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# Past and Present Applications of Synroc

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# **Classes of Nuclear Waste**

- Low-level (mining waste, hospital wastes; less than 100 MBq/L)
- Intermediate level (secondary wastes from nuclear power plant operations; more than 100M Bq/L)
- TRU= actinide-bearing waste having > 100 nCi/g (for example 1.6 ppm of <sup>239</sup>Pu or 140 ppm of <sup>237</sup>Np)

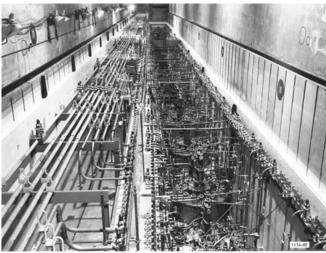
$$(1Ci = 37GBq)$$

High-level: spent power plant fuel or reprocessing waste ~10<sup>13</sup>-10<sup>14</sup> Bq/L



- Spent fuel in storage (many thousands of MT from the ~400 power reactors worldwide)
- Acidic liquid wastes from reprocessing fuel (~1000 Ci/L)
- Defence wastes from Pu production (~ 1 Ci/L; millions of litres in US). Neutralised for storage in SS tanks but tank leakage can occur and gas buildup a problem-mostly process chemicals





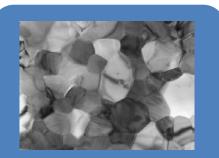
Savannah River Site -- interior of canyon



# **Waste Forms for HLW**

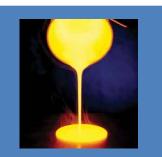
- Via the addition of certain materials, produce by chemical design a near-water insoluble solid (the waste form) plus minimum secondary waste.
- Requirements:
  - Relatively easy to fabricate, even though intensely radioactive (no dust or liquid spray)
  - Low volatility losses of RN during processing
  - High waste loading
  - Nearly insoluble in a range of hot and cold groundwaters

# **Types of Wasteforms**



#### Ceramic

- HLW / ILWLattice substitution
- 10<sup>-5</sup> g/m²/d



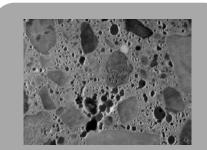
#### Glass

- HLW / ILW
- Glass network incorporation
- $10^{-3} \text{ g/m}^2/\text{d}$



### **Glass Ceramic**

- HLW / ILW
- Composite glass-ceramic
- Elements targeted to either ceramic or glass
- 10<sup>-3</sup> -10<sup>-5</sup> g/m²/d



#### Cement

- LLW
- Continuous porosity
- Diffusion release
- Waste ions located in pore water



# **PAST APPLICATIONS**

# **Synroc Titanate Minerals**

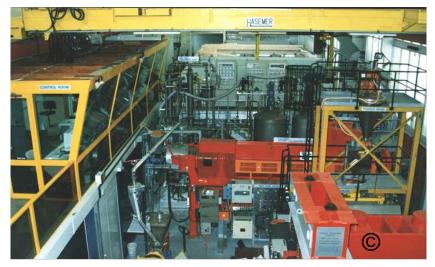
### Composition and mineralogy of synroc-C (20 wt%)

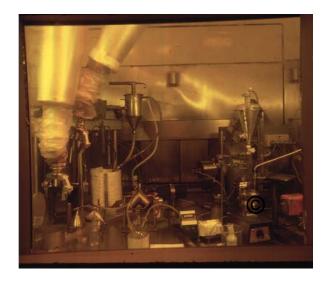
- Much more leach resistant in water than silicates and phosphates of supercalcine
- 10-100 times more resistant than borosilicate glasses in short-term MCC-1 tests

Phase	Wt.%	Radionuclides in lattice	
Hollandite, BaAl <sub>2</sub> Ti <sub>5</sub> O <sub>14</sub>	30	Cs, Rb	
Zirconolite, CaZrTi <sub>2</sub> O7	30	RE, Zr, An	
Perovskite, CaTiO <sub>3</sub>	20	20 Sr, RE, An	
Ti oxides, mostly TiO <sub>2</sub>	15	none	
Alloy phases	5	5 Tc, Pd, Ru, Rh, Mo, Ag, Cd, Se, Te	

