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Waste Forms for the Immobilization of Uranium Waste Streams from Mo-99 Production

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ANSTO, *Australian Nuclear Science and Technology Organisation*

Work basis

- Funded by NNSA with work being done by NESA and ANSTO

Alkaline Process: Waste streams

1: UOx + Na/Fe/Ni/Cr oxides + FP

2: As in 1, with majority of U extracted

3: Al_2O_3 ion exchanger + FP

- All more active than LLW, typically 10^{12} Bq/L
- For conservatism chose mainly HLW waste forms and HLW immobilisation criteria

Waste Forms

- Mix the waste with selected additives to make solid material that is relatively insoluble in water
- Major HLW waste forms that can immobilise the full range of FPs + actinides are glass, synroc, and alumina-based ceramics .
- Long-lived in Nature
- Cementitious products for less active wastes

Waste Form Design Strategy

- Maximize waste loading to increase cost savings
  - by utilizing waste components to advantage via 30 years experience in WF design

- Optimize durability to lower environmental risk
  - by incorporating waste in very durable mineral analog phases & high durability glasses

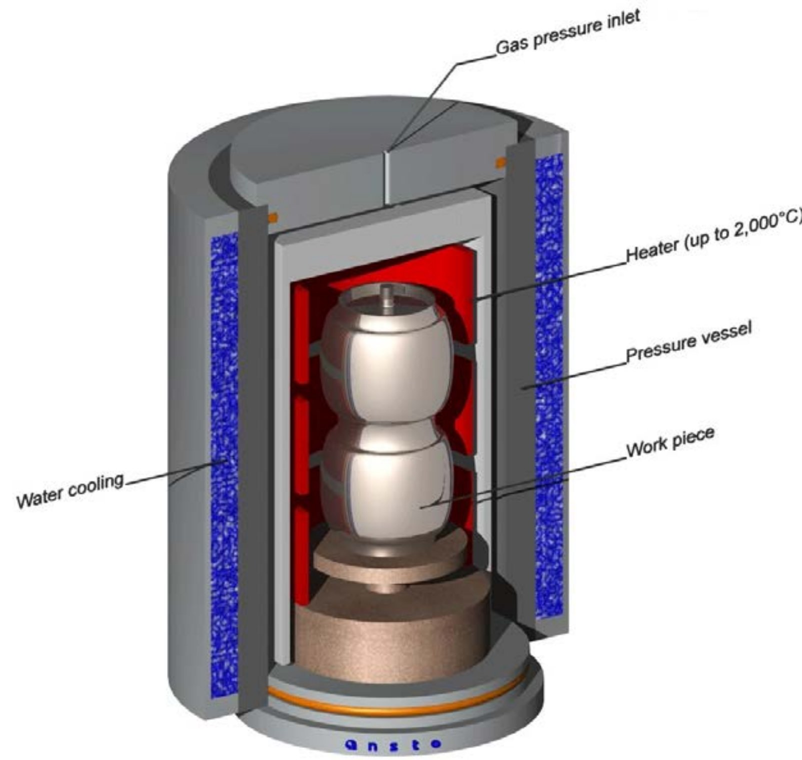
- Increase flexibility to accommodate process and waste variations
  - via in built chemical buffering & multiphase waste forms

- Integrate optimal consolidation technology
  - process should place minimal constraints on the chemistry of the waste form and reduce or eliminate off-gas emissions

Integrated waste form and process technology to achieve maximum benefits

Making and characterizing waste forms

- Hot isostatic pressing for waste form production mainly
- Microstructure and leaching
- Radiation effects would be minimal in these HLW forms and mechanical properties never an issue
- Simulated FPs and natural U



Leaching and characterization of waste streams 1-3

- Substituted ~0.2 wt% of FPs
- XRD, SEM
- MCC-1 - ~1cm squares in ~25 mL of water
- PCT – 1g 75-150 micron particles/10 mL of water
- Thermal stability and compressive strength

Waste forms and scaleup

- Many ceramics, glasses, glass-ceramics, geopolymer cements at ~50g scale
- Scaled up to a few kg those samples which passed downselect criteria- performance, processing, preconceptual engineering

ANSTO Synroc HIP Treatment Technology

Waste Stream 1 (WS1)

