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# Nuclear waste immobilisation using glass and crystalline materials

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Joint ICTP-IAEA  
International School on  
Nuclear Waste Vitrification



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# I. Background

TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT OR REVISION OF A RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)

		Case Country A <sup>1</sup>	Case Country B <sup>2</sup>	Case Country C <sup>3</sup>	Case Country D <sup>4</sup>	Case Country E <sup>5</sup>					
Technical options to be considered in strategy formulation stage											
TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT OR REVISION OF A RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)											
		Case Country A <sup>1</sup>	Case Country B <sup>2</sup>	Case Country C <sup>3</sup>	Case Country D <sup>4</sup>	Case Country E <sup>5</sup>					
LILW	TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT OR REVISION OF A RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)										
	Liquid waste (resulting from):	Case Country A <sup>1</sup>	Case Country B <sup>2</sup>	Case Country C <sup>3</sup>	Case Country D <sup>4</sup>	Case Country E <sup>5</sup>					
• Chemical precipitation	Liquid waste conditioning options: • Cementation; • Bituminization; • Polymerization; • Vitrification	All options require consideration	All options require consideration	Some options may be considered	Some options may be considered						
• Evaporation											
• Ion exchange											
• Membrane filtration (filters/membranes)											
• Incineration (sludge)											
Gaseous waste (resulting from):	TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT OR REVISION OF A RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)										
• Off-gas scrubbers	Solid and solidified waste conditioning options: • Packaging; • Containerization; • Overpacking; • High integrity containers	All options require consideration	All options require consideration	All options require consideration	Some options may be considered						
• Filters											
• Gas separation											
• Solid waste											
• Fragmentation											
• Incineration	Storage: • Storage for decay; • Storage awaiting disposal; • Prolonged (long time) storage	All options require consideration	All options require consideration	All options require consideration	Some options may be considered						
• Compactors											
• Melting											
• Disposal of LLW:						All options require consideration	All options may require consideration	Some options may be considered	Some options may be considered	may be considered	Fully required
• Geological repository											
• Disposal of ILW:	Requires consideration	Requires consideration	May be considered	Not applicable	Not applicable	Not applicable	Fully required				
• Geological repository											



TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT OR REVISION OF A RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)

	Case Country A <sup>1</sup>	Case Country B <sup>2</sup>	Case Country C <sup>3</sup>	Case Country D <sup>4</sup>	Case Country E <sup>5</sup>
HLW and spent fuel					
Spent fuel storage: • Wet storage in pools; • Dry storage in containers/vaults	All options require consideration	All options require consideration	All options may require consideration	Not applicable	Not applicable
Spent fuel conditioning for disposal: • Encapsulation; • Overpacking for disposal	All options require consideration	All options require consideration	May be considered	Not applicable	Not applicable
High level solid waste processing: • Fragmentation	Requires consideration	Requires consideration	May be considered	Not applicable	Not applicable
High level liquid waste conditioning: • Vitrification; • Packaging for storage/disposal; • Overpacking	All options require consideration	Not applicable	Not applicable	Not applicable	Not applicable
HLW storage: • Storage awaiting disposal; • Long term storage	All options require consideration	All options require consideration (for spent fuel)	Some options may be considered	Not applicable	Not applicable



TABLE II-3. ELEMENTS TO BE CONSIDERED DURING DEVELOPMENT RADIOACTIVE WASTE MANAGEMENT STRATEGY (cont.)

	Case Country A <sup>1</sup>	Case Country B <sup>2</sup>	Case Country C <sup>3</sup>	Case Country D <sup>4</sup>	Case Country E <sup>5</sup>
Disposal of spent fuel/HLW: • Geological repository with/without retrievability	Requires consideration	Requires consideration (for spent fuel)	Some options may be considered	Not applicable	Not applicable
Disused sealed radiation sources					
Repatriation to the original manufacturer	Requires consideration	Requires consideration	Requires consideration	Requires consideration	Not applicable
Processing: • Encapsulation; • Immobilization in metal matrix	All options require consideration	All options require consideration	All options require consideration	All options require consideration	Not applicable
Conditioning for storage and disposal:	Requires	Requires	Requires	Requires	Not applicable

<sup>1</sup> Radioactive waste from nuclear power plants, front and back end fuel cycle facilities, wide use of nuclear R&D facilities, and extensive nuclear applications in industry and medicine.

<sup>2</sup> Radioactive waste from nuclear power plants, wide use of nuclear R&D facilities, extensive nuclear applications in industry and medicine. No fuel cycle facilities.

<sup>3</sup> Radioactive waste from limited use of nuclear R&D facilities, research reactor, limited use of nuclear applications in industry and medicine. No nuclear power plant, no fuel cycle facilities.

<sup>4</sup> Radioactive waste from limited use of nuclear applications in industry and medicine. No reactors, no fuel cycle facilities, no nuclear R&D.

<sup>5</sup> Only NORM waste is generated.

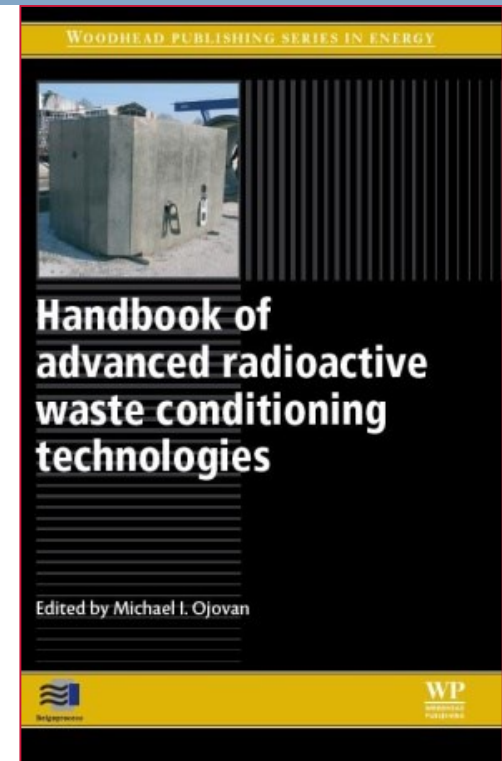
## II. Vitreous and crystalline wasteforms

The *wasteform* is the waste in its physical and chemical form after treatment and/or immobilization (resulting in a solid product) prior to packaging.

**A number of matrices have been used for waste immobilization and those include glass, ceramic, cement, polymer and bitumen.**

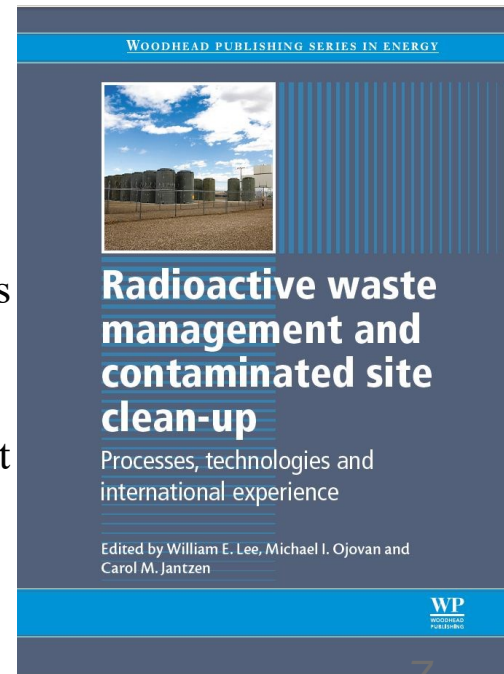
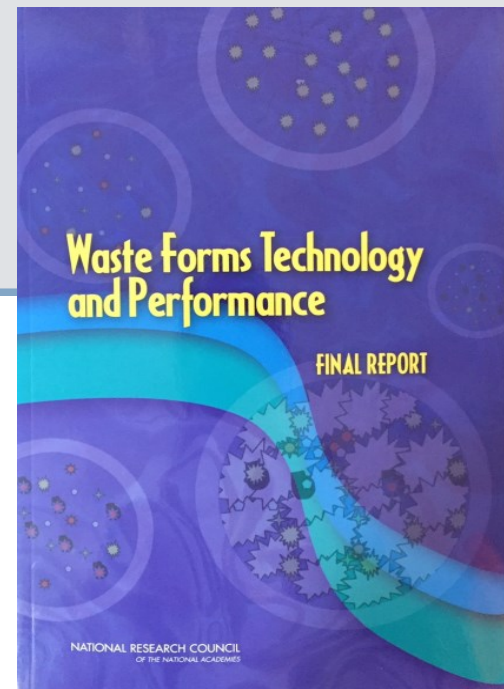
Radioactive and chemically hazardous constituents of waste can be immobilized into a wasteform material through two processes:

- (1) Bound into the material at atomic scale (*chemical incorporation*), or
- (2) Physically surrounded and isolated by the material (*encapsulation*).



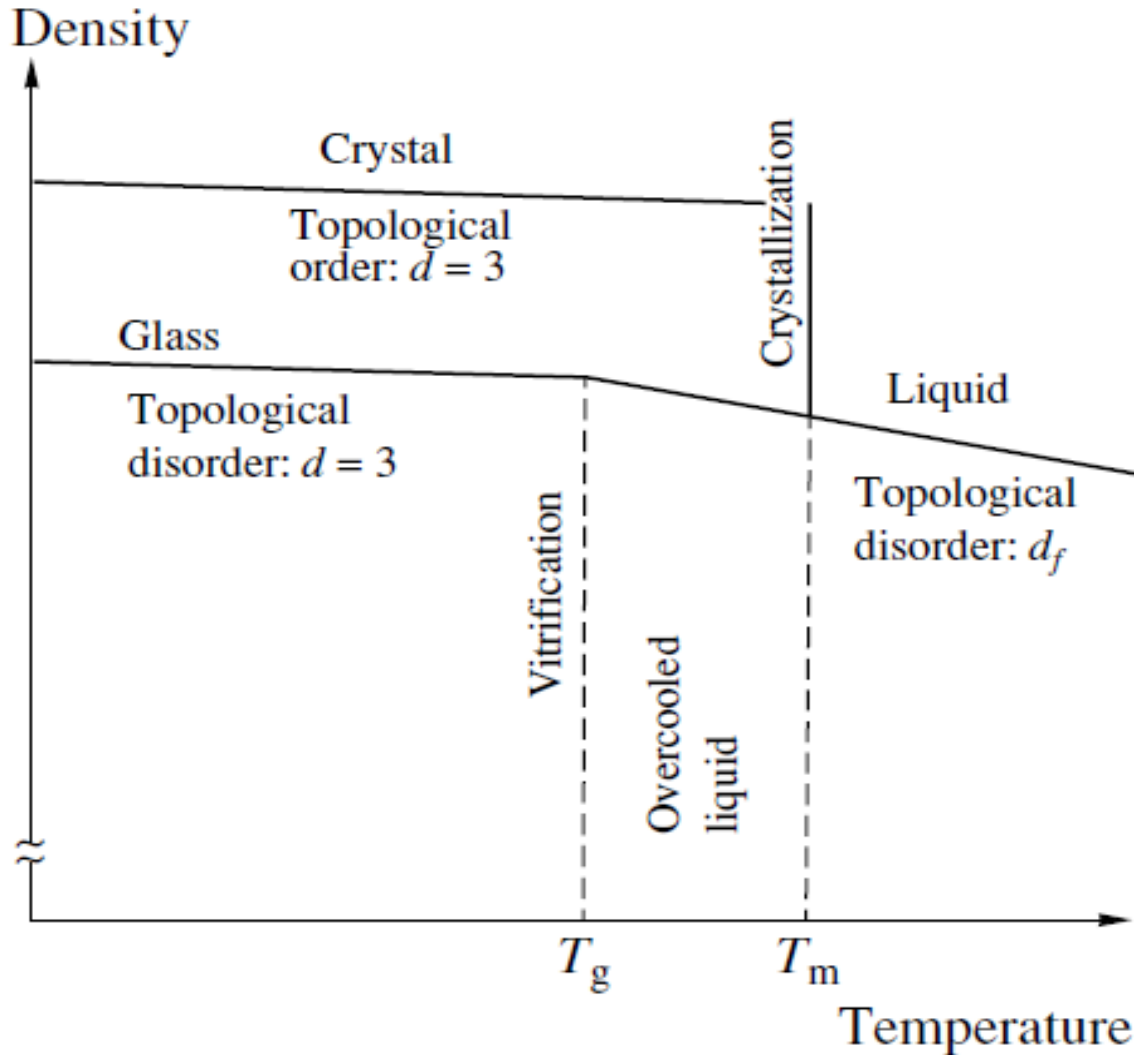
## Important factors for wasteform materials:

- **Waste loading;**
  - able to accommodate a significant amount of waste (typically 25-45 weight %) to minimize volume.
- **Ease of production;**
  - accomplished under reasonable conditions.
- **Durability;**
  - low rate of dissolution to minimize the release of radioactive and chemical constituents.
- **Radiation stability;**
  - high tolerance to radiation effects from the decay of radioactive constituents.
- **Chemical flexibility;**
  - able to accommodate a mixture of radioactive and chemical constituents with minimum formation of secondary phases.
- **Availability of natural analogues;**
  - availability of natural mineral or glass analogues may provide important clues about the long-term performance.
- **Compatibility with the intended disposal environment.**
  - compatible with the near-field environment of the disposal facility.



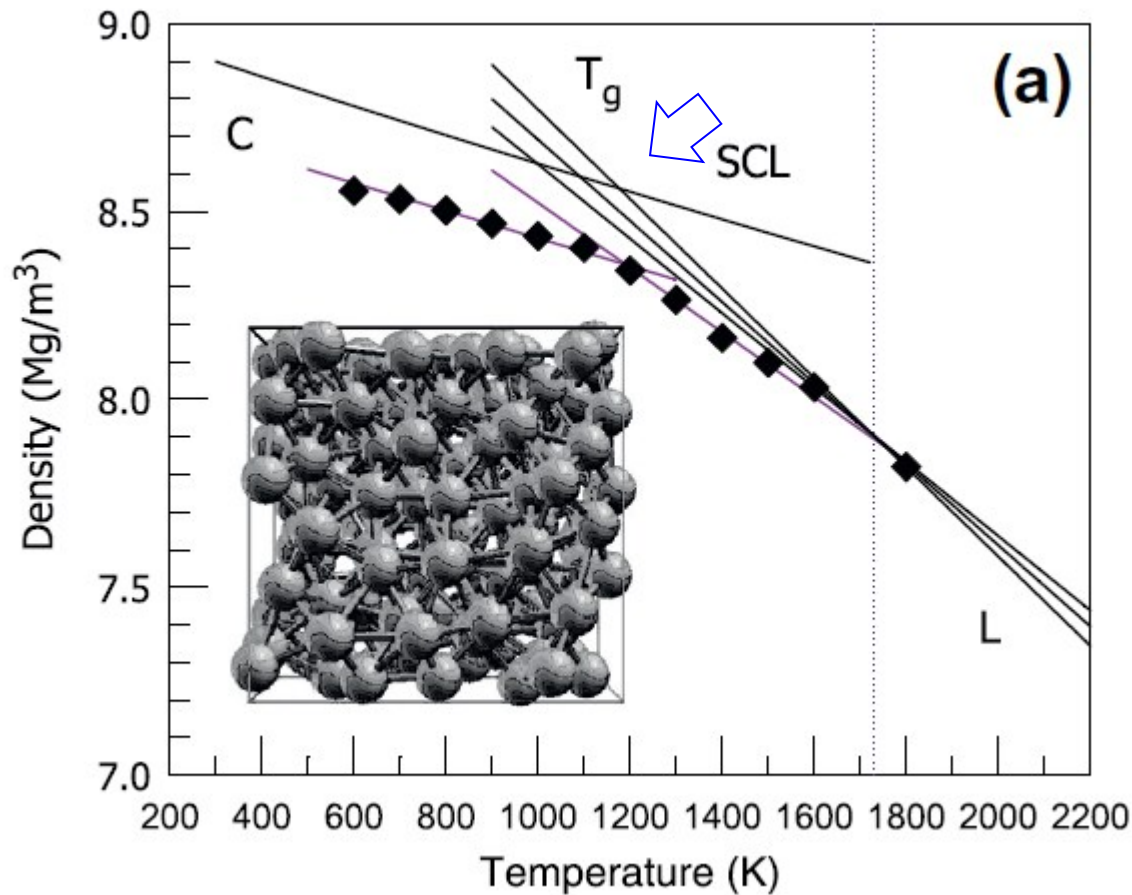
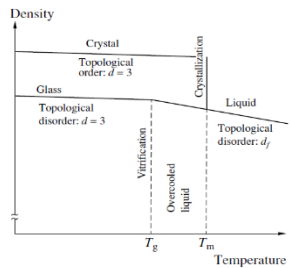
Wasteform	Features	Limitations	Secondary waste
<p><b>Glasses</b></p> <p><b>Vitrification</b></p>	<p>Proven method to condition liquid HLW as well as ILW and LLW</p> <p>High flexibility in terms of the glass formulation range</p> <p>High reliability of the immobilization process</p> <p>High glass throughput</p> <p>High durability of the final wasteform</p> <p>Small volume of the resulting wasteform</p>	<p>High initial investment and operational costs</p> <p>Complex technology requiring high qualified personnel</p> <p>Generally not economical for LLW and ILW</p> <p>Need to control off-gases</p> <p>Need to control variations in waste feed</p> <p>High specific energy consumption</p>	<p>Off-gases</p> <p>Filters. Scrub Solutions</p> <p>Used Melters</p> <p style="text-align: center;"><b>1</b></p>
<p><b>Ceramics</b></p>	<p>Possible to incorporate higher levels of actinides than borosilicate glass</p> <p>Waste form is more stable and hence is more durable than glass</p> <p>Expected to be suitable for long term isolation since it simulates natural rocks</p>	<p>Limited experience. Most efforts have been research-based. There are not known commercial installations in operation at present. Generally considered not economical for LLW and ILW. The ceramic (e.g. Synroc) waste form must be tailored to suit the particular characteristics of the nuclear waste to be immobilized</p>	<p>Filters</p> <p>Off-gases</p> <p>Scrub Solutions</p> <p style="text-align: center;"><b>2</b></p>
<p><b>Glass-composite materials</b></p>	<p>Combine features of both crystalline and glassy materials. Higher waste loading.</p> <p>Higher compatibility</p> <p>Higher stability compared glasses</p>	<p>Limited experience</p> <p style="text-align: center;"><b>1</b> + <b>2</b></p>	<p>Off-gases</p> <p>Filters. Scrub Solutions</p> <p>Used Melters</p>





Glasses are solid amorphous materials which transform into liquids upon heating through the glass transition e.g. *the solid-like behaviour of glasses is separated from liquid-like behaviour at higher temperatures by the glass transition temperature,  $T_g$ .*

**Fig. 2.** Changes in the density and Hausdorff dimension of the bond network for configurons in crystalline and amorphous materials depending on temperature.

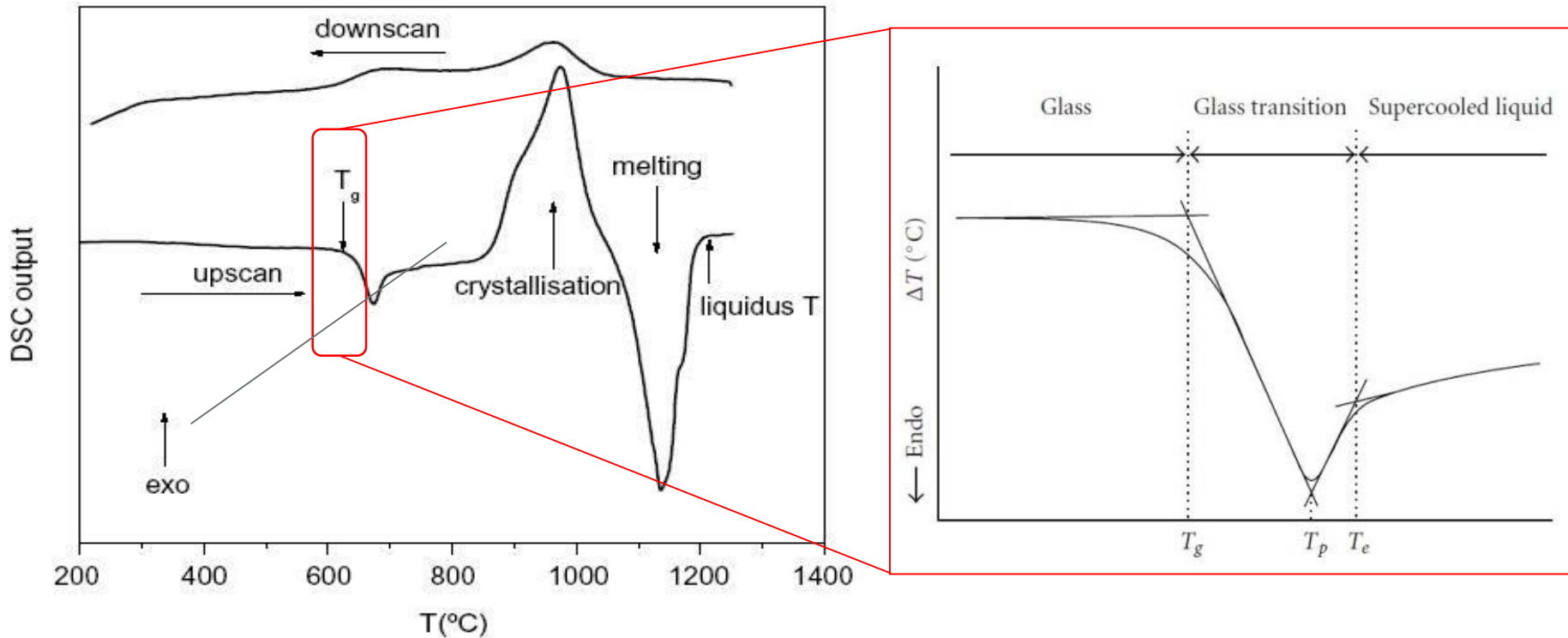


**Fig. 1.** (a) Solid lines – density versus temperature diagram for Ni according to literature data. Diamonds represent the results of ab initio MD simulation. Several plots for liquid Ni represent data from different literature sources. The insert – atomic structure of Ni cell obtained in an MD simulation at 1000 K. The dotted line represents the liquidus temperature. The data for (a) is taken from Ref. [11] with

*D.V. Louzguine-Luzgin / Journal of Alloys and Compounds 586 (2014) S2–S8*

Liquid-glass transition has been considered as a **second order phase transition** in which a supercooled melt yields, on cooling, a glassy structure and properties similar to those of crystalline materials e.g. of an isotropic solid material.

Y. Yue / *Journal of Non-Crystalline Solids* 345&346 (2004) 523–527



Differential scanning calorimetric (DSC) measurements on a basaltic glass. 'Exo' means exothermic response to the heating or cooling process. The measurements are performed in argon at the heating and cooling rate 20°C/min.

