP

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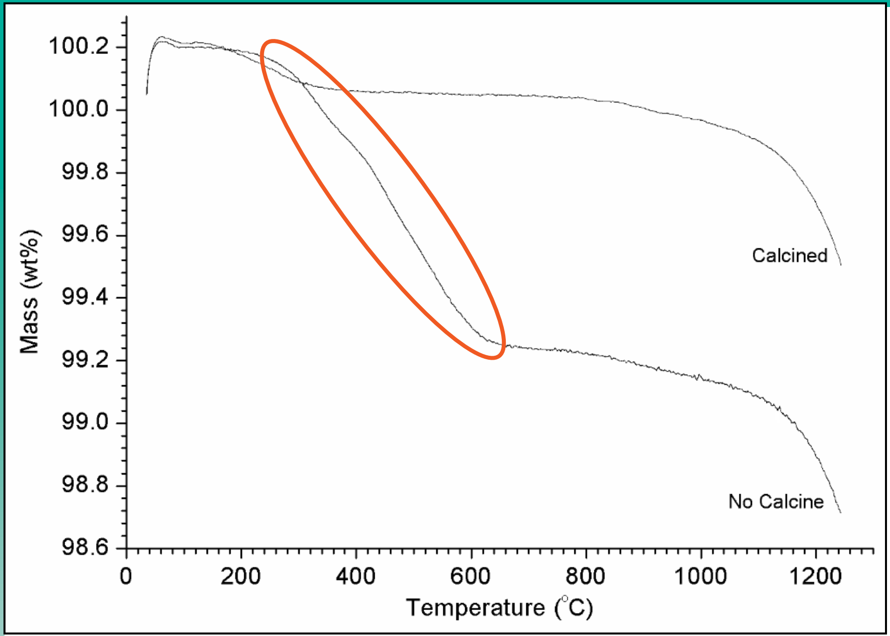
Results



TG: Platinum crucible, 10 °C/min, 1250 °C

Mass loss agrees with our hypothesis that volatiles are being released or a reagent is decomposing to produce a gas.

REAGENTS USED

SiO_2
Na_2SiO_3 - anhydrous
Al_2O_3
$Na_2B_4O_7$ - anhydrous
$CaTiO_3$
ZrO_2
TiO_2

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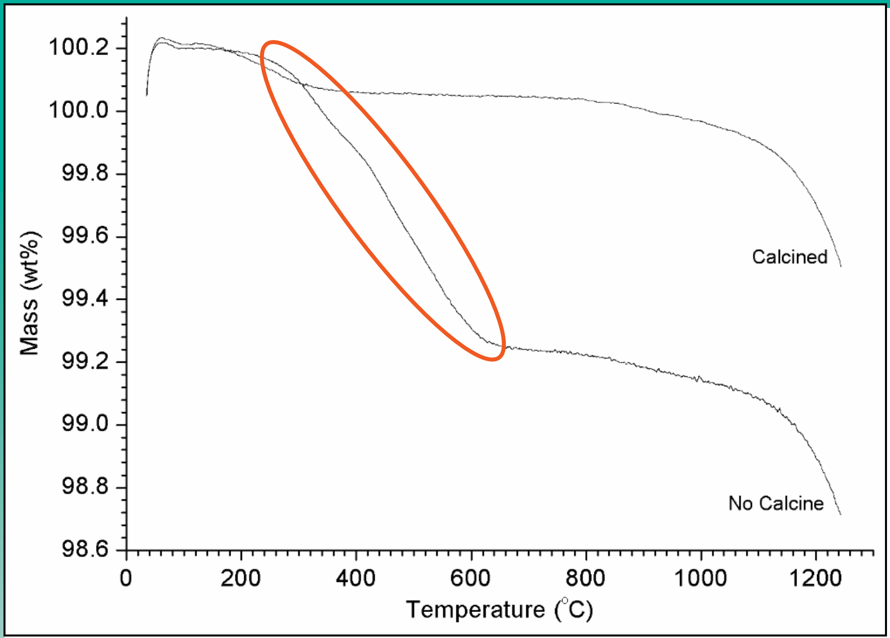
Results



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ZrO_2

TiO_2

$$Na_2B_4O_7.10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$$

$$Na_2(B_4O_5.(OH)_4).8H_2O \xrightarrow{\text{57-142 °C}} Na_2B_4O_5(OH)_4 + 8H_2O$$

$$Na_2B_4O_5(OH)_4 \xrightarrow{\text{142-602 °C}} Na_2B_4O_7 + 2H_2O$$

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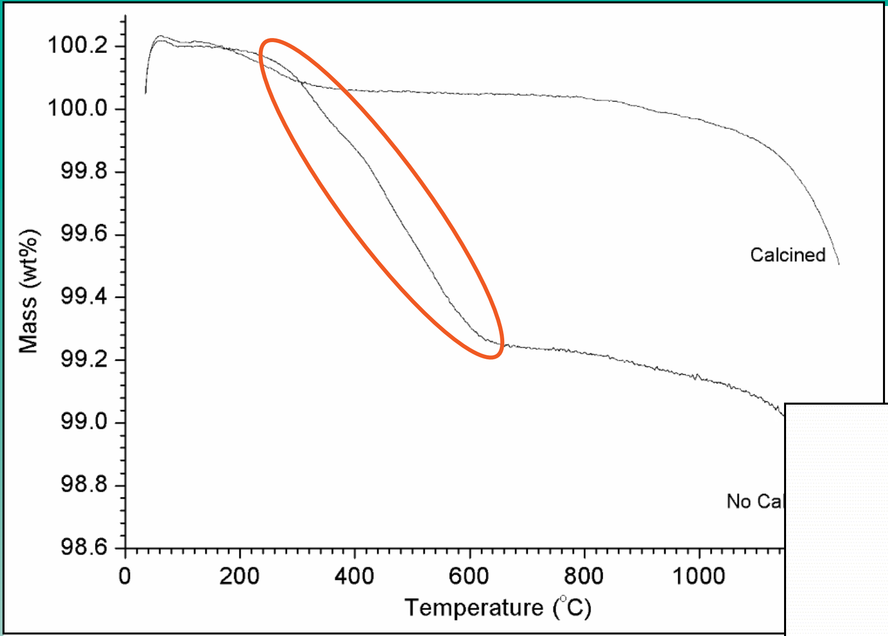
Dehydration kinetics of Borax by thermal analysis, A. Ekmekyapar et al. 1997

