Development in the Back End of the Fuel Cycle – Indian Perspectives

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GCNEP-IAEA TM on ‘Strategies and Opportunities for the Management of Spent Fuel from Power Reactors in the Longer Timeframe November 25-29, 2019 at GCNEP, Bahadurgarh, INDIA
Radioactive Waste Management

• A case of Sustainable Development
  – Multidisciplinary Area of Research

• R&D Focus is towards
  – Minimizing environmental discharges
  – Minimising waste volumes for disposal

• Adoption of Recycle and Reuse Strategy
Examples of Process Development and its Deployment

- **Partitioning of HLW**
  - Radiotoxicity reduction
  - Reduction of waste for disposal
  - Plants operational at Trombay & Tarapur

- **Spent Solvent Management**
  - Conversion to aqueous compatible waste
  - Waste Volume Reduction
  - Plants operational at Trombay, Tarapur and Kalpakkam

- **Alpha Solid Waste Management**
  - Handling of radiotoxic waste
  - Very high levels of decontamination required
  - Demonstration Plants operational at Trombay
  - Treatment Plant being set up at Trombay
Indian Nuclear Fuel Cycle: Today

- U (natural)
- UOX fuel
- PHWR
- Non α waste (L&IL)
- Volume Reduction
- Near Surface Disposal
- PUREX
- Heavy metal α Bearing HLW
- Vitrification
- Interim Storage
- Repository
- Reprocessing of carbide fuel
  - Mixed Carbide fuel For Fast breeder test reactor
  - Mixed Oxide fuel for Prototype Fast Breeder Reactor

Reprocessing Facility, Tarapur
Vitrification Facility, Trombay
Vitrified Waste Storage Facility, Tarapur
Partitioning of High Level Radioactive Waste : A Changing Scenario !!
Partitioning of minor actinides from HLLW leads to **reduction of radio toxicity** of the waste addressing:
- Long term concerns for repositories,
- simplified repository design
- increase in public acceptance

 Such a strategy also favours **recovery of useful fission products**

 Minor actinides so separated can be **transmuted** in accelerator driven sub critical systems (ADSS) or fast breeder reactors (FBRs)

 Special **tailor made matrices** for separated radionuclide – Alternate development

**Demonstration of partitioning process: consequence of industrial scale availability of novel solvents**
Development of a Facility for partitioning of HLW

- Solvent system Characterization
  - Extraction properties
  - Physical properties
  - Degradation behaviour

- Bulk availability of solvent

- Cell worthy contactor

- Performance Evaluation
  (Inactive Engineering Studies)

  - Conv. Engg inputs
    (radiochemical)

  - Solvent effectiveness
  - Contactor effectiveness
  - Metering effectiveness
  - Phase monitoring

  - Terminal Stream management
  - On-site constraints
  - Engineering Flow sheet
  - Equipment sizing/layout

- Active Facility Design
Operational Engineering Scale Partitioning Facilities in India

• **Actinide Separation Demonstration Facility : Tarapur**
  - Operational since Nov. 2013 & being operated on demonstration basis
  - Three cycles operated simultaneously at Processing rate ~ 30L/hr
  - Demonstrated actinide partitioning from HLW along with An/Ln separation
  - All secondary waste streams suitably addressed

• **Solvent Extraction Facility, Trombay**
  - Operational since January 2015 & is under continuous operation
  - Continuously pre-treats high salt loaded legacy waste at Trombay leading to separation of active constituents from bulk of the inactive constituents
  - Recovery of Cs-137 and its conversion to caesium pencil – Spin Off
  - Strontium-90 recovery for societal benefits – Spin Off

*Adoption of such partitioning schemes – beneficial for wastes from HFRR, LWR etc*
### Solvent Systems Deployed

#### ASDF Tarapur

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Process Description</th>
<th>Solvent Composition</th>
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<tr>
<td>Cycle 1</td>
<td>U Separation</td>
<td>30% TBP in n-dodecane</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>An + RE separation</td>
<td>0.2 M TEHDGA in 30% IDA in dodecane</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>An/Ln Separation</td>
<td>0.2 M D2EHPA in n-dodecane (TALSPEAK)</td>
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#### Solvent Extraction Facility, Trombay