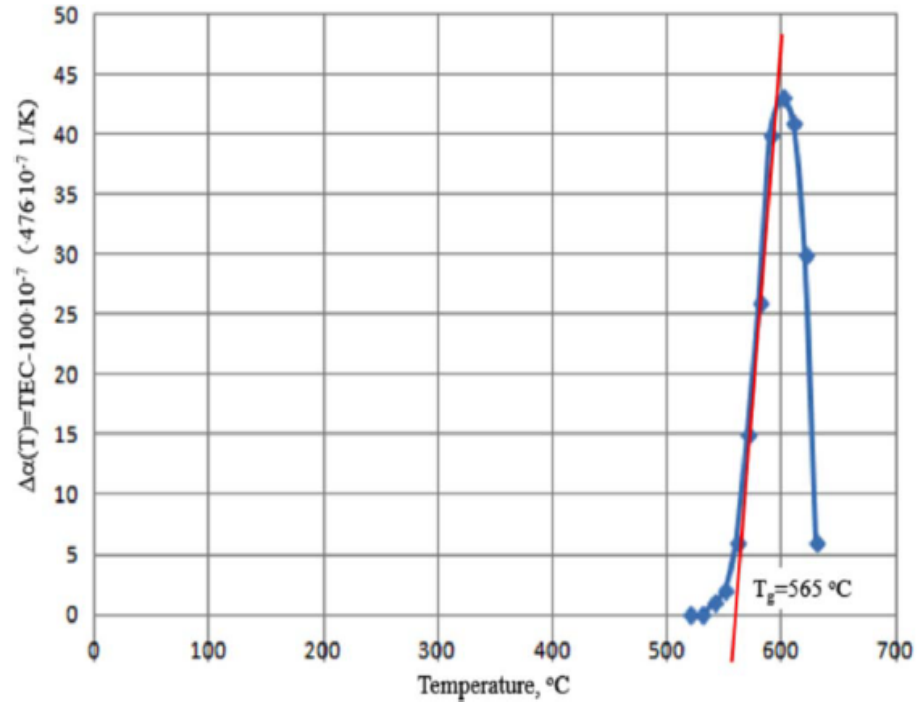
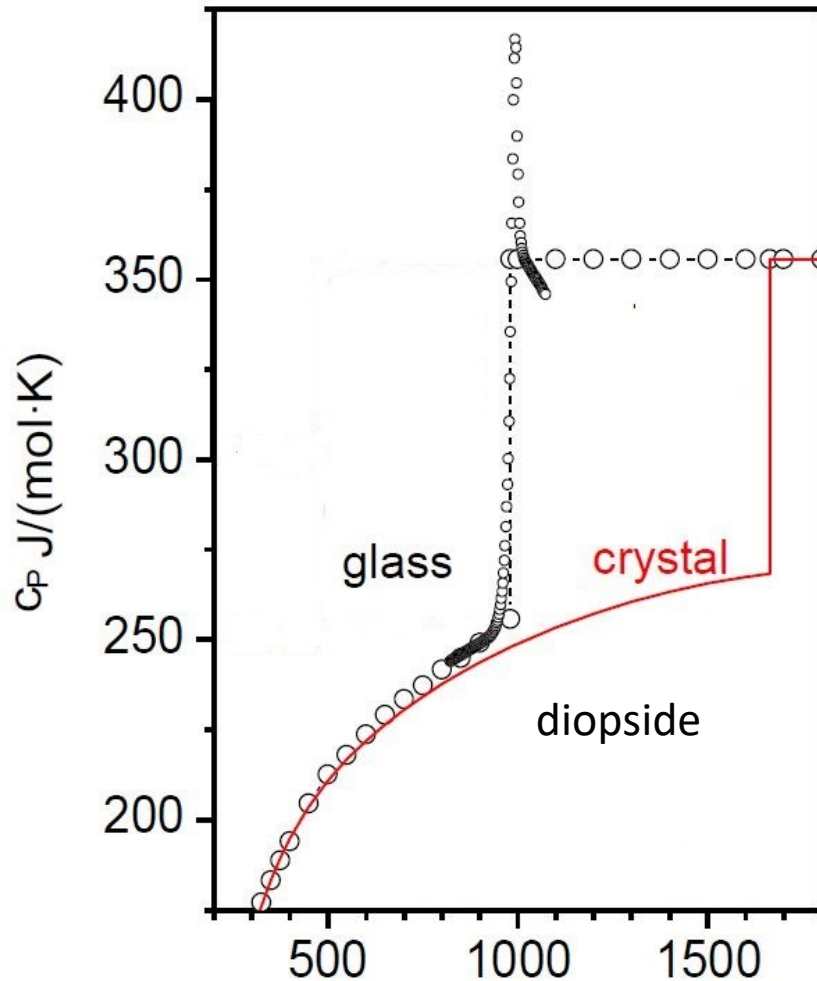
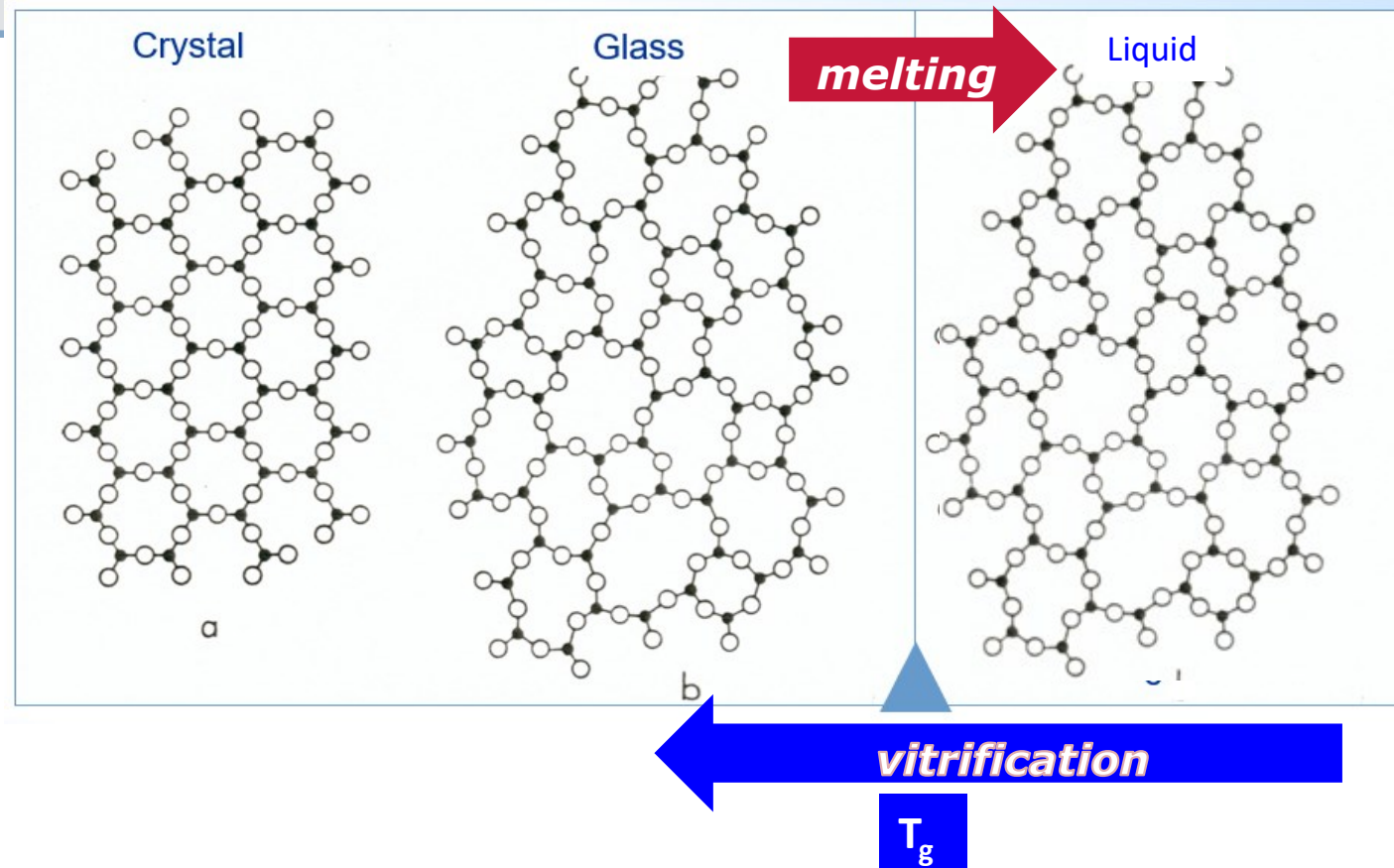


Fig. 4.1. Temperature dependence of deviation of thermal expansion coefficient (TEC) from its value in the glassy state  $\Delta\alpha(T) = \text{TEC} - 100 \cdot 10^{-7}$  of a high-sodium borosilicate glass 60.  $\text{SiO}_2 \cdot 10 \cdot \text{B}_2\text{O}_3 \cdot 3 \cdot \text{Al}_2\text{O}_3 \cdot 20.5 \cdot \text{ZrO}_2 \cdot 20 \cdot \text{Na}_2\text{O}$  designed for nuclear waste immobilisation near the glass transition temperature  $T_g = 565^{\circ}\text{C}$  (given in units of  $476 \cdot 10^{-7} 1/\text{K}$ ).

M.I. Ojovan / Journal of Non-Crystalline Solids 382 (2013) 79–86

$$C_p, \alpha_{\infty} \frac{1}{|T - T_g|^{0.59}}$$

# What is structural difference between a Glass and an Liquid?



Glasses are typically formed on rapid cooling of melts so avoiding crystallisation since little time is allowed for the ordering processes.



C. A. Angell and K. J. Rao, "Configurational excitations in condensed matter, and the "bond lattice" model for the liquid-glass transition," *The Journal of Chemical Physics*, vol. 57, no. 1, pp. 470–481, 1972.

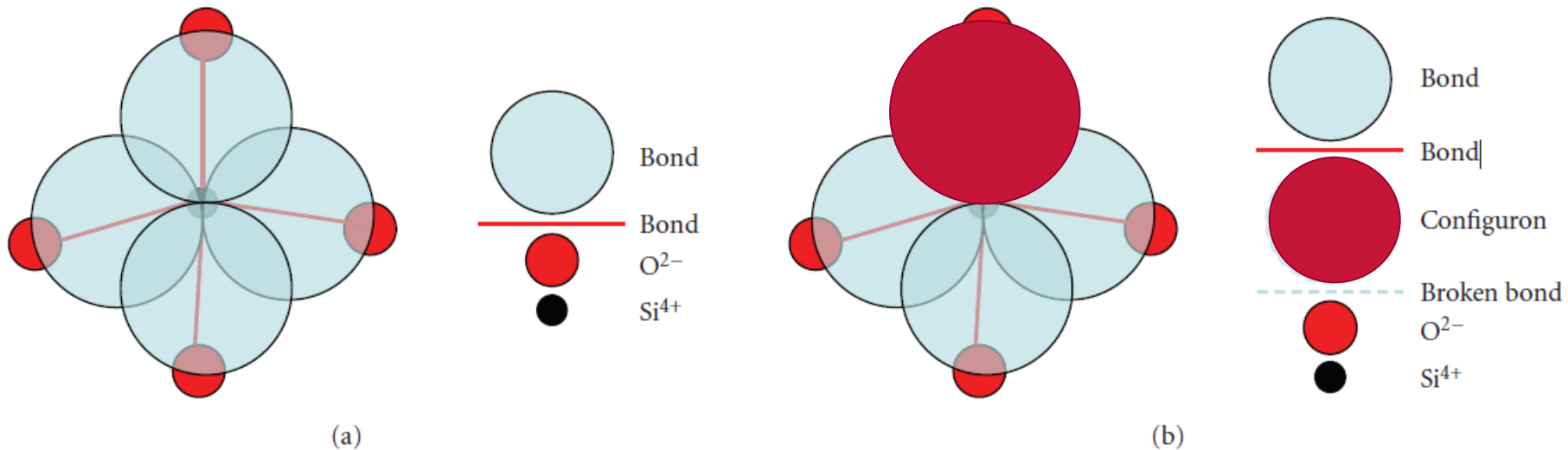


FIGURE 12: (a) Schematic of 4 covalent bonds (b) and one broken bond in SiO<sub>2</sub>.

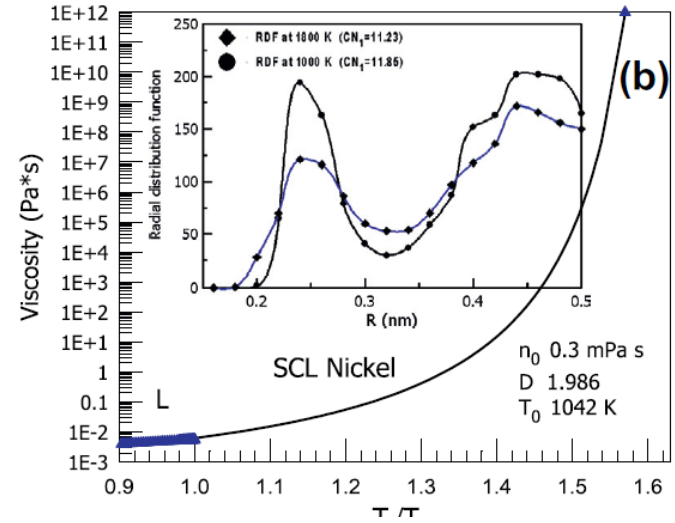
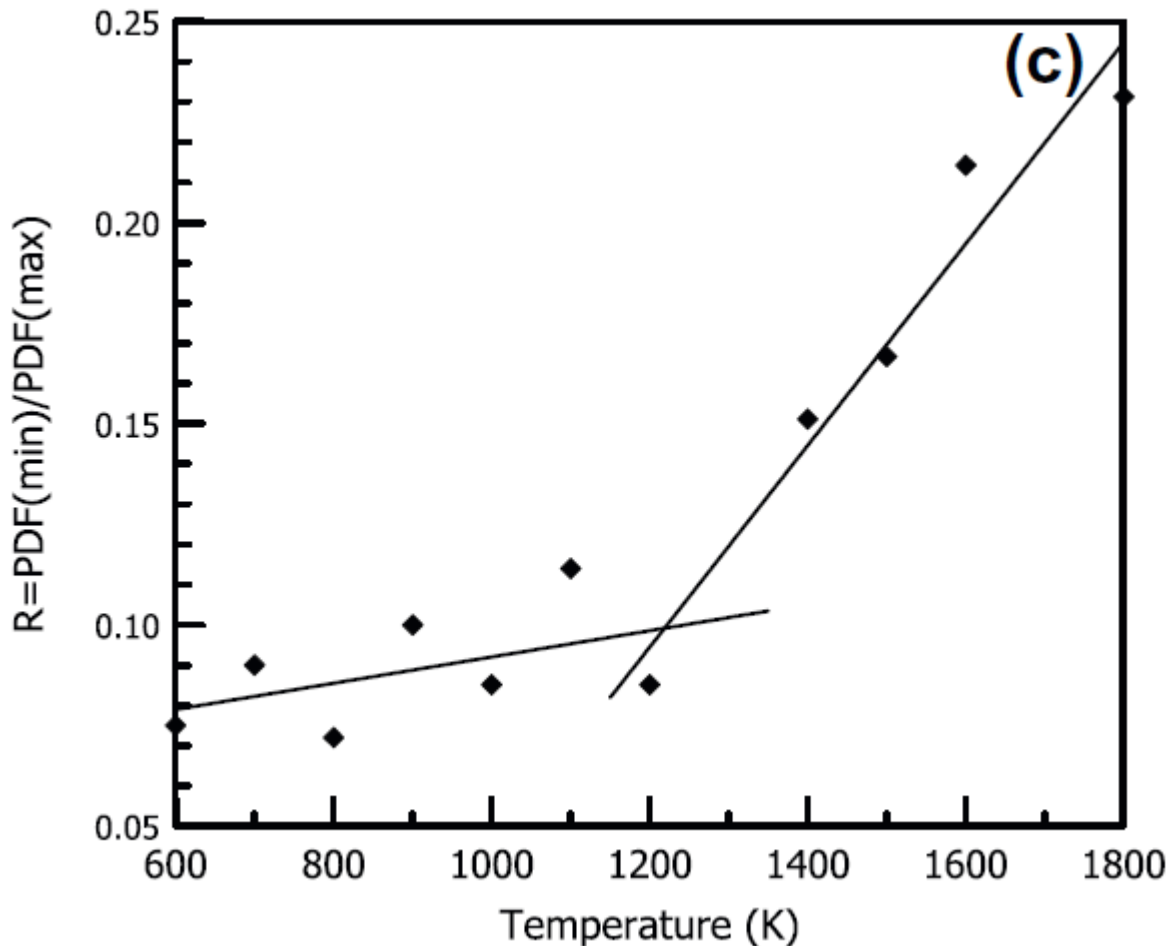
Advances in Condensed Matter Physics  
Volume 2008, Article ID 817829, 23 pages  
doi:10.1155/2008/817829



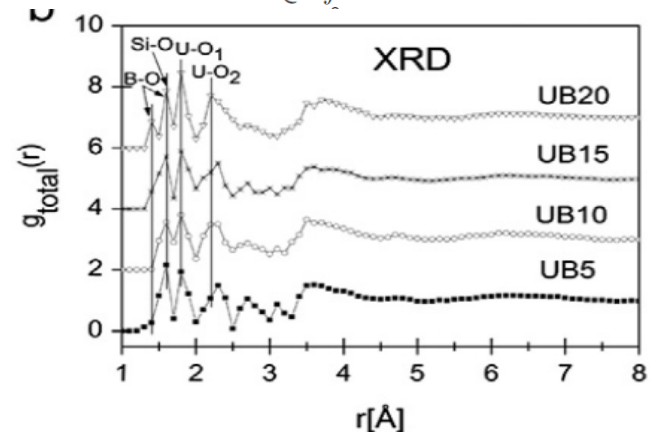


*D.V. Louzguine-Luzgin / Journal of Alloys and Compounds 586 (2014) S2–S8*

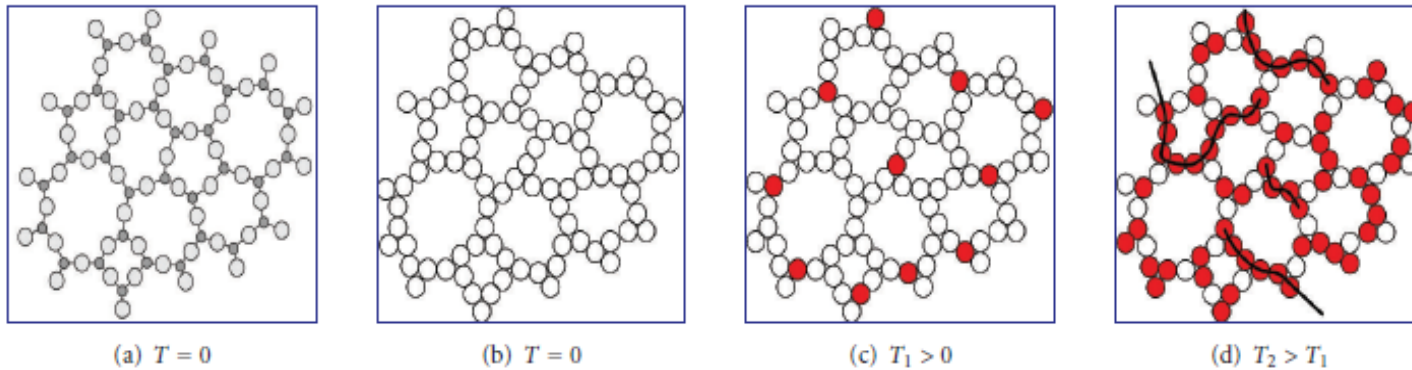
$$\mathfrak{R} = \text{PDF}(R)_{\min} / \text{PDF}(R)_{\max}$$



$$S_{ij}(Q) = 1 + \frac{4\pi\rho_0}{Q} \int_0^{r_{\max}} r [g_{ij}(r) - 1] \sin Qr dr,$$



*M. Fábián et al. / Journal of Non-Crystalline Solids 380 (2013) 71–77*



$T_g$

$$C_p, \alpha \propto \frac{1}{|T - T_g|^{0.59}}$$

FIGURE 11: Schematic of disordered bond lattice model of an amorphous material: (a) distribution of atoms in amorphous phase at  $T = 0$ ; (b) distribution of bonds in amorphous phase at  $T = 0$ ; (c) distribution of bonds in amorphous phase at  $T_1 > 0$ ; (d) distribution of bonds in amorphous phase at higher temperatures  $T_2 > T_1$  when configuron clustering occurs.

M.I. Ojovan. Viscosity and Glass Transition in Amorphous Oxides, *Advances in Condensed Matter Physics*, **2008**, Article ID 817829, 23 pages (2008). <http://www.hindawi.com/journals/acmp/2008/817829/ref/>

$$T_g = \frac{H_d}{S_d + R \ln [(1 - \phi_c) / \phi_c]}$$

Physica B 523 (2017) 96–113

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Physica B

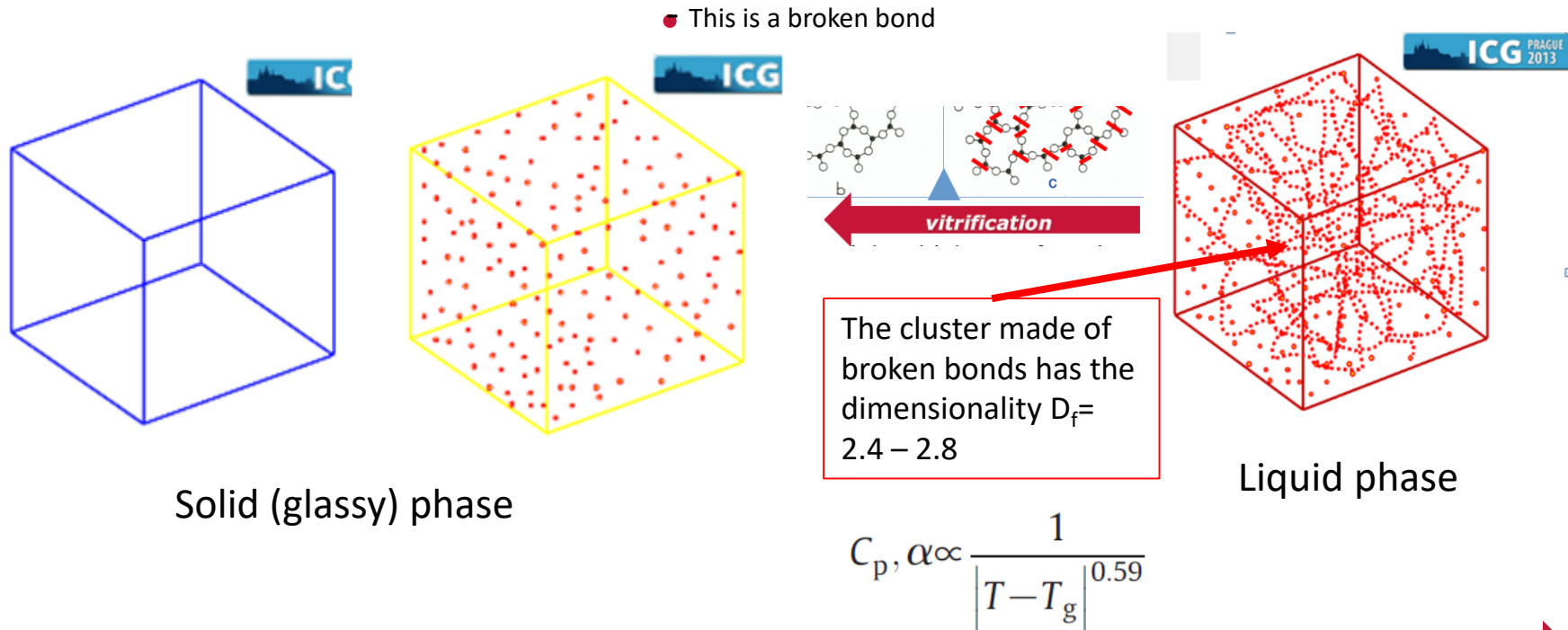
journal homepage: [www.elsevier.com/locate/physb](http://www.elsevier.com/locate/physb)

On relaxation nature of glass transition in amorphous materials  
Damba S. Sanditov<sup>a,b</sup>, Michael I. Ojovan<sup>c,d,\*</sup>

Physica B **523** (2017) 96–113: The glass transition belongs to a class of critical phenomena generically termed **topological phase transitions** which are amenable to the scaling approach and characterised by diverging length and time at the transition.

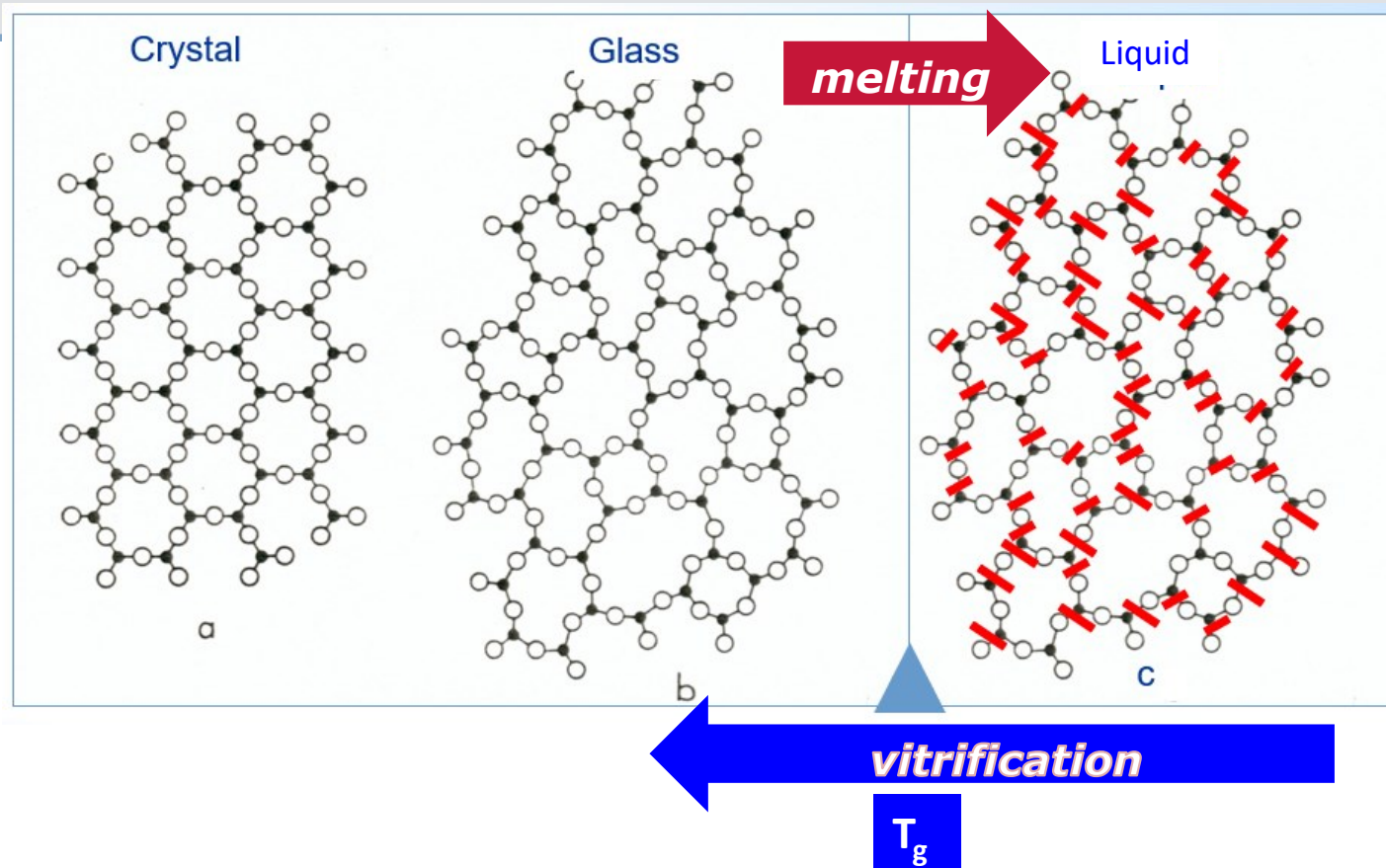
Structurally the difference between glasses and liquids become evident for broken bonds (configurons).