Results



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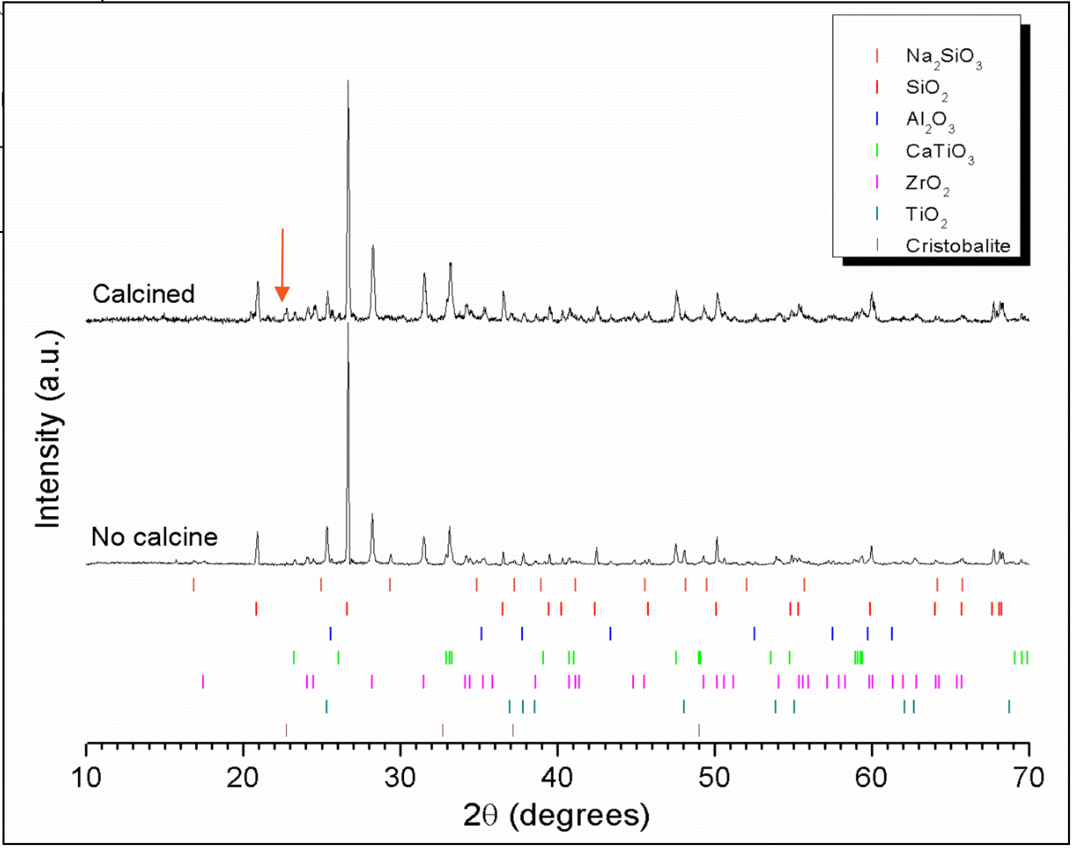

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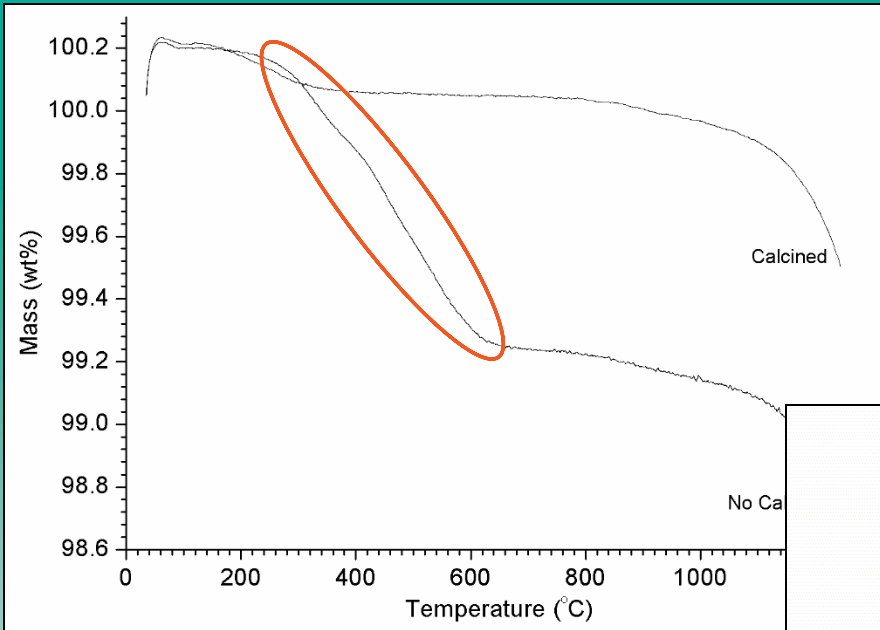
Results



