Incineration and vitrification technologies for radioactive waste

Speakers:
Etienne FOURCY (ORANO DM2D), etienne.fourcy@orano.group
Maxime FOURNIER, (CEA/DE2D/SEVT) maxime.fournier@cea.fr
Summary

- Thermal process solution for fission products
  - Benefits sought
  - Vitrification process: world overview
  - Orano-CEA experience: history and processes

- Thermal processes for legacy and orphan wastes
  - **Organic waste**: pyrolysis, calcination, incineration
  - Focus on **PIVIC project**: incineration-vitrification
  - Focus on **DEM’N MELT project**: in-can vitrification
Part 1

Thermal process solution for fission products
Thermal solution for fission products

Benefits sought

- These **High Level Long Life wastes** can not be treated by traditional technologies (such as grouting…)

- Only **vitrification** (allowed by a thermal process) can neutralize the hazardous characteristics of the waste and can produce an inert, very stable wasteform, suitable with disposal safety

  - Vitrification sought thanks to a thermal treatment

  - *(Not volume reduction, nor chemical stabilization)*
Thermal solution for fission products

Benefits sought

Chemical composition of the vitreous matrix: SiO$_2$, Na$_2$O, B$_2$O$_3$, Al$_2$O$_3$

Fission products incorporation (FP$_2$O$_3$...) in the matrix
Vitrification process
Fission products vitrification in the world

- Two major processes in the world for HLW

**Continuous 2 steps processes**

- AVM (FR), R7T7 (FR), WVP (GB), Tarapur (IN)

**Liquid fed melter (1 step)**

- PAMELA (BE), Mayak (RU), TVF (JP), DWPF (US), WVDP (US), Trombay (IN), VEK (DE)

Startup or construction: RRP (JP), WTP (US)
Vitrification process
Fission products vitrification in the world

- One step feeding melter

Advanced CCIM with direct liquid feeding

- R&D stage
- The goal is to simplify the process by avoiding the calcination step (1 process step)
- To increase the vitrification capacity thanks to a large diameter which allows high evaporation capacity
Vitrification process
Fission products vitrification in the world

- 2 steps feeding melters:
  - **Heating mode**: Joule (resistor) or induction (direct or indirect),
  - **Crucible design**: hot or cooled metallic walls

- **Hot melter by indirect induction**
  - Standard solution used at La Hague (5 lines)
  - Heat is induced **in the crucible walls** which heat the glass in a second step
  - Walls are not cooled
  - 2 process steps with calcinator

- **Cold crucible by direct induction**
  - 1 line at La Hague
  - Heat is inducted **directly in the glass**
  - Crucible walls are cooled which creates a protection glass layer on the inner crucible wall
  - Allows to go higher in treatment temperature
  - Allows vitrification of corrosive species
  - 2 process steps with calcinator

NON-CONFIDENTIAL
Orano-CEA experience
History of vitrification in France

- 1950’s: Choice of borosilicate glass
- 1960’s: Hot-wall Metallic Induction Melter
- 1970’s: Two-step Vitrification Process
- 1978: AVM Start-up
- 1980’s: CCIM Initial Studies
- 1989: R7 Start-up
- 1992: T7 Start-up
- 1996: Mechanical Stirring
- 2001: CFA Platform Development
- 2004: Inactive CEA Platforms
- 2010: CCIM in R7
Orano-CEA experience

History of vitrification in France: Gulliver (1963-66)

Process
- discontinuous
- graphite crucible
- resistive heating

Results
- 50 blocks of 4 kg
- 2 to 3 kCi/glass L
- 250 L of solution treated (5 L/block)

Gelation
- Glass frit
- FP solution

Heating
- 1150 °C

Demolding
- Suction cup
Orano-CEA experience
History of vitrification in France: PIVER (1969-80)

**Process**
- metal crucible
- inductive heating
- glass pouring
- 5 kg/h of glass

**Results**
- 28 000 L of FP solution treated
- 12 000 kg of glass
- 164 operations of 170 L each
Orano-CEA experience
Continuous 2 steps process
Orano-CEA experience
Orano La Hague R7/T7 vitrification facilities
Orano-CEA experience
Orano La Hague R7/T7 vitrification records

- **20,000+** universal canisters produced:
  - R7 facility (**3 lines** commissioned in **1989**)
    - Line B equipped with CCIM technology
    - Lines A&C equipped with Hot Melter technology
  - T7 Facility (**3 lines** commissioned in **1992**)
    - All lines equipped with Hot Melter technology