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<td>30% TBP in n-dodecane</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>Cs Separation</td>
<td>0.03 M Calyx Crown (CC6) in 50% IDA in dodecane (1,3 Di n octyloxy Calix[4] arene crown 6)</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>Sr, Ce and An Separation</td>
<td>0.4 M TEHDGA in 10% IDA in dodecane</td>
</tr>
</tbody>
</table>
Separation of Minor Actinides from High Level Liquid Waste - Challenges

- **Spent Fuel** → **Reprocessing** → **High Level Waste**
  - U, Pu, Np
  - Solvent Extraction based Minor Actinide partitioning

- **Fission products** - Cs, Sr, Ru etc
- **Rare Earths**
- **Minor Actinide** - Np, Am, Cm
- **Trace of U, Pu**

- **Extractant**
- **Phase Modifier**
- **Diluent**

- **Trivalent minor actinides**, Am$^{3+}$ & Cm$^{3+}$, not effectively extractable by PUREX Solvent (TBP)

- **Characteristics of novel solvent system**
  - Good extraction & stripping behaviour with respect to minor actinides
  - Inevitable co-extraction of trivalent lanthanides
  - Low extraction of fission products
  - High chemical & radiation stability
  - Acceptable physical properties including inflammability, volatility and chemical hazard – in cell application

- **Separation of minor actinides (MAs) from co-extracted Lanthanides (Lns)**
  - necessary for transmutation of MAs (Lns are neutron poisons)

- **Plant scale adoption**
  - Efficient contacting devices
  - Remote operation & maintenance
1. Massively shielded enclosures, equipped to carry out earmarked processes
   - Series of isolated cells: aids in carrying out maintenance in a particular cell
   - Series of connected cells (access corridors) aids in material movement during construction, and aids flexibility
   - Vertical Compartments vs. full height

2. Cell Top
   - Designed with end plugs – this aids material entry during construction and also facilitates taking out decontaminated equipment after its life

3. Embedded pipes and plates
   - Embedded pipes: Ease of connection between active and inactive areas
   - Embedded Plates: Aids support the equipment inside the cell
   - Embedded Plugs: Gives access for maintainance
1. Material handling devices:
   • EOT crane, Master Slave Manipulators, Servo Manipulators, Shielding Windows

2. Remotisation and remote handling devices
   • Extensive instrumentation leading to remote operations from control room

3. Appropriately designed Recesses for
   • Sampling systems

4. Elaborate Ventillation & Off gas Systems
Commissioning of the Partitioning Facilities

- Performance of the cycles
  - Metering of feed & solvent
  - Stable operation of mixer-settlers with Detection & maintenance of interphase
  - Mass transfer performance check (extraction & stripping of markers)

- Instrumentation parameters
  - mixer-settlers & density pots
  - Tanks

- aq./org. detection and separation provisions in the various equipments
  - Density pots
  - Rework tank
The Actinide Separation Demonstration Facility, Tarapur & Solvent Extraction Facility, Trombay

- Throughput to match vitrification process
- Multi step process based on solvent extraction
- All secondary streams suitably addressed
- Facilities has been designed as per the conventional basis of design of radiochemical plant

Overall Layout of the integrated Facility
· ASDF which is based on indigenous efforts, inaugurated by Hon. President of India on November 15, 2013.
· Has treated 13 m$^3$ of High Level Liquid Waste (HLLW) till date

**Performance**

Cycle 1 - 99.65% removal of residual U& Pu
Cycle 2 - 99.95% removal of alpha activity
Cycle 3 - 97.8 % An/Ln separation

With the successful commissioning of this facility, India has taken a lead role towards reducing the long term concerns of HLLW, an endeavor pursued globally.
Overall Block Diagram for ASDF/SSMF, SSSF, Tarapur

