Development of host matrices for high-level nuclear waste (HLW)

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Current matrix development research programs

- **Development of borosilicate glass matrix**

  - **equivalent to basaltic glass**

- **Development of sphene based glass ceramics**

  - **equivalent to devitrified basaltic glass**

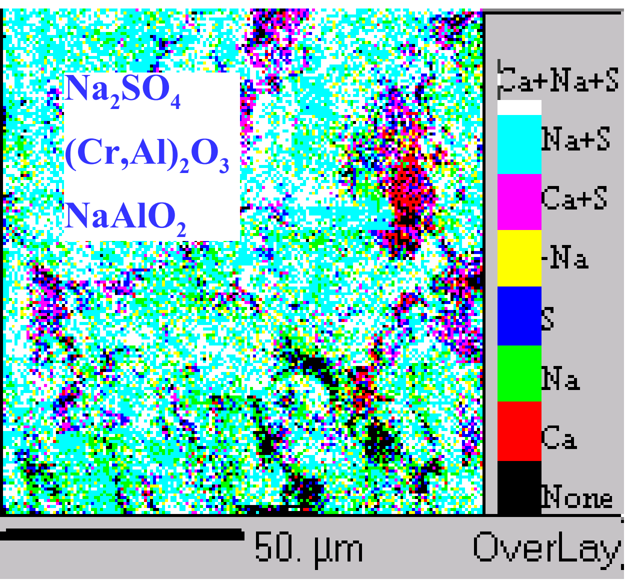
- **Development of SYNROC (synthetic rock)**

  - equivalent to TiO_2 rich bulk composition metamorphosed at granulite facies condition

Example

Development of borosilicate glass matrices for sulfate rich high level nuclear waste

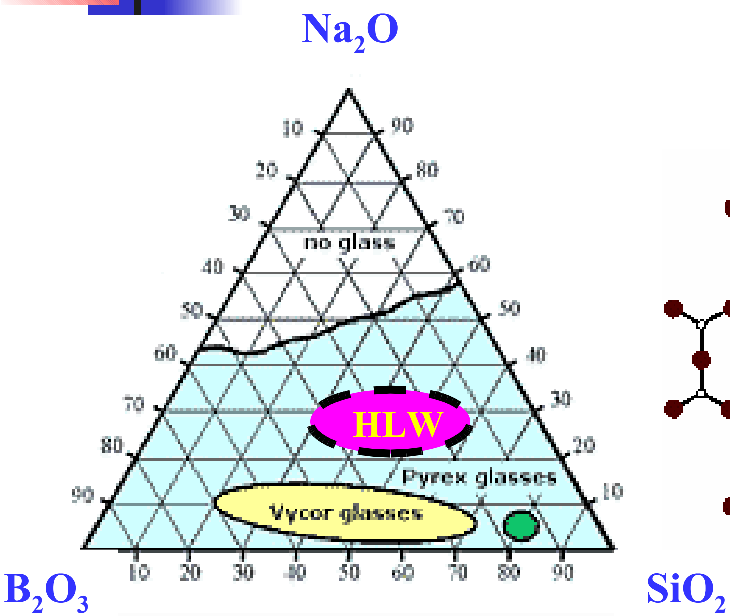
Problems with sulfate rich high level waste

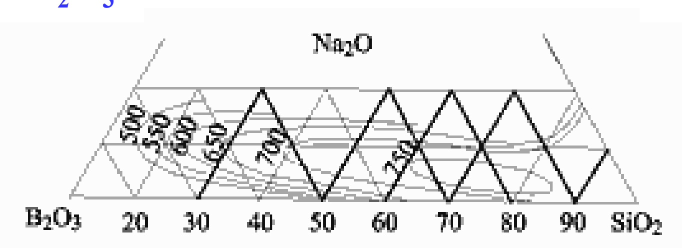


- Lower solubility in silicate melt forms **water soluble yellow phase**
- Due to lower density (~2-2.5 gm/cc) floats on waste glass melt (3-3.5 gm/cc) & prevents escape of gas bubbles causing **frothing & bumping**
- Higher **corrosion** of pot materials
- gets partially volatilized and **clogs off-gas system**
- ^{137}Cs and ^{90}Sr get partitioned into yellow phase & being **water soluble** provide easy release of radioactive fission products to nature

