Uranium encapsulation into glass

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JOINT ICTP-IAEA INTERNATIONAL SCHOOL ON
NUCLEAR WASTE VITRIFICATION

ICPT, TRIESTE

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1. Enriched Uranium problem

Enriched Uranium

MTR Reactor

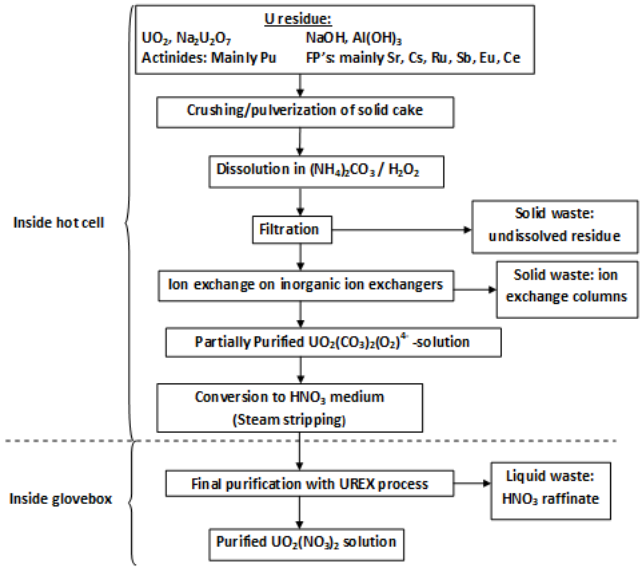
- Old reactor spent fuel (MTR fuel)
- U(m) ≥ 45%

Medical isotope production

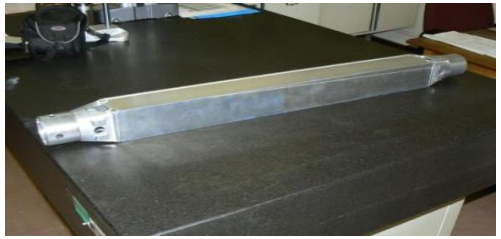
- Residue from dissolved target plates
- U(m) ≥ 45%

2. Alkaline reprocessing of MTR fuel (Research Reactor)

Country	Reactor (Age)	production per week (6dCi)	Processing Facility	Processing facility capacity (6dCi)	target type	processing
Canada	NRU (57)	4680	MDS Nordion	7200	HEU	acid (HNO_3)
Netherlands	HFR (53)	4680	Covidien	3500	HEU	alkaline (NaOH)
Belgium	BR-2 (53)	7800	IRE	2500	HEU	alkaline (NaOH)
South Africa	Safari-1 (49)	3000	NTP	3000	LEU	alkaline (NaOH)
Australia	OPAL (8)	1000	ANSTO Health	1000	LEU	alkaline (NaOH)
Argentina	RA-3 (47)	400	CNEA	900	LEU	alkaline (NaOH)
France	OSIRIS (48)	1200	IRE		HEU	
Czech Republic	LVR-15 (57)	2800	IRE		HEU	
Poland	MARIA (40)	1920	Covidien		HEU	
Russian Federation	RIAR:three (40)	900	IPPE	unknown	HEU	acid (HNO_3)

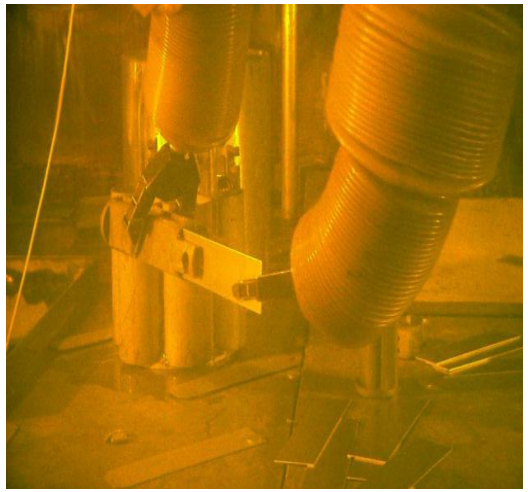


Schematic representation of the alkaline route to recover uranium bases on residue from Mo-99 target plates



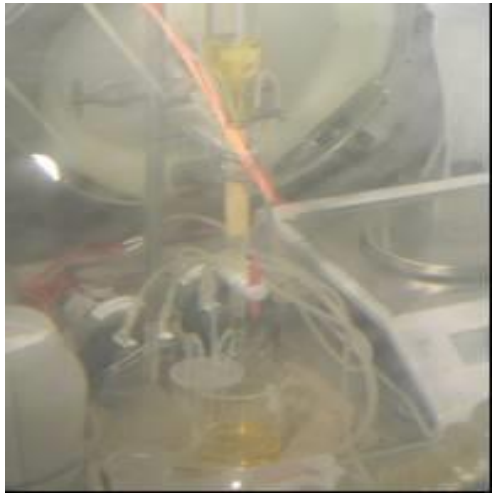
Alkaline re-processing chemistry of MTR spent fuel and Mo-99 residue from target plates identical