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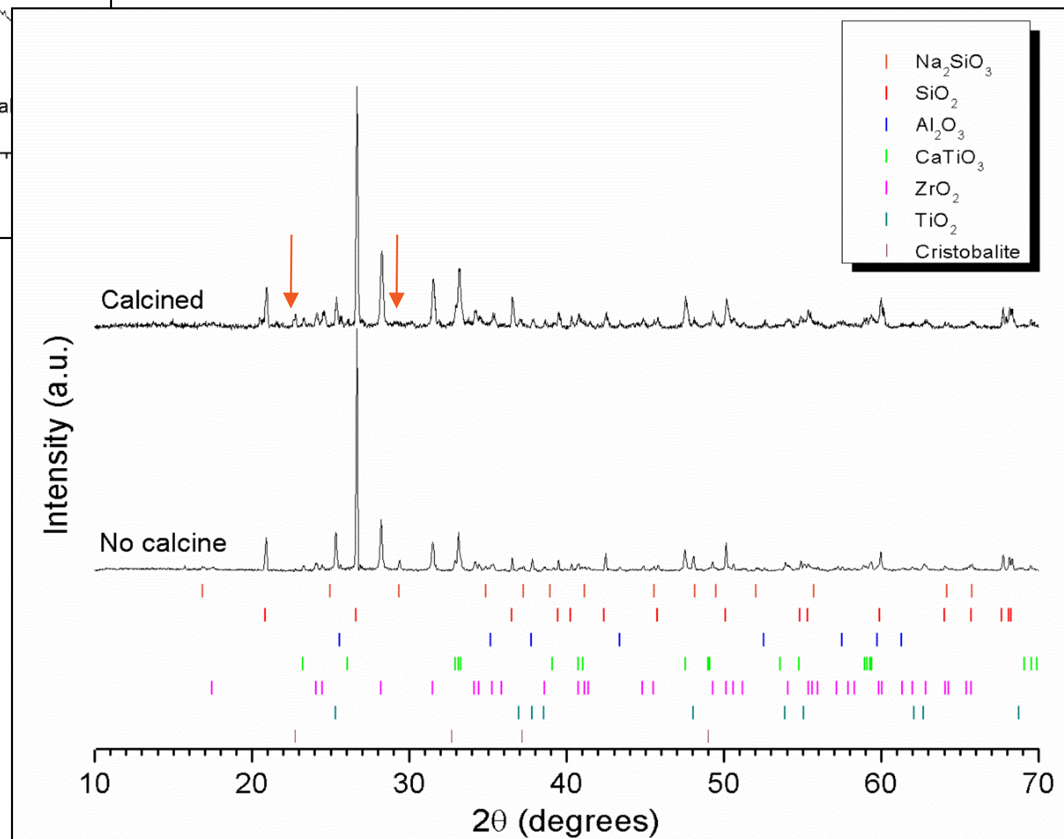
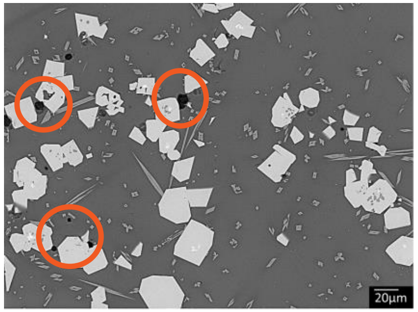
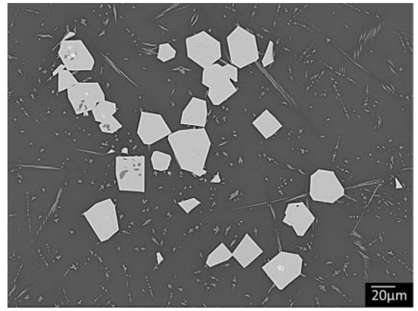
TiO_2