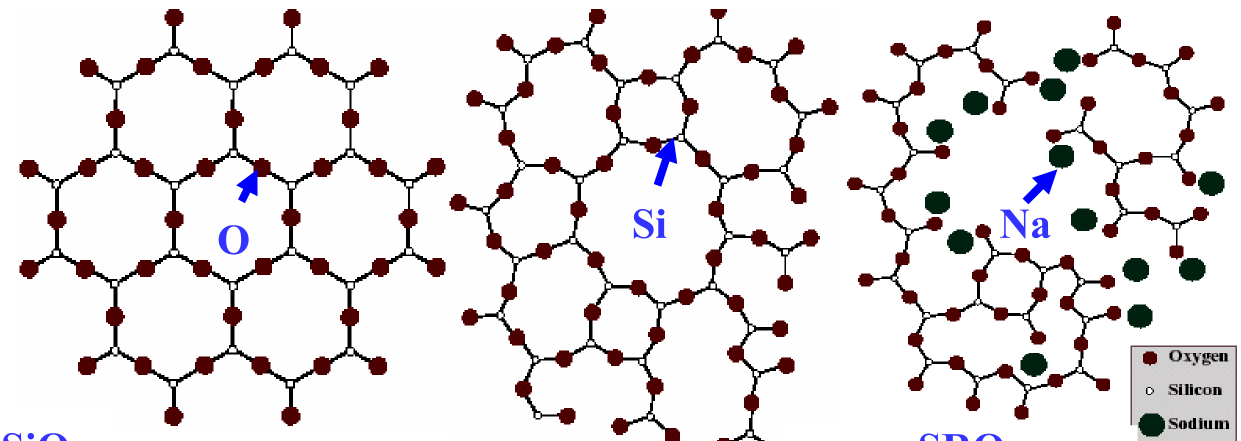
Borosilicate matrix

Choice of matrix = f (waste compositions)