2. Alkaline reprocessing of MTR fuel (Research Reactor)



Dissolving step

Residue from dissolving (NaOH) process



Isolating uranium from solid residue

High enriched Uranium waste to be conditioned

3. Uranium waste to be conditioned for disposal

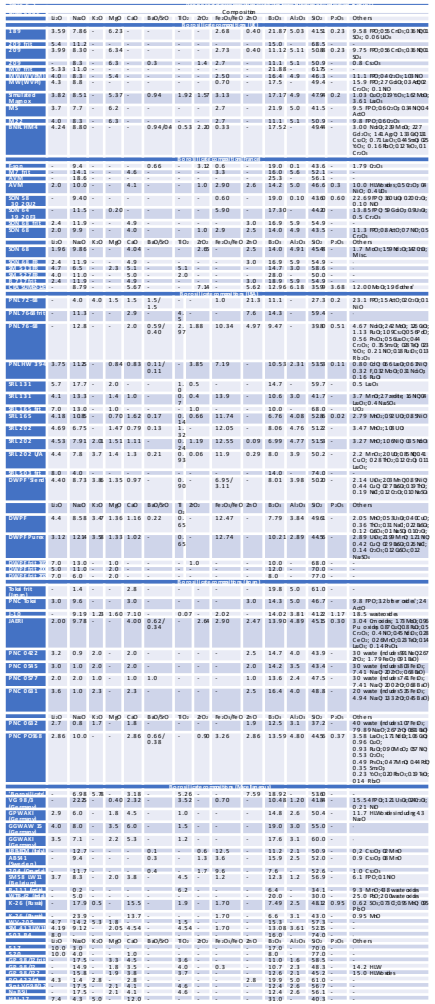
Waste characterization

Nuclide	Bq/g residue
Co-60	1.99E+04
Nb-95	2.95E+04
Zr-95	1.90E+04
Ru-106	4.24E+05
Sb-125	1.45E+06
Cs-137	3.22E+06
Ce-144	8.90E+05
Pr-144	7.86E+05
Eu-154	7.09E+04
Eu-155	2.46E+06
Fe	99.7 % m/m
Al	83 % m/m
U	98 %

Approximate solubility limits

Element	Solubility limit, wt.%
Al, Si, P, Pb	25
Li, B, Na, Mg, K, Ca, Fe, Zn, Rb, Sr, Cs, Ba, Fr, Ra, U	15 -25
Ti, Cu, F, La, Ce, Pr, Nd, Gd, Th, Bi, Zr	5 - 15
Mn, Cr, Co, Ni, Mo	3 - 5
C, S, Cl, As, Se, Tc, Sn, Sb, Te	1 - 3
H, He, N, Ne, Ar, Br, Kr, Ru, Rh, Pd, Ag, I, Xe, Pt, Au, Hg, Rn	< 0.1

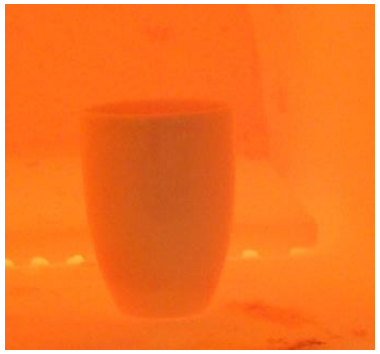
Literature search



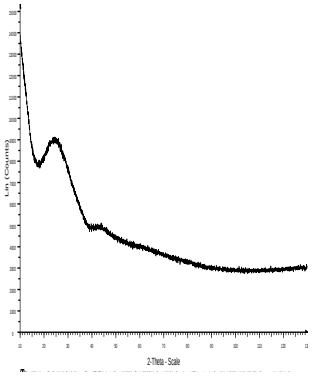
4. Initial Uranium vitrification studies

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
7% Fe	Fe_2O_3	0.100
1.5% Cr	Cr_2O_3	0.022
1% Al	$Al(OH)_3$	0.029
U(VI)	$Na_2U_2O_7$	0.736
U(IV)	UO_2	0.111
^{60}Co	CoO	6.30×10^{-8}
^{95}Nb	Nb_2O_5	1.26×10^{-9}
^{95}Zr	ZrO_2	2.45×10^{-3}
^{106}Ru	RuO_2	9.14×10^{-4}
^{125}Sb	Sb_2O_3	3.41×10^{-6}
^{137}Cs	$CsOH.H_2O$	1.03×10^{-5}
^{144}Ce/ ^{239}Pu	CeO_2	1.59×10^{-3}
^{144}Pr	Pr_6O_{11}	6.15×10^{-4}
^{154}Eu/ ^{155}Eu	Eu_2O_3	2.13×10^{-5}
^{90}Sr	SrO	5.73×10^{-4}
Se	SeO_2	3.72×10^{-5}
Y	Y_2O_3	3.35×10^{-4}
Mo	MoO_3	6.34×10^{-4}
Rh	Rh_2O_3	2.45×10^{-4}
Pd	PdO	1.24×10^{-4}
Ag	AgO	2.38×10^{-6}
Cd	CdO	5.32×10^{-6}
Sn	SnO_2	1.34×10^{-5}
Te	TeO_2	1.81×10^{-4}
La	La_2O_3	6.42×10^{-4}
Nd	Nd_2O_3	2.13×10^{-3}
Sm	Sm_2O_3	3.72×10^{-4}
Gd	Gd_2O_3	4.99×10^{-6}
Total surrogate mixture mass		**1.010**

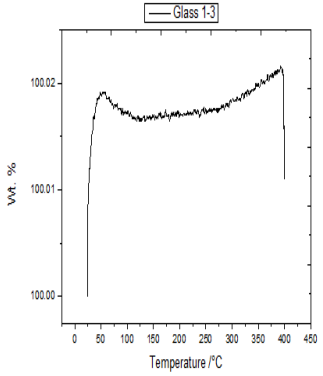
GLASS FRIT (containing 85% Uranium)