They form percolation clusters in liquids, whereas in glasses they are point-type defects

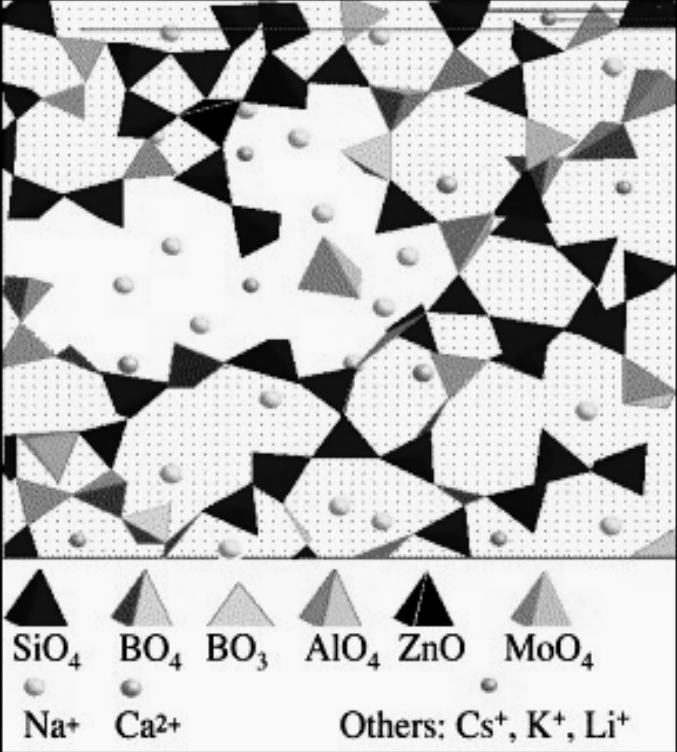


**melting**

M.I. Ojovan / Journal of Non-Crystalline Solids 382 (2013) 79–86



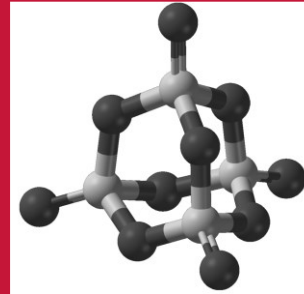
Structurally the difference between glasses and liquids becomes evident if we consider broken bonds!

Type of Glass	Major Structural Components		Comments
<p style="text-align: center;"><b>Alkali Borosilicate</b></p>	<p><math>(\text{SiO}_4)^{-4}</math>, <math>(\text{BO}_4)^{-5}</math>, <math>(\text{BO}_3)^{-3}</math> and some <math>(\text{AlO}_4)^{-5}</math> and <math>(\text{FeO}_4)^{-5}</math> structural units to which alkali, alkaline earth, and waste species bond.</p>	<p>Atomic structure of a French nuclear waste glass: unshaded region shows formation of a <math>(\text{Na,Cs})_2\text{MoO}_4</math> cluster.</p> 	<p>Ease of processing, melt temperatures 1150-1200°C to minimize volatility; cold cap production if feasible minimizes volatility; most waste cations highly soluble in glass; overall waste solubility 25-40 wt%; made by Joule Heated Melting (JHM), Advanced JHM known as AJHM, Cold Crucible Induction Melting (CCIM) or Hot Isostatic Pressing (HIP).</p>

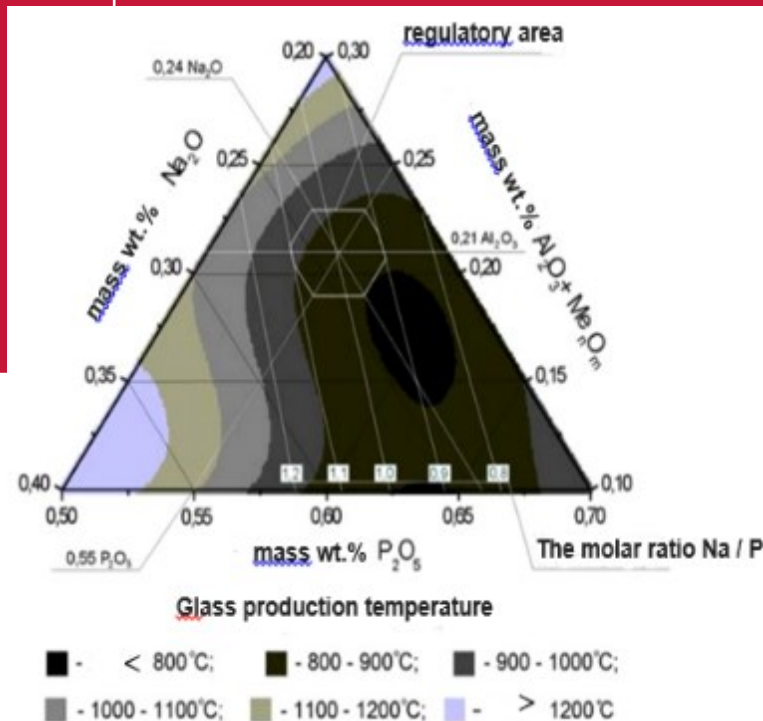
# Alkali Aluminophosphate

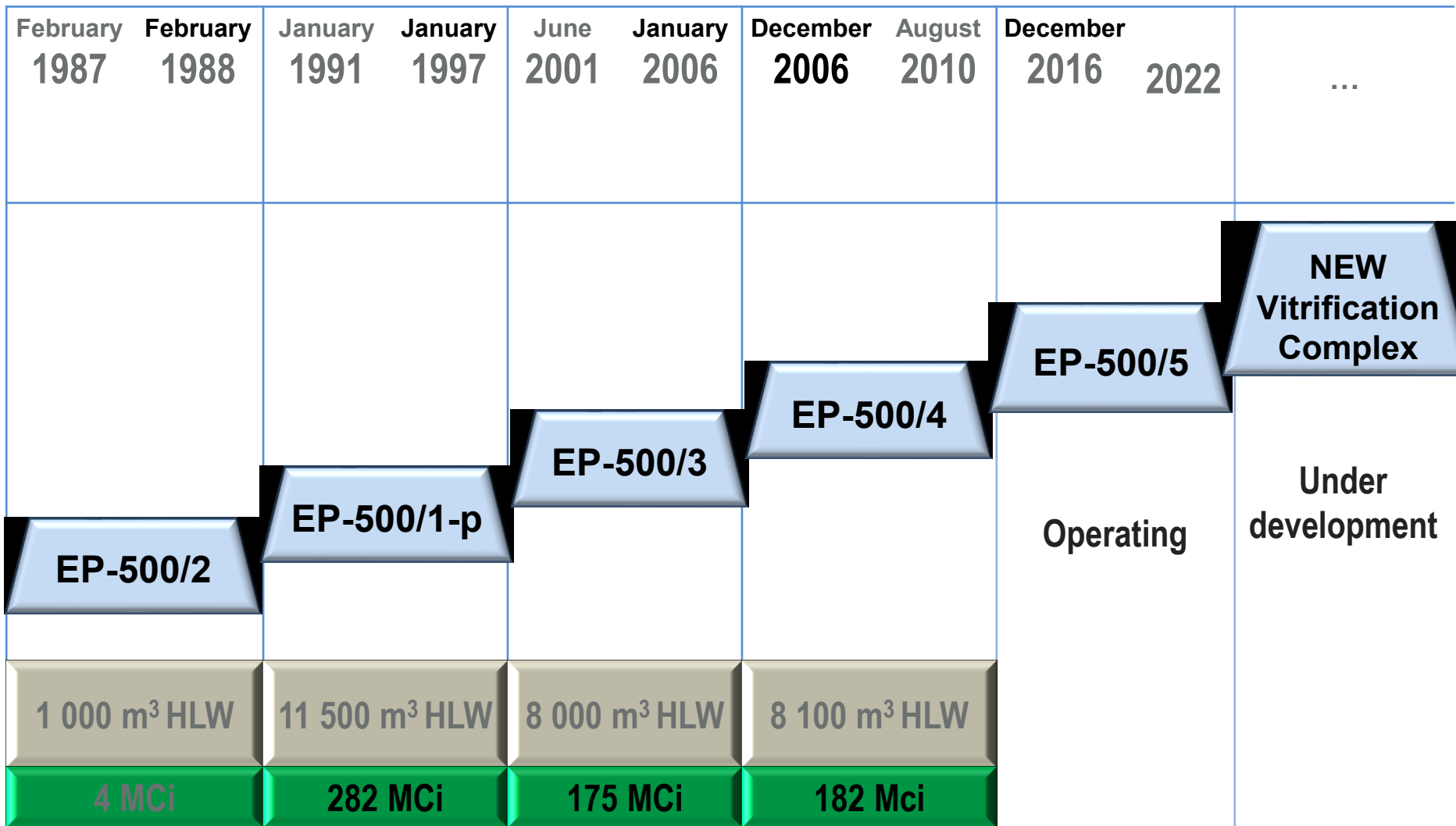
$(PO_4)^{-3}$  and  $(AlO_4)^{-5}$  structural units to which alkali, alkaline earth, and waste species bond

Atomic structure of phosphate glass with  $P_4O_{10}$  cage like structures which provides the basic building block for phosphate glass formers.



Melts at lower temperatures than silicate or borosilicate systems; most cations readily incorporated; accommodates >10 wt% sulfate; corrosive to materials of construction; tendency to devitrify; durability comparable to borosilicate glass if alumina content is sufficient; composition ~ 24-27 Na<sub>2</sub>O, 20-24, Al<sub>2</sub>O<sub>3</sub> + Me<sub>m</sub>O<sub>n</sub>, 50-52 P<sub>2</sub>O<sub>5</sub> where Me<sub>m</sub>O<sub>n</sub> is an actinide or rare earth oxide; JHM, AJHM, CCIM.

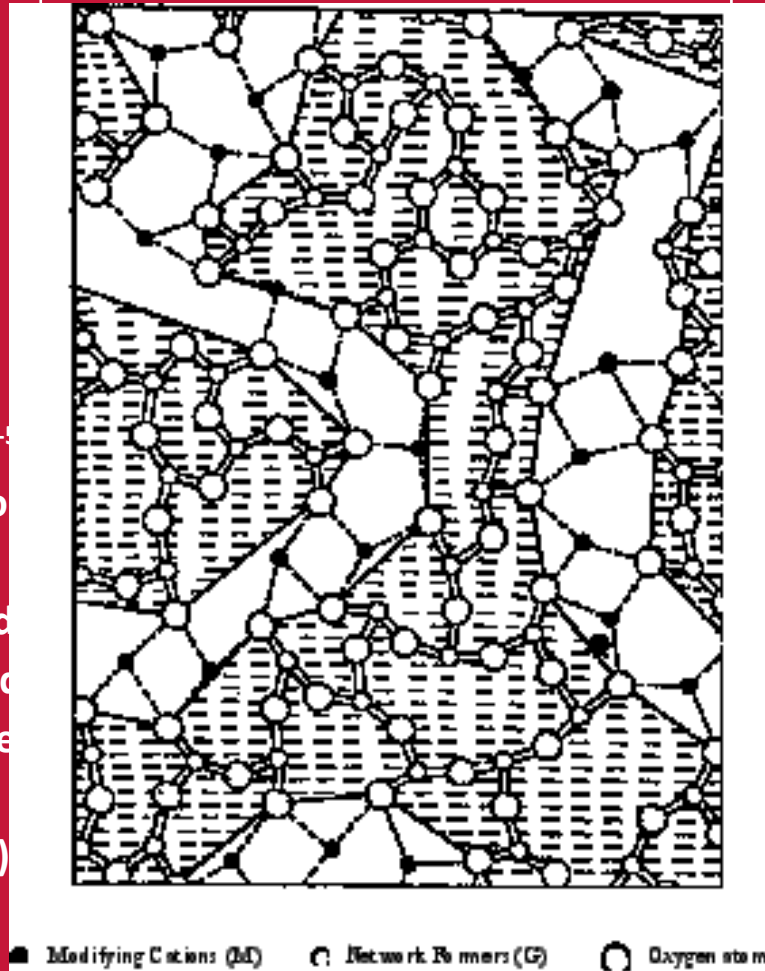




Aluminosilicate  
glasses  
and/or  
alkali  
aluminosilicate  
glasses

$(\text{SiO}_4)^{-4}$  and  $(\text{AlO}_4)^{-5}$  structural units to which alkali, alkaline earth, and waste species bond – (similar structure to borosilicate glasses when  $(\text{BO}_4)^{-5}$  are present)

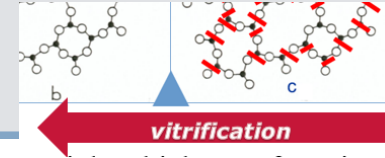
Atomic structure of a simple generic  $\text{M}_2\text{O}_3(\text{G}_2\text{O}_3)_2$  glass (M is modifying cations, G represents tetrahedral cations). The shaded regions are the PR regions. The un-shaded regions represent the percolation channels or DR regions (from ).



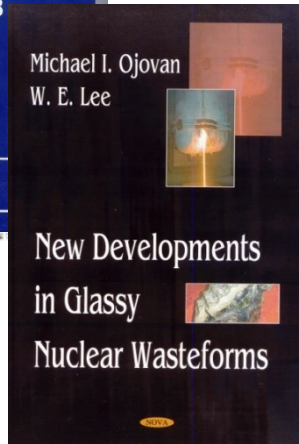
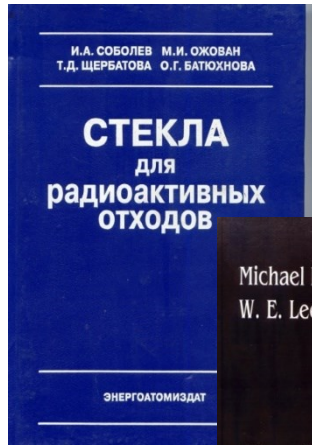
Melt temperature of 1600°C causes volatilization of radionuclides; waste loading dependent on rapid cooling, e.g. 10 wt%  $\text{UO}_2$  if cooled rapidly while 10 wt% if cooled slowly; improved durability over borosilicate glass; CIM, HIP



Waste vitrification is attractive because of:



- High capability of glass to immobilise various elements,
- Simple production technology adapted from glass production industry,
- Small volume of the resulting wasteform,
- High chemical durability of glasses in natural environment and
- High tolerance of glasses to radiation damage.



## Vitrification of Radioactive Wastes

Nuclear energy continues to receive considerable attention as a potential solution to issues such as global warming. However, the management of radioactive nuclear waste remains an obstacle to a true 'Nuclear Renaissance.'

James C. Marra\* and Michael I. Ojovan\*\* discuss.

Glass International April 2014

### Vitrification:

Vitrify: to convert (something) into glass or a glass-like substance, typically by exposure to heat.

Late Middle English: From French vitrifier or based on Latin vitrum 'glass'.

Facility	Waste type	Melting process	Operational period	Performance
R7/T7, La Hague, France	HLW	IHC <sup>1</sup>	1989/1992	6555 tonnes in 16885 canisters, 262·10 <sup>6</sup> TBq to 2012
AVM, Marcoule, France	HLW	IHC	1978 – 2012	1357 tonnes in 3306 canisters, 22·10 <sup>6</sup> TBq to 2012
R7, La Hague, France	HLW	CCM <sup>2</sup>	2010 –	GCM: U-Mo glass 76 tonnes in 190 canisters to 2012
WVP, Sellafield, UK	HLW	IHC	1990 –	2200 tonnes in 5615 canisters, 33·10 <sup>6</sup> TBq to 2012
DWPF, Savannah River, USA	HLW	JHCM <sup>3</sup>	1996 –	6300 tonnes in 3591 canisters, 1.8·10 <sup>6</sup> TBq to 2012
WVDP, West Valley, USA	HLW	JHCM	1996 – 2002	570 tonnes in 570 canisters, 0.9·10 <sup>6</sup> TBq
EP-500, Mayak, Russia	HLW	JHCM	1987 –	~6200 tonnes, 643 10 <sup>6</sup> Ci
CCM, Mayak, Russia	HLW	CCM	Pilot plant	18 kg/h by phosphate glass
Pamela, Mol, Belgium	HLW	JHCM	1985 – 1991	500 tonnes in 2201 canisters, 0.5·10 <sup>6</sup> TBq
Karlsruhe, Germany	HLW	JHCM	2009 – 2010	55 tonnes in 140 canisters, 0.8·10 <sup>6</sup> TBq
Tokai, Japan	HLW	JHCM	1995 –	70 tonnes in 241 canisters (110 L), 0.4·10 <sup>6</sup> Ci to 2007
Radon, Russia	LILW	JHCM	1987-1998	10 tonnes
Radon, Russia	LILW	CCM	1999	> 30 tonnes
Radon, Russia	ILW	SSV <sup>4</sup>	2001 – 2002	10 kg/h, incinerator ash
Bohunice, Slovakia	HLW	IHC	1997 –	1.53 m <sup>3</sup> in 211 canisters
WIP, Trombay, India	HLW	IHPTM <sup>5</sup>	1985-2002, 2002 –	18 tonnes, 110·10 <sup>3</sup> Ci to 2012
AVS, Tarapur, India	HLW	IHPTM	2006 –	10 tonnes in 100 canisters, 0.15·10 <sup>6</sup> TBq
WIP, Kalpakkam, India	HLW	JHCM	Testing	
WTP, Hanford, USA	LLW	JHCM	1998 –	~ 1000 tonnes to 2000
VPC, SEPEC Site, China	HLW	JHCM	Testing	
Taejon, Korea	LILW	CCM	Testing	

Michael I. Ojovan  
William E. Leo  
Stepan N. Kalmykov

Third edition

An Introduction to  
**Nuclear Waste  
Immobilisation**



- Radiation durability of glass is very high and is above orders of GGy.

250

An Introduction to Nuclear Waste Immobilisation

**Table 17.2** Typical Properties of Glasses for Nuclear Waste Immobilisation

Glass Type	Density (g/cm <sup>3</sup> )	Compressive Strength, (MPa)	NR <sup>a</sup> (10 <sup>-6</sup> g/cm <sup>2</sup> day)	TEC <sup>b</sup> , (1/K)	T <sub>max</sub> <sup>c</sup> , K (°C)	Damaging Dose <sup>d</sup> (Gy)
Borosilicate	2.7	22–54	0.3 (Cs) 0.2 (Sr)	8 × 10 <sup>-6</sup>	≥823 (550)	>10 <sup>9</sup>
Phosphate	2.6	9–14	1.1 (Cs) 0.4 (Sr)	1.5 × 10 <sup>-6</sup>	≥723 (450)	>10 <sup>9</sup>

<sup>a</sup>IAEA test protocol for 28th day.

<sup>b</sup>TEC – thermal expansion coefficient.

<sup>c</sup>T<sub>max</sub> is the maximum allowed temperature of glass representing the limit of its thermal stability. T<sub>max</sub> is defined as the temperature above which the radionuclide NR's increase >10<sup>2</sup> times. By definition T<sub>max</sub> < T<sub>g</sub>.

<sup>d</sup>Irradiation has a small impact on glasses and the damaging dose is the absorbed dose above which the radionuclide NRs increase several times.

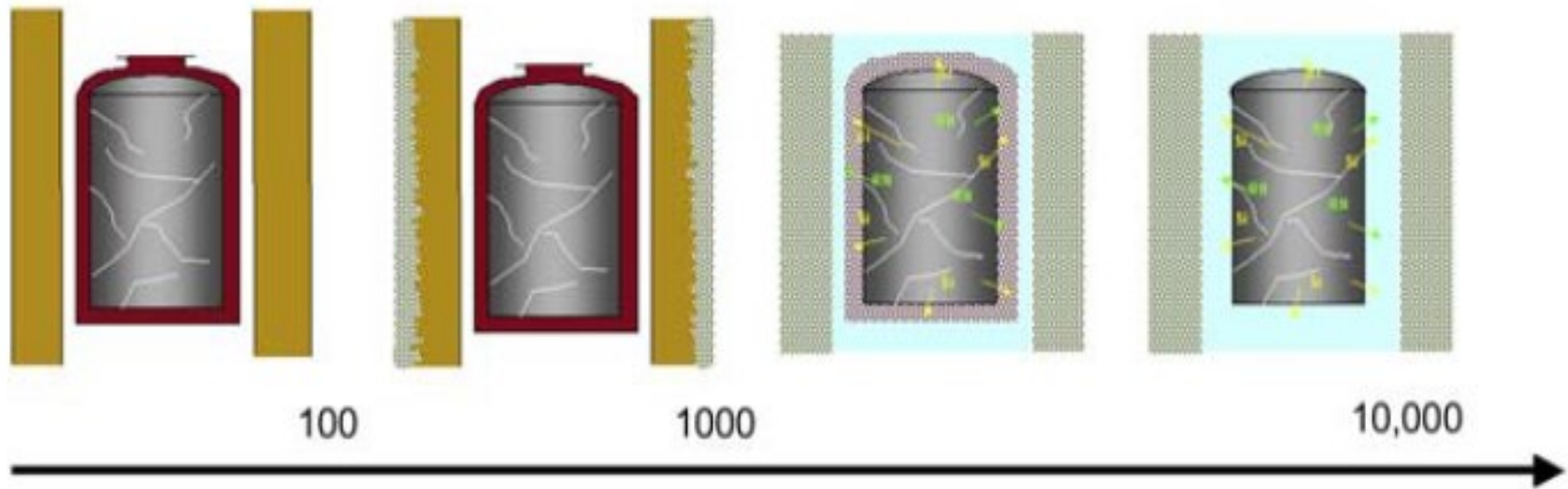


Figure 23.5 Schematic of alteration to packaged glass wasteform in wet repository environment with time (in years). *Courtesy Stephane Gin, CEA France.*

REVIEW ARTICLE OPEN

# A comparative review of the aqueous corrosion of glasses, crystalline ceramics, and metals

Gerald S. Frankel<sup>1</sup>, John D. Vienna<sup>2</sup>, Jie Lian<sup>3</sup>, John R. Scully<sup>4</sup>, Stephane Gin<sup>5</sup>, Joseph V. Ryan<sup>2</sup>, Jianwei Wang<sup>6</sup>, Seong H. Kim<sup>7</sup>, Wolfgang Windl<sup>1</sup> and Jincheng Du<sup>8</sup>

All materials can suffer from environmental degradation; the rate and extent of degradation depend on the details of the material composition and structure as well as the environment. The corrosion of silicate glasses, crystalline ceramics, and metals, particularly as related to nuclear waste forms, has received a lot of attention. The corrosion phenomena and mechanisms of these materials are different, but also have many similarities. This review compares and contrasts the mechanisms of environmental degradation of glass, crystalline ceramics, and metals, with the goal of identifying commonalities that can seed synergistic activities and advance the current knowledge in each area.