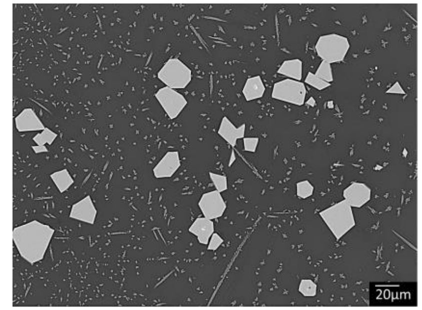
Microstructure



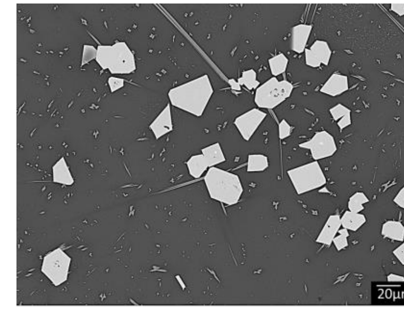
300 °C bake out



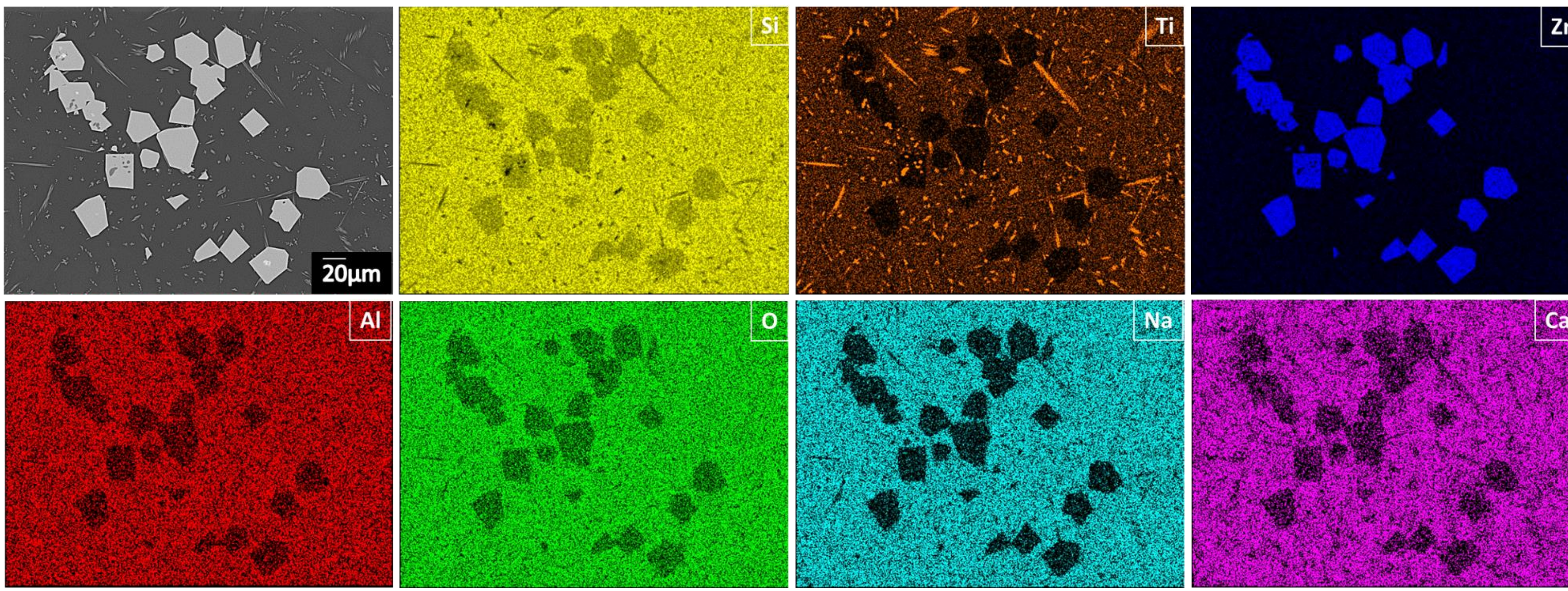
600 °C bake out



600 °C calcine +
300 °C bake out

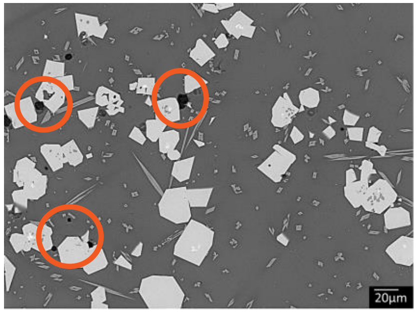


600 °C calcine

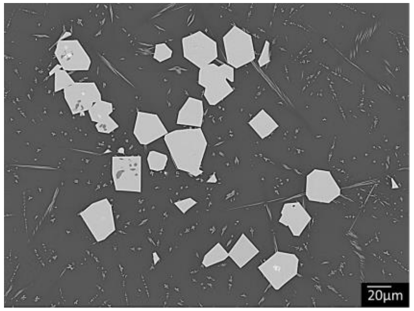


Sample C: 600 °C calcine + 300 °C bake out.

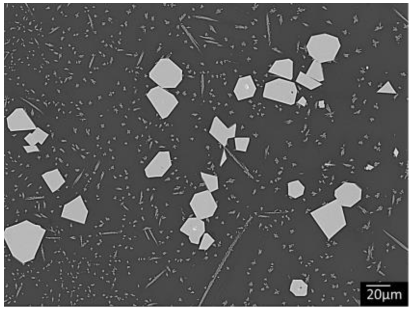
Phase assemblage



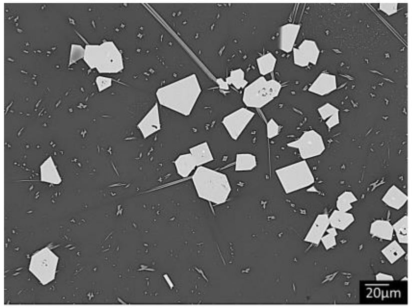
300 °C bake out



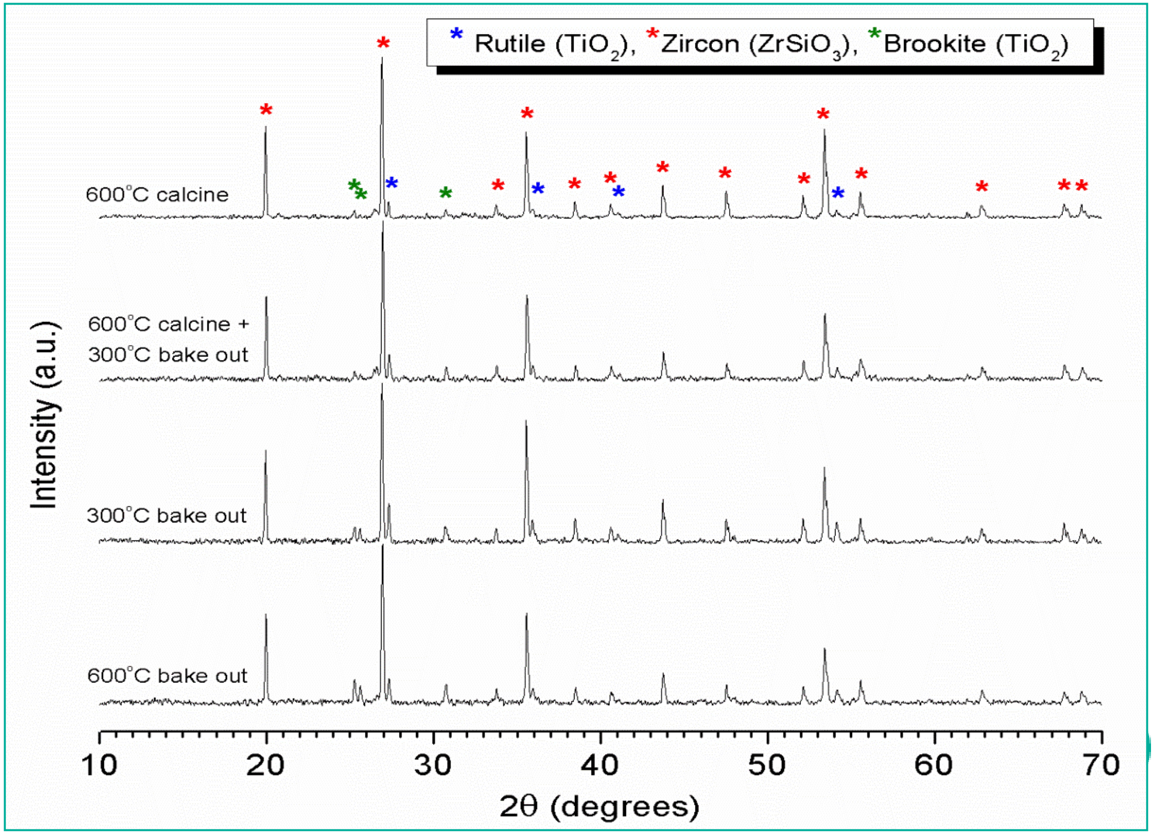
600 °C bake out



600 °C calcine +
300 °C bake out



600 °C calcine



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Summary

	Sample			
	300°C bake out	600°C bake out	600°C calcine +300°C bake out	600°C calcine
Total can evacuation time (min)	**960** (±2.5)	**480** (±2.5)	**150** (±2.5)	**45** (±2.5)
Packing density (g/cm³)	1.66 (±0.08)	1.57 (±0.08)	1.37 (±0.07)	1.38 (±0.07)
Final density (g/cm³)	2.43 (±0.12)	2.66 (±0.13)	2.69 (±0.13)	2.57 (±0.13)
Densification (%)	31.80 (±1.59)	40.91 (±2.05)	49.19 (±2.46)	46.51 (±2.33)

300 °C bake out can was very porous as expected from TG data showing a mass loss between 300-600 °C.