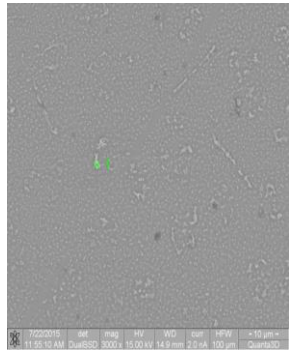
BUTTON MANUFACTURING



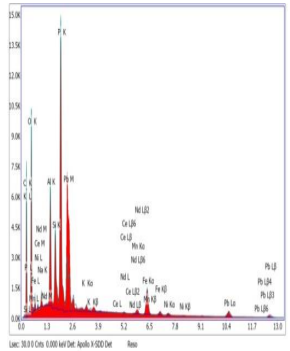
XRD



TGA



SEM



EDX

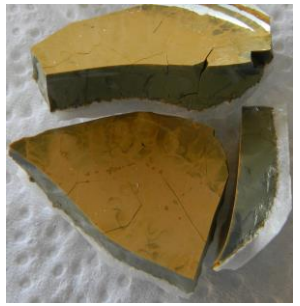
Element	Upper limit on leach rate (g/m²/d)
B	0.06
Na	0.13
Al	0.01
Si	0.03
Ca	0.01
Cr	0.00
Fe	0.00
Ni	0.00
Zn	0.00
Se	0.00
Sr	0.00
Zr	0.00
Ru	0.00
Ag	0.00
Sb	0.08
Cs	0.03
Ba	0.00
Ce	0.00
Nd	0.00
U	0.00

PCT-leaching

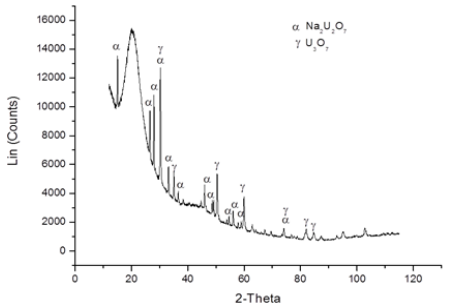
CHARATERIZATION

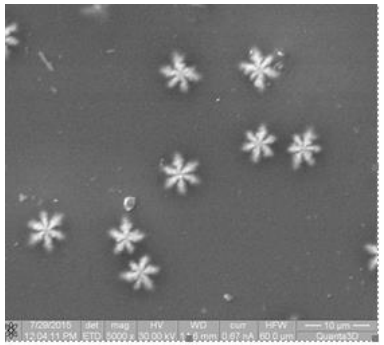
4. Initial Uranium vitrification studies

Properties	WS3-G-03	WS3-G-04	WS3-G-05	WS3-G-06	WS3-G-07
Processing Conditions	Melt	Melt	Melt	Melt	Melt
Process Conditions	1200ºC air	1200ºC air	1200ºC air	1300ºC air	1300ºC air
Target Phases	Sodium alumino borosilicate-3	Sodium alumino borosilicate-4	Sodium alumino borosilicate-5	Phosphate *P_2O_5: PbO (Average 1:1)*	Phosphate *P_2O_5: PbO (Average 1:1)*
Waste Form Properties					
Waste Form Density (g/mL)	2.07 g/cm^3	3.25 g/cm^3	3.36 g/cm^3	3.6 g/cm^3	3.6 g/cm^3
Waste Loading (wt.% as oxide)	20	20	40	10	20
Compressive Strength	29 Mpa	28.5 Mpa	29 Mpa	25 Mpa	25 Mpa
Thermal Stability	<0.5%	<0.5%	<0.5%	<0.5%	<0.5%
Chemical Durability	PASS	PASS	PASS	PASS	PASS
PCT-B test at 90°C for 7 days	PASS	PASS	PASS	PASS	PASS



sodium diuranate





5. Upscaled vitrification using RF technology in modified glovebox

Special glovebox for high mass of Uranium to be vitrified

5. Upscaled conditioning using RF technology

USA Type Borosilicate glass matrix (24 wt% loading)

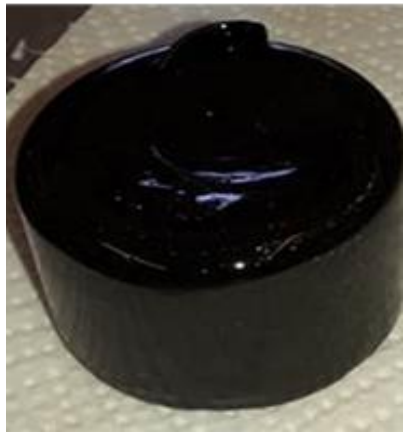
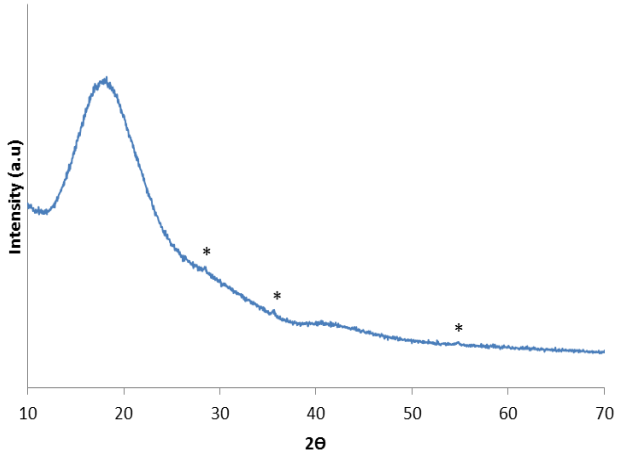
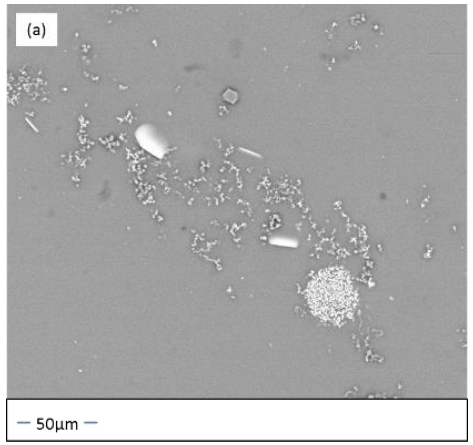