- For **CCIM**, facilities operation record since **2010**
  - Several runs of **UMo FP** (graphite type reactor) products vitrification between 2010 and 2017
  - ~ **600** universal canisters
Part 2
Thermal processes for legacy and orphan wastes
Legacy and orphan wastes

- D&D operations = large volumes of radioactive waste generation, mainly LLW
- Some types of waste cannot be easily conditioned or disposed, or have no disposal route… e.g., legacy waste.
Pyrolysis-calcination of organic waste
The example of the IRIS process

- **IRIS**: Solid Incineration Research Facility Commissioned in CEA/DAM since 1999
- **Organic solids** from nuclear applications
- Two steps process: **pyrolysis and calcination**
- High volume reduction factor of inlet wastes
Pyrolysis-calcination of organic waste
The example of the IRIS process
Plasma incineration of organic liquids
The examples of IDOHL and ELIPSE processes

- **IDOHL**: Organo-Halogenated Liquids Destruction Facility
  *Installation de Destruction des OrganoHalogénés Liquides*

- **ELIPSE**: Submerged Plasma Process for Liquid Treatment
  *Elimination de Liquides par Plasma Sous Eau*
Plasma incineration of organic liquids
Halogen organic liquids: the IDOHL process

Example for a LLW with high amount of chloride
CHCl₃ contaminated with ³H and ¹⁴C

CHCl₃ + H₂O + 1/2 O₂ ⇌ 3HCl + CO₂

- Liquid waste (Cl, F) directly introduced in a RF oxidizing plasma (4-5 kW, > 1MHz)
- Small flows: 100-400 g·h⁻¹
- No (or very low) mineral content.
- Secondary waste depending on gas treatment: cemented lime (dry process) or another solution (wet process)
- To be commissioned in CEA/DRF in 2019

<table>
<thead>
<tr>
<th>CHCl₃ feed rate (g·h⁻¹)</th>
<th>O₂ (NL·min⁻¹)</th>
<th>CHCl₃ destruction (%)</th>
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<tr>
<td>100</td>
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<td>99.95</td>
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<tr>
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<tr>
<td></td>
<td>28</td>
<td>99.98</td>
</tr>
</tbody>
</table>

\[ P_{\text{elec.}} = 4.2 \text{ kW} \quad Q_{\text{Ar}} = 40 \text{ NL/mn} \]
\[ Q_{\text{O₂}} = 7-27 \text{ NL/mn} \quad Q_{\text{waste}} = 100-400 \text{ g·h}^{-1} \]
Plasma incineration of organic liquids with mineral load: the ELIPSE process

- DC arc oxygen plasma torch (~ 30 kW, 200 NL·min⁻¹ O₂) submerged in aqueous solution
- Waste continuously introduced in the plasma plume with a high flow of 1-3 L·h⁻¹ (up to 6 L·h⁻¹)
- Compact and cold process (with an only hot point: the plasma zone)
- The submerged reactor:
  - Quenches and washes gases
  - Cools the reactor
  - Avoids corrosion
- Secondary waste: cemented filters

Example: for TBP/Dodecan, between 99.7 and 99.9% of destruction at 5 L·h⁻¹.

\[
\begin{align*}
\text{C}_{12}\text{H}_{27}\text{PO}_4 + 18\text{O}_2 & \rightarrow \text{H}_3\text{PO}_4 + 12\text{CO}_2 + 12\text{H}_2\text{O} \\
\text{C}_{12}\text{H}_{26} + (37/2)\text{O}_2 & \rightarrow 12\text{CO}_2 + 13\text{H}_2\text{O}
\end{align*}
\]
Incineration-vitrification of organic waste
The example of the SHIVA process

- A “3 in 1” process with one objective: the confinement of the activity in a matrix with a good long term behavior.
Incineration-vitrification of organic waste
The example of the SHIVA process

A plasma torch is used to heat a gas at a very high temperature.
In SHIVA, a gas consisting of O and Ar is projected through an electric arc created between the two electrodes above the molten glass bath.
Incineration-vitrification of organic waste
The example of the SHIVA process

The relatively high gas pressure favors collisions between particles and the transmission of energy between them. The plasma can thus reach temperatures up to 4000 °C, 7000 °F.
Incineration-vitrification of organic waste
The example of the SHIVA process

At such temperatures, the waste is reduced to ashes, the glass matrix is melted: the radioelements can then be trapped and the gases are completely burned.
Incineration-vitrification of organic waste
The example of the SHIVA process

The molten glass containing the radionuclides is poured to obtain a waste package consisting of a container, a confinement matrix and radionuclides immobilized in the matrix.
Incineration-vitrification of organic waste
The example of the SHIVA process
The PIVIC project is a partnership between ORANO, CEA and ANDRA.