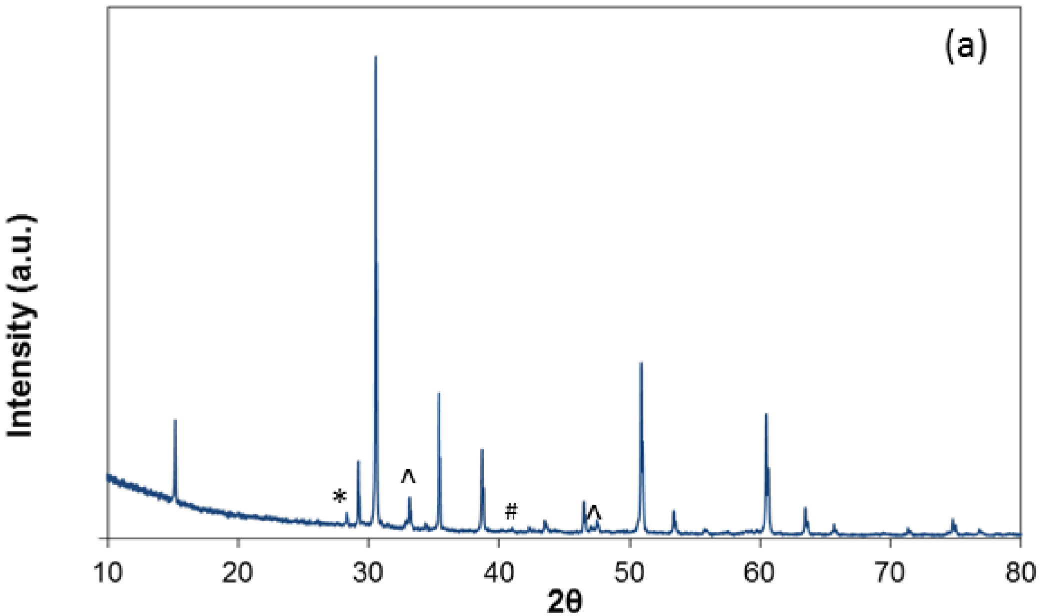
- Fe_2O_3 (10); Cr_2O_3 (2.2); NiO (1.3); Al_2O_3 (1.9); $Na_2U_2O_7$ (72.5); UO_2(10.9) + FP oxides (1.2)

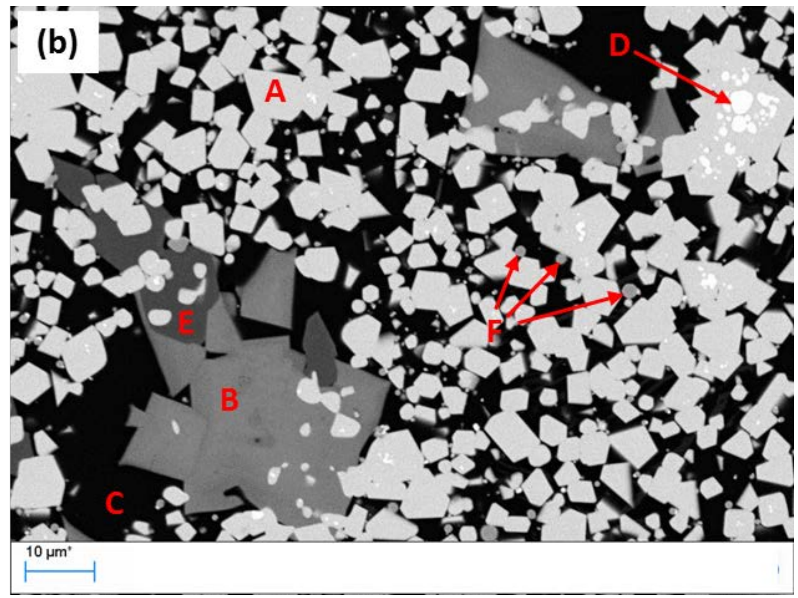
- Main waste forms were pyrochlore-structured $CaUTi_2O_7$ (synroc group) + 10 or 20 wt% glass additives (U and FP hosts, additional thermal conductivity above T_g)