The phase assemblage and microstructure remained the same independent of the processing route.

The total time required to evacuate the canisters before crimping and sealing was dramatically reduced by calcining the whole batch overnight at 600 °C.

Further tests are to be performed to underpin whether the mass loss is due to the removal of water from borax or the decomposition of Na_2SiO_3.

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Aims

Optimise the processing route and parameters whilst maintaining ease of production.

Understand and control the crystalline phase assemblage and stability.

Effect of glass composition

- Target matrix: High fraction zirconolite glass-ceramics.
- Samples at NNL revealed multiple crystalline phases forming.
- The yield of zirconolite was seen to change as a function of the glass phase composition.

Method

50:50 vol% glass : ceramic

Glass Phase: $Na_2Al_{1+x}B_{1-x}Si_6O_{16}$
x = 0, 0.2, 0.4, 0.6, 0.8, 1.0

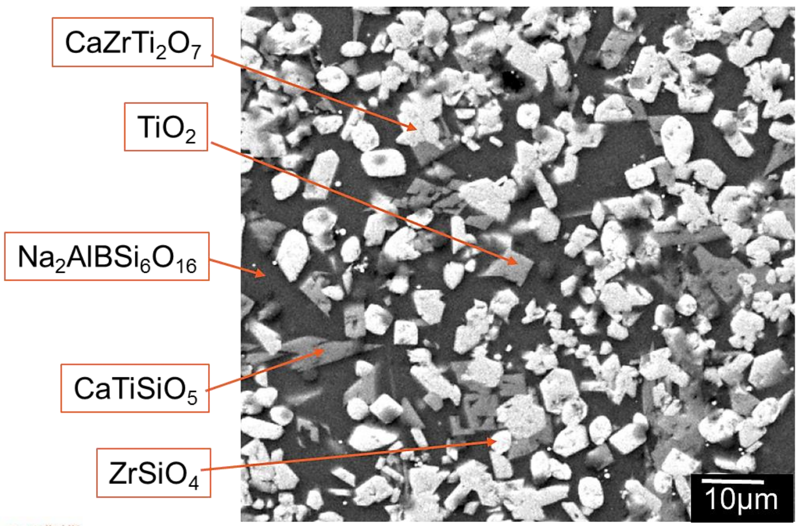
HIP: 1250 °C, 100 MPa, 2 hr

$$CaTiO_3 + ZrO_2 + TiO_2 \rightarrow CaTiSiO_5 + ZrSiO_4 + TiO_2$$

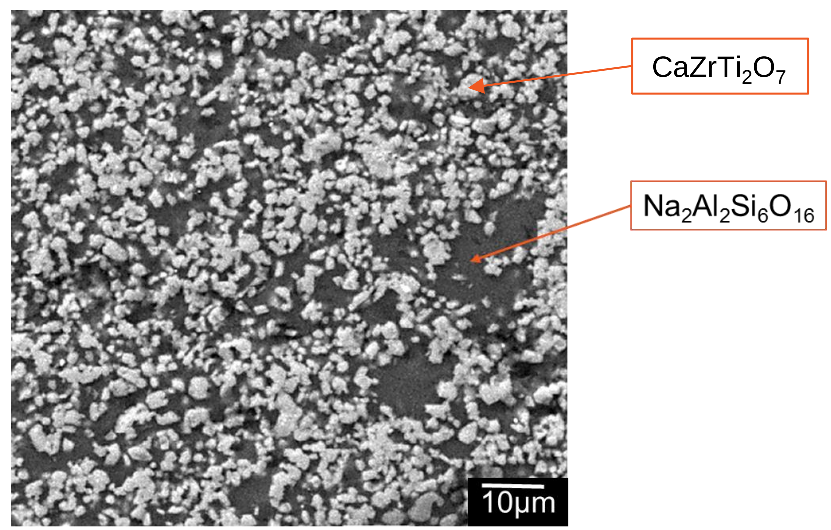
$$CaTiO_3 + ZrO_2 + TiO_2 \rightarrow CaZrTi_2O_7 + 2[SiO_2]$$

$$\mathbf{CaTiSiO_5 + ZrSiO_4 + TiO_2 \rightleftharpoons CaZrTi_2O_7 + 2[SiO_2]}$$

1Al : 1B



2Al : 0B



Published in Journal of Nuclear Materials, "The influence of glass composition on crystalline phase stability in glass-ceramic wasteforms." E. Maddrell, S. Thornber, N. C. Hyatt, 2014