It is supported by the French government program: “Programme d’Investissements d’Avenir” whose management has been entrusted to Andra.
PIVIC project
Summary

- The transuranic mixed metallic and organic waste
- Mineralization scenario: the PIVIC process
  - Industrial Specification and Technical Challenges for the PIVIC development
  - Functions of the PIVIC process
  - Heart of the PIVIC process
  - The PIVIC Package
  - Structuring tools of the PIVIC project
- State of R&D main progress
  - Fusion Module: Low frequency induction melting concept validation
  - Fusion Module: Stirring and homogenization
  - Glass formulation
  - Package description
  - Combustion module conception
- Conclusions and perspectives
PIVIC project

Alpha waste

- **ILW** mainly coming from MOX fuel utilities in France (MELOX)
- Packaged in 120 L drums for interim storage
- **Rich in alpha emitters** (U, Pu, Am, as oxides)
- **Various compositions:**
  - **Organics** (PE, neoprene, PVC, wipes, glovebox windows, …)
  - **Metallic** and various elements (electric equipment, defective mechanical products, tools…) made mainly of stainless, copper or aluminum,
  - Filters (HEPA, grinding machine prefilters, labs filters, …)
  - Fiberglass, ceramics pieces
PIVIC project

Goals

Full destruction of organic matter • Stabilization of actinides in a solid matrix

Expected benefits:

• Provide **better safety** in final disposal thanks to the removal of **reactive** material (organic material are mineralized) and to the production of a **stable matrix**.

• Preserve disposal resources thanks to a noticeable reduction of the **volume** of actual waste packaging to be disposed of (volume reduction up to 7).
PIVIC project
Pros and Challenges

- Full destruction of organic material, confinement of radionuclides, and reduction of volume
- No pre-treatment (no grinding, no sorting)
- Final package compliant with the French geological disposal CIGEO
- Start operations in 2035
- Mean rate of 2,000 drums treated per year
- Challenges: manage criticality, corrosion, waste composition variability and uncertainty
PIVIC project
Process

- Basic design requirements:
  - a limited number of apparatus,
  - as compact as possible,
  - a minimum inlet of gas to minimize the size of gas treatment,
  - a minimum generation of secondary waste,
  - a resistance to aggressive corrosion.
PIVIC project
Process

- Direct waste feeding
  - No grinding nor sorting of the waste
  - Gradual lowering of the load
  - 2-steps treatment: organic combustion, metal fusion in the crucible
  - Pure oxygen plasma combustion

- Full destruction of organic materials
  - Compact off gas treatment system
  - Water cooled metallic walls: no refractory to be changed

- In Can Melting
  - Metallic parts melted in the can
  - Addition of glass
  - Electromagnetic stirring
  - No draining

- Final package
  - Biphasic metal and glass matrix
  - Highly inert and stable material
  - Volume reduction by a factor of 7
PIVIC project
Process

Introduction chamber
Combustion chamber (oxygen plasma)
Fusion Module (direct induction)

Patent Number: WO 2015/018905
Date of Patent: Feb. 12, 2015
PIVIC project
The final waste package

- A metallic / glass biphasic canister
  - No metal oxidation required
  - Metallic bottom and glass supernatant

- Final package
  - 2 canisters stacked in final package

- Metallic phase
  - Mainly stainless steel, copper, aluminum alloy
  - Fusion at 1450 °C

- Aluminosilicate glass
  - Preferred to a borosilicate glass
  - Fusion at 1250 °C
PIVIC project
Development planning

2012
Phase 1
Exploratory R&D

Phase 2
Proof of concepts

Benchscale mockup trials

2020
Phase 3
Integration and tuning

Feasibility demo

Design and manufacturing of the industrial building

2025
Phase 3
Qualification

2030

PIVIC Facility

PIVIC Prototype

FUSION Module Full Pilot

PIVIC Full Pilot

Benchscale

Full-scale mockup trials
# PIVIC project

## Main topics of R&D

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<th>Process Development</th>
<th>Containment Material Development</th>
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<td>Can docking and sealing</td>
<td>Combustion management</td>
<td>Glass composition tuning</td>
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<td>Waste feeding</td>
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<td>Off gas treatment</td>
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PIVIC project
State of R&D main progress

Fusion Module: low frequency induction melting concept

- Validation of the multilayer cooled IN CAN low frequency induction melting
  - 30 can produced (200 kg of metallic alloy – Stainless/Al/Cu, 50 kg of glass)