WS1 Wasteform

HIP Canister properties		
	unHIPed	HIPed
Diameter (mm)	86.7	70.4
Height (mm)	122.2	67.8
Mass of sealed can (g)	1253.0	1254.4
Can volume (cm^3)	675	210
Sample density (g/cm^3)	1.52	4.83
Mass of can contents (g)	862.6	
Volume reduction (%)	**69%**	

XRD and Microstructure





- Leach results OK

Waste Stream 2 (WS2)

- Composition: Fe_2O_3 (33.7); Cr_2O_3 (5.9); NiO(3.6); Al_2O_3 (16.6); Na_2O (3.3), UO_3 (30.2); UO_2 (5.3): FP (1.5)

- Targeted pyrochlore $CaUTi_2O_7$ + TiO_2 ceramic, HIPed at 1250^oC/100MPa.
- Generally good properties but high Cs leaching due to $CsAlTiO_4$ formation

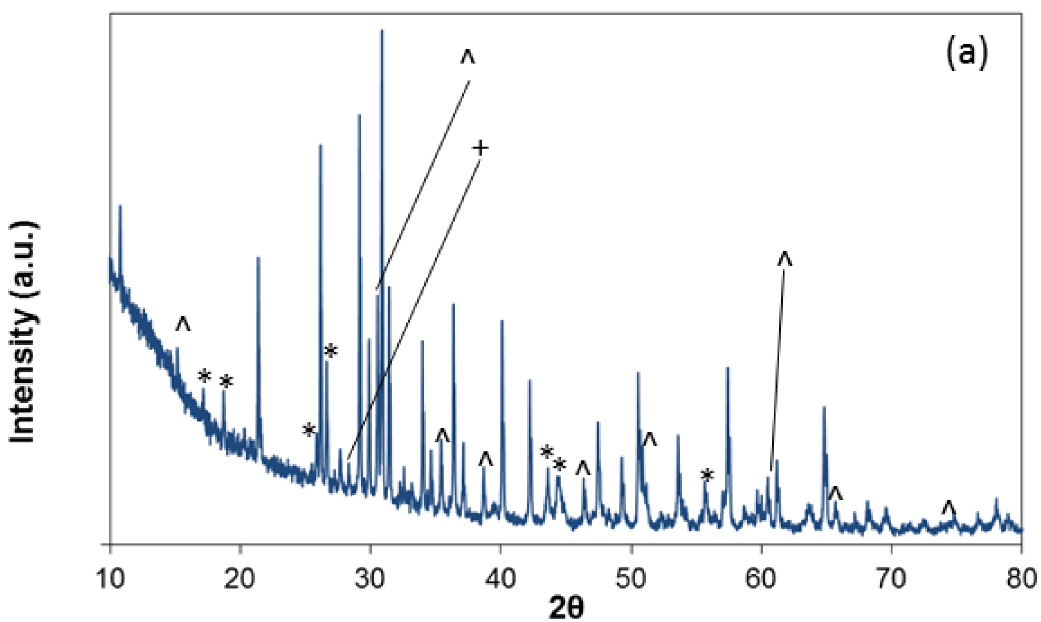
Pyrochlore + 20% glass for WS2

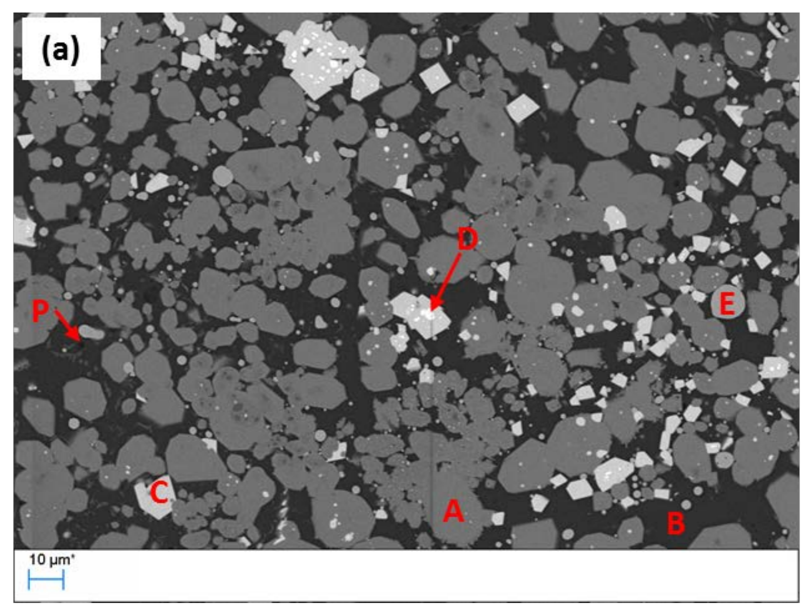
HIP Canister properties		
	unHIPed	HIPed
Diameter (mm)	86.8	70.6
Height (mm)	122.1	83.0
Mass of sealed can (g)	1372.97	1373.7
Can volume (cm^3)	675	295
Sample density (g/cm^3)	1.72	3.7
Mass of can contents (g)	979.6	
Volume reduction (%)	56	