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Journal of Nuclear Materials 484 (2017) 357–366

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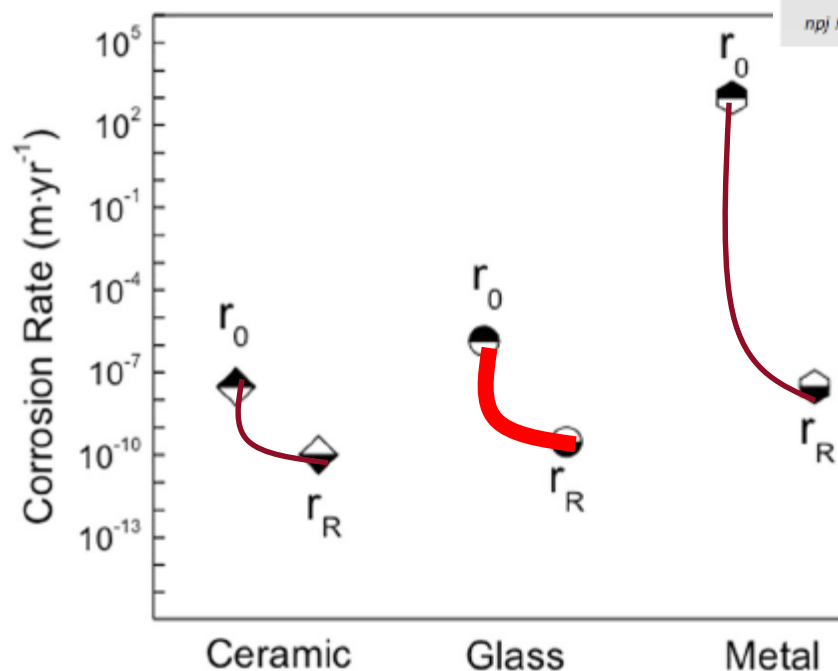


Journal of Nuclear Materials

journal homepage: [www.elsevier.com/locate/jnucmat](http://www.elsevier.com/locate/jnucmat)

## Modelling aqueous corrosion of nuclear waste phosphate glass

Pavel P. Poluektov<sup>a</sup>, Olga V. Schmidt<sup>a</sup>, Vladimir A. Kascheev<sup>a</sup>, Michael I. Ojovan<sup>b,\*</sup>



**Fig. 7** Summary of estimates of initial rates of corrosion,  $r_0$ , and residual or steady state rates,  $r_R$ , for ceramics, glasses and corrosion-resistant metal alloys. The very high initial rate shown for metal passivation is a consequence of the very short timescale ( $\mu\text{s}$ ) over which such rates can be measured for metals

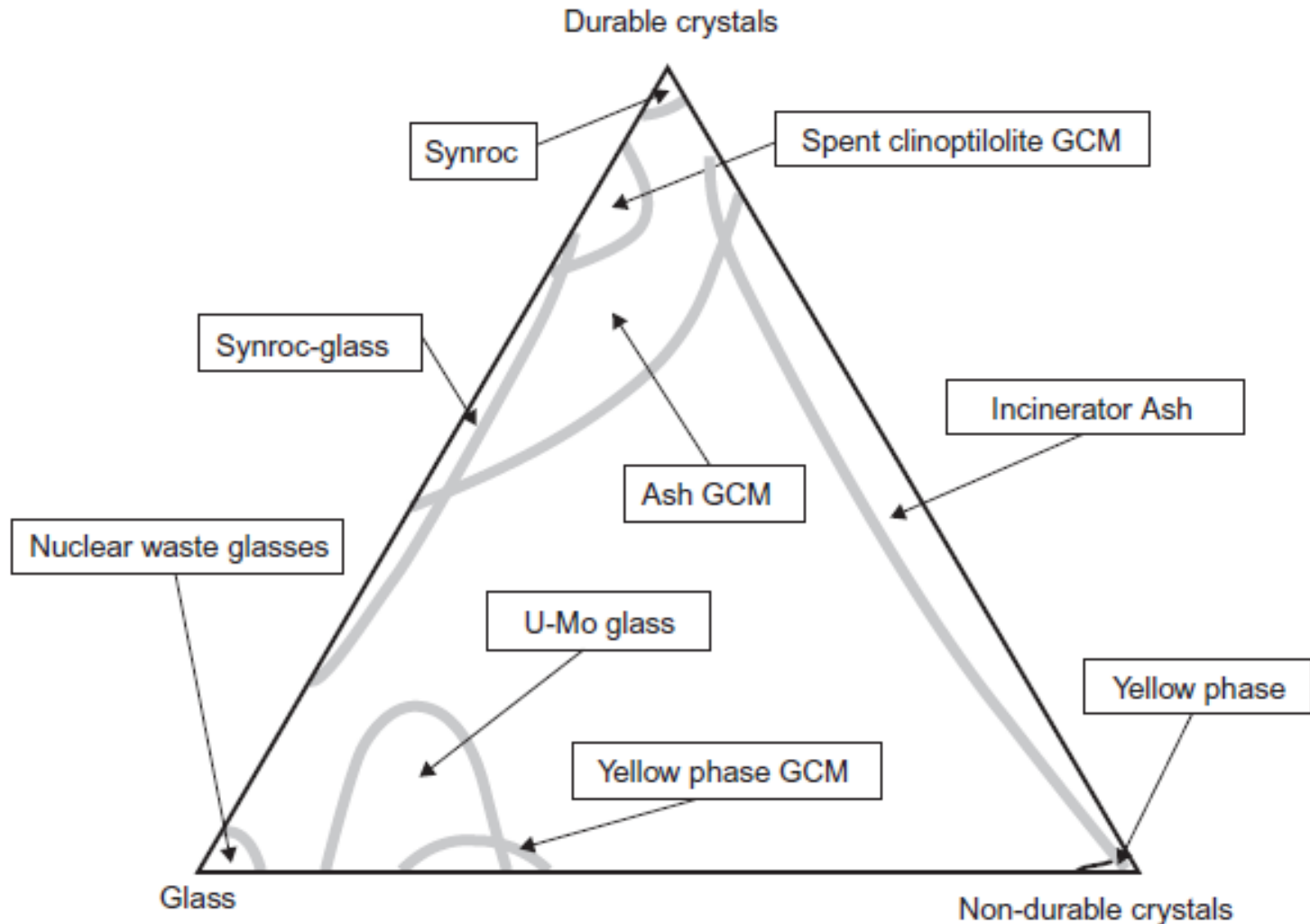


Figure 18.7 Phase composition of nuclear wasteforms.

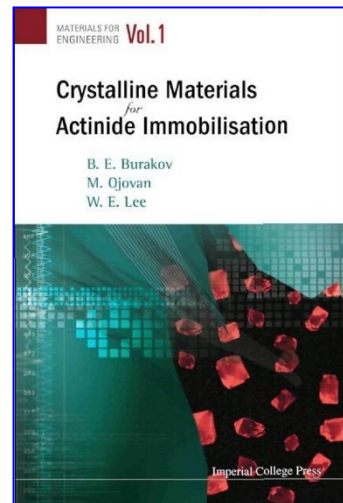
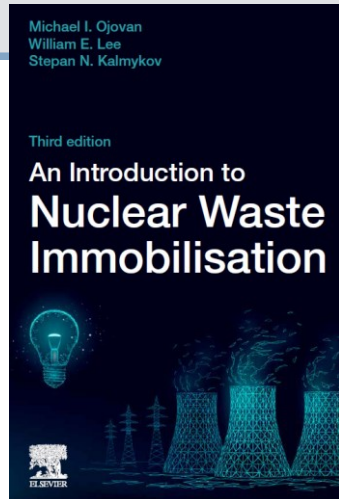
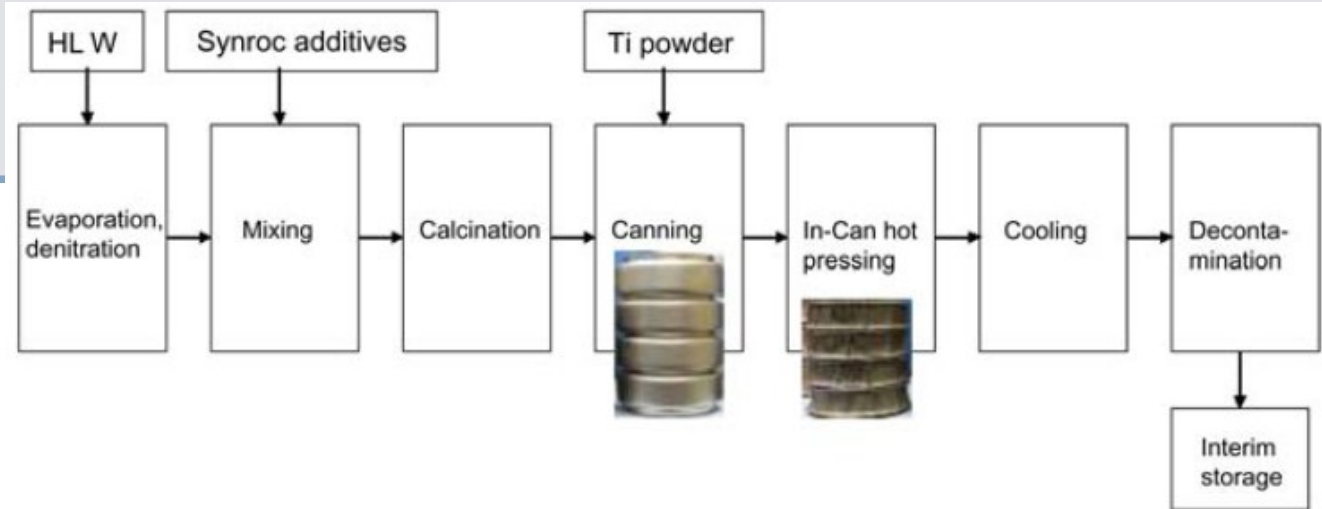


Table 20.2 Potential ceramic wastefoms for actinide immobilisation

Composition type	Mineral name	Ideal formula
Simple oxides	Zirconia	ZrO <sub>2</sub>
Complex oxides	Pyrochlore	(Na,Ca,U) <sub>2</sub> (Nb,Ti,Ta) <sub>2</sub> O <sub>6</sub> , Gd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub>
	Murataite	(Na,Y) <sub>4</sub> (Zn,Fe) <sub>3</sub> (Ti,Nb) <sub>6</sub> O <sub>18</sub> (F,OH) <sub>4</sub>
	Zirconolite	CaZrTi <sub>2</sub> O <sub>7</sub>
	Perovskite	CaTiO <sub>3</sub>
Silicates	Zircon	ZrSiO <sub>3</sub>
	Thorite	ThSiO <sub>3</sub>
	Garnet	(Ca,Mg,Fe <sup>2+</sup> ) <sub>3</sub> (Al,Fe <sup>3+</sup> ,Cr <sup>3+</sup> ) <sub>2</sub> (SiO <sub>4</sub> )
	Britholite	(Ca,Ce) <sub>5</sub> (SiO <sub>4</sub> ) <sub>3</sub> (OH,F)
Phosphates	Titanite	CaTiSiO <sub>5</sub>
	Monazite	LnPO <sub>4</sub>
	Apatite	Ca <sub>4-x</sub> Ln <sub>6+x</sub> (PO <sub>4</sub> ) <sub>y</sub> (O,F) <sub>2</sub>
	Xenotime	YPO <sub>4</sub>
	NZP <sup>a</sup>	NaZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>
	Th-pyrophosphate <sup>a</sup>	Th <sub>4</sub> (PO <sub>4</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>7</sub>

<sup>a</sup>These phases do not occur naturally.

B.E. Burakov, M.I Ojovan, W.E. Lee. *Crystalline Materials for Actinide Immobilisation*, Imperial College Press, London, 198 pp. (2010).

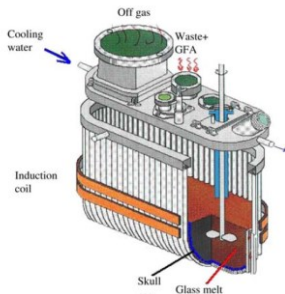


**Table 20.3** Sintering parameters for some host ceramics

Mineral	Monazite	Zircon	Zirconolite	Zirconia	Apatite	Synroc
Temperature, °C	900–1200	1450	1300–1800	1400–1600	700	1100–1300
Pressure, MPa	29		150	80	25	14–21

**Table 20.5** Melting parameters for some host ceramics

Mineral	Murataite	Zirconia	Zirconolite	Perovskite	Hollandite	Synroc B and C
T, °C	1400–1500	2650	1530	1975	1600	1400–1550



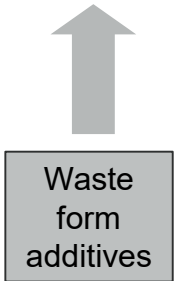
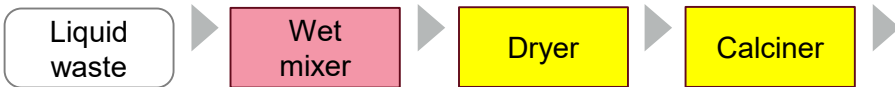




The Australian Nuclear Science and Technology Organisation (Ansto) said on 9 April that construction of a first-of-a-kind facility to immobilise waste from the production of molybdenum-99 (Mo-99) is expected to be completed in early 2020. The new facility will use Ansto Synroc technology to immobilise waste from Mo-99 production, known as SyMo. The Mo-99 is produced in Ansto's OPAL multipurpose reactor. "Today, Ansto Synroc combines waste form design and process technologies to immobilise and terminate nuclear wastes creating a technology tailored for intermediate level liquid waste," said Gerry Triani, Ansto Synroc Technical Director. "It is also a flexible platform technology that can be modified to suit other waste streams."

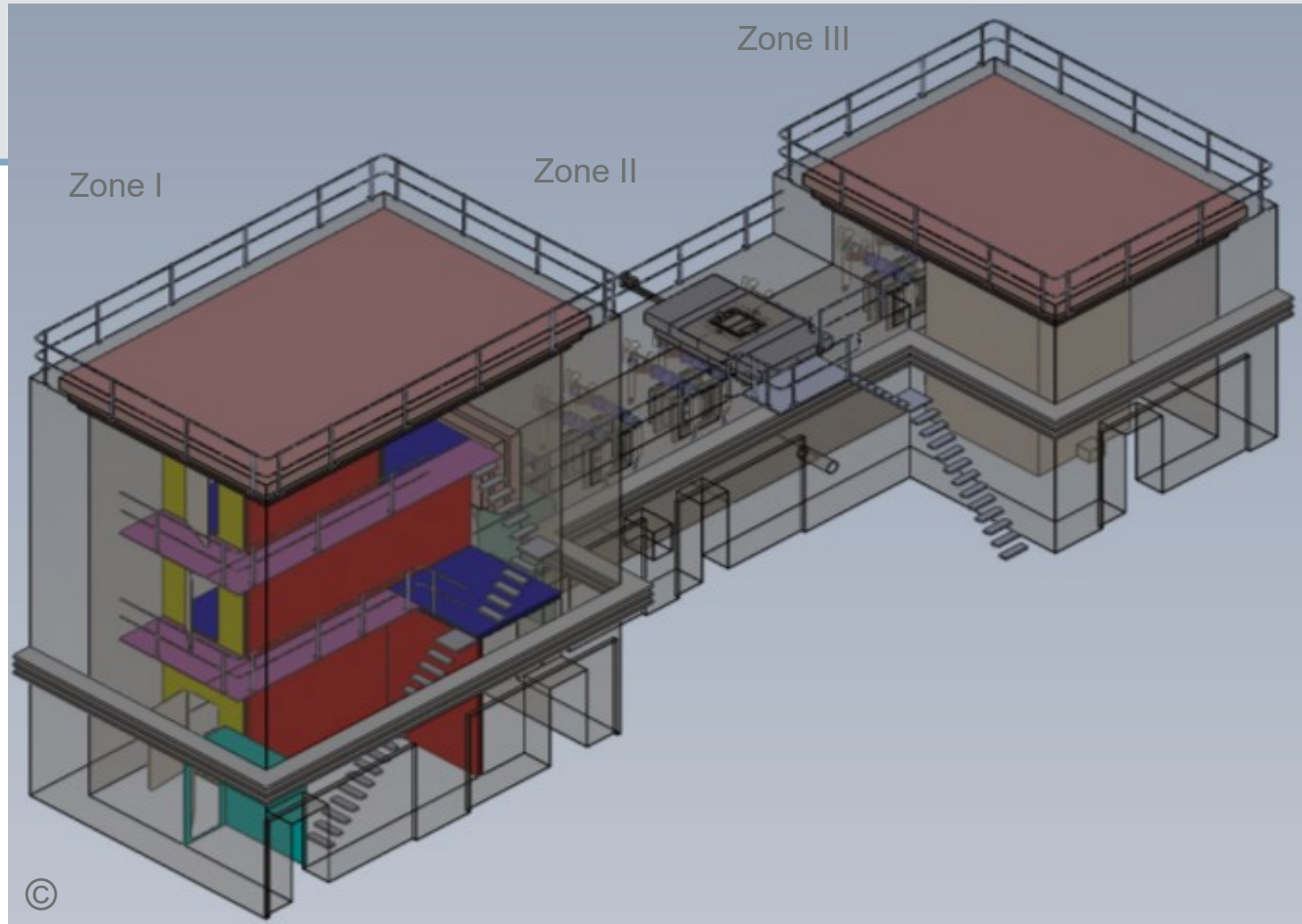
In Australia the 'SyMo' Facility (Synroc-Molybdenum) will operate a world first process line utilising a **fully integrated HIP based technology**; <https://www.neimagazine.com/news/newsansto-to-complete-new-mo-99-waste-facility-in-2020-7156356>

**POWDER PROCESSING**



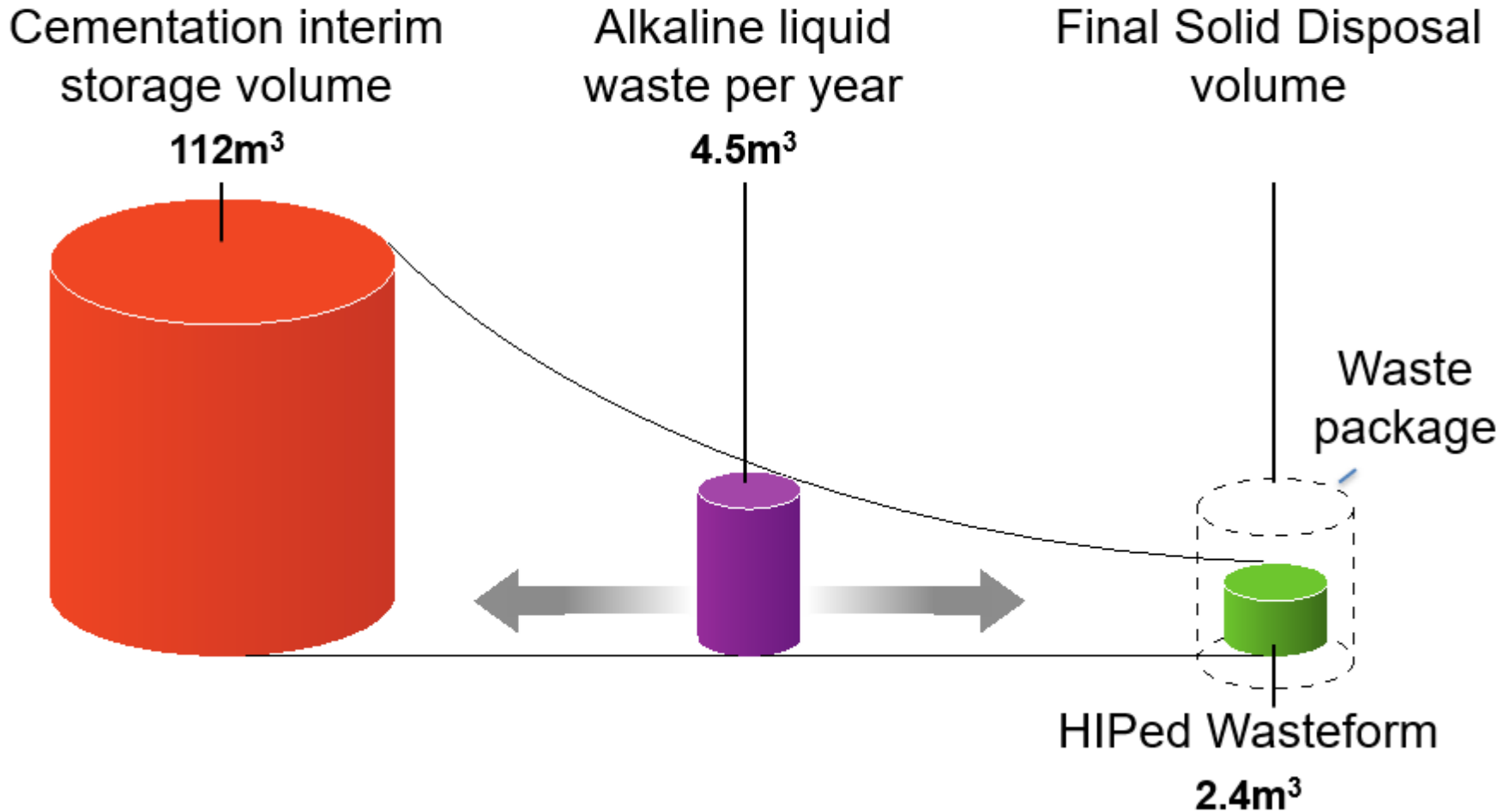
**CAN PROCESSING**





G Triani, R.L. Holmes, D.T. Chavara, E.R. Vance, M Smith, A Abboud, B Bigrigg, N Scales, D.J. Gregg. Synroc Waste Treatment Plant for fission-based Molybdenum-99 Production. Report presented at MRS Symposium on Scientific Bases for Nuclear Waste Management. Sydney 2017.

# Comparison of consolidated volume



See: <https://mo99.ne.anl.gov/2018/pdfs/presentations/S8-P1.pdf>

[https://mo99.ne.anl.gov/documents/Feasibility Review Report030914.pdf](https://mo99.ne.anl.gov/documents/Feasibility_Review_Report030914.pdf)

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## Ansto to complete new Mo-99 waste facility in 2020

16 April 2019



Print



Email


The Australian Nuclear Science and Technology Organisation (Ansto) said on 9 April that construction of a first-of-a-kind facility to immobilise waste from the production of molybdenum-99 (Mo-99) is expected to be completed in early 2020. The new facility will use Ansto Synroc technology to immobilise waste from Mo-99 production, known as SyMo. The Mo-99 is produced in Ansto's OPAL multipurpose reactor. "Today, Ansto Synroc combines waste form design and process technologies to immobilise and terminate nuclear wastes creating a technology tailored for intermediate level liquid waste." said Gerry Triani, Ansto Synroc Technical Director. "It is also a flexible platform technology that can be modified to suit other waste streams."

Table 20.4 Comparison of Synroc matrix parameters with nuclear waste glasses


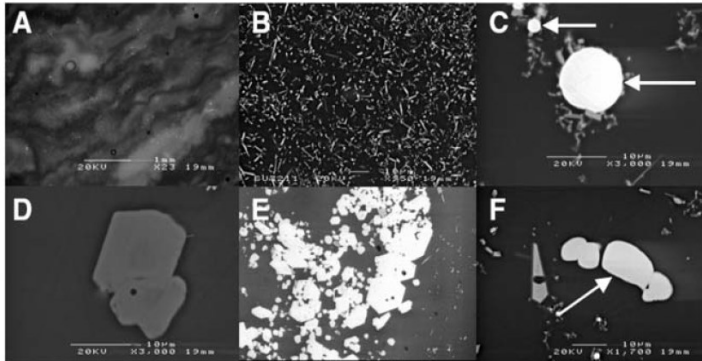
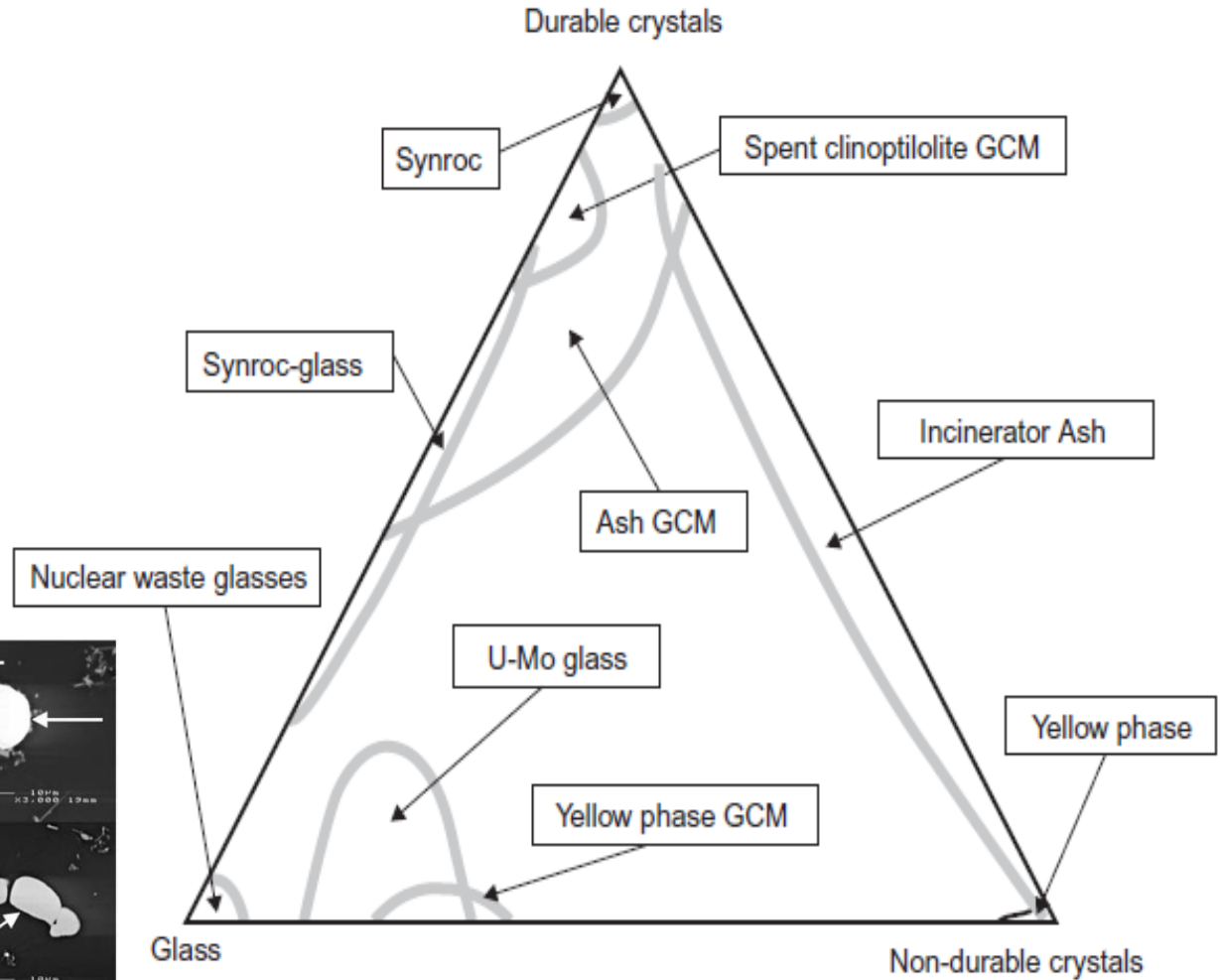
Parameter		Phosphate glass	Borosilicate glass	Synroc	
				Sintered	Melted
Density, g/cm <sup>3</sup>		2.6	2.6	4.35	3.8–4.4
Heat conductivity, W/m K		0.74	1.1	2.1	1.7
Temperature conductivity, cm <sup>2</sup> /s		$2.9 \times 10^{-3}$		$10^{-2}$	
Linear dilatation coefficient, $10^{-6}$ , 1/K		1.5	8.1	10.5	8–10
Heat capacity, J/g K		0.96	0.9	0.55	0.5–0.7
Compressive strength, MPa		10	80	547	500–600
Microhardness, GPa			7.2	8.4	8.0–8.5
NR, g/cm <sup>2</sup> day	Cs	$1.1 \times 10^{-6a}$	$10^{-4}$	$< 3 \times 10^{-6}$	$5 \times 10^{-5}$
	Sr	$4 \times 10^{-7a}$	$7 \times 10^{-6}$	$6.5 \times 10^{-7}$	$10^{-6}$
	An		$10^{-5}$	$10^{-7}–10^{-8}$	$10^{-7}–10^{-8}$

<sup>a</sup>Data for room temperature.