- 30% TBP
- HLW
- U Removal Cycle
- TEHDGA
- U Lean HLW
- MA Separation Cycle
- D2EHPA
- Ac/Ln Group Separation Cycle
- MA Lean HLW
- U Lean HLW
- Ac. Product Storage
- Rare earth solution for vitrification/cementation
- for Vitrification
- Recovered dodecane casking
- Spent Solvent from PREFRE
- Storage
- Spent Solvent Management Facility
- Aq. After Alkaline Hydrolysis & Carbonate solution for immobilization
- Novel solvent casking
Basic process: Decontamination of HLW by Solvent Extraction

High-Level Waste (HLW) with Radioactivity:
- Gross $\alpha$: $4.5 \text{ mCi/L}$
- Gross $\beta$: $10.2 \text{ Ci/L}$

Solvent Extraction:
- 1st Cycle: U
- 2nd Cycle: Cs
- 3rd Cycle: Ce, Sr, An

Raffinate (ILW, Short Lived):
- Gross $\alpha$: $5-7 \times 10^{-4} \text{ mCi/L}$
- Gross $\beta$: $5-30 \text{ mCi/L}$

To Tk4 after neutralization.

Spent Solvents:
- Evaporation & vitrification
- Cementation
- Solvent washings

Conversion to Cs Pencil

Recycle/Treatment:
- U Solution Recycle
- VWP (HL)
- CWP (L&IL)
Observations & Further Planning

- Developmental efforts are being directed towards increasing the process efficiency of An/Ln Separation.

- R&D focus on increased waste loading in glass

- Spent Solvent Management and secondary waste stream management

Camphor Bistriazinyl Pyridine
Bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyrdine

Carbamate Waste Stream

- DBP destruction by ozonisation
- Destruction of carbonate
- To Precipitate Out HM as sludge as metal hydroxide at 10 PH
- Treatable ILW to TRIX for Cs-Sr removal
- Filtration
Management of Spent Organic Solvent
✓ Organic wastes normally fall in the category of **Non-High Level Waste**

✓ Volumetric generation of organic wastes is very low compared to its radio active contaminant equivalent aqueous waste streams

✓ **Organic waste deserve special attention both on account of radioactivity as well as their organic nature**
✓ Alkaline hydrolysis process for spent PUREX solvent – Degraded TBP
✓ Dodecane to recycle / incineration
### Management of Organic Wastes

**Modified Alkaline Hydrolysis Process**  
(3 Phase separation with recycle of NaOH phase)

**Typical operation data**

<table>
<thead>
<tr>
<th>Waste stream</th>
<th>Molarity</th>
<th>Volume (litres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed spent TBP</td>
<td>NA</td>
<td>200</td>
</tr>
<tr>
<td>Bottom phase (Left over alkali +</td>
<td>8-9 M alkaline</td>
<td>40 (20+20)</td>
</tr>
<tr>
<td>bottom middle phase)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle phase (Na-DBP + Butanol reach + entrapped Dodecane)</td>
<td>&lt; 1 M alkaline</td>
<td>80-90</td>
</tr>
<tr>
<td>Top phase (Dodecane)</td>
<td>NA</td>
<td>110-120</td>
</tr>
</tbody>
</table>

Total Spent solvent Managed by this process: ~ 13000 litres (2012 onwards). Leads to a volume reduction factors of 6-10
Recycling of Diluent in Reprocessing Plants

Test for Recyclability : Pu Retention Test

Fresh diluent : Recovered Diluent
3 x $10^{-3}$ mg/L 6.23 x $10^{-3}$ mg/L

Diluent taken up for recycling at Trombay and Tarapur
Management of Organic Wastes

Future Trends and Developments

✓ Vacuum distillation for bulk recovery of TBP+ n-Dodecane– Engineering Scale Facility at Tarapur yielding promising results

✓ Industrial scale deployment of use of recovered dodecane. – Being carried out in phased manner at both Trombay and Tarapur

✓ Identification of suitable solvent wash reagents/Separation processes for purification of novel solvents and their recycle and reuse.
Alpha Solid Waste Management
Cat IV waste by physical nature

Activity > 4000 Bq/g
Cellulosic waste:
- Cotton rugs
- Cotton wool
- Absorbent paper
- Tissue paper
- Filter cloth
- Cello tape