- Adjusted composition: $CaUTi_2O_7$ + 20% glass, same HIP conditions

Pyrochlore + glass for WS2

- Microstructure- major pyrochlore, minor perovskite ($CaTiO_3$), minor glass, minor UO_2, trace loveringite, FP-bearing alloys
- U and FPs located in the different phases
- Excellent leaching behaviour (all PCT rates <0.2 $g.m^{-2}.day$





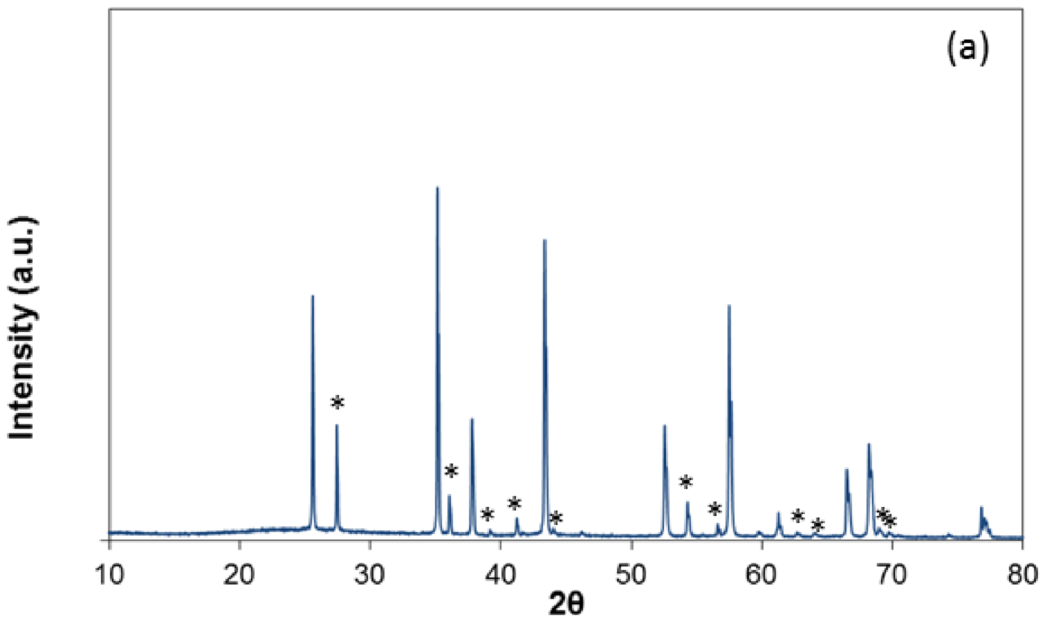
Waste stream 3

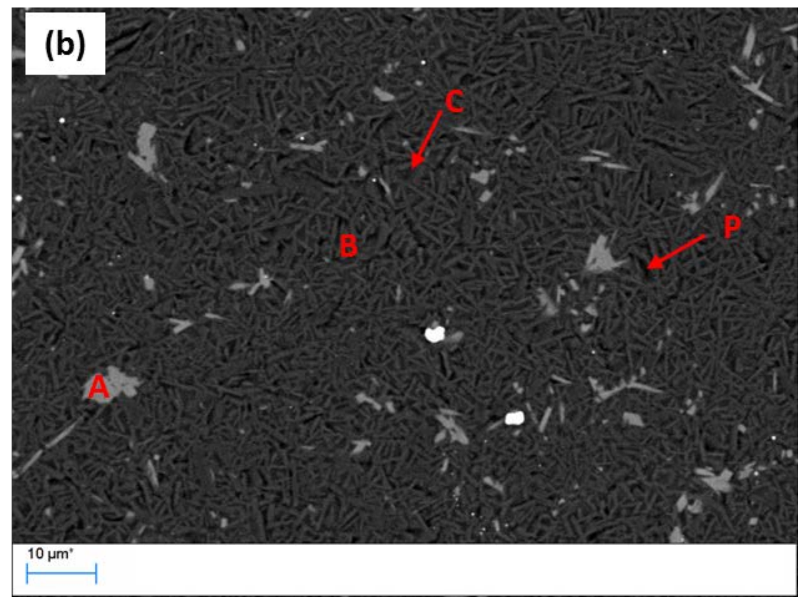
HIP Canister properties		
	unHIPed	HIPed