Michael I. Ojovan  
W. E. Lee



New Developments  
in Glassy  
Nuclear Wasteforms

Phase composition of nuclear wasteforms.

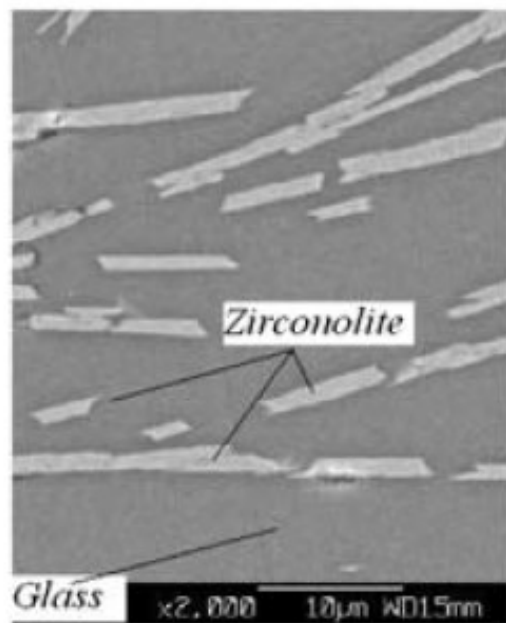
Figure 19.8 Gas bubbles (A) and crystalline phases (B–F) in an as-cast British Magnox waste simulant glass. (B) RuO<sub>2</sub>, (C) Pd, (D) Cr, Fe, Ni-spinels, (E) lanthanide-rich phase and (F) Zr-rich phase. Courtesy P.B. Rose, ISL, University of Sheffield.

Glass composite materials (GCM's) are used to immobilise glass-immiscible waste components such as sulphates, chlorides, molybdates and refractory materials requiring unacceptably high melting temperatures. GCM's comprise both vitreous and crystalline components.

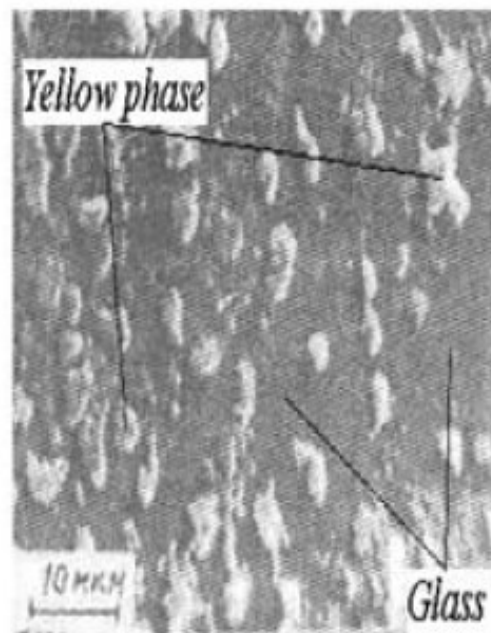
**Table 19.4** Approximate solubility limits of elements in silicate glasses

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	Less than 0.1

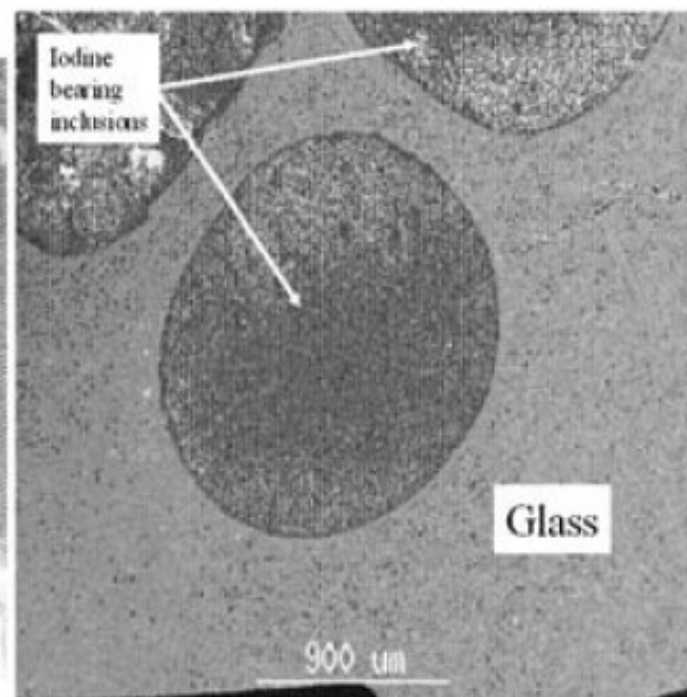
342 An Introduction to Nuclear Waste Immobilisation



(A)



(B)

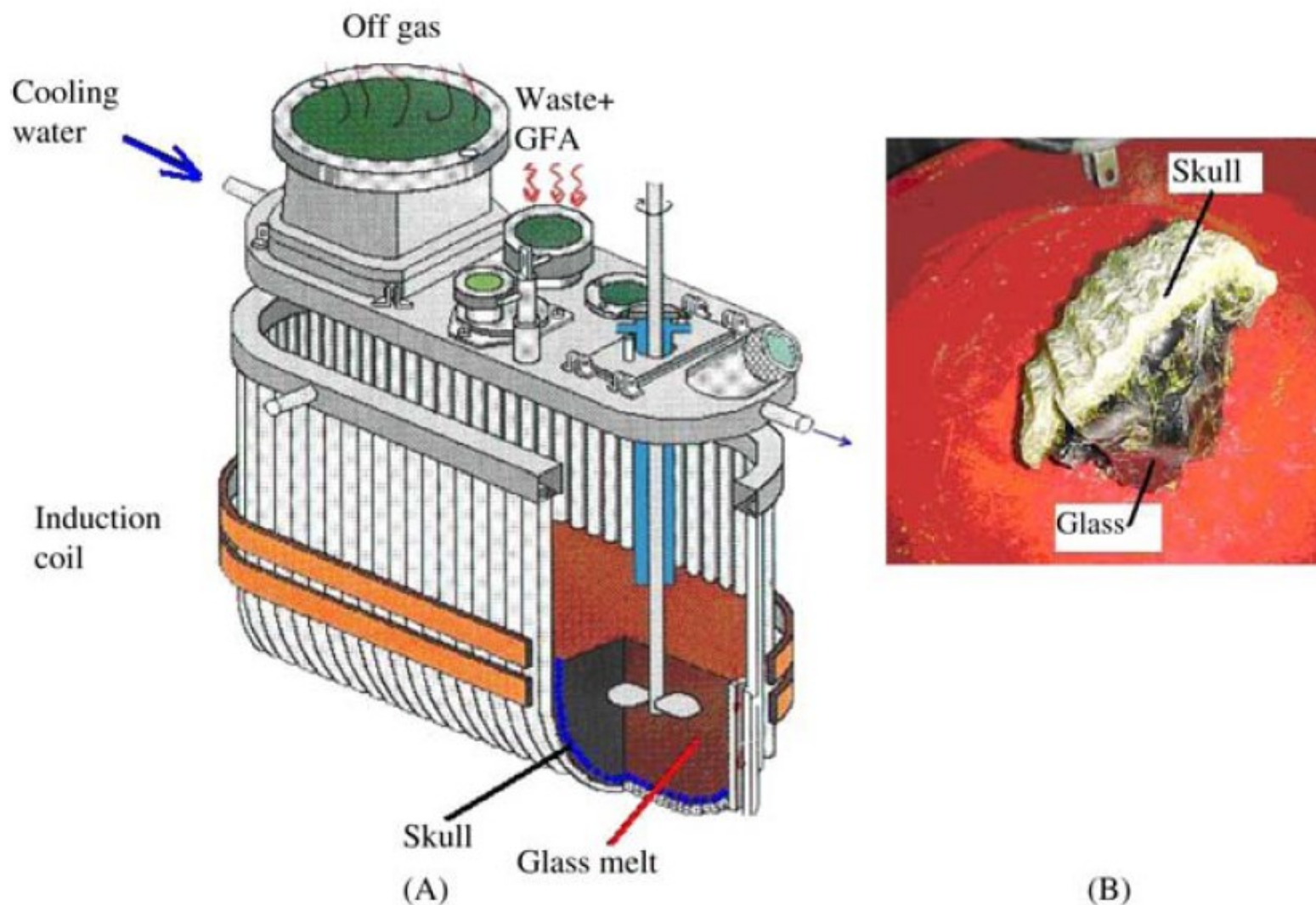


(C)

D S Perera, E R Vance, R L Trautman, B D Begg WM'04 Conference, Tucson, AZ

**Figure 19.12** Waste encapsulation in GCMs: Microstructure of (A) Synroc-glass with zirconolite crystalline phase; (B) GCM for immobilising yellow phase; (C) GCM for immobilising iodine. GCM, Glass-composite material. *Courtesy Dan Perera, ANSTO.*



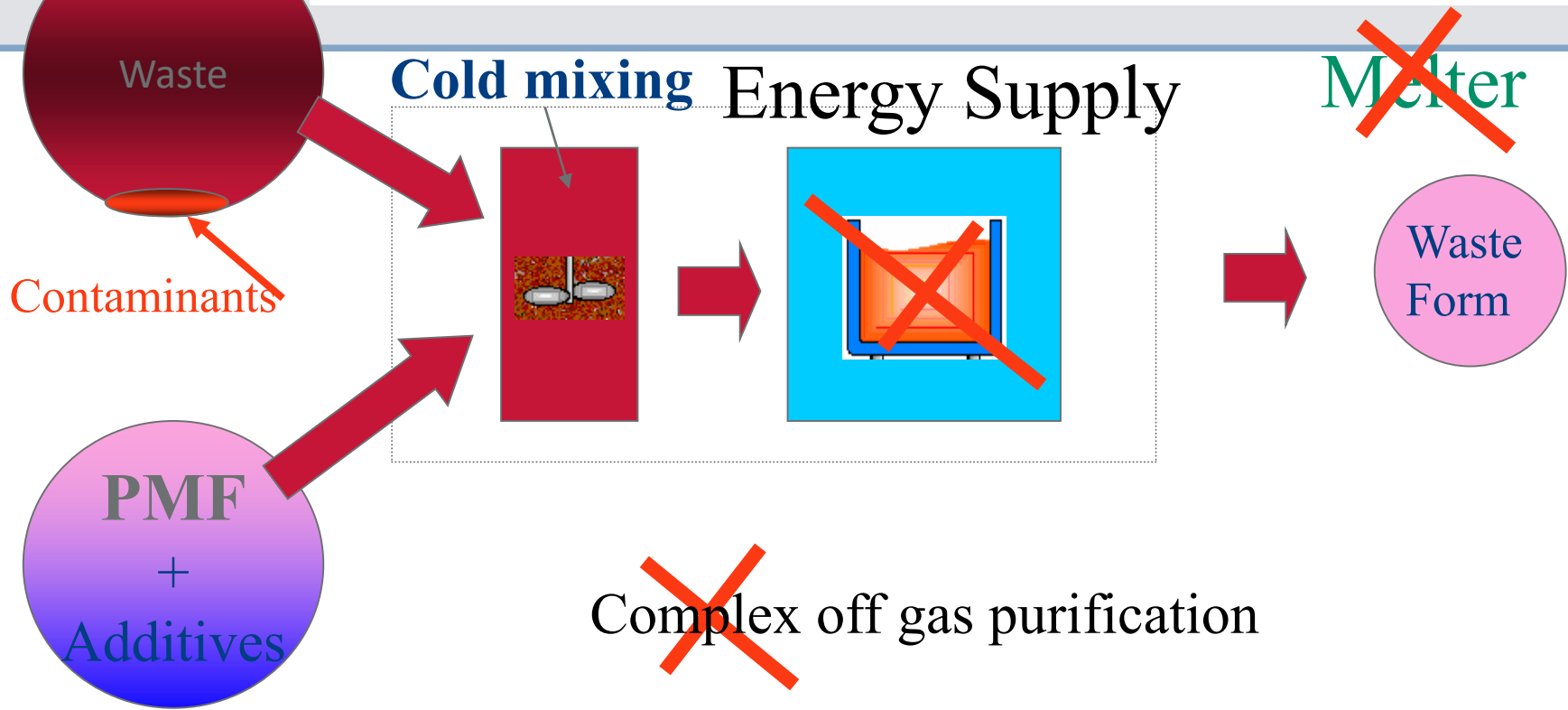


**Figure 19.26** (A) Schematic of Russian stainless steel CCM. The stirrer in this CCM enables production of GCM. (B) A sample of glass from the CCM: the white layer is a part of the glass forming batch (skull) that remains unmelted. GCM, Glass-composite material; CCM, cold crucible melters.

**Table 19.10** Basic properties of borosilicate glasses and Russian yellow phase glass-composite material (GCM)

Parameter	Borosilicate glasses for high sodium waste	GCMs	
Waste oxide content, wt.%	30–35	30–35 + up to 15 vol.% of yellow phase	
Viscosity, Pa s, at 1200°C	3.5–5.0	3.0–6.0	
Resistivity, $\Omega$ m, at 1200°C	0.03–0.05	0.03–0.05	
Density, g/cm <sup>3</sup>	2.5–2.7	2.4–2.7	
Compressive strength, MPa	80–100	50–80	
Leach rate, g/cm day, (28-day International Atomic Energy Agency test)	<sup>137</sup> Cs	$10^{-5}$ – $10^{-6}$	$\sim 10^{-5}$
	<sup>90</sup> Sr	$10^{-6}$ – $10^{-7}$	$10^{-6}$ – $10^{-7}$
	Cr, Mn, Fe, Co, Ni	$\sim 10^{-7}$ – $10^{-8}$	$10^{-7}$ – $10^{-8}$
	Rare earth elements (REE), Actinides (An)	$\sim 10^{-8}$	$\sim 10^{-8}$
	Na	$10^{-5}$ – $10^{-6}$	$10^{-4}$ – $10^{-5}$
	B	$< 10^{-8}$	$\leq 10^{-8}$
	SO <sub>4</sub> <sup>2-</sup>	$\sim 10^{-5}$ – $10^{-6}$	$\sim 10^{-4}$ – $10^{-5}$ with up to 15 vol.% yellow phase

# GCM via Self-Sustaining Vitrification



SSV produces Waste Forms without external power supply ensuring minimisation of emission of contaminants (carry over).

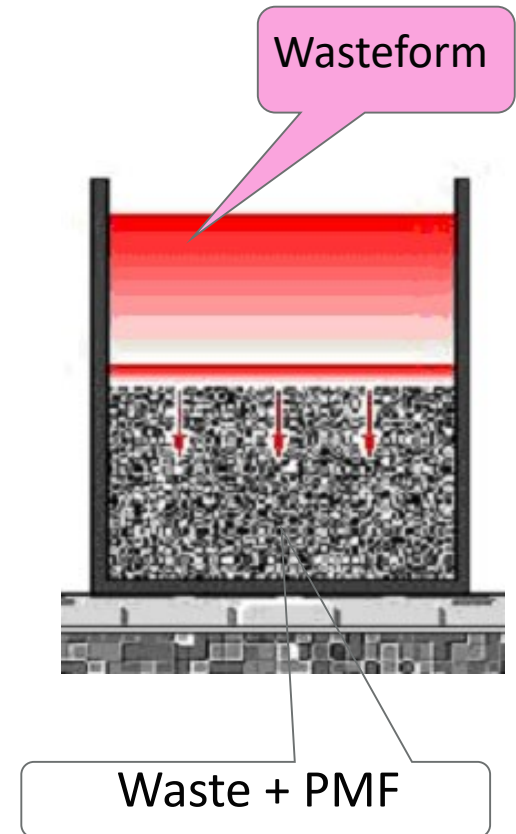
## Waste + PMF (+Additives) → Wasteform + Heat

**Waste:** a mixture of metal oxides including contaminants.

**PMF:** a specially designed blend of heat generating components.

**Additives** can be required to enhance the efficiency of process and to obtain a high quality wasteform

**Suitable PMF** composition ensures an efficient immobilising process and a qualitative wasteform.



The waste should be:

1. In a powder form to enable good mixing with PMF;
2. Dry enough to avoid release of large amounts of gas on melting.

**Examples:**

Ashes produced by incinerating hazardous (toxic and radioactive) waste,

Soils contaminated both by heavy metals and radionuclides,

Spent inorganic ion-exchangers.

Characteristics of radioactive wastes

Characteristic		Ash residue	Soil	Clinoptilolite
Content in the waste, Wt. %	SiO <sub>2</sub>	28.10	75.28	68.02
	P <sub>2</sub> O <sub>5</sub>	19.21	–	–
	CaO	25.80	0.73	2.71
	Na <sub>2</sub> O	4.47	1.51	1.57
	K <sub>2</sub> O	6.40	2.79	3.01
	Fe <sub>2</sub> O <sub>3</sub>	2.90	4.91	1.44
	Al <sub>2</sub> O <sub>3</sub>	3.65	7.63	11.34
	CuO	1.53	0.17	–
	MgO	5.14	1.44	0.53
	MnO	1.11	–	0.06
	SO <sub>3</sub>	1.76	–	0.32
	LOI at 900°C	-	5.51	11.11

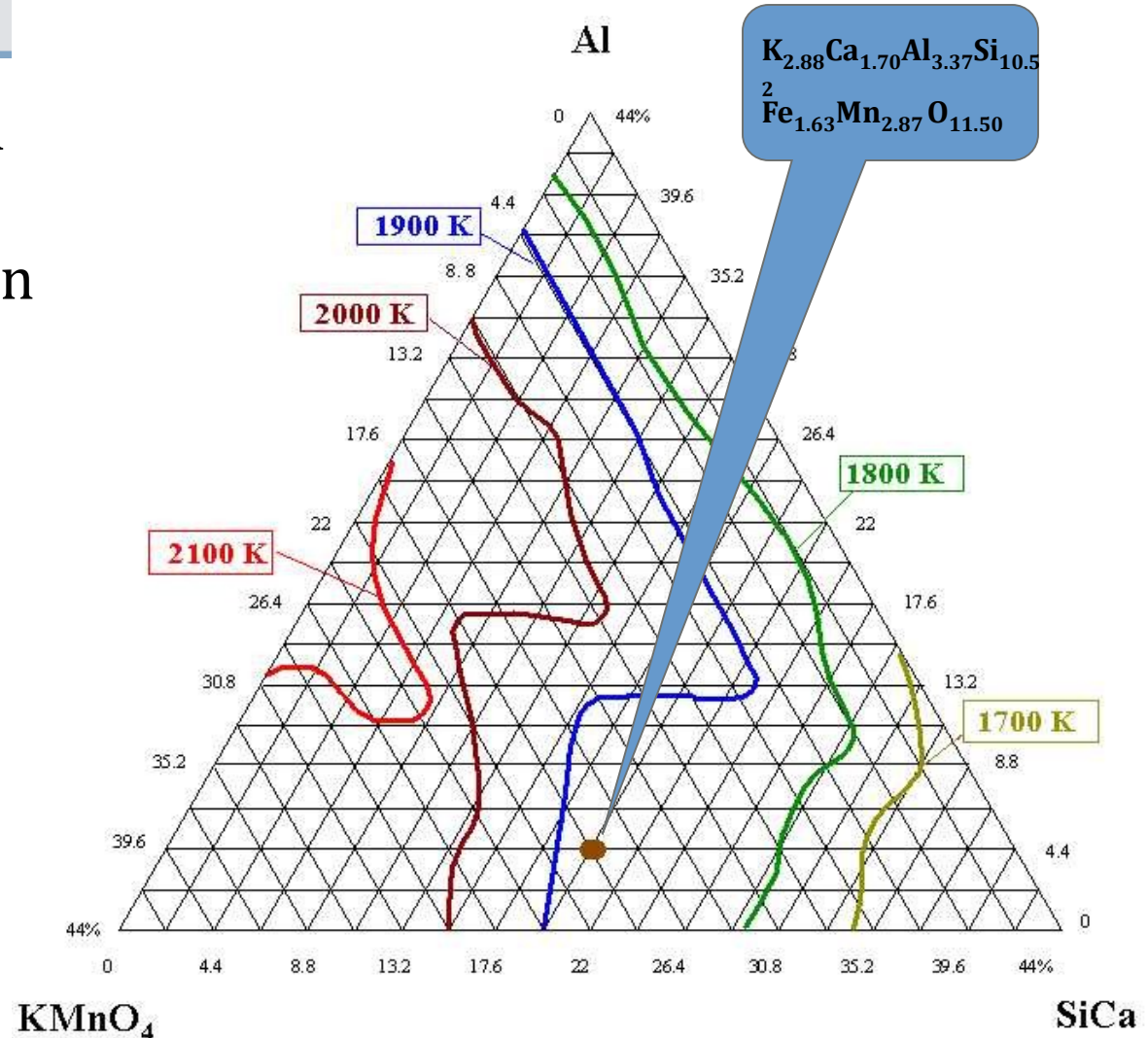
Characteristics of radioactive wastes

Characteristic		Ash residue	Soil	Clinoptilolite
Specific radio activity, Bq/kg	$\Sigma \beta$ by $^{137}\text{Cs}$	$10^5 - 10^6$	$10^3 - 10^5$	$10^3 - 10^5$
	$\Sigma \alpha$ by $^{239}\text{Pu}$	$10^5 - 10^7$	$\leq 10^3$	-
	$\Sigma \beta$ by $^{90}\text{Sr} + ^{90}\text{Y}$	$7.7 \cdot 10^5$	$3.6 \cdot 10^3$	$4.6 \cdot 10^5$
	$^{137}\text{Cs}$	$1.3 \cdot 10^5$		$7.0 \cdot 10^5$
	$^{90}\text{Sr}$	$1.5 \cdot 10^5$		$7.0 \cdot 10^5$
	$^{238}\text{U}$	$3.2 \cdot 10^4$		$1.8 \cdot 10^2$

Thermodynamic simulation is applied to design PMF and model immobilisation process.

These result in determining the appropriate PMF composition and PMF/waste ratio.

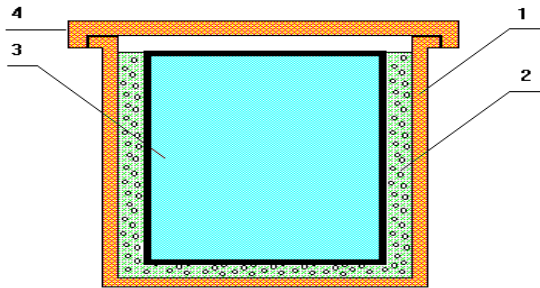
Equilibrium temperatures in a composition of ash and PMF.