- The stainless steel canister is correctly cooled

- The internal ceramic liner has sufficient corrosion resistance to glass & metal
The metallic fraction is strongly agitated by the EM forces
- Velocity 0.1 m.s\(^{-1}\)

Glass phase dragged by the molten metal
- Velocity 0.01 m.s\(^{-1}\)
Glass composition

• Glass phase in the final PIVIC waste is made of:
  - Ashes (incineration of organics: Si, Al, Ca, K, Mg, Na, P, Zn, Fe, Ba, Ti)
  - Minerals (filters, glass fibers)
  - Oxidation of metallic elements (Al, Cr…)
  - Glass additives

• Why is PIVIC glass design challenging?
  - Metal melted at high temperature (↑ volatility)
  - Wide range of waste composition
  - Highly reducing conditions and glass/metal interaction
    - Reduction of some elements in the metallic state (Si⁰!, ↑ volatility)

Consequences: Glass frit not easy to design
PIVIC project
State of R&D main progress

Package description

- Good macroscopic separation of glass and metal phases
  - Without Al the glass is homogeneous with low crystallization
  - High Al concentration leads to a more crystallization (Al$_2$O$_3$, Si-Al phases…)

- Ashes from organics incineration
  - Dissolved in the glass
  - Rapid incorporation

- The actinides simulants (Hf, Ce) are mainly in the glassy matrix
  - Dissolved in the glass
  - Or in crystalline form for high Al concentration
In-Can Vitrification
Focus on DEM’N MELT project

The DEM’N MELT project is a partnership between CEA, ORANO, ECM and ANDRA.

It is supported by the French government program: “Programme d’Investissements d’Avenir” whose management has been entrusted to Andra.
**DEM’N MELT project**

**Main principles**

- Originally developed for CEA needs for defense waste vitrification. Integrates feedback from La Hague vitrification facility.

- Decisions from Orano & CEA to customize the process for nuclear waste coming from D&D:
  1. Adaptation of In-Can vitrification process for High Level Wastes
  2. Treatment of solid or liquid wastes (compatible with sludge)
  3. Compact unit allowing several systems operated in parallel
  4. Maintenance by remote manipulators integrated in the design
  5. Fit for D&D operations:
     - Decommissioning in-situ
     - Low amount of secondary wastes

- **Targeted capacity: 1 container per day** (around 300 kg per container)
DEM’N MELT project
Main principles

- **A simple and robust process**
  - Canister in a furnace (no pouring)
  - Simple resistance heating
  - Thermal homogenization (no stirrer)
  - Liquid feeding of the canister (1 step, no calciner)
  - Corrosion resistant (single use crucible)
In the frame of the DEM’N MELT project, a new prototype is under building to develop a vitrification tool adapted to D&D:

- **Capacity**: 300 kg of glass per canister
- **Process**: All the process being included in a 20 feet ISO container to be easily deployable on an existing D&D site
- **Dismantling**: Designed to cost for a short duration of use as a decommissioning tool aimed to be dismantled after treatment operations
- **Secondary Wastes**: Producing a small amount of secondary wastes

Available in S2/2020
DEM’N MELT project
In Can Melter vitrification process
Main operation sequences:

- Preloaded can is transferred and connected to the feed header
- The furnace jackets are closed
- OGTS residues are recycled in the process
- The glass can is allowed to cool inside the furnace until the glass is solidified
- The furnace jackets are opened and the glass can is evacuated
DEM’N MELT project
Example of two vitrification lines with carrousel distribution
DEM’N MELT project
Example of hot cell implementation

- Movable crane
- Glass frit supply
- 2 Working stations
- Sleeve supply
- S Crossing
- Dust collector
- Rotating tray+ push/pull chain
- Condensing unit
- Weighing station
- Furnace
- Conveyor
- Spin rail
DEM’N MELT project
Final product optimization

- Using CSD « Universal Canister for Vitrified products » for final waste packaging
- Compatible with existing transport cask, storage design, etc.

For example 5 m³:
- with a shielding
- with 3 m³ useful
- 9 cans per Concrete container
Thermal processes for legacy/orphan wastes

Conclusions

- A **panel of technologies** available for the development of **new waste conditioning solutions**:  
  - For an activity range up to HA waste

- **Thermal treatment solution** is to be chosen according to:
  - Objectives to be reached:
    - To stabilize wastes
      - Vitrification or not?
    - To reduce the volume of waste
    - Both?
  - The waste inventory
    - Quantities at stakes ➔ Utility capacities?
    - Chemical composition ➔ volatility and corrosion resistance of the utility?
    - Activity level ➔ Utility volume and maintenance facilities?
      Secondary waste volumes?
Thank you for your attention!