Process: Dissolution in presence of electro catalyst
CELLULOSIC WASTE TREATMENT (GB-03)
Inactive trials

Demonstrate in-situ generation of Ag-II in a divided cell and destruction of various types of cellulosic waste based on silver mediated electrolytic dissolution process

Experimental loop

1) Process system involving reactor, generator, intercooler and recirculation pump
2) Off-gas system involving scrubbers, scrubber tank, pump for circulation of scrubber solution, air ejector
3) Instrumentation system with PRVs, valves, transmitters and display units for temp, level density and pressure
4) DC power supply system
5) Chiller unit
Alpha Demonstration Facility

• **A Glove Box Train**: Set up to demonstrate the alpha solid waste treatment processes

• Treatment mainly intended for **cellulosic wastes** – Based on Ag++ mediated electrochemical processes

• Ultrasound decontamination systems – **Rubber and plastics**

• Facility **retrofitted** in an available area of WIP

*Feedback of these trials being used for designing a full scale treatment facility at Trombay*
Pyrolysis Process Development for alpha bearing waste

Observations & Results

**Weight of Char (g)**

- Labcoat: 0.5
- Blotting Paper: 1.08
- Postmortem Gloves: 1.98
- Surgical Gloves: 4.1
- Viton Tube: 6.1
- Neoprene Gauntlet: 8.03
- PVC: 8.69
- Monsoon Tape: 9.2

**Mass Reduction Factor (MRF)**

- Labcoat: 100.0
- Blotting Paper: 46.3
- Postmortem Gloves: 25.3
- Surgical Gloves: 12.2
- Viton Tube: 8.2
- Neoprene Gauntlet: 6.2
- PVC: 5.8
- Monsoon Tape: 5.4

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Labourcoat Blotting Paper PVC **Monsoon Tape** Surgical Gloves Postmortem Gloves Viton Tube Neoprene Gauntlet Neoprene Gauntlet
Thank You For Your Kind Attention!

"Not all of us can do great things. But we can do small things with great love." ...Mother Teresa
### HLW Management: Partitioning Scenarios (a Study)

<table>
<thead>
<tr>
<th></th>
<th>1. Direct Vitrification</th>
<th>2. HLW partitioning Scenario 1</th>
<th>3. HLW partitioning Scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Glass for GDF</td>
<td>50 Kg/T</td>
<td>26 Kg/T (An &amp; Ln - 8% Ln loading limit)</td>
<td>7 Kg/T (5 year cooled fuel)</td>
</tr>
<tr>
<td>Cs-Sr Glass for SSDF</td>
<td>-</td>
<td>20 Kg/T</td>
<td>20 Kg/T</td>
</tr>
<tr>
<td>Lean FP Glass for NSDF</td>
<td>-</td>
<td>22 Kg/T</td>
<td>22 Kg/T</td>
</tr>
<tr>
<td>Cement Product for NSDF</td>
<td>-</td>
<td>-</td>
<td>Short lived REs (?)</td>
</tr>
</tbody>
</table>

**Basis of Calculation**
- Alpha loading based on $10^{19}$ $\alpha$/gm: He accumulation limit.
- In case of Transmutation with multiple recycling this will reduce to substantial low value.
- Heat bearing $\beta\gamma$ loading based on the centreline temperature limitation of glass ($500^\circ$ C), the calculated maximum heat load for canister size of 100 kg is 2000 W. This will corresponds to Cs-Sr loading of $\sim$4.5%.

**Focus Areas**
- Separation & Management of long lived FP Tc$^{99}$ & I$^{129}$ needs to be addressed
- Disposal scenario for Cs to include long lived Cs$^{135}$ (based on its radio toxicity contribution)
Evolving Fuel Cycle

- **U (Natural)**
  - PHWR
  - U ( ~ 1.2% Enriched)
- **U (enriched) MOX Fuel**
  - LWR
  - U (depleted)
- **MOX Fuel**
  - FR
  - PUREX MA partitioning
  - Recovery of FPs
  - Am, Np
  - Storage ~ 100 years
  - Pu
  - Heterogeneous Recycling
  - Irradiated Pins (high specific activity, short life)
  - Pu

(FPs)