Diameter (mm)	86.6	62.5
Height (mm)	122.6	71.4
Mass of sealed can (g)	938.70	939.60
Can volume (cm^3)	625	238
Sample density (g/cm^3)	1.0	3.33
Mass of can contents (g)	558.0	
Volume reduction (%)	**62**	

- 99% + alumina ion exchanger, rest FPs
- Waste form target: Alumina + glass & TiO_2

Alumina-glass-rutile waste form for WS3

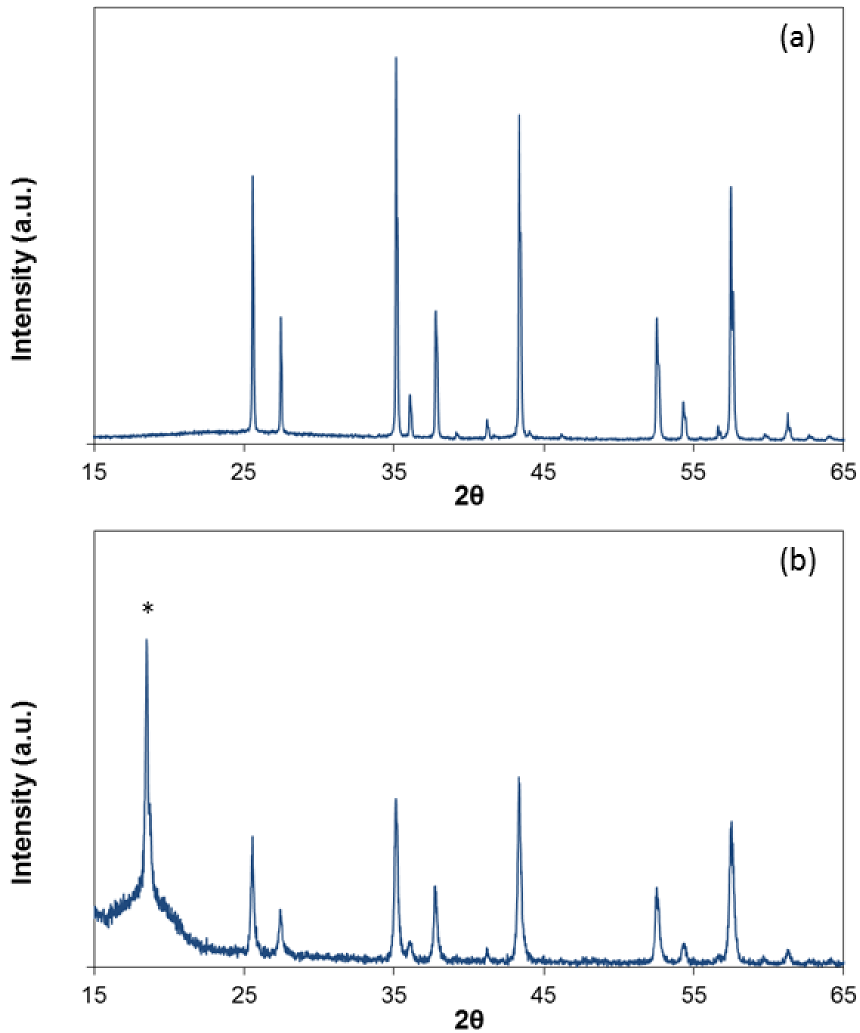
- Microstructure picture showing designated phases + some FPs in metal alloys
- FPs in the targeted phases