# **Synroc Titanate Minerals**

- 1980s Original synroc-C and its processing technology developed
- Specifically targeted towards immobilising high level waste (HLW) from the reprocessing of spent nuclear fuel from power reactors (PUREX type PW-4b type waste)
- Synroc technology was not sufficiently mature to compete with borosilicate glass (US DOE decision in 1981 to immobilize SRNL HLW in borosilicate glass)
- Glass became the defacto baseline process for the immobilisation of HLW.





SDP – conceptual plant (1980s)

# What makes waste problematic for glass

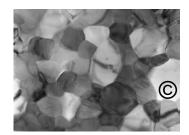
### Switch in focus to "problematic" wastes

 High concentrations of refractory metal oxides like alumina and zirconia

low waste loadings in pourable borosilicate glasses

- Require high processing temperature
  - increase in volatile fission product loss
- Chemistry viscosity / conductivity / crystallisation
- Corrosive off-gas (eg. HCI)
- High concentrations of toxic and radioactive elements
- Relatively low waste loadings achievable (plutonium / U).
- Harder to extract fissile material
- Orphan wastes where volumes are low





# **ANSTO Synroc – HIPing**



## **Benefits from HIP route:**

- Zero emissions from high temperature densification
- Significant waste volume reduction (impact on long term storage)
- High density with minimal temperature (grain size)
- Versatile Capable of producing a wide range of waste forms
- No contact between waste and process equipment

## **Excess Weapons Plutonium Immobilization**

- Excess impure weapons Plutonium
- Project in the 1990s with US Labs

Competitively selected by the US DOE to immobilize excess impure weapons plutonium in 1997

(written into the Waste Acceptance System Requirements Document)

# **Idaho National Laboratory Calcines**

### Waste Description:

• 4400 m<sup>3</sup> heterogeneous calcine, consisting of layered binsets (alumina, zirconia, zirconia-sodium blends reflecting different reprocessed fuel assemblies)

<b>Alumina Calcine</b> ~90% Al <sub>2</sub> O <sub>3</sub> ~5% alkali ~3% HgO	<b>Zirconia Calcine</b> ~50% CaF <sub>2</sub> ~25% ZrO <sub>2</sub> ~15% Al <sub>2</sub> O <sub>3</sub> ~0-8% CdO	
	~15% Al <sub>2</sub> O <sub>3</sub>	

### Calcine challenges for glass...

- Low solubility in glass
- Detrimental to glass properties e.g viscosity
- Corrosive to melter or off-gas system

### Impact is to significantly reduce maximum achievable waste loading for glass, What about a glass-ceramic waste form.

# **Idaho National Laboratory Calcines**

Consolidation: Matrix: Waste loading: Durability (PCT-B): Final volume: (relative to untreated calcine) Temp:

Pressure: Off-gas: HIP glass-ceramic **60-90%** 10-100 x EA glass 15-45% reduction