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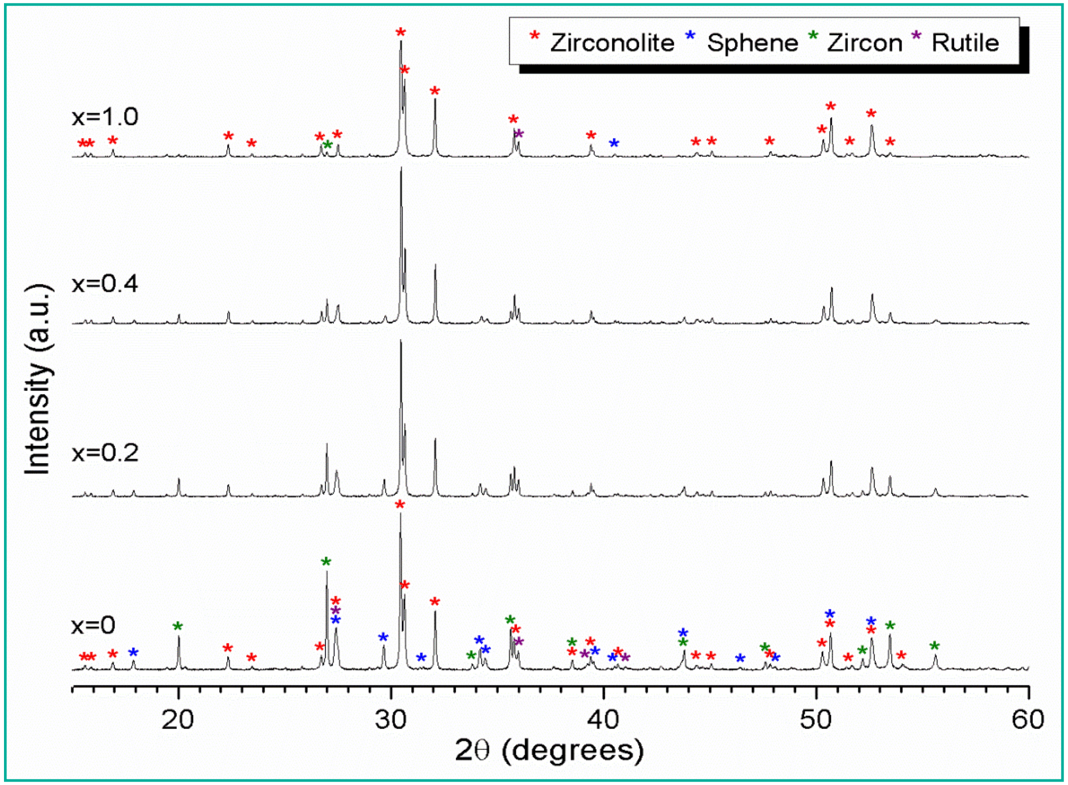

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Next steps

- Develop a matrix to construct a phase map to determine an optimum composition for producing high fraction zirconolite glass-ceramics.
- All cans will be processed with a 600 °C calcination plus 300 °C bake out to optimise product quality and throughput.
- Maximise waste loading capacity and study wasteform properties – Ce, U/Th.

Conclusion

- High-fraction zirconolite glass-ceramics are being developed by hot isostatic pressing as future wasteforms for Pu-residue immobilisation.

- “Pre-HIP” processing parameters have been studied to optimise product quality and throughput such that a “high temperature calcine plus low temperature bake out” route will be used throughout the remainder of this project.

- Zirconolite has been seen to form unfavourably as part of 2 competing reactions.

- The yield of zirconolite depends on the glass phase and current experiments are trying to underpin the mechanism controlling the crystalline phase stability.

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Acknowledgements

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ANY QUESTIONS?

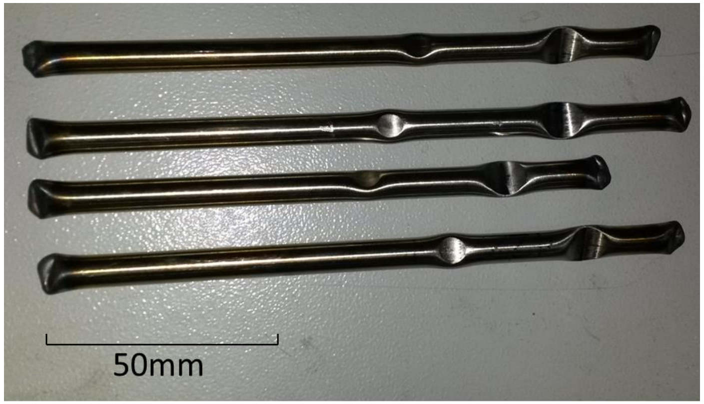
Contents

Zirconia full ceramics

- Pu-residues contaminated with chlorine due to the decomposition of PVC storage bags.
- Want to retain chlorine in the wasteform in a separate phase from Pu.

Waste-stream	Samples	Method
20 wt% Pu loading 3 wt% Cl contamination 4 wt% H2O	20 wt% Ce loading 3 wt% Cl contamination 20 wt% Gd loading	300 °C bake out 1250 °C, 100 MPa, 2 hrs

Sample	Additions
A	nothing
B	0.5 wt% aeroxide
C	Nothing, milled wet in heptane
D	0.5 wt% aeroxide, milled wet in heptane
E	0.5 wt% aeroxide + $Ca_2P_2O_7$ (5:1 molar ratio of Ca:Cl)
F	0.5 wt% aeroxide + $Ca_2P_2O_7$ (2:1) molar ratio of Ca:Cl)