Immiscibility region

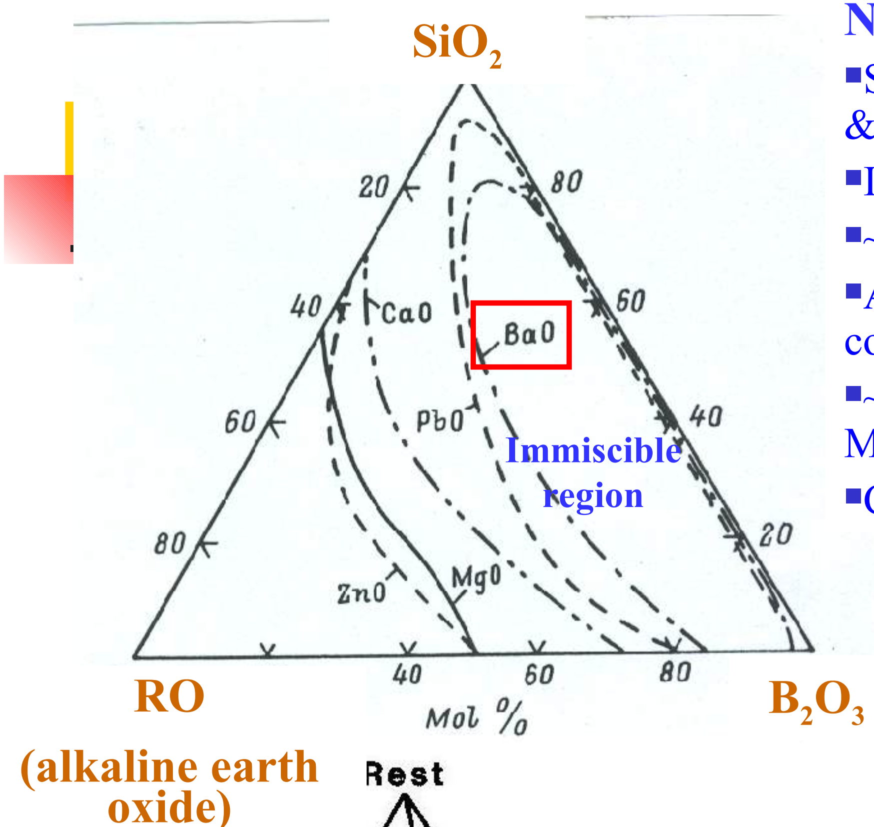


SRO+LRO
Cryst. Silica

SRO
Amp. Silica

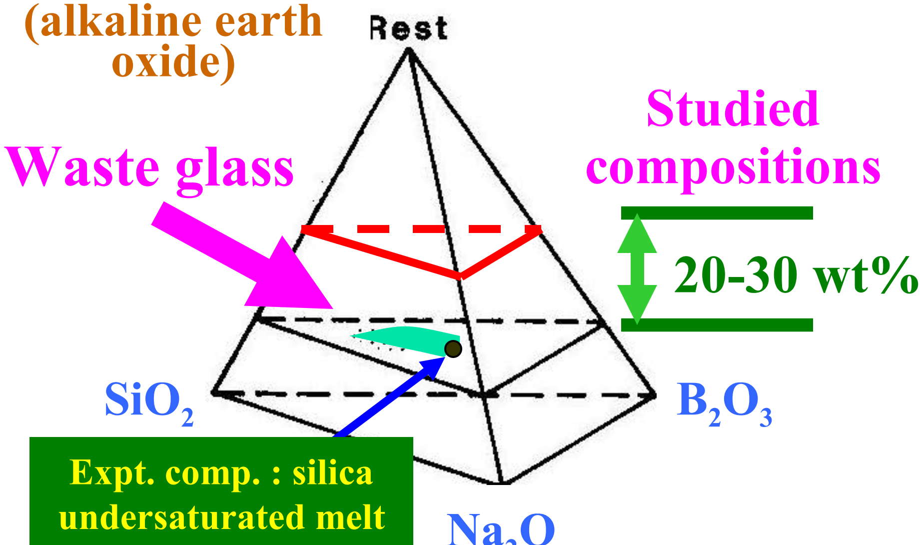
SRO
Amp. Na silicate

Sodium barium borosilicate waste glass



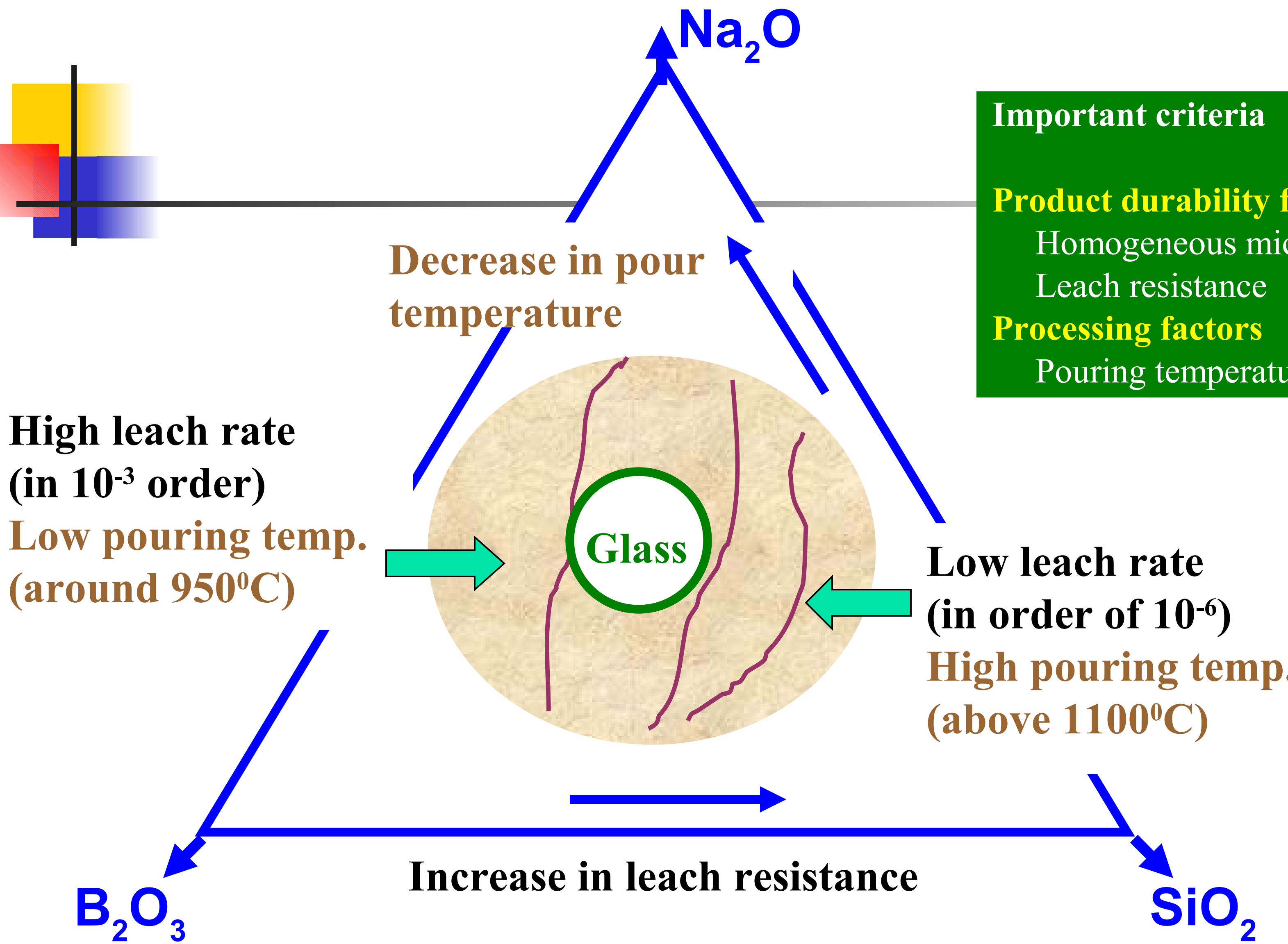
Natural data

- S in minerals occur in S^{2-} (sulfide), S^0 (native), S^{4+} (sulfite) & S^{6+} (sulfate state).
- In waste glass S always occur as sulfate.
- ~370 sulfate minerals with ~140 structure types are known.
- Among anhydrous sulfates Barite structure is most common.
- ~Barite deposits are known from Early Archean (~3500 Myrs) to recent.
- Complete solid solution between Barite-Celestine occurs



Compound	Melting point (^{0}C)	Solubility in 100 parts	Free energy (at 1000^{0}C, kJ/mole)
$PbSO_4$	1090	0.004	-459.54
Na_2SO_4	**884**	**19.5**	**-874.73**
Cs_2SO_4	995	179.0	-880.11
$CaSO_4$	1400	0.20	-950.74
$SrSO_4$	1600	0.013	-973.69
$BaSO_4$	**1580**	**0.0002**	**-976.29**