Table 3-15 Glass properties for WS1-G-01	
Physical property	Value
Diameter (mm)	41
Height (mm)	30
Mass (g)	157.70
Volume (cm^3)	49.1
Density (g/cm^3)	3.21*
Compressive strength (MPa)	34

Element	Upper limit on leach rate ($g/m^2/d$)
B	0.06
Na	0.13
Al	0.01
Si	0.03
Ca	0.01
Cr	0.00
Fe	0.00
Ni	0.00
Zn	0.00
Se	0.00
Sr	0.00
Zr	0.00
Ru	0.00
Ag	0.00
Sb	0.08
Cs	0.03
Ba	0.00
Ce	0.00
Nd	0.00
U	0.00





WS1-G-01 indicating a predominantly amorphous structure with very weak peaks (*) assigned to RuO_2 (JCPDS 03-065-2824).

5. Upscaled conditioning using RF technology

USA Type Borosilicate glass matrix (24 wt% loading)

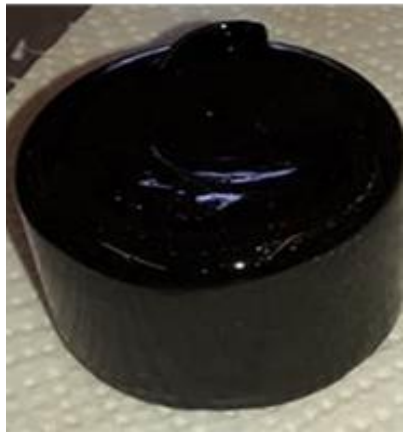
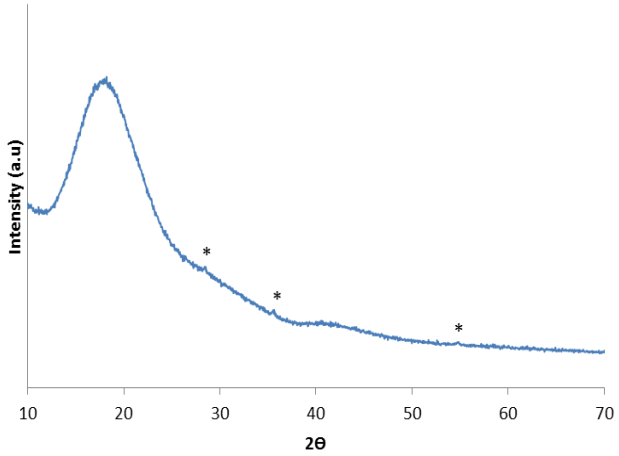
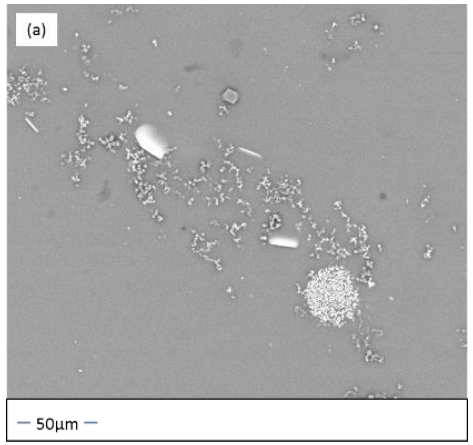


Table 3-15 Glass properties for WS1-G-01	
Physical property	Value
Diameter (mm)	41
Height (mm)	30
Mass (g)	157.70
Volume (cm^3)	49.1
Density (g/cm^3)	3.21*
Compressive strength (MPa)	34

Element	Upper limit on leach rate ($g/m^2/d$)
B	0.06
Na	0.13
Al	0.01
Si	0.03
Ca	0.01
Cr	0.00
Fe	0.00
Ni	0.00
Zn	0.00
Se	0.00
Sr	0.00
Zr	0.00
Ru	0.00
Ag	0.00
Sb	0.08
Cs	0.03
Ba	0.00
Ce	0.00
Nd	0.00
U	0.00





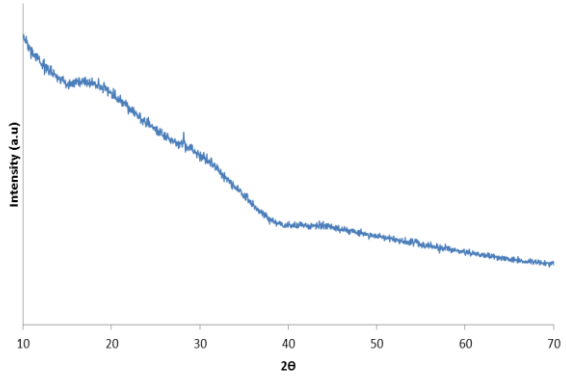
WS1-G-01 indicating a predominantly amorphous structure with very weak peaks (*) assigned to RuO_2 (JCPDS 03-065-2824).