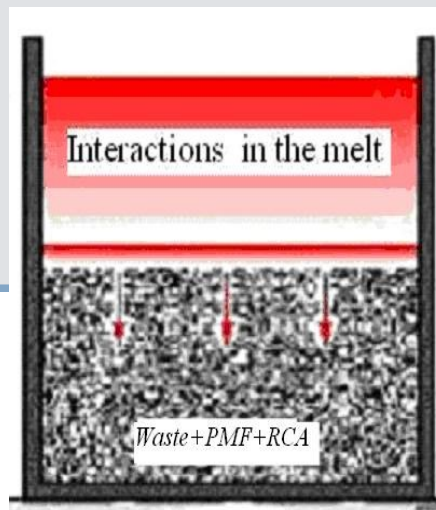
Self-sustaining immobilisation was performed for waste to PMF ratios of 0.82 – 1.50.

Double wall crucible-containers made of carbon steel of 3, 5 and 10 dm<sup>3</sup> volumes were used.



1-carbon steel drum, 2-refractory backfill,  
3-waste+PMF mixture, 4-lid.





Propagation velocity of the combustion wave is about 1 mm/s.

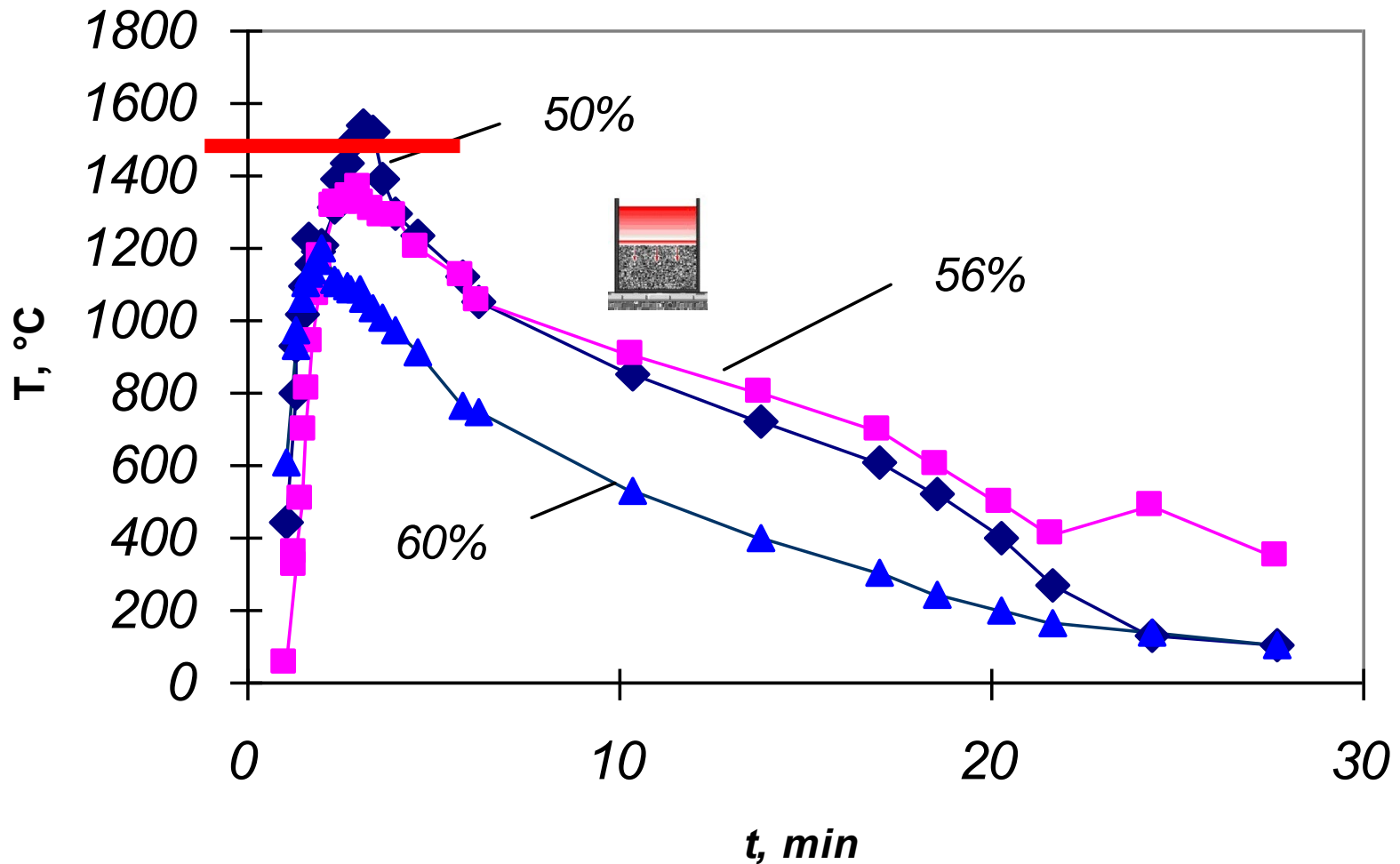


Initiating of  
the process

Container ready for ignition.



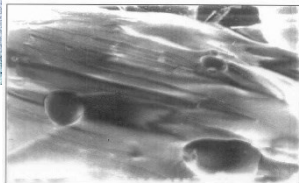
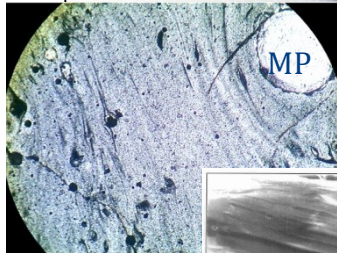
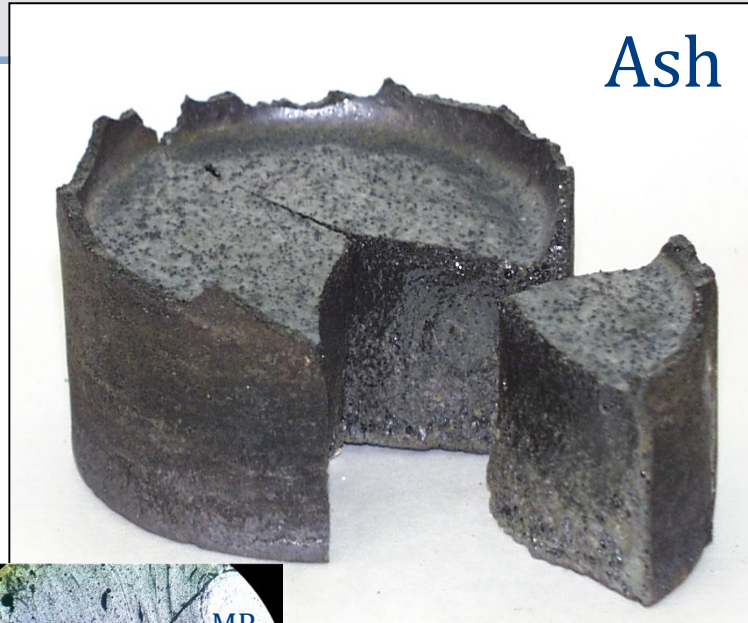
SSV Process.



Thermograms of self-sustaining vitrification.  
Left for ash residue for PMF/ash wt. ratios as 1 - 50/50, 2 - 44/56, 3 - 40/60.

## Parameters of SSI

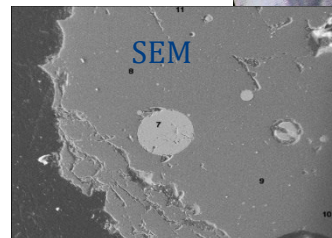
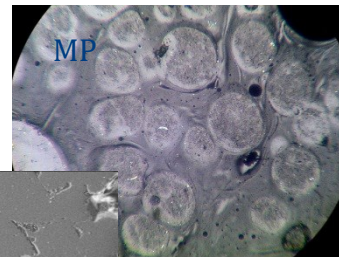
Waste content, wt. %			Maximum process temperature, °C	Aerosols carryover, wt. %	<sup>137</sup> Cs carryover, %
Ash residue	Soil	Clinoptilolite			
50 -	-	-	1530	1.9	0.9
56 -	-	-	1350	1.4	0.4
60 -	-	-	1200	1.0	0.3
-	45	-	1900	2.2	3.1
-	50	-	1620	1.8	1.9
-	56	-	1530	1.0	1.3
-	-	50	1564	3.6	0.8
-	-	55	1476	2.4	1.1



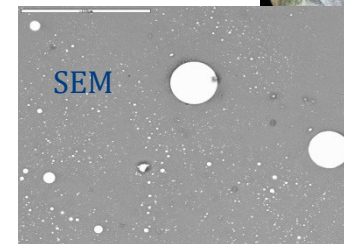
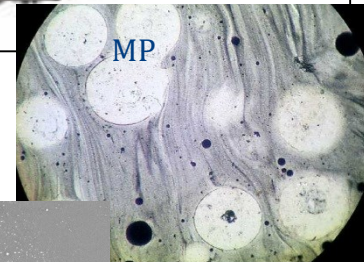
SEM 400x magnification, 50 wt.%

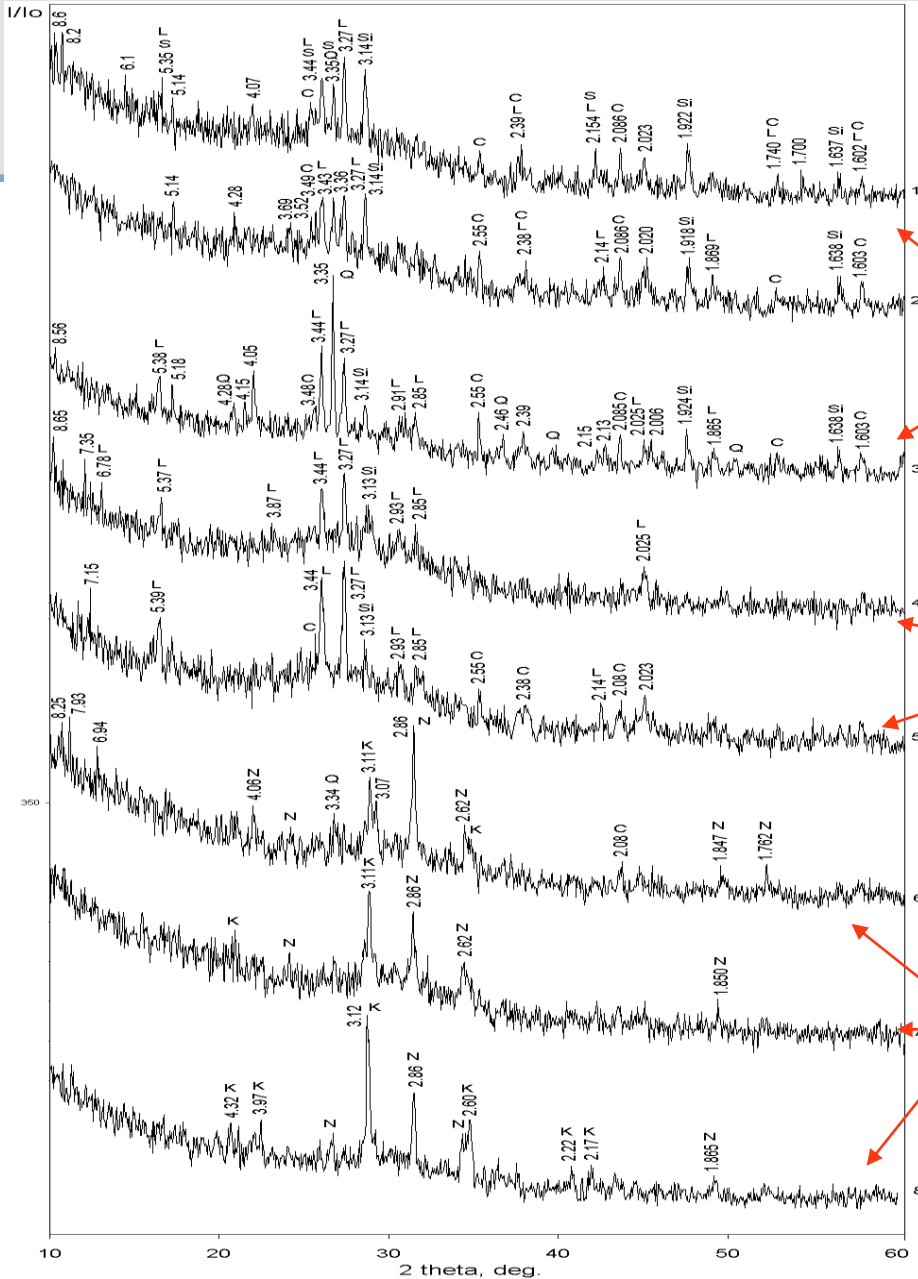


b) 200x magnification, 60 wt.%



### Clinoptilolite





1- soil 45 %,  
2- 50 %,  
3- 56 %

4- clinoptilolite 50 %,  
5-55 %,

6 - ash residue 60  
%,  
7 -56 %,   
8 -50 %.

C- corundum,  
K- calcilite,  
L- leicite ,  
S- sillimanite,  
N-  
nagelshmidtite, Q  
- quartz.

Evidence of high  
temperature  
interaction between  
components of the  
PMF

Vitrified product phases able to incorporate waste elements.

Phases

Potential contaminants

Glassy



Pb, Zn, Rb, Sr, Cs, Ra, U, La, Ce, Pr, Th, Co, Ni, Mo, and up to 1-3 wt.%: C, S, Cl, As, Se, Te, Sn, Sb, Te.

Nagelschmidtite  $\text{Ca}_7(\text{PO}_4)_2(\text{SiO}_4)_2$

Sr, REE<sup>III</sup>, An<sup>III,IV</sup> (U, Pu), Pb, S

Sodium-calcium silicophosphate  $\text{Na}_2\text{Ca}_4(\text{PO}_4)_2(\text{SiO}_4)$

Sr, REE<sup>III</sup>, An<sup>III,IV</sup> (U, Pu), Pb, S

Kaliophilite (K[AlSiO<sub>4</sub>])

K, Rb, Cs, Fe



Characteristics of the end product

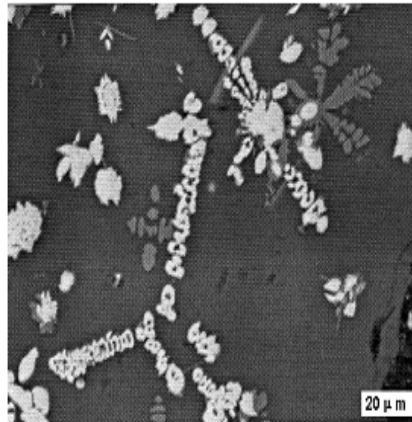
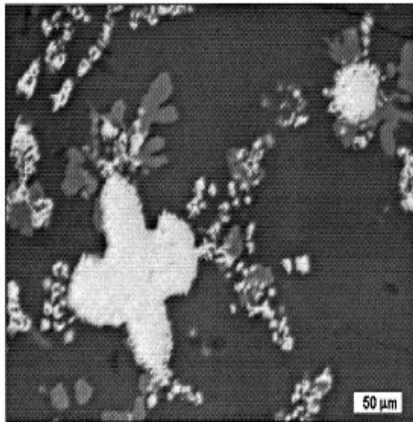
Waste content, wt. %			Density, g/cm <sup>3</sup>	Compressive strength, MPa	Leaching rate, g/cm <sup>2</sup> ·day	
Ash residue	Soil	Clinoptilolite			<sup>137</sup> Cs	<sup>239</sup> Pu
50	-	-	2.8	20	$9.0 \cdot 10^{-6}$	$5.4 \cdot 10^{-6}$
56	-	-	2.8	17	$4.9 \cdot 10^{-6}$	$2.8 \cdot 10^{-6}$
60	-	-	3.0	16	$7.9 \cdot 10^{-5}$	$7.0 \cdot 10^{-5}$
-	45	-	2.4	10	$1.0 \cdot 10^{-5}$	-
-	50	-	2.0	10	$8.1 \cdot 10^{-6}$	-
-	56	-	1.5	8	$2.1 \cdot 10^{-6}$	-
-	-	50	1.85	12	$\sim 6 \cdot 10^{-6}$	-
-	-	56	1.74	9	$\sim 8 \cdot 10^{-6}$	-



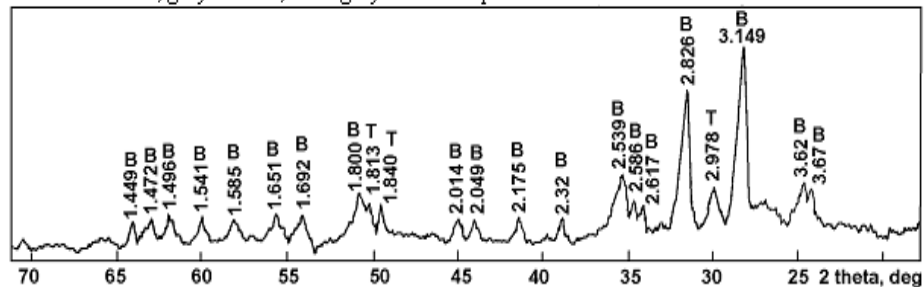


Additives were found to incorporate long-lived isotopes of carbon, uranium, plutonium (actinides) in the target crystalline phases (e.g. carbides, zirconolite, zirconia).

*Waste + PMF + Additives → Waste Form + Heat*



SEM images in backscattered electrons of the material produced using exothermic mixture. White - zirconia, gray - metal, dark-gray - vitreous phase.



XRD pattern of the material produced using exothermic mixture.

B - baddeleyite, T - tetragonal zirconia.

Leaching rate ( $\text{g/m}^2\cdot\text{d}$ ) for mineral-like block (MCC-1 test at  $90^\circ\text{C}$  during 7\* and 28\*\* days).

	Our material*	Synroc-C	Waste glass PNL 76-68**
Mass	0.01	0.005**	0.42
Al	0.01	<0.01**	n.a.***
B	0.75	-	1.12
Ca	0.012	0.0065**	0.068
Ce	$5,1 \cdot 10^{-4}$	$10^{-4}-10^{-3}$ *	n.a.
K (Cs)	0.15	(0.033)**	(1.03)
Si (Ti)	$7 \cdot 10^{-4}$ ( $1 \cdot 10^{-4}$ )	(< $5 \cdot 10^{-5}$ )**	0.73
Zr	< $1 \cdot 10^{-3}$	< $6 \cdot 10^{-4}$ *	-

# GCM OBTAINED VIA SINTERING

*J.M. Juoi et al. / Journal of Nuclear Materials 372 (2008) 358–366*

## Host Borosilicate Glass melting and Characterisation

- DTA, XRD and ICP-AES analysis



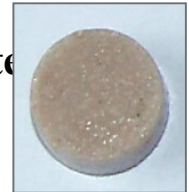
## Impregnation of Cs on natural clinoptilolite and characterisation

- DTA, XRD and ICP-AES analysis



## Sintering of pellets

- **Sintered at 750°C for 2 hours with 2°C/min heating and cooling rate**
- Both Cs-Clino and glass size <math><75\mu\text{m}</math>.
- 13mm diameter pellet using 78.3 Mpa.
- Glass to Cs-clino ranging from 1:1 up to 1:10 glass to Cs-clino vol. ratio



## Leaching Test

- Based on ASTM C1220-98 standard.
- In deionized water, at 40°C for 7 days.
- surface area to volume ratio  $(S/V)=10.0\text{m}^{-1}$ .

## Microstructural Analysis


- Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) analysis.



Table 1  
Cs-clino parameters

Analyses	Results
ICP-MS (wt%)	Cs – 21.0
XRD	Potassium sodium aluminium silicate hydrate $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$
Mean particle size (mm)	0.564
Density ( $\text{g cm}^{-3}$ )	$2.00 \pm 0.23$

Table 2  
Properties of borosilicate glass used as matrix

Composition (wt%)	Oxide	Batch <sup>a</sup>	ICP <sup>b</sup>
	SiO <sub>2</sub>	50.05	50.43
	Na <sub>2</sub> O	16.72	14.00
	CaO	16.61	16.80
	Al <sub>2</sub> O <sub>3</sub>	2.60	2.74
	TiO <sub>2</sub>	1.56	1.58
	B <sub>2</sub> O <sub>3</sub>	9.34	10.37
	Li <sub>2</sub> O	3.12	2.46
	K <sub>2</sub> O	–	0.75
	Total		100
$T_g$ (°C)	488 ± 2		
Density (g cm <sup>-3</sup> )	2.60 ± 0.10		

<sup>a</sup> Calculated from batch composition.

<sup>b</sup> Calculated based on elemental composition obtained by ICP-AES.

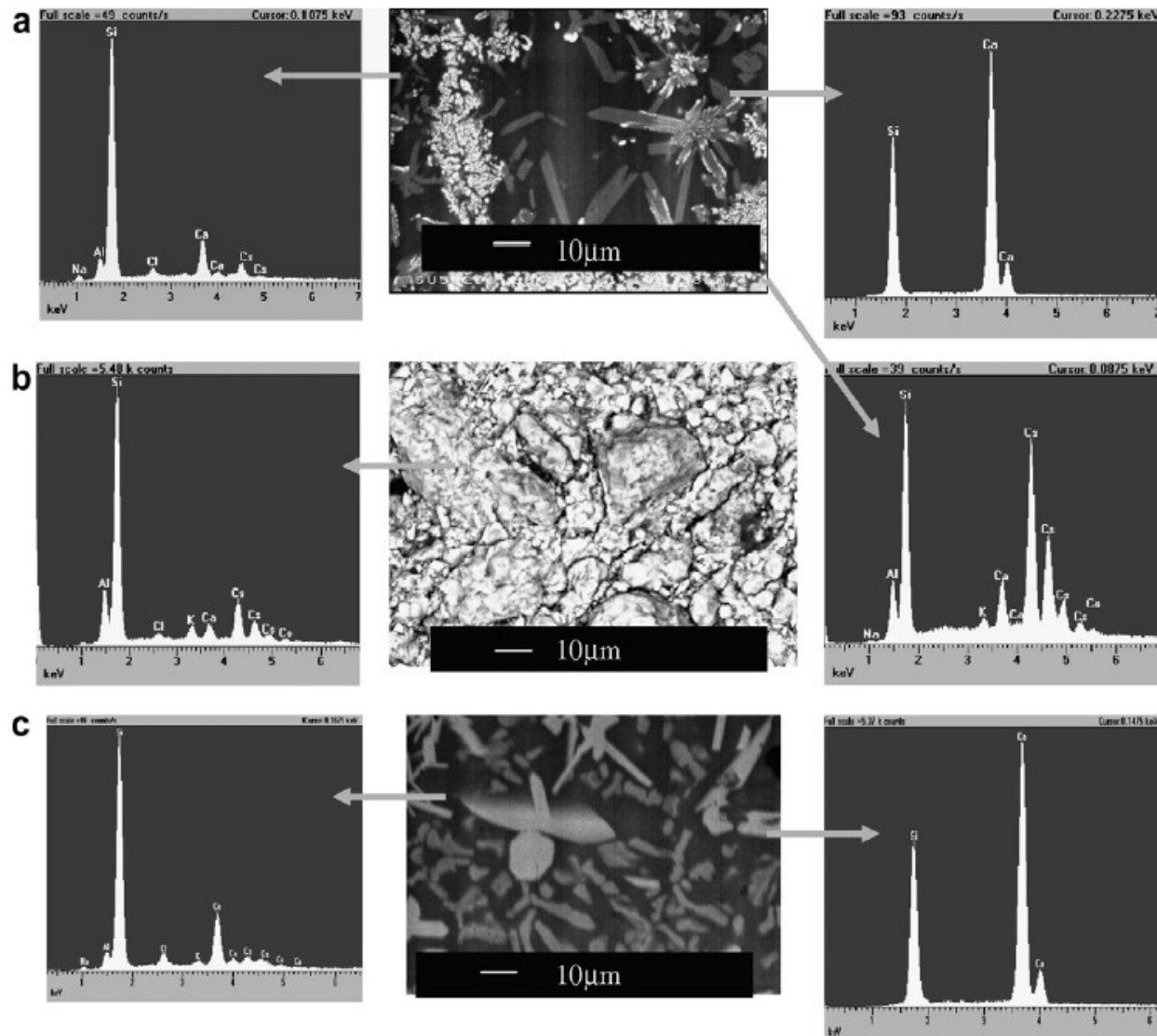


Fig. 1. BEI image and EDS of each phase of (a) GCM wasteform with 1:1 glass to Cs-clino volume ratio (b) sintered Cs-clino only and (c) sintered borosilicate only.