1300°C

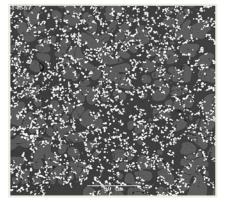
100 MPa

very low



2009



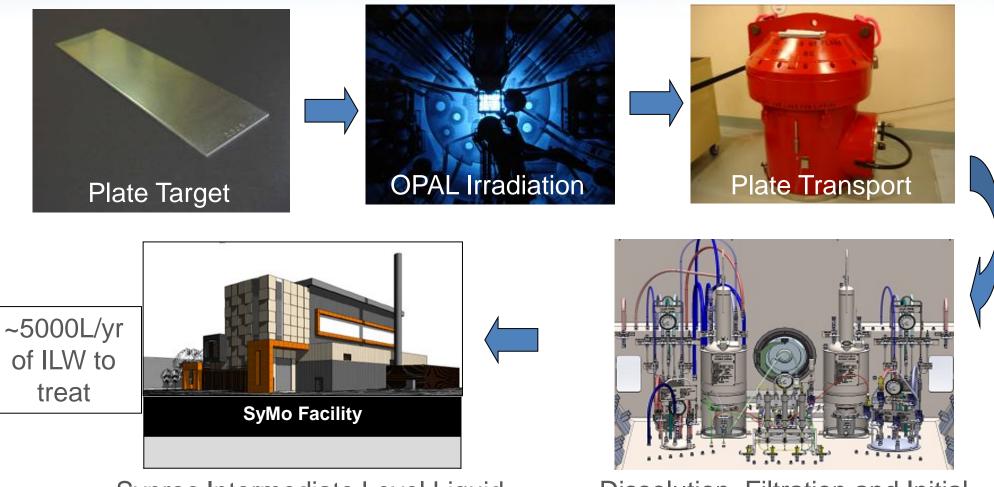


JHM borosilicate glass **20-35%** 10 x EA glass 100+% increase

1150°C medium-high

# **PRESENT APPLICATIONS**

# **ANM Production Cycle**



Synroc Intermediate Level Liquid Waste Treatment Plant Project Dissolution, Filtration and Initial Ion-exchange Purification: ILLW

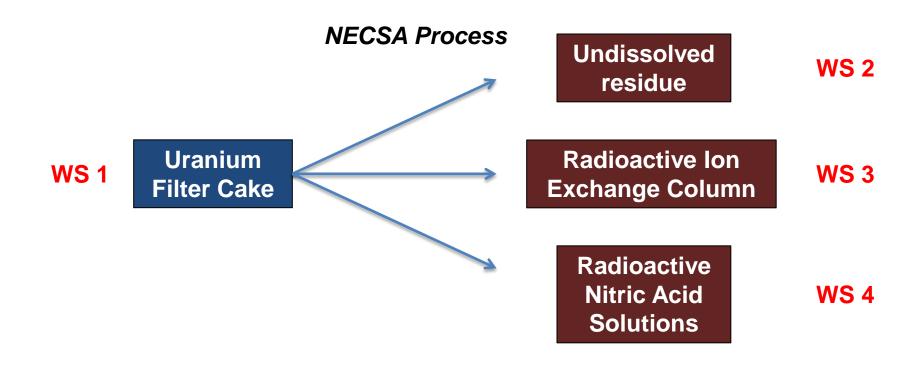




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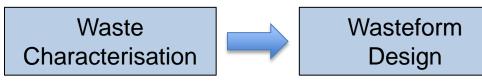


- Funded by U.S. Department of Energy's (DOE) National Nuclear Security Administration (NNSA)
- The demonstration of practical and economically feasible technologies to treat the waste arising from Mo-99 production
- Nearly all of the Mo-99 is produced in reactors by irradiation of HEU targets
- Provide an additional incentive for conversion to an LEU process
- NECSA
  - Legacy HEU wastes arising from the Mo-99 recovery process that meets the NNSA's non-proliferation objectives
- ANSTO Synroc
  - Extensive waste form expertise
  - Knowledge and capability waste treatment technologies



### Work Order 1

• Benefitted from differing expertise



Work Order 2

• Phase 1:

Over 100 small scale samples fabricated

All characterised

Measured against pre-established evaluation criteria

~ 15 formulations recommended for scale-up



### Work Order 2

• Phase 2:

 Up-scale to ~ 1 L (up to 6 L)
All characterised and evaluated
Some up to 80 wt.% waste loading and 60% volume reduction
U-extraction from final HEU-bearing wasteform

Only feasible technology to process all Mo-99 wastes is either HIP or vitrification.



# **CURRENT RESEARCH PROJECTS**

- FLiNaK pyroprocessing waste
- Agl sodalite (with NNL) and Cul
- CRADA
- Engineered waste form for spent fuel
- HIPed wasteform revisit from 1990s PIP project

# Conclusion

- Focus on waste that is problematic for vitrification
- Working toward cost estimates for Mo-99 production wastes using LEU.
- Substantial progress is being made in several projects, notably immobilisation of ANM waste



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