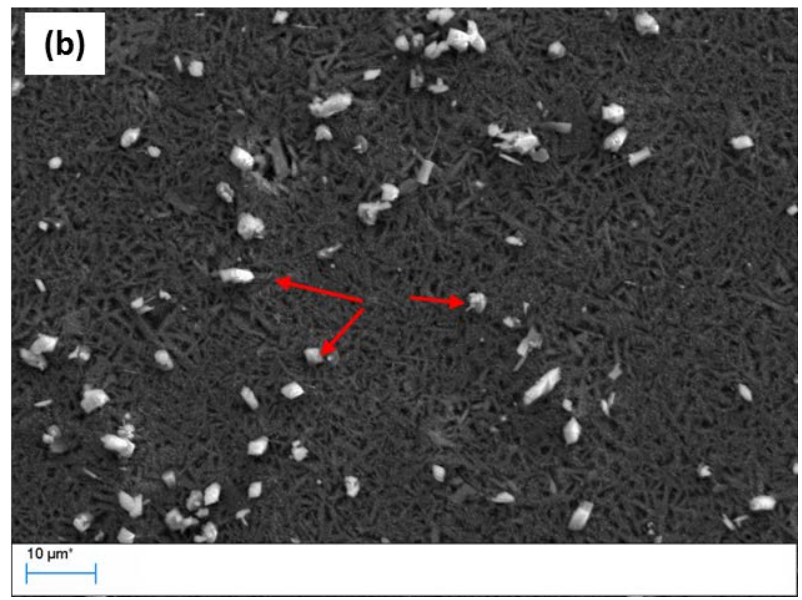


- PCT leach rates <0.2 $g.m^{-2}.day$ at 90ºC

WS3



- Norstrandite alteration layer covered surface after 90 days



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Alumina-glass-rutile waste form for WS3

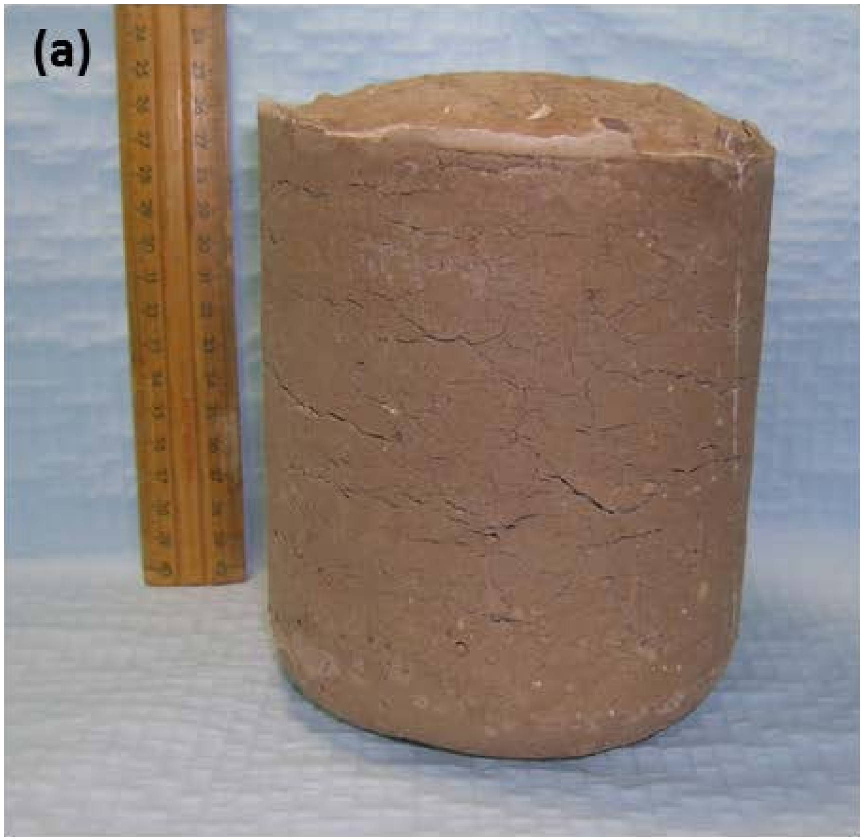
- Larger HIP can containing 6.3 kg of waste form gave broadly similar results