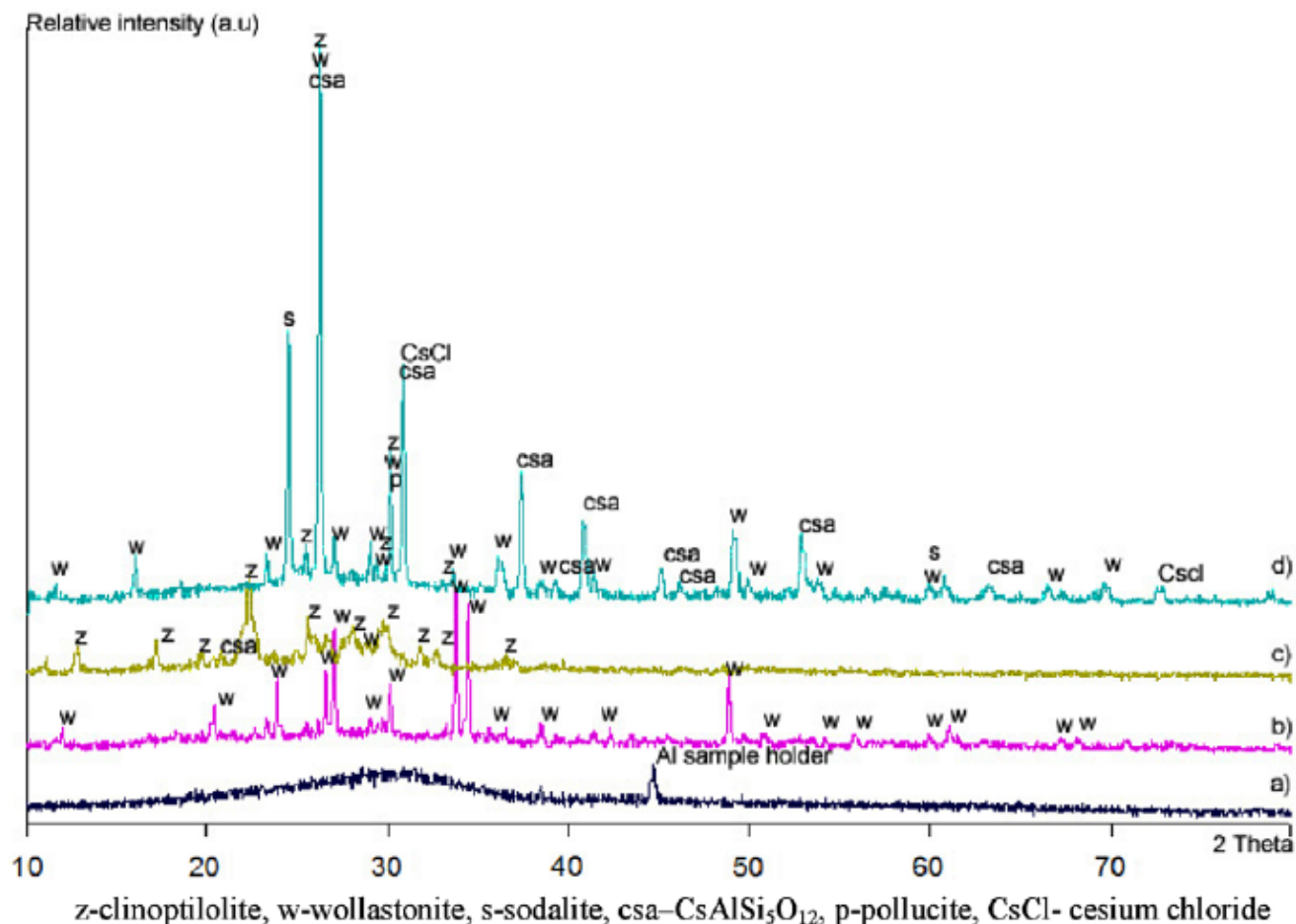


Fig. 2. XRD of (a) unheat-treated host glass, (b) sintered host glass only, (c) sintered Cs-clino only and d) sintered GCM wasteform with 1:1 glass to Cs-clino volume ratio after 2 h at 750 °C.

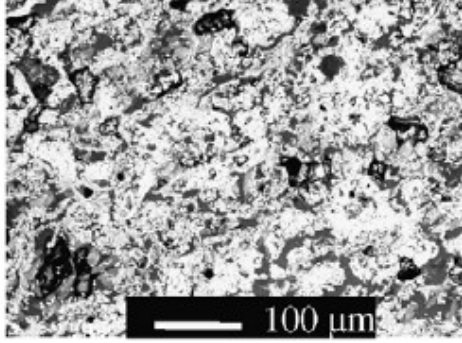
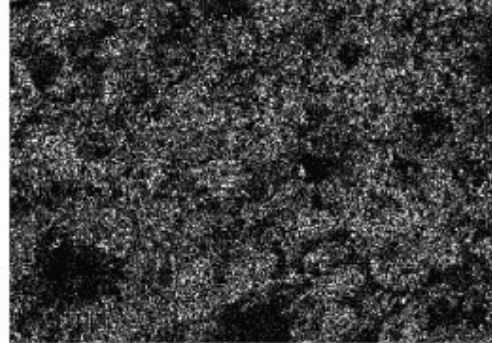
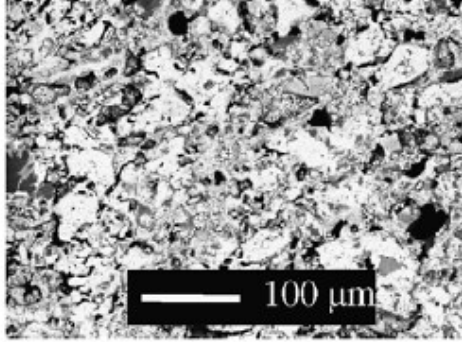
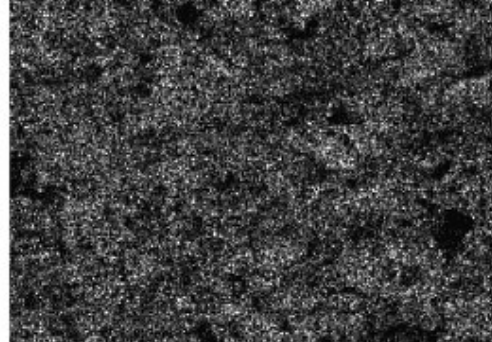
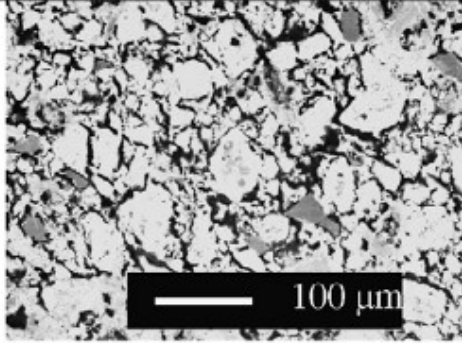
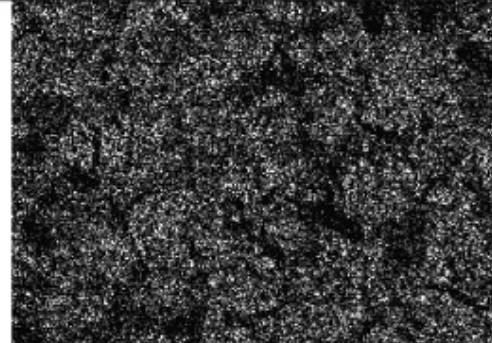
Glass to Cs-clino (Volume ratio) (Waste loading, mass%)	BEI Micrograph	Cesium Map
1:2 (59%)		
1:4 (73%)		
1:5 (80%)		

Fig. 3. Microstructural changes and Cs distribution in the GCM wastefrom with increased waste loading.

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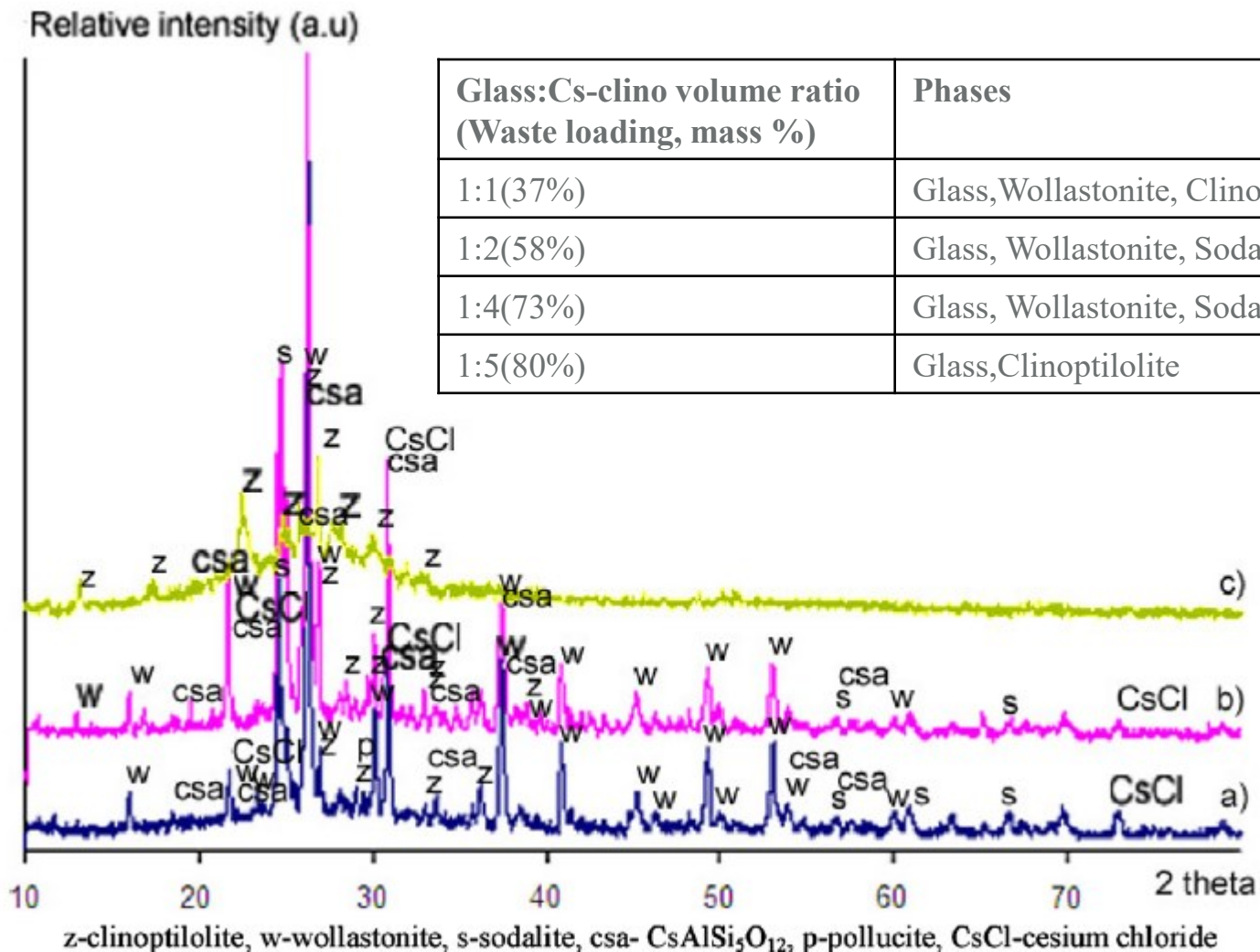


Fig. 4. XRD of GCM with glass to Cs-clino volume ratio respectively (a) 1:2, (b) 1:4 and (c) 1:5 after 2 h at 750 °C.



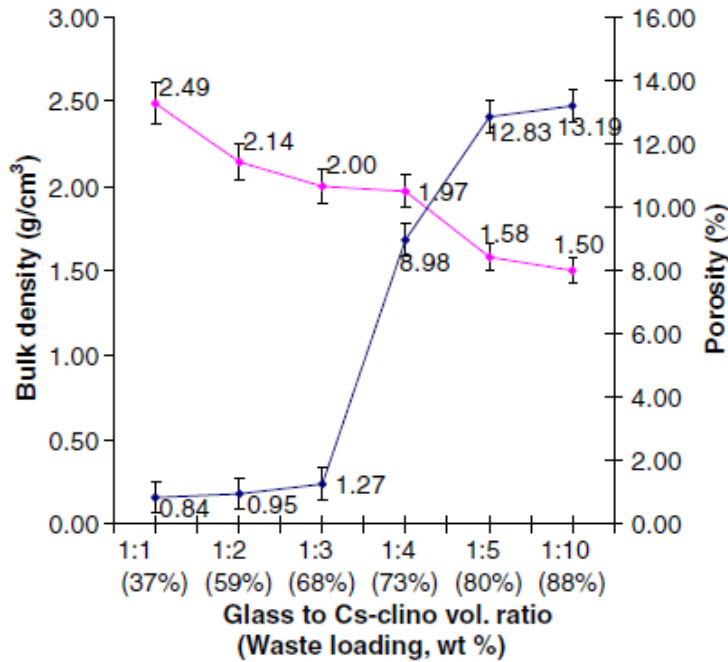


Fig. 5. Bulk density and porosity of glass composite wasteform with the increase of waste loading.

•Up to waste loading  $\sim 73\%$  mass microstructure of the GCM ensures complete encapsulation of clinoptilolite particles and  $NR_{Cs}$  of the GCM below  $6.35 \cdot 10^{-6} \text{g/cm}^2 \cdot \text{day}$ .

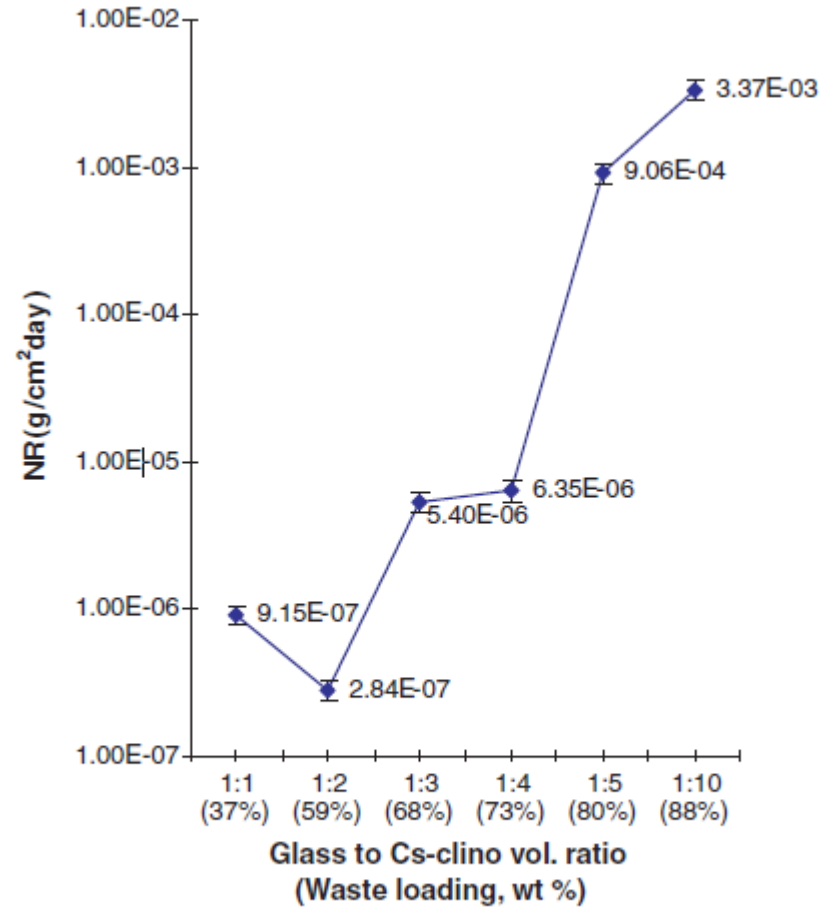
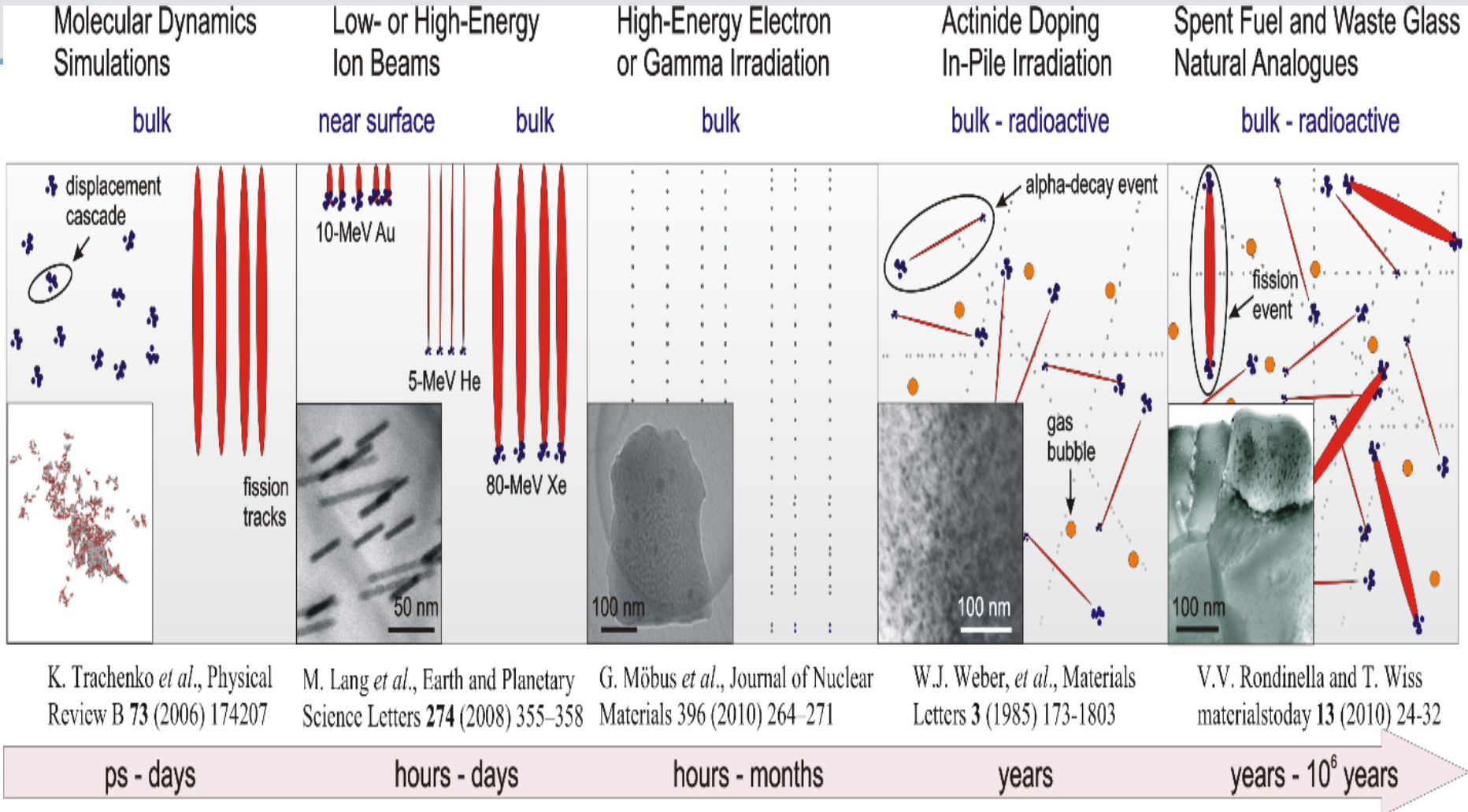


Fig. 6. Cesium normalized leaching rates of glass composite wasteform with the increase in waste loading.

# III. Radiation effects





The Abdus Salam  
**International Centre  
 for Theoretical Physics**  
 www.ictp.it



## Joint ICTP/IAEA Workshop on radiation effects in nuclear waste forms and their consequences for storage and disposal

12 - 16 September 2016

Miramare, Trieste, Italy



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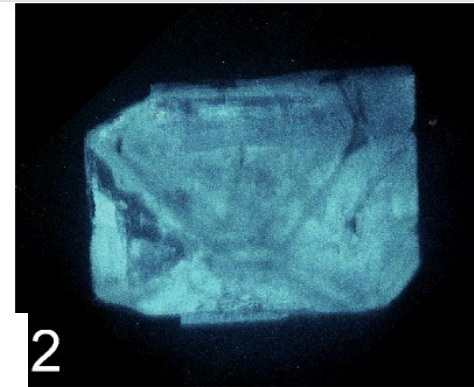
- Role of irradiation at different stages of material use in the nuclear industry;
- Nuclear waste forms and envisaged irradiation storage and disposal conditions;
- Behaviour of materials containing actinides and long lived radionuclides;
- Experimental techniques to investigate and simulate radiation effects;
- Theoretical/computational methods to investigate and simulate radiation effects;

# I. Zircon ( $\text{Zr}_{0.977}\text{Pu}_{0.023}\text{SiO}_4$ ) containing 2.4 wt.% $^{238}\text{Pu}$



1

$10^{16}$   $\alpha$ -decays/g



2

2



3

$2 \times 10^{17}$   $\alpha$ -decays/g



4

$5 \times 10^{17}$   $\alpha$ -decays/g



5

$22 \times 10^{17}$   $\alpha$ -decays/g



6

$51 \times 10^{17}$   $\alpha$ -decays/g

## II. Pu-monazite, $\text{PuPO}_4$

containing

7.2 wt. %  $^{238}\text{Pu}$

is very **unstable** under self-irradiation.

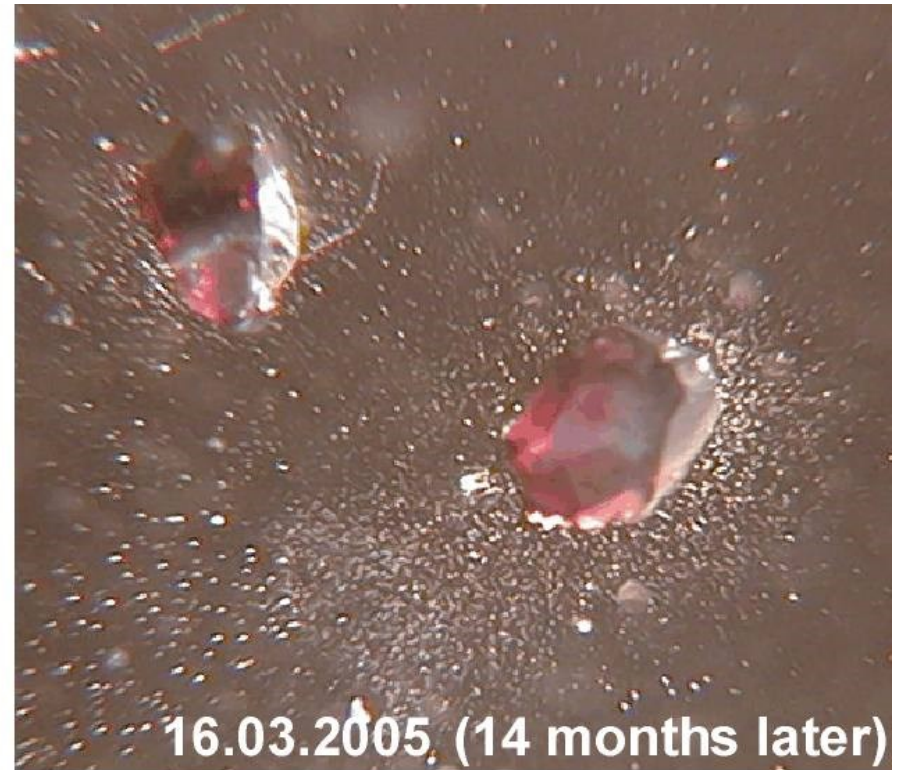
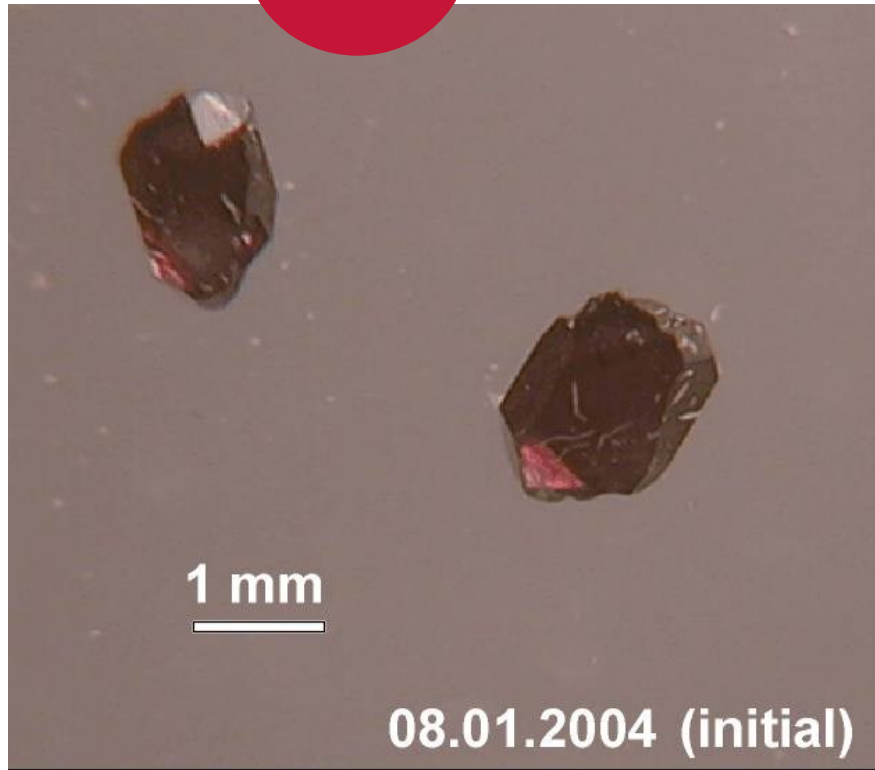
Strong swelling was seen and even breaking into separate pieces.