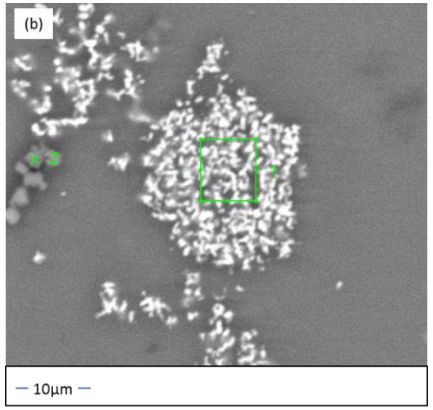
5. Upscaled conditioning using RF technology

Loffler type glass matrix (24 wt% loading)

Table 3-25 Physical properties for Glass WS1-G-03	
Physical property	Value
Diameter (mm)	41
Height (mm)	34
Mass (g)	152.0
Volume (cm^3)	50
Density (g/cm^3)	3.04*
Compressive strength (MPa)	34

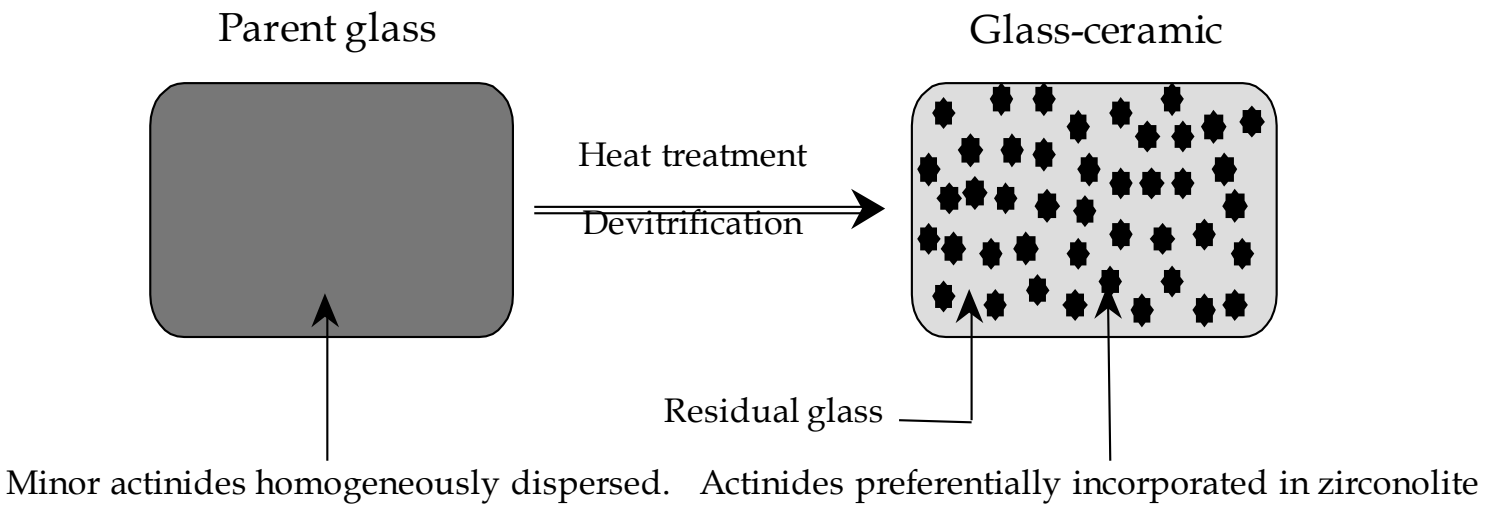
Element	Upper limit on leach rate ($g/m^2/d$)
B	0.10
Na	0.07
Al	0.01
Si	0.04
Ca	0.00
Cr	0.00
Fe	0.00
Ni	0.00
Zn	0.00
Se	0.00
Sr	0.00
Zr	0.00
Ru	0.00
Ag	0.00
Sb	0.16
Cs	0.02
Ba	0.00
Ce	0.00
Nd	0.00
U	0.00

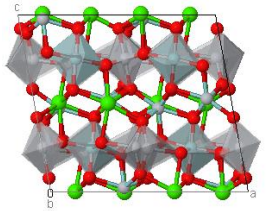




WS1-G-03 indicating a predominantly amorphous structure with very weak peaks (*) assigned to RuO_2 (JCPDS 03-065-2824).

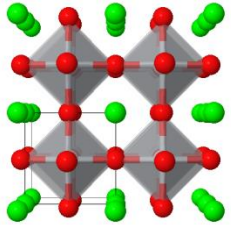
6. Composite glasses for U and FP





Zirconolite: 30%

Act^{3+}, Ln



Perovskite: 20%

Na, Act^{4+}, Ln

Content

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2. Alkaline reprocessing of MTR fuel (Research Reactor)
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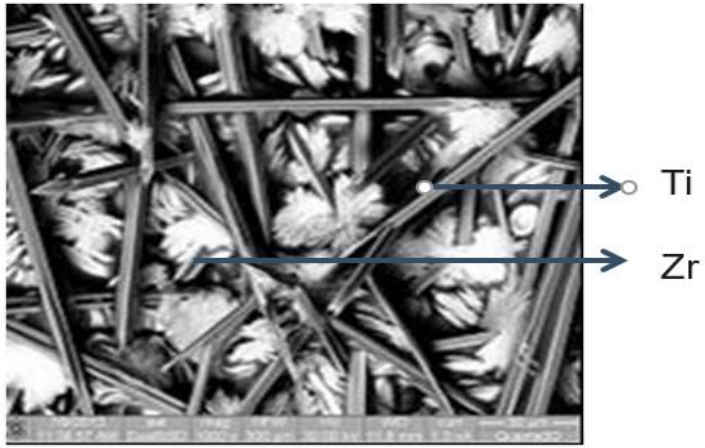
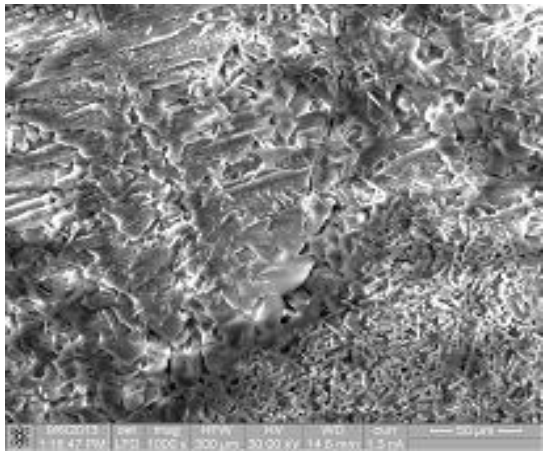
5. Upscaled conditioning using RF technology
6. Composite glasses for U and FP
7. Conclusion