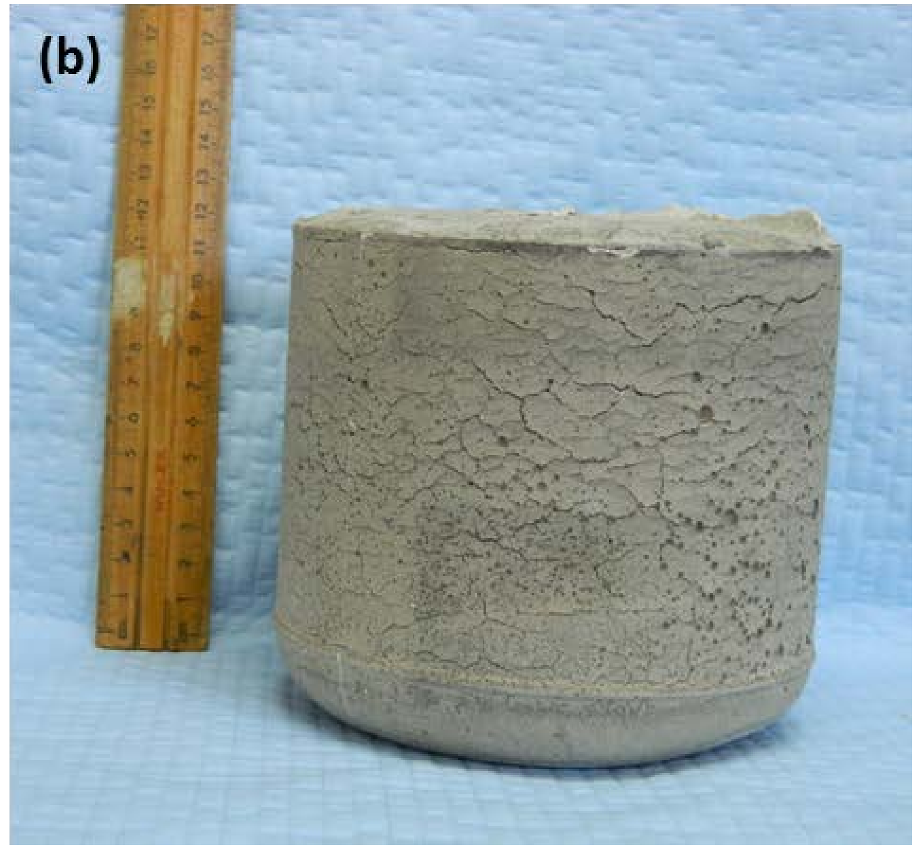
Geopolymer for WS3

- Mixed metakaolin and sodium silicate solution with Na/Al=1 and Si/Al=2 with 40 wt.% WS3
- Small-scale experiments using strong agitation and exit of air bubbles (~80g) looked good and could heat to 500^{o}C without fracture
- At ~3kg level could had to pour into container- more water necessary

WS3 –Large sample

- Curing at 90-130^{o}C plus 500^{o}C





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WS3

- Compressive strength only ~3MPa
- But passed PCT (Na < 1g.m^{-2}.day) by a factor of ~20 and ANS 16.1 tests easily (for Na vs logarithmic “pass mark” of 6).
- Leaching mainly due to diffusion of non-network ions in pore water
- Because the waste is an ion exchanger, very low FP apparent leaching but Na results real
- Suspect limited stability for real waste

Conclusion and Final Remarks

- Ceramic and glass-ceramic waste forms are preferred with “economic” waste loadings of ~30 - 70 wt %.
- Large volume reduction ~ 50% - 70%
- HIPing flexible technology suitable for several tonne quantities of waste and can be applied to all waste streams
- Geopolymers less durable and prone to radiation effects

- ANSTO in detailed engineering stage for a HIP facility to treat its own ILW from Mo-99 production
- Building to commence in 2017

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