¼" crimped HIP cans

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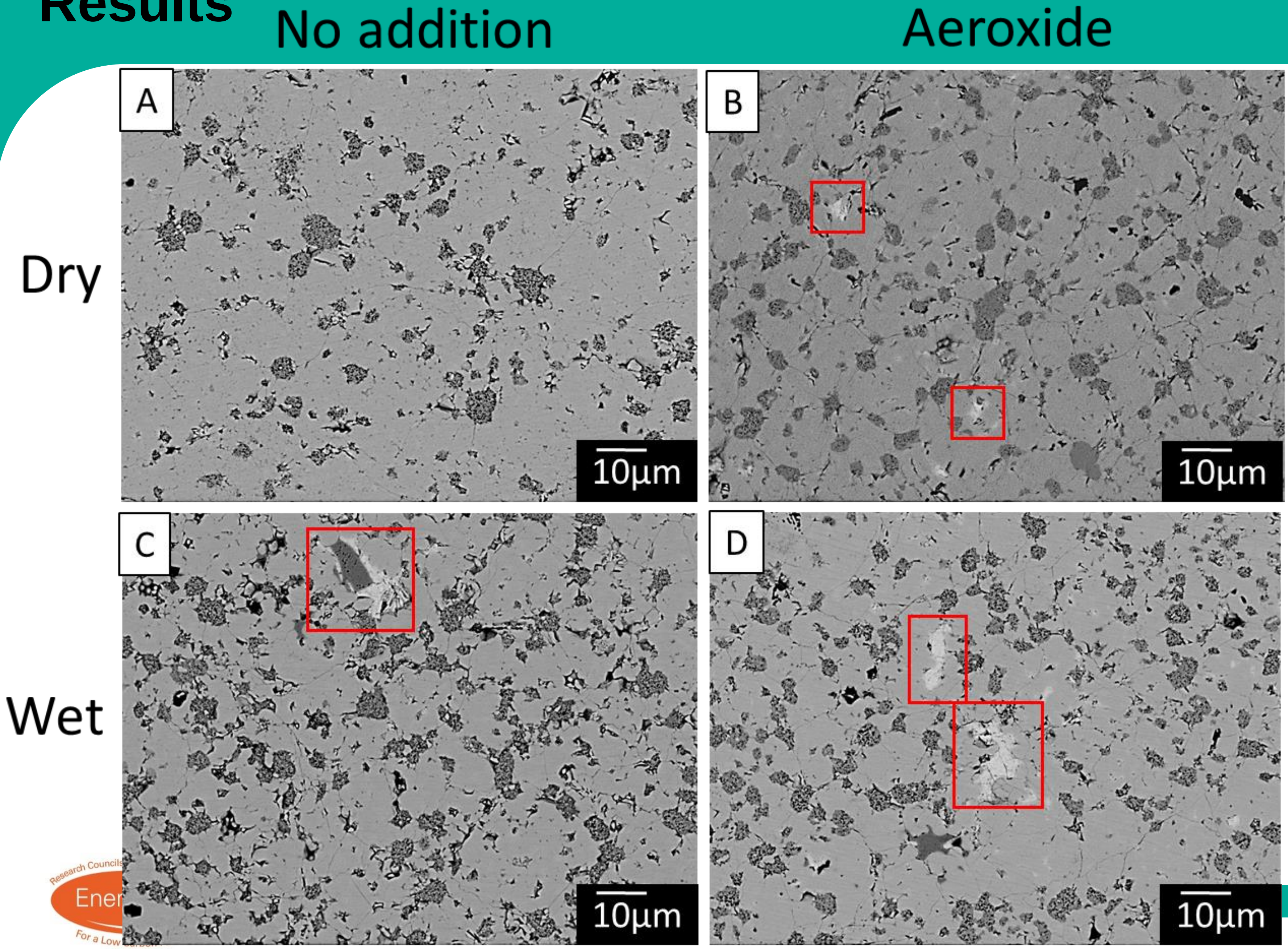
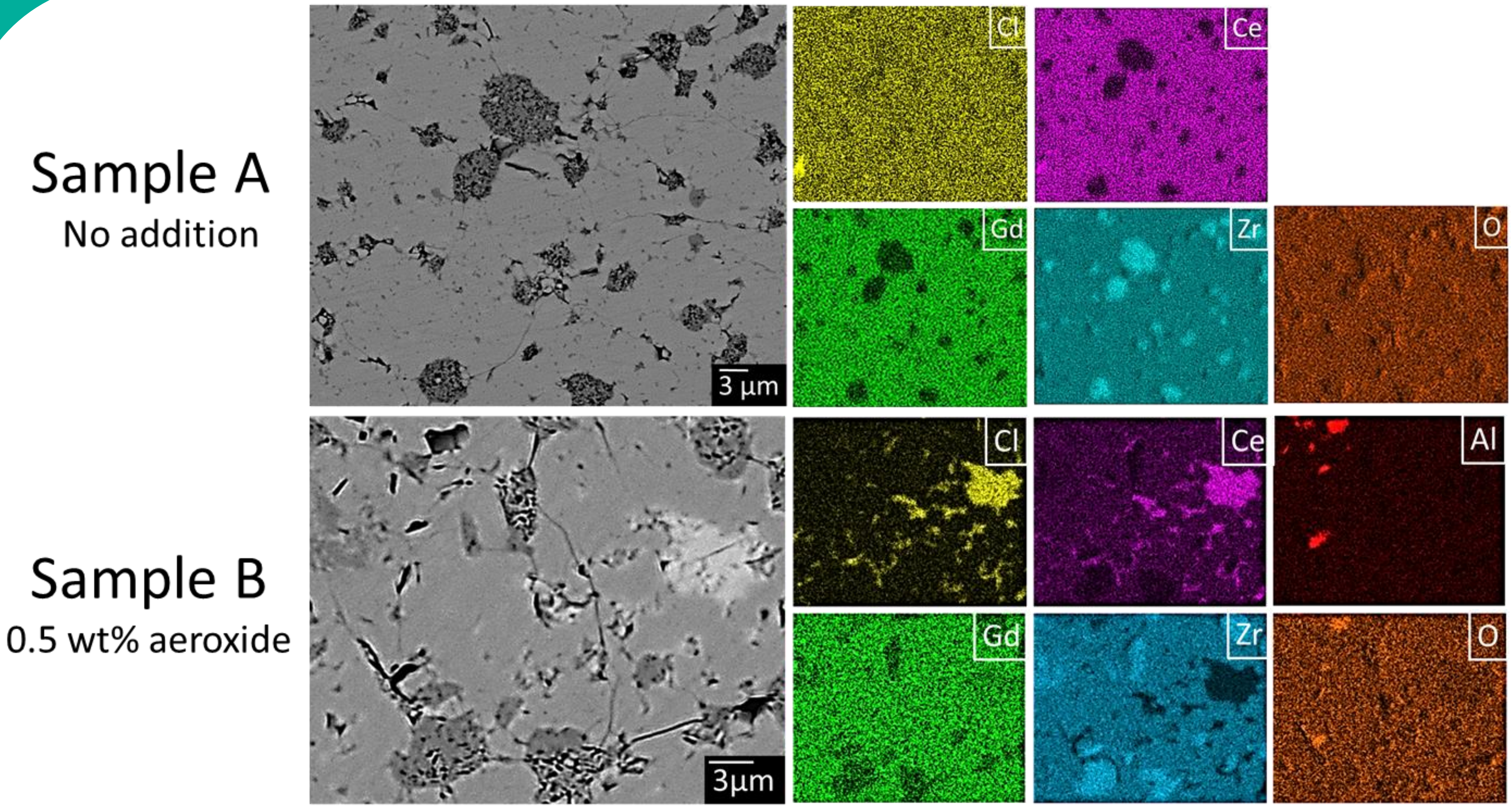
Results



Results



The addition of 0.5 wt% aeroxide inhibits the separation of the cerium and the chlorine.