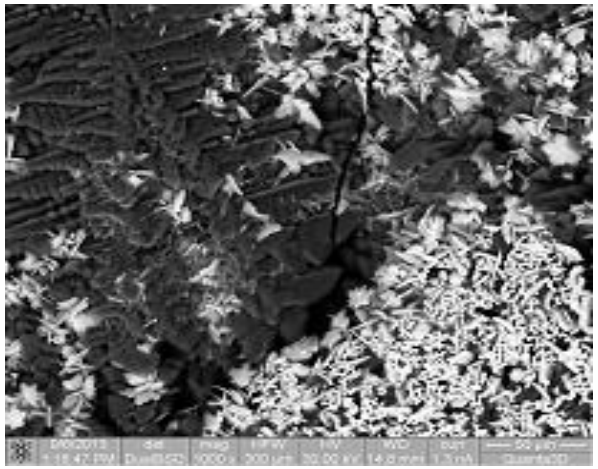
6. Composite glasses for U and FP



GCM (borosilicate glass) containing
10% Titanate : 10% Zirconia



GCM (borosilicate glass) containing
20% Titanate : 10% Zirconia



GCM (borosilicate glass) containing
10% Titanate : 20% Zirconia

GCM (lead iron phosphate glass) containing
10% Titanate : 10% Zirconia

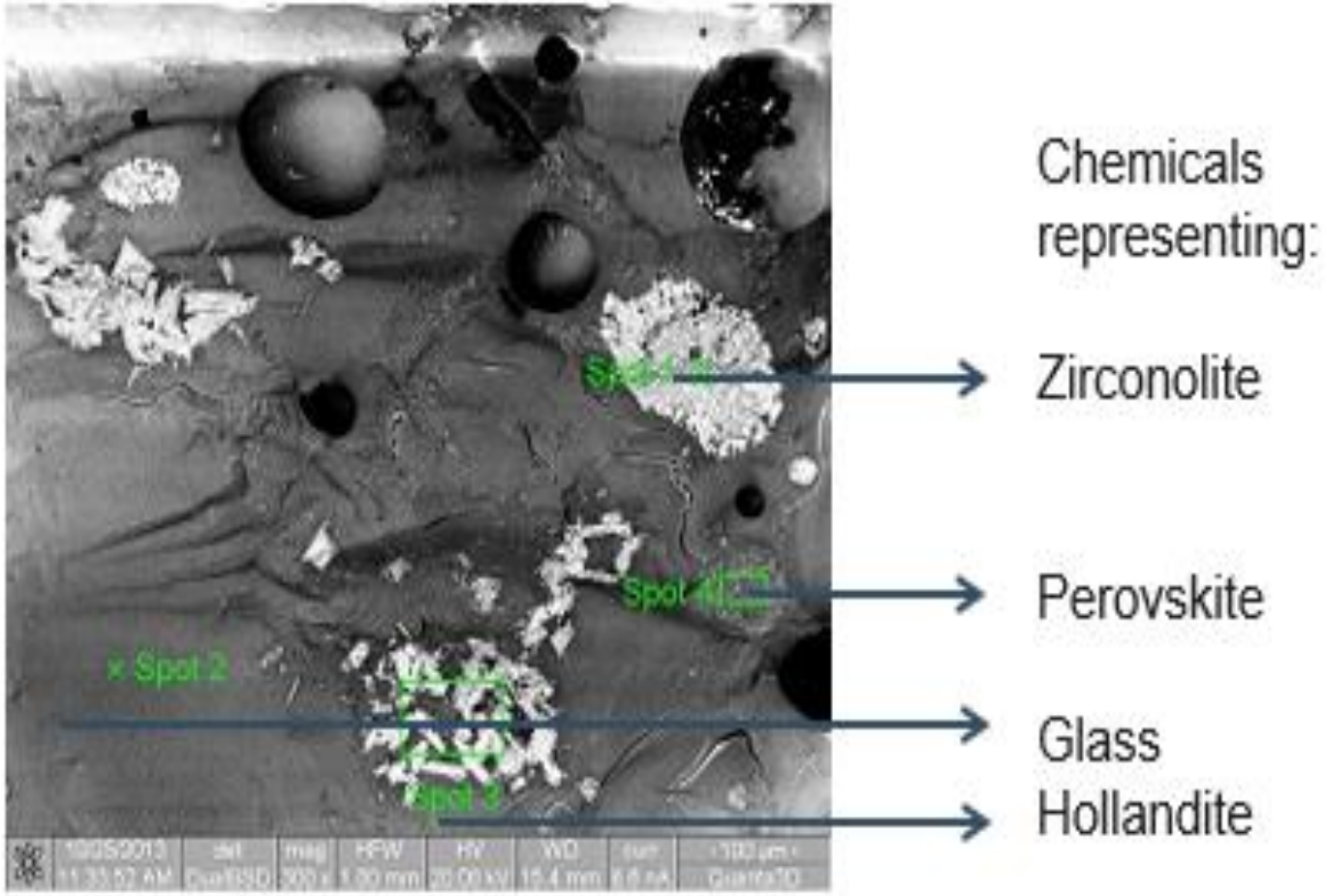
6. Composite glasses for U and FP

Al borosilicate glass with ceramic forming components added

43.3 Wt% SiO_2 : 6.3 Wt% B_2O_3 :
18.8 Wt% Al_2O_3 : 2.5 Wt% CaO :