Single crystals Eu-monazite,  $(\text{Eu}_{0.937}\text{Pu}_{0.063})\text{PO}_4$  with  
4.9 wt.%  $^{238}\text{Pu}$ .

7 years after synthesis at accumulated dose

$52 \cdot 10^{17}$   $\alpha$ -decay/g

2

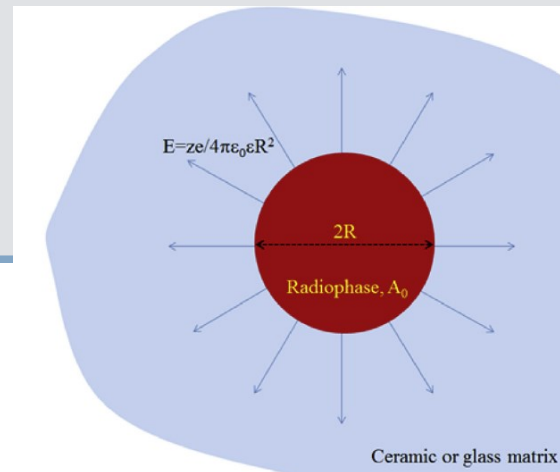


Mechanical destruction: *Is that a result of alpha-decay?*

*What is the mechanism of aerosol/colloid formation ?*

M.I. Ojovan, B.E. Burakov, W.E. Lee. Radiation-induced Microcrystal Shape Change as a Mechanism of Wasteform Degradation. *Journal of Nuclear Materials* **501C** (2018) 162-171.

Experiments with actinide-containing insulating wasteforms such as devitrified glasses containing  $^{244}\text{Cm}$ , Ti-pyrochlore, single-phase La-monazite, Pu-monazite ceramics, Eu-monazite and zircon single crystals containing  $^{238}\text{Pu}$  indicate that mechanical self-irradiation-induced destruction may not reveal itself for many years (even decades). The mechanisms causing these slowly-occurring changes remain unknown therefore in addition to known mechanisms of wasteform degradation such as matrix swelling and loss of solid solution we have modelled the damaging effects of electrical fields induced by the decay of radionuclides in clusters embedded in a non-conducting matrix. Three effects were important: (i) electric breakdown; (ii) cluster shape change due to dipole interaction, and (iii) cluster shape change due to polarisation interaction. We reveal a critical size of radioactive clusters in non-conducting matrices so that the matrix material can be damaged if clusters are larger than this critical size. The most important parameters that control the matrix integrity are the radioactive cluster (inhomogeneity) size, specific radioactivity, and effective matrix electrical conductivity. We conclude that the wasteform should be as homogeneous as possible and even electrically conductive to avoid potential damage caused by electrical charges induced by radioactive decay.



Journal of Nuclear Materials 501 (2018) 162–171

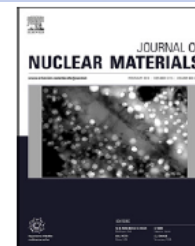


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## Radiation-induced microcrystal shape change as a mechanism of wasteform degradation

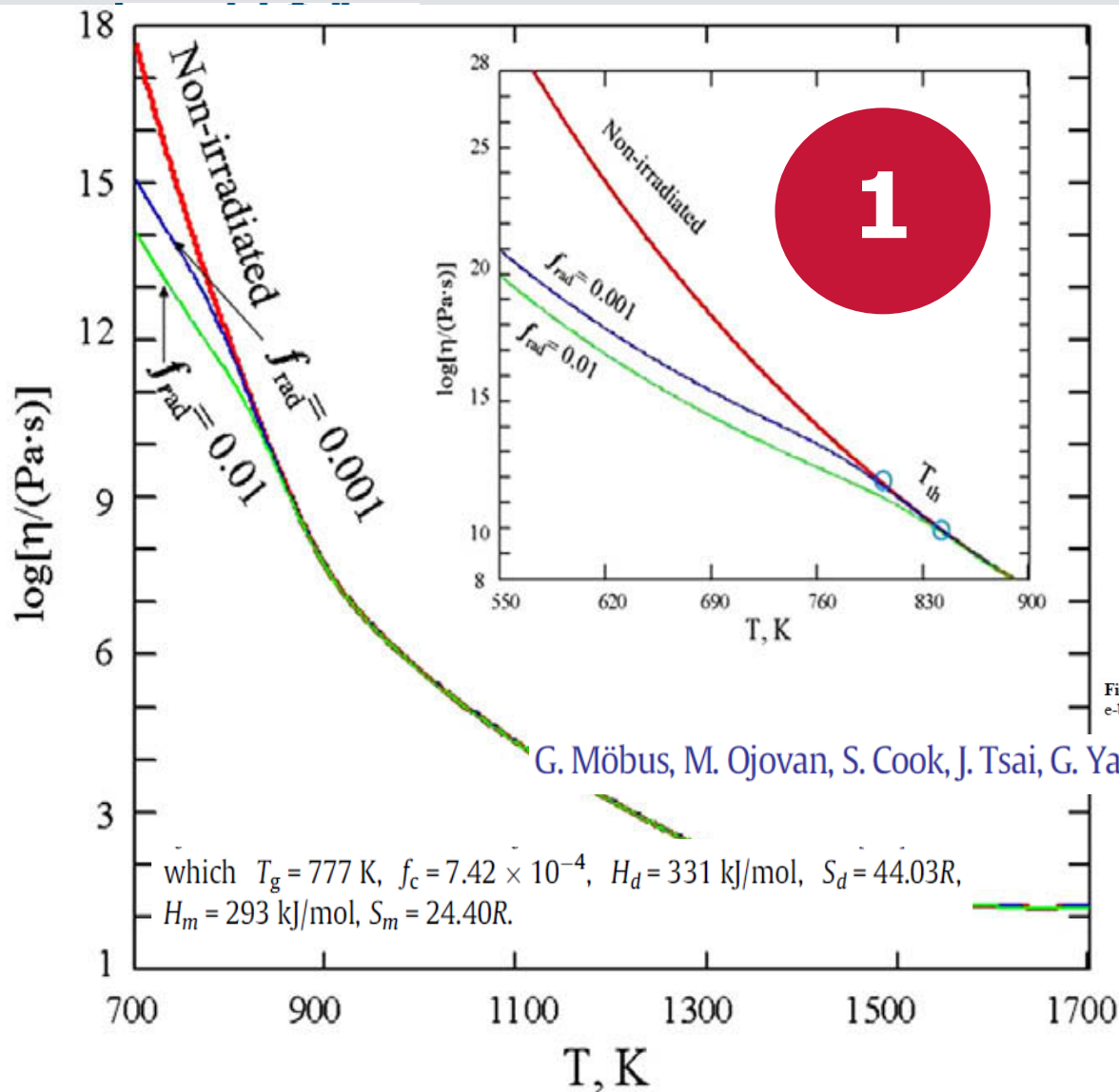
Michael I. Ojovan <sup>a, c, \*</sup>, Boris E. Burakov <sup>b</sup>, William E. Lee <sup>c</sup>

<sup>a</sup> Department of Radiochemistry, Lomonosov Moscow State University, Leninskie Gory, 1, Bd. 3, Moscow, 119991, Russia

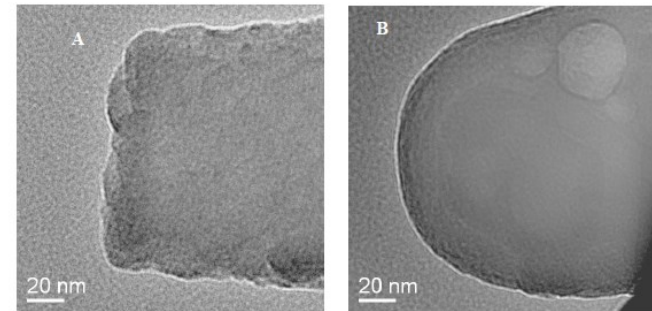
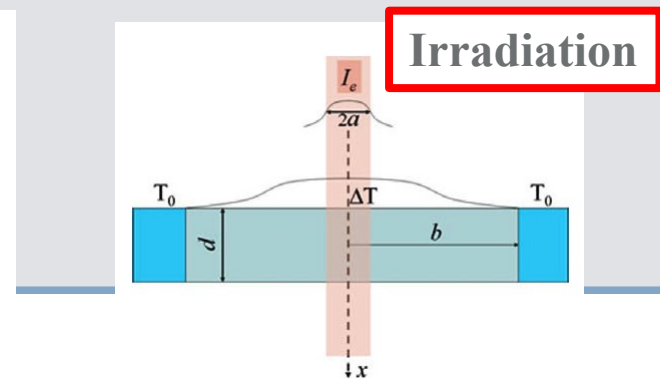
<sup>b</sup> V.G. Khlopin Radium Institute, 28, 2-nd Murinskiy Ave., St. Petersburg, 194021, Russia

<sup>c</sup> Centre for Nuclear Engineering and Department of Materials, Imperial College London, SW7 2AZ, London, UK



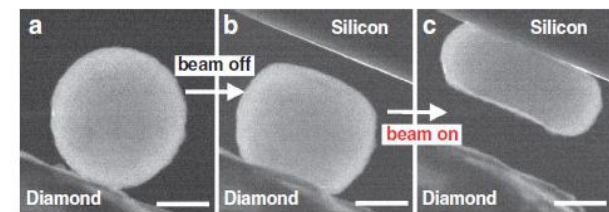


**Fig. 9.** Viscosities of non-irradiated and electron beam irradiated amorphous soda lime silicate system  $70\text{SiO}_2\text{21CaO9Na}_2\text{O}$  as a function of temperature for two dimensionless electron flux densities ( $f_{\text{rad}} = \alpha_e I_e$ ) 0.01 and 0.001.



**Figure 3.** Transformation of rugged glass fibre end (A) into hemisphere (B) under the 4 nA TEM e-beam continuous irradiation over 30 min.

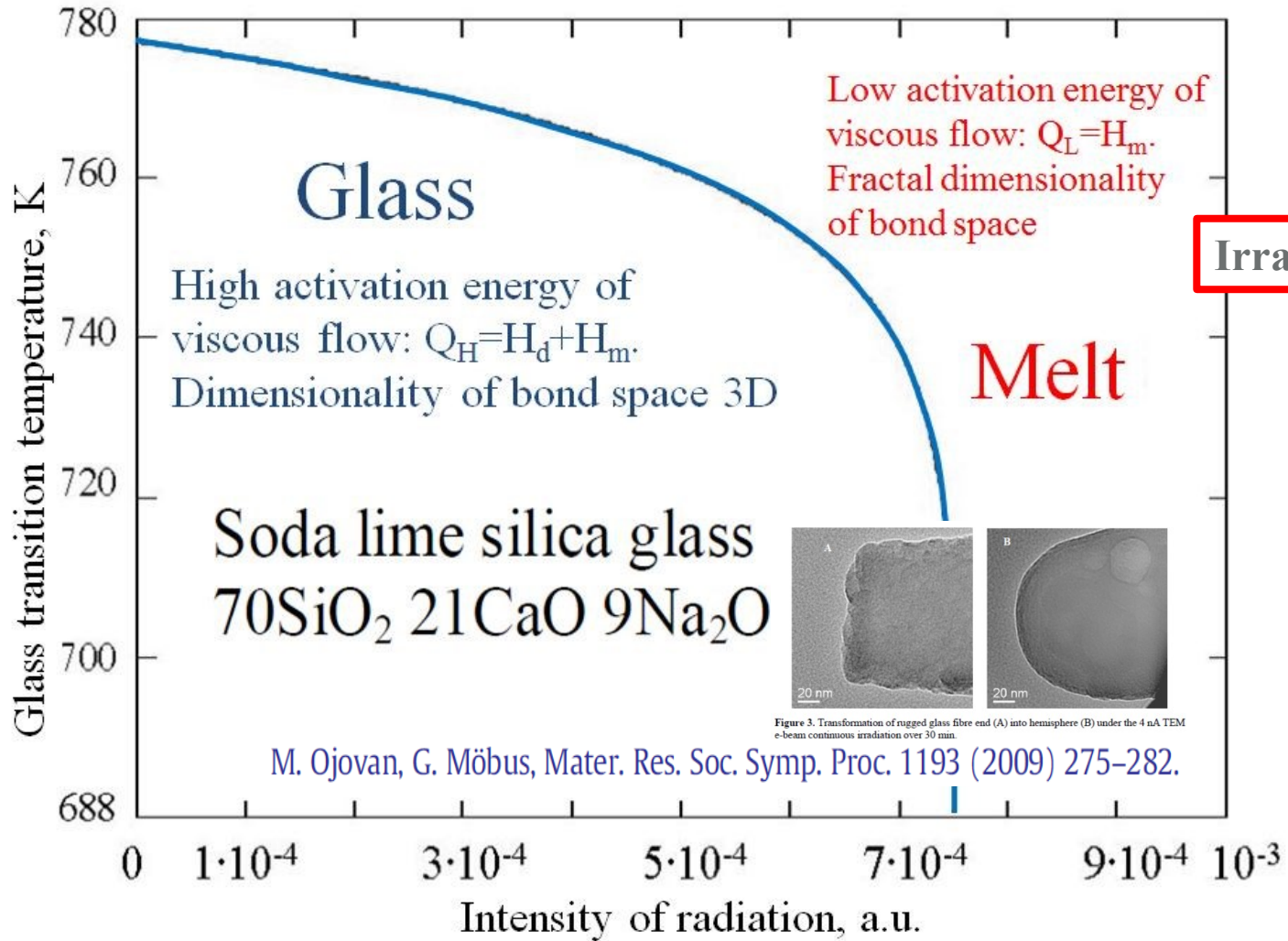
G. Möbus, M. Ojovan, S. Cook, J. Tsai, G. Yang, *J. Nucl. Mater.* 396 (2–3) (2010) 264–271.



**Figure 1 |** Nanocompression of amorphous silica particle inside a transmission electron microscope (TEM). Two consecutive compression runs were performed with the electron beam being off and on, respectively.

K. Zheng et al., *Nature Communications*, 1:24, 1 (2011).





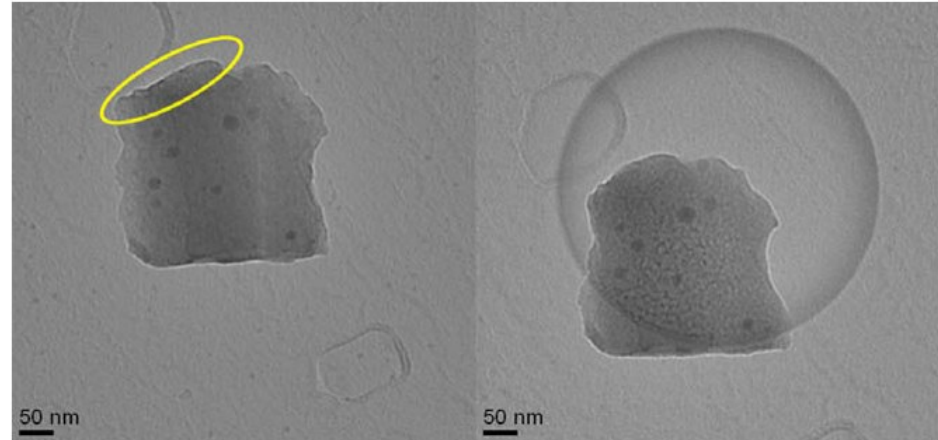
Irradiation

1

## Phase separation, bubble formation in nuclear glasses ...

### ➤ Modification of the glass viscosity

- Very high dose rate (**10 orders of magnitude higher than expected in HLW glass**)
- Bond Breaking



Favors oxygen bubbles and phase separation

$$\eta_R(T) = \eta(T) / [1 + \alpha_e I_e [1 + C \exp(D / RT)]]$$

$\eta(T)$  viscosity of an non-irradiated material,  
 $\alpha_e$  efficiency of electron beam bond breaking and annihilation  
 $A_e I_e$  dimensionless electron flux density

Ojovan, *Mater. Res. Soc. Symp. Proc. Vol. 1193 (2009)*  
 Möbus, *JNM 396 (2010)*

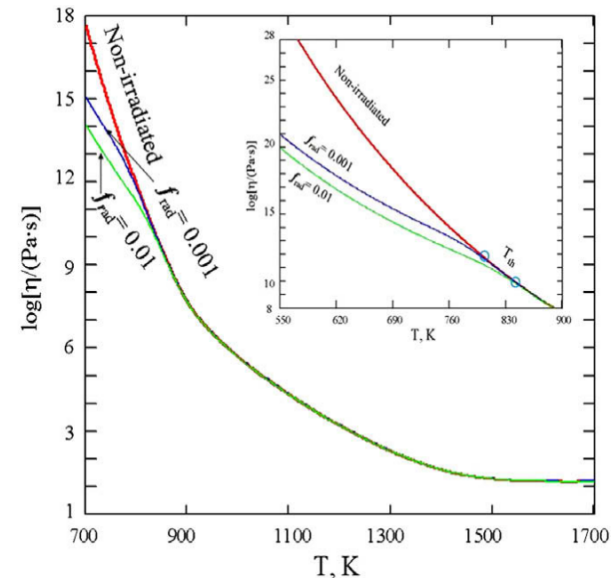
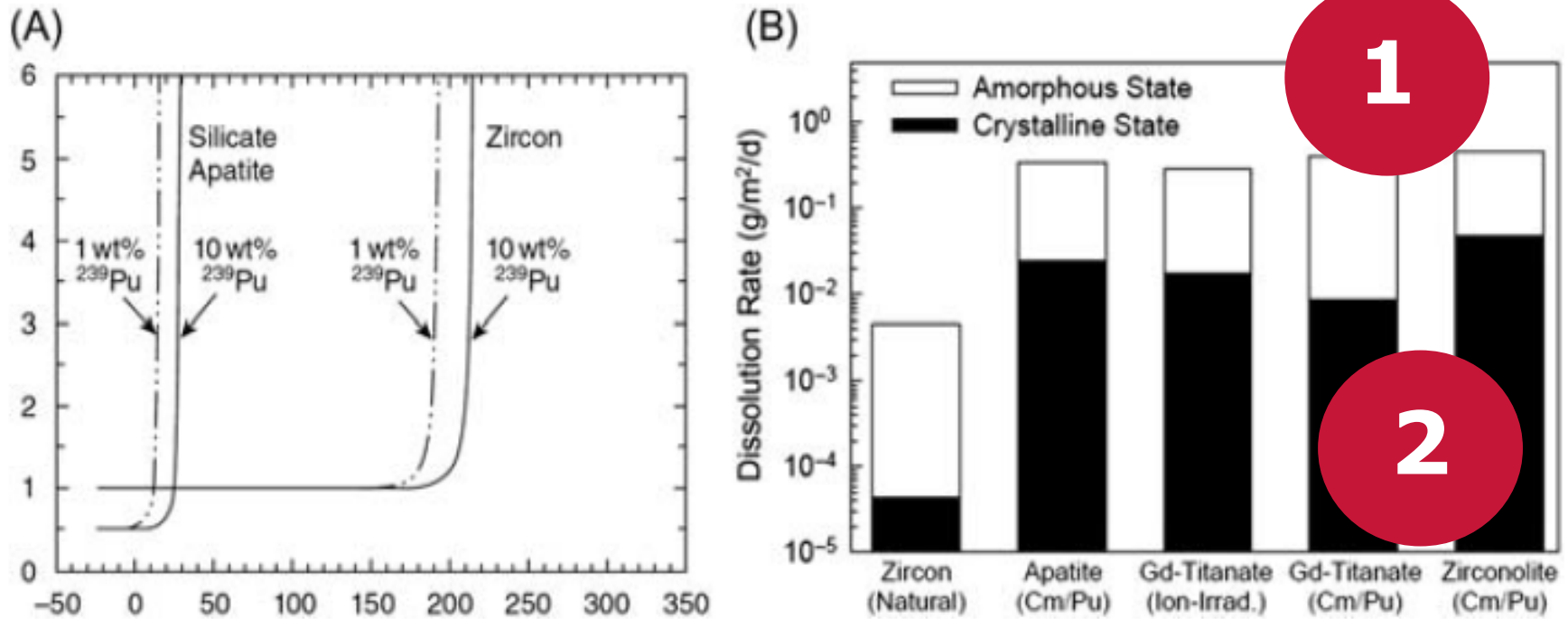


Fig. 9. Viscosities of non-irradiated and electron beam irradiated amorphous soda lime silicate system  $70\text{SiO}_2/21\text{CaO}/9\text{Na}_2\text{O}$  as a function of temperature for two dimensionless electron flux densities ( $f_{\text{rad}} = \alpha_e I_e$ ) 0.01 and 0.001.



**Figure 23.16** (A) Critical amorphisation dose (vertical axis:  $\times 10^{19}$  alpha-decays per g) as a function of materials temperature (horizontal axis:  $^{\circ}\text{C}$ ). (B) Wasteform dissolution rate increases caused by radiation amorphisation. *Courtesy William J. Weber, University of Tennessee, US.*

Molecular Dynamics  
Simulations

Low- or High-Energy  
Ion Beams

High-Energy Electron  
or Gamma Irradiation

Actinide Doping  
In-Pile Irradiation

Spent Fuel and Waste Glass  
Natural Analogues

bulk

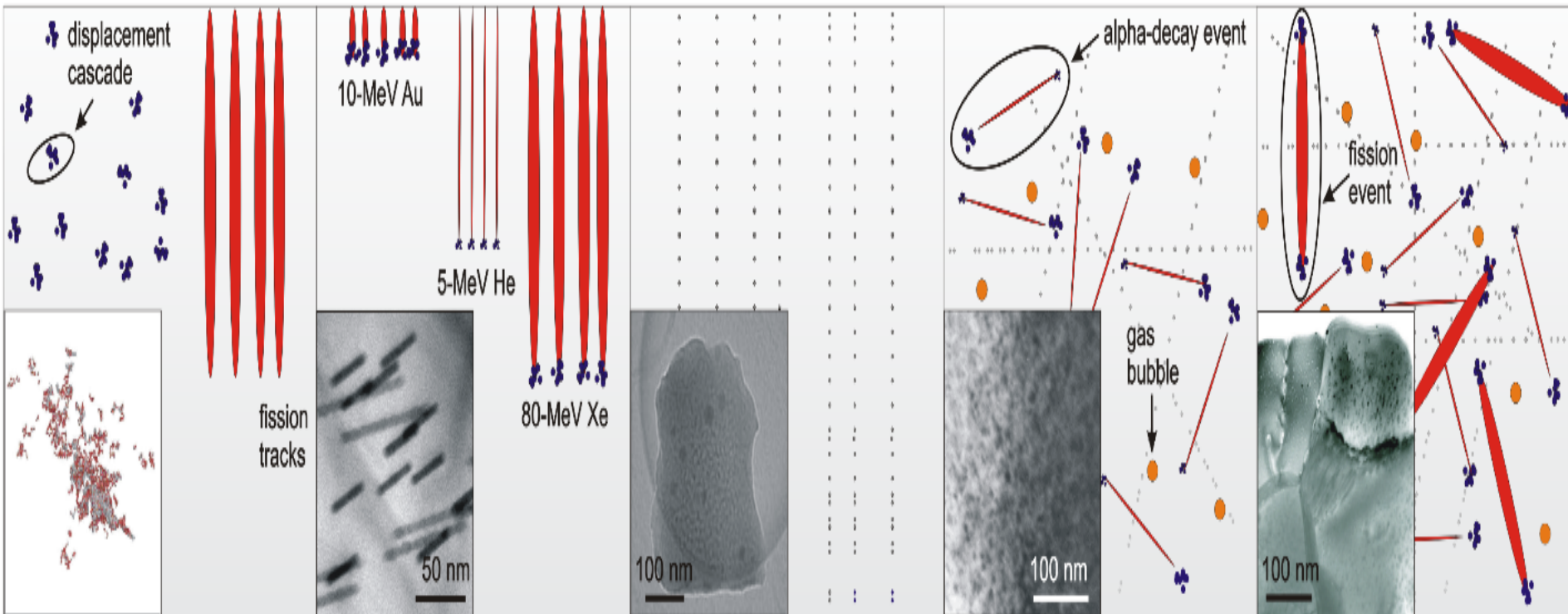
near surface

bulk

bulk

bulk - radioactive

bulk - radioactive



K. Trachenko *et al.*, Physical  
Review B **73** (2006) 174207

M. Lang *et al.*, Earth and Planetary  
Science Letters **274** (2008) 355–358

G. Möbus *et al.*, Journal of Nuclear  
Materials **396** (2010) 264–271

W.J. Weber, *et al.*, Materials  
Letters **3** (1985) 173–1803

V.V. Rondinella and T. Wiss  
materialstoday **13** (2010) 24–32

ps - days

hours - days

hours - months

years

years -  $10^6$  years

## References:

- 1. *An Introduction to Nuclear Waste Immobilisation*, M.I. Ojovan, W.E. Lee, S.N. Kalmykov. Elsevier, Amsterdam, 3<sup>rd</sup> Edition (2019).   **
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- 4. *New Developments in Glassy Nuclear Wasteforms*. M.I. Ojovan, W.E. Lee. Nova Science Publishers, New York, 131p. (2007). **