Results

Sample E

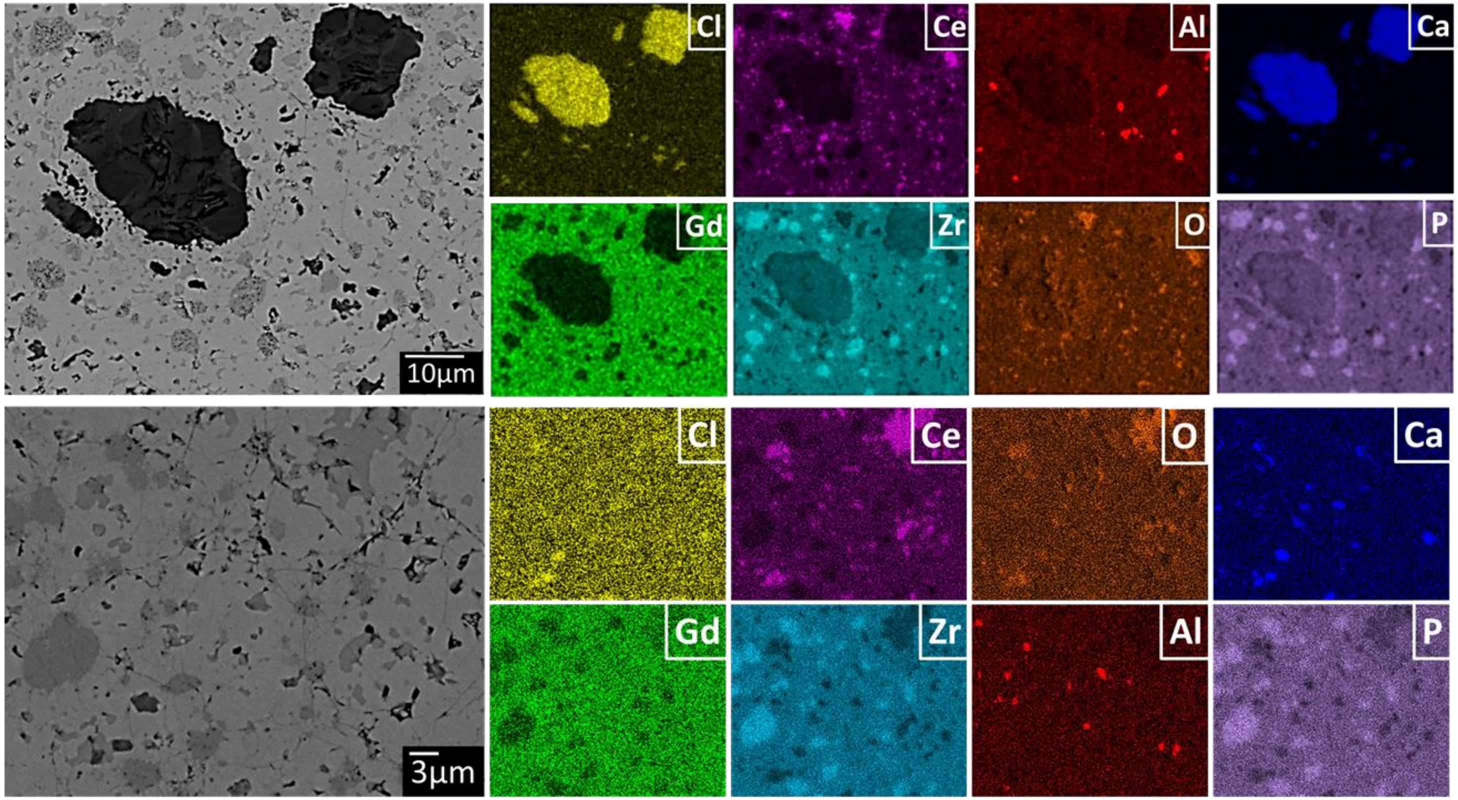
$Ca_2P_2O_7$ 5:1 ratio

0.5 wt% aeroxide

Sample F

$Ca_2P_2O_7$ 2:1 ratio

0.5 wt% aeroxide



$Ca_2P_2O_7$ successfully separates the chlorine from the cerium but destabilises the zirconia phases resulting in residual CeO_2.

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Summary

- Changes in the processing parameters inhibit the separation of cerium and chlorine.
- Aeroxide added as a milling lubricant had a detrimental effect on waste digestion.
- $Ca_2P_2O_7$ successfully separated the chlorine and cerium into different phases however destabilised the zirconium containing phases resulting in residual CeO_2 in the matrix.

Future Work

- Ongoing experiments trying to stabilise the zirconia matrix whilst retaining Ce/Cl separation by reducing the Ca:Cl ratio further.
- Repeat the matrix with zirconolite
- Scale up HIP cans to see if such results can be reproduced.

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- High-fraction zirconolite glass-ceramics are being developed by hot isostatic pressing as future wasteforms for Pu-residue immobilisation.
- “Pre-HIP” processing parameters have been studied to optimise product quality and throughput such that a “high temperature calcine plus low temperature bake out” route will be used throughout the remainder of this project.
- Zirconolite has been seen to form unfavourably as part of 2 competing reactions.
- The yield of zirconolite depends on the glass phase and current experiments are trying to underpin the mechanism controlling the crystalline phase stability.
- The retention and separation of chlorine into a zirconia ceramic has been promising however further is in ongoing to achieve desired phases and optimum waste loading capacity.

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