7.5 Wt% BaO : 3.4 Wt% Na_2O :

Basic chemicals to form

6.0 Wt% Perovskite
6.0 Wt% Hollandite
6.0 Wt% Zirconolite



SEM image of Glass-ceramic matrix:300x Mag

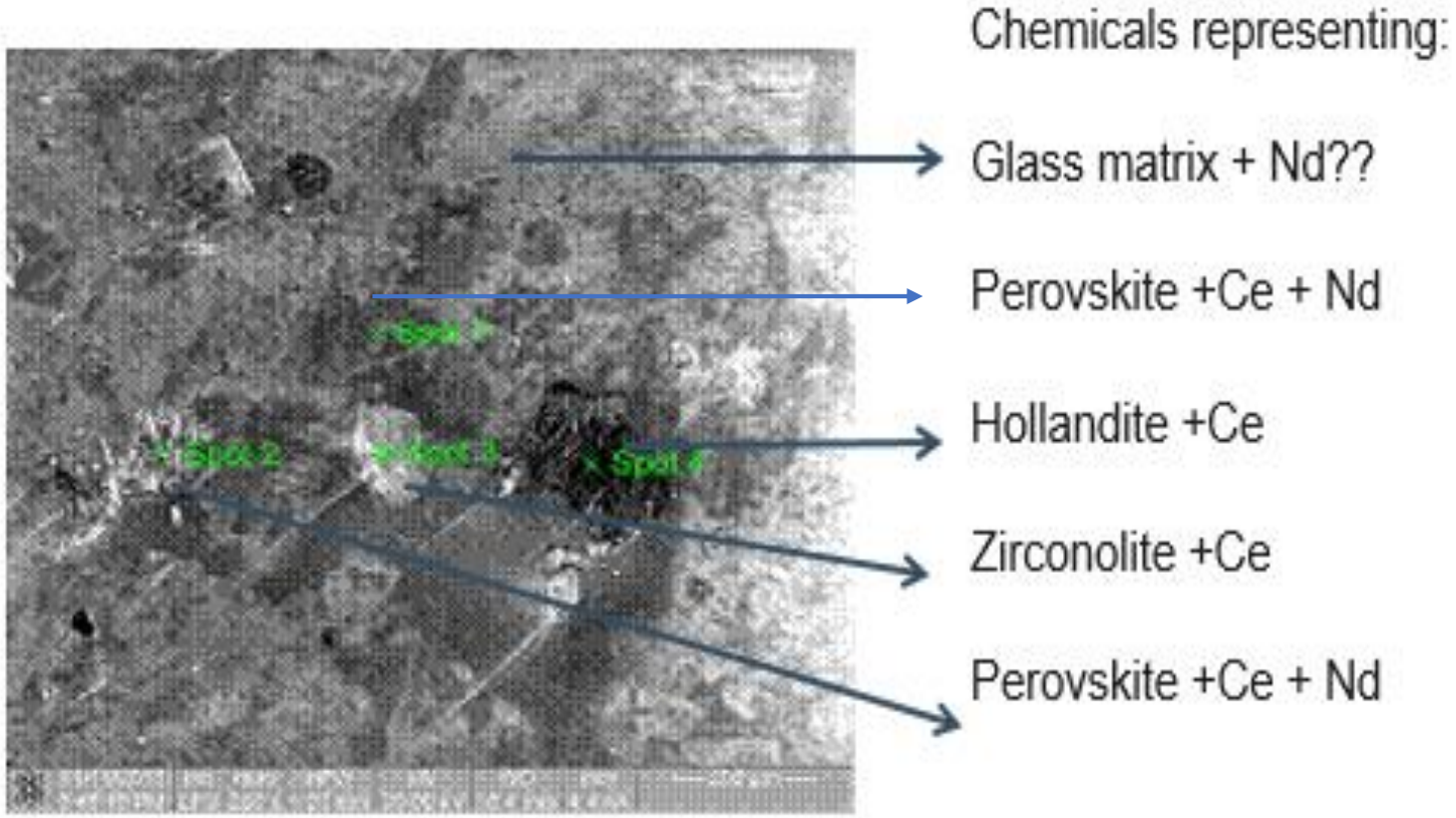
6. Composite glasses for U and FP

Al borosilicate glass with real ceramic-forming components and two FP's

43.3 Wt% SiO_2 : 6.3 Wt% B_2O_3 :
18.8 Wt% Al_2O_3 : 2.5 Wt% CaO :
7.5 Wt% BaO : 3.4 Wt% Na_2O :
4.8 Wt% Nd_2O_3: 4.0 Wt% CeO_2

Basic chemicals to form

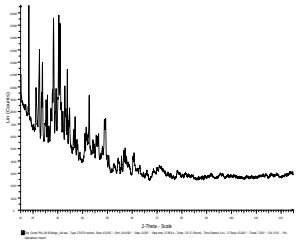
5.0 Wt% Perovskite
5.0 Wt% Hollandite
5.0 Wt% Zirconolite