Optimization of Waste glass composition

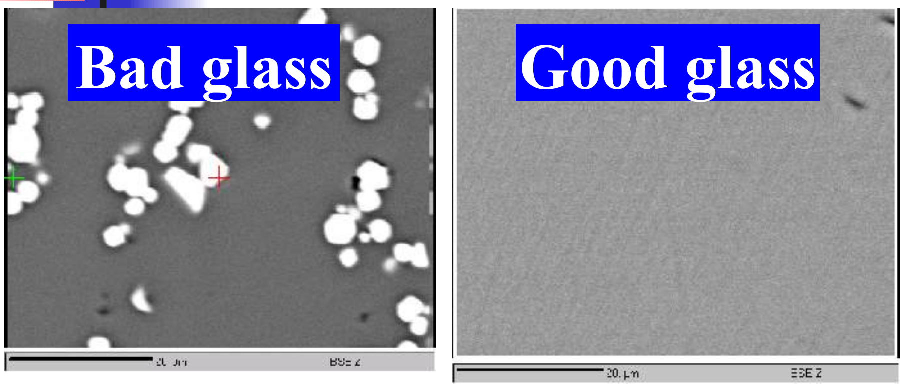


Important criteria

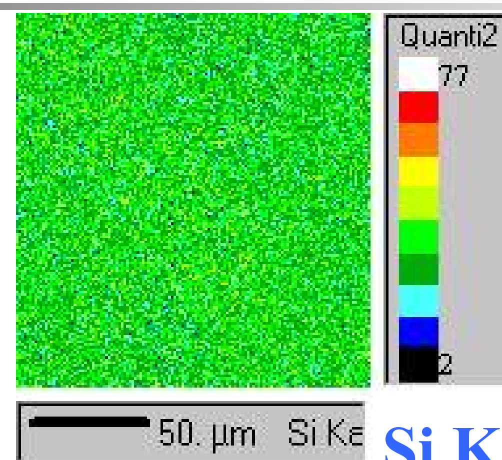
Product durability factors
- Homogeneous microstr.
- Leach resistance

Processing factors
- Pouring temperature

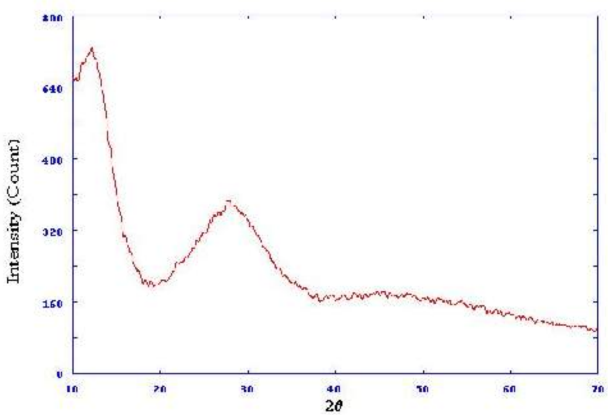
Homogeneity of sodium barium borosilicate waste glass



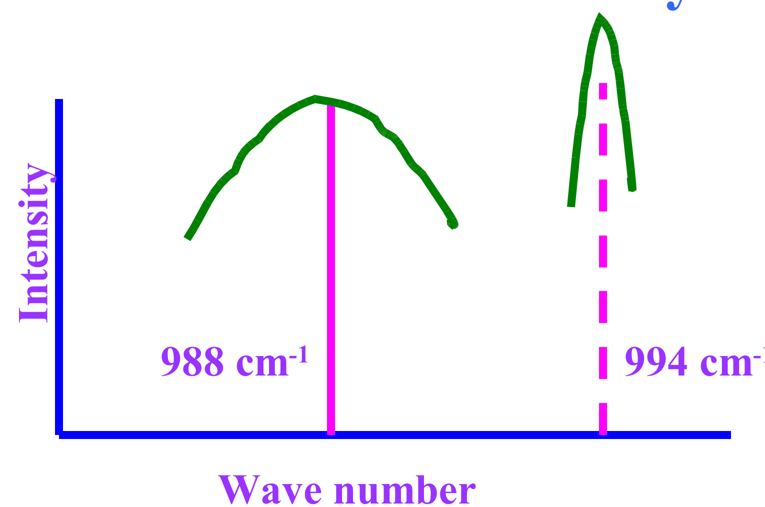
BSE image



Si Kα X-ray image



XRD spectrum



Raman spectrum (Schematic)

Leach resistance of waste glass

Leachate analysis

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Leaching study

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Glass surface

Diffusion:

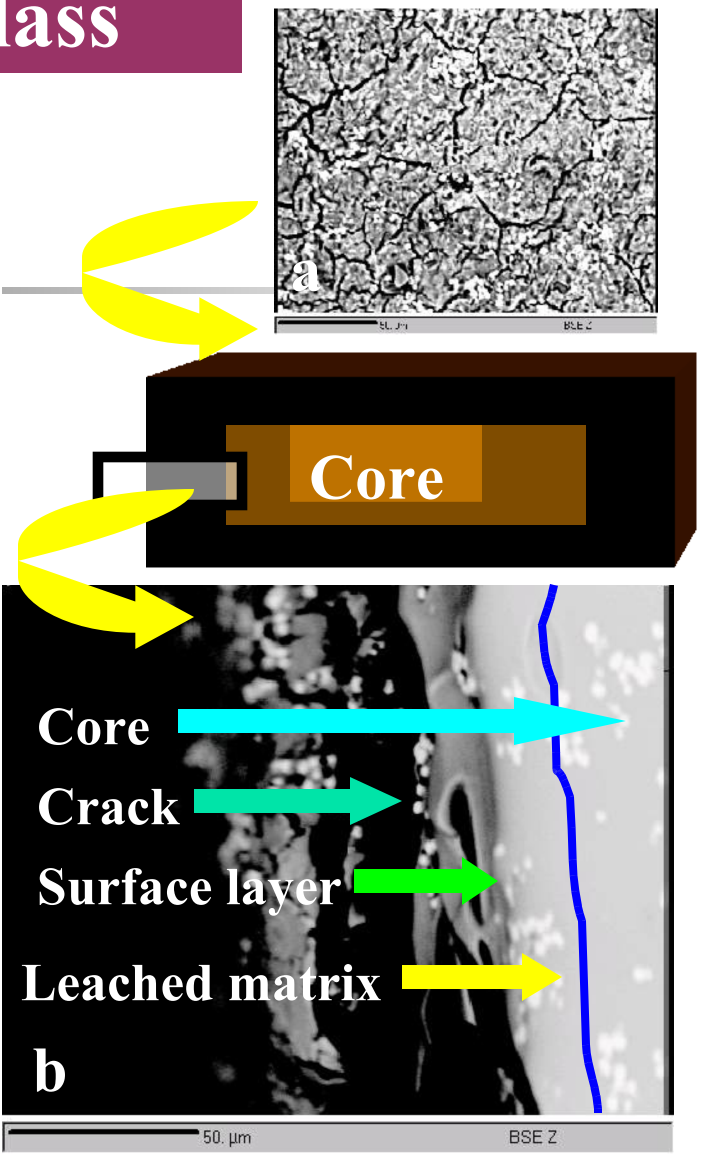
$\equiv Si\text{-}O\text{-}M + H^+ \leftrightarrow \equiv Si\text{-}O\text{-}H + M^+$

[low temperature]

Dissolution:

$\equiv Si\text{-}O\text{-}Si\equiv + H_2O \leftrightarrow 2\equiv Si\text{-}O\text{-}H$

[high temperature]

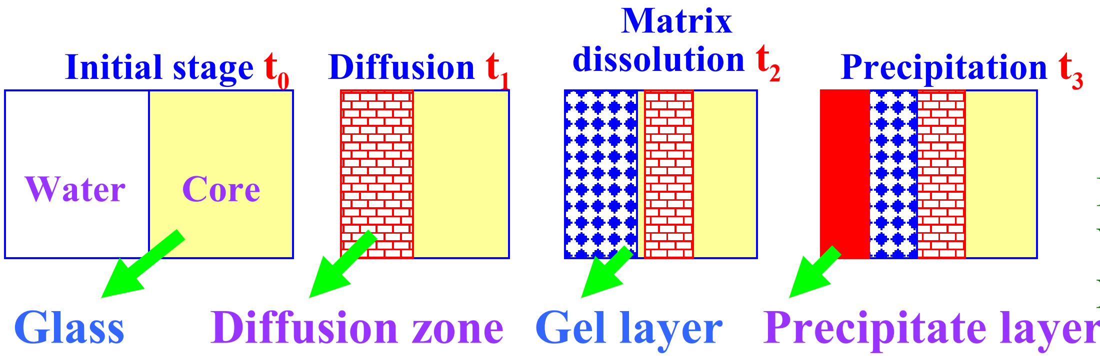


Phases on precipitate. layer:

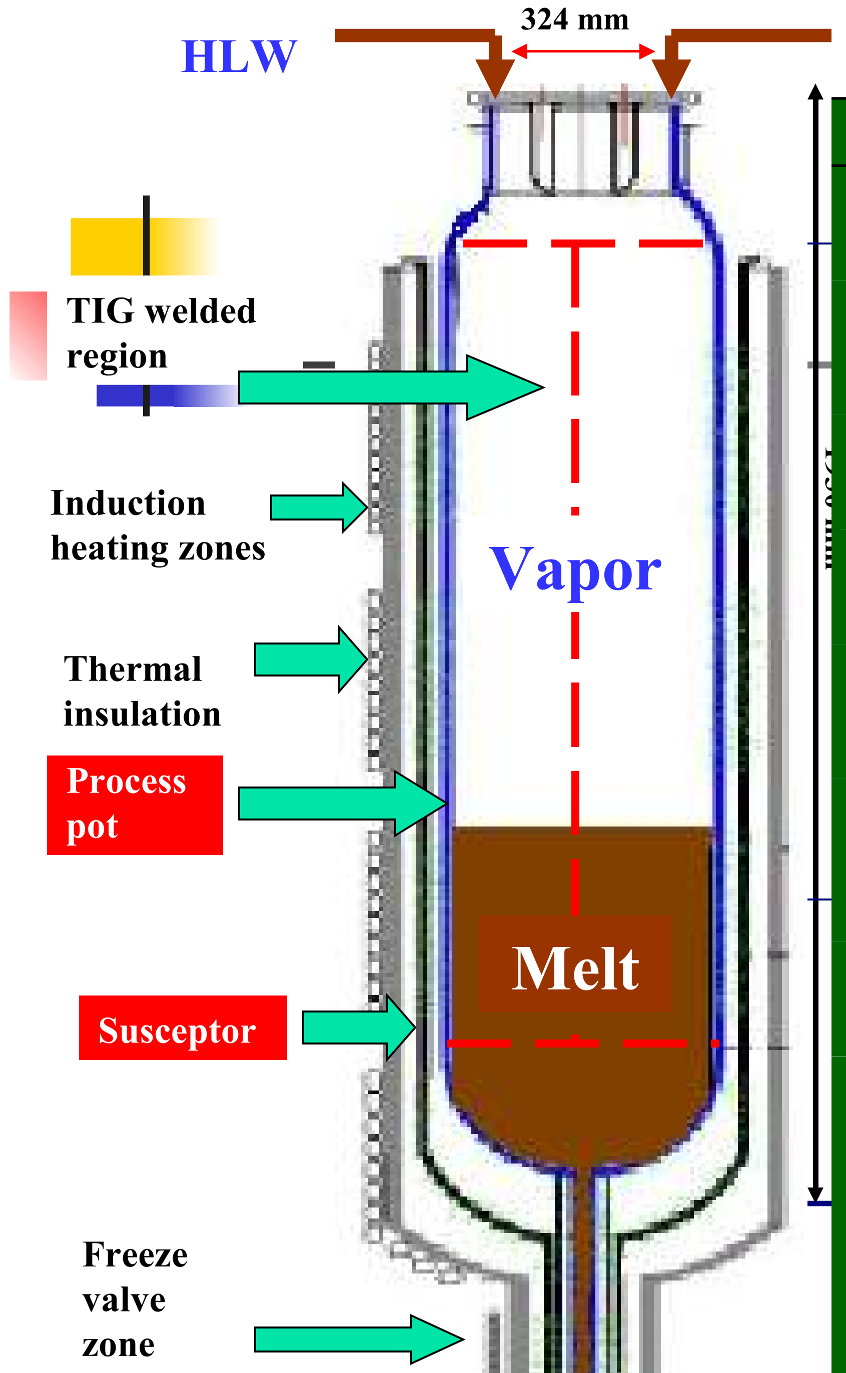
Waste glass: smectites, zeolite

Natural glass: saponite, smectite, zeolite

Evolution of glass surface with time (t)

