Past and Present Applications of Synroc

E. R. Vance, D. J. Gregg and D. T. Chavara
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 $^{239}$Pu or 140 ppm of $^{237}$Np)
  
  \[
  (1\text{Ci} = 37\text{GBq})
  \]
- **High-level**: spent power plant fuel or reprocessing waste
  \[
  \sim 10^{13}-10^{14} \text{ Bq/L}
  \]
HLW

- 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
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 / ILW
- Lattice substitution
- $10^{-5}$ g/m$^2$/d

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

Glass Ceramic
- HLW / ILW
- Composite glass-ceramic
- Elements targeted to either ceramic or glass
- $10^{-3}$-$10^{-5}$ g/m$^2$/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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Wt.%</th>
<th>Radionuclides in lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollandite, BaAl$_2$Ti$<em>5$O$</em>{14}$</td>
<td>30</td>
<td>Cs, Rb</td>
</tr>
<tr>
<td>Zirconolite, CaZrTi$_2$O$_7$</td>
<td>30</td>
<td>RE, Zr, An</td>
</tr>
<tr>
<td>Perovskite, CaTiO$_3$</td>
<td>20</td>
<td>Sr, RE, An</td>
</tr>
<tr>
<td>Ti oxides, mostly TiO$_2$</td>
<td>15</td>
<td>none</td>
</tr>
<tr>
<td>Alloy phases</td>
<td>5</td>
<td>Tc, Pd, Ru, Rh, Mo, Ag, Cd, Se, Te</td>
</tr>
</tbody>
</table>
• 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.
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. HCl)

• 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)*
Waste Description:

- 4400 m³ heterogeneous calcine, consisting of layered binsets (alumina, zirconia, zirconia-sodium blends reflecting different reprocessed fuel assemblies)

<table>
<thead>
<tr>
<th>Alumina Calcine</th>
<th>Zirconia Calcine</th>
</tr>
</thead>
<tbody>
<tr>
<td>~90% Al₂O₃</td>
<td>~50% CaF₂</td>
</tr>
<tr>
<td>~5% alkali</td>
<td>~25% ZrO₂</td>
</tr>
<tr>
<td>~3% HgO</td>
<td>~15% Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>~0-8% CdO</td>
</tr>
</tbody>
</table>

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: HIP CCIM JHM
Matrix:
Waste loading:
Durability (PCT-B):
Final volume: (relative to untreated calcine)
Temp: 1300°C
Pressure: 100 MPa
Off-gas: very low

HIP
- glass-ceramic
- 60-90%
- 10-100 x EA glass
- 15-45% reduction

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

Temp: 1150°C
Pressure: -
Off-gas: medium-high

2009
PRESENT APPLICATIONS
ANM Production Cycle

Plate Target → OPAL Irradiation → Plate Transport

~5000L/yr of ILW to treat

SyMo Facility

Synroc Intermediate Level Liquid Waste Treatment Plant Project

Dissolution, Filtration and Initial Ion-exchange Purification: ILLW
ANSTO Synroc – NECSA Project

- 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
ANSTO Synroc – NECSA Project

NECSA Process

Uranium Filter Cake

Undissolved residue
WS 2

Radioactive Ion Exchange Column
WS 3

Radioactive Nitric Acid Solutions
WS 4
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
- AgI sodalite (with NNL) and CuI
- 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
Thank you