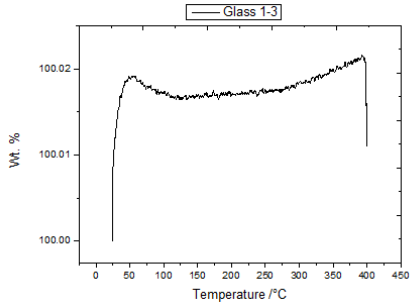


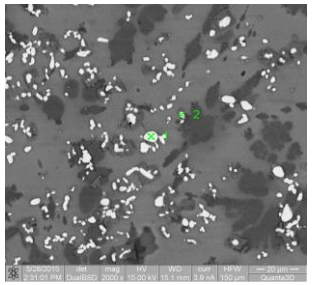
SEM image of GCM with surrogates:250 x Mag

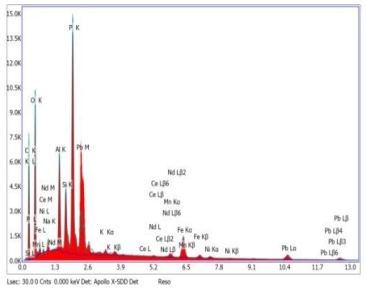
6. Composite glasses for U and FP

Element/ Nuclide	Surrogate compound	Mass of surrogate (g)
7% Fe	Fe_2O_3	0.100
1.5% Cr	Cr_2O_3	0.022
1% Al	$Al(OH)_3$	0.029
U(VI)	$Na_2U_2O_7$	0.736
U(IV)	UO_2	0.111
^{60}Co	CoO	$6.30x10^{-8}$
^{95}Nb	Nb_2O_5	$1.26x10^{-9}$
^{95}Zr	ZrO_2	$2.45x10^{-3}$
^{106}Ru	RuO_2	$9.14x10^{-4}$
^{125}Sb	Sb_2O_3	$3.41x10^{-8}$
^{137}Cs	$CsOH.H_2O$	$1.03x10^{-5}$
$^{144}Ce/\ ^{239}Pu$	CeO_2	$1.59x10^{-3}$
^{144}Pr	Pr_6O_{11}	$6.15x10^{-4}$
$^{154}Eu/\ ^{155}Eu$	Eu_2O_3	$2.13x10^{-5}$
^{90}Sr	SrO	$5.73x10^{-4}$
Se	SeO_2	$3.72x10^{-5}$
Y	Y_2O_3	$3.35x10^{-4}$
Mo	MoO_3	$6.34x10^{-4}$
Rh	Rh_2O_3	$2.45x10^{-4}$
Pd	PdO	$1.24x10^{-4}$
Ag	AgO	$2.38x10^{-6}$
Cd	CdO	$5.32x10^{-6}$
Sn	SnO_2	$1.34x10^{-5}$
Te	TeO_2	$1.81x10^{-4}$
La	La_2O_3	$6.42x10^{-4}$
Nd	Nd_2O_3	$2.13x10^{-3}$
Sm	Sm_2O_3	$3.72x10^{-4}$
Gd	Gd_2O_3	$4.99x10^{-6}$
Total surrogate mixture mass		**1.010**









Element	Upper limit on leach rate ($g/m^2/d$)
B	0.06
Na	0.13
Al	0.01
Si	0.03
Ca	0.01
Cr	0.00
Fe	0.00
Ni	0.00
Zn	0.00
Se	0.00
Sr	0.00
Zr	0.00
Ru	0.00
Ag	0.00
Sb	0.08
Cs	0.03
Ba	0.00
Ce	0.00
Nd	0.00
U	0.00

Added Basic chemicals to form
5.0 Wt% Perovskite
5.0 Wt% Hollandite
5.0 Wt% Zirconolite

Properties	WS3-GC-02	WS3-GC-03	WS3-GC-04	WS3-GC-05
Processing Conditions	Melt	Melt	Melt	Melt
Process Conditions	1. 1300 °C, 2. 600 °C, 3. 900 °C In air	1. 1300 °C, 2. 600 °C, 3. 900 °C In air	1. 1300 °C, 2. 600 °C, 3. 900 °C In air	1. 1300 °C, 2. 600 °C, 3. 900 °C In air
Target Phases	Borosilicate glass with 30% Al and 5% perovskite 5% zirconolite	Borosilicate glass with 30% Al and 5% perovskite 5% zirconolite	Brorsilicate glass with 30% Al and 5% perovskite 5% zirconolite	Phospate glass with 30% Al and 5% perovskite 5% zirconolite
Waste Form Properties				
Waste Form Density (g/mL)	2.42 g/cm^3	2.17 g/cm^3	2.01 g/cm^3	2.01 g/cm^3
Waste Loading (wt.% as oxide)	40	38	22	20
Compressive Strength	30MPa	32MPa	35MPa	29 Mpa
Thermal Stability	<0.1%	<0.1%	<0.1%	<1%
Chemical Durability	PASS	PASS	PASS	PASS
PCT-B test at 90°C for 7 days	PASS	PASS	PASS	PASS

7. Summary

Vitrification of Uranium waste

1. Alkaline reprocessing technology possible for Al-U Type fuels
2. Selective removal of enriched U possible (with traces of other activities)
3. High waste loadings of Uranium into glass possible (24% waste - 20 wt. % U previous literature 1.2 %)
4. Glass matrix with 25 wt.% loading pass all WAC requirements for disposal (Compression, stability, leaching)
5. High waste loadings of Uranium into glass-ceramics (composite glasses) possible (24% waste - 12 wt. % U - no available literature values)
6. Glass-ceramic matrix with 12 wt.% loading pass all WAC requirements for disposal (Compression, stability, leaching)

8. References

1. L. Stassen Necsa report AC-UMo0101-REP-10001
2. L. Stassen Necsa report NWR-UMo01-REP-14026
3. Necsa report RC-PVLG-0027 (2007).