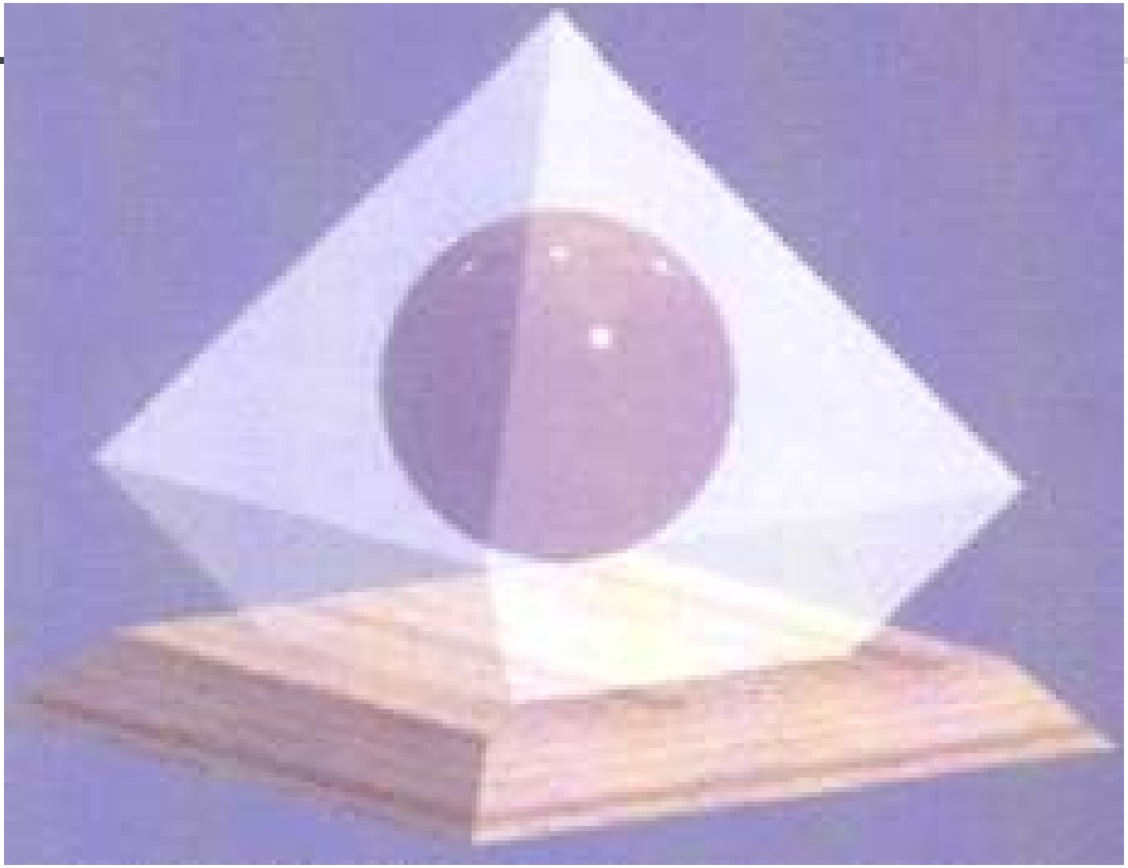


Plant scale experience



Features	Data
Composition (wt%)	$SiO_2 + B_2O_3$-50.5%, Na_2O + BaO – 28.5% Waste oxides: 21.0
Pouring temp. (°C)	Base glass: 950, Waste glass: 925
Homogeneity	Amorphous and homogeneous
Leach rate (after 700 days leaching)	~ 2.32×10^{-6} gm $cm^{-2}.day^{-1}$
Glass transition temp. (°C)	496
Viscosity (dPa.s)	50 at pouring temperature
Density (gm/cm^3)	~3.0
Thermal Conductivity at 100°C ($W\ m^{-1}\ {}^oC^{-1}$)	0.92
Impact Strength (RIAJ)	0.84
Plant scale operation	•No excessive foaming •No accumulation of yellow phase •No unusual release of waste and glass components in off-gas system •13000 Kgs of VWP prepared safely

Thank you



The glass sphere, which can be held in palm, represents the amount of vitrified waste arising from life long use of nuclear energy by an average Indian family for all its electricity needs