IDAHO CALCINE HLW TECHNOLOGY PROGRAM

DIETER A. KNECHT
Idaho Chemical Processing Plant

HLW Status

- 3,500 m$^3$ HLW calcine and 7,500 m$^3$ HLW liquid currently stored at ICPP

- Land Disposal Restriction Storage Prohibitions prohibit storage of mixed high-level waste after May 1992. Mixed waste must have a demonstrated acceptable treatment in order to be stored or the generator must obtain statutory relief in the form of a variance petition

- DOE Order 5820.2A directs that all new and readily retrievable HLW be processed and disposed of in a geologic repository according to the requirements of the Nuclear Waste Policy Act
IDAHO CHEMICAL PROCESSING PLANT
HLW PROGRAM JUSTIFICATION

- EM HLW Program goal in 5-YR Plan - successful deployment of HLW disposal

- Recommendation of Ahearne Advisory Committee on Nuclear Facility Safety to convert DOE HLW to form suitable for disposal

- Specifications for HLW disposal in Nuclear Waste Policy Act, Regulations of DOE, NRC and EPA, and DOE-RW Waste Acceptance Specifications

- DOE Waste Reduction Policy Statement, 40 CFR 264.75 (h) and (i) and Pollution Prevention Act of 1990 require reduced waste volume

- DOE LDR Case-by-Case Extension Application and Temporary No-Migration Petition require completion of HLW Immobilization by 2014
DOE Defense HLW Background

- Three defense HLW sites: Savannah River (SRS), Hanford, and Idaho (ICPP)

- Defense Waste Management Plan issued to comply with Public Law 97-90
  - Reference plans for disposal of defense HLW and TRU
  - Orderly transition of HLW processing by 1994 at SRS, 1999 at Hanford, and 2014 at ICPP (current estimate)
  - Increased near-term ICPP funding required to support Plan
The Defense Waste Management Plan

June 1983

U.S. Department of Energy
Assistant Secretary for Defense Programs
Washington, DC 20585

PUBLIC LAW 97-90, 1982

REFERENCE PLANS FOR DISPOSAL OF HLW AND TRU FROM ATOMIC ENERGY DEFENSE ACTIVITIES
EXECUTIVE SUMMARY

Public Law 97-90, the Department of Energy National Security and Military Applications of Nuclear Energy Authorization Act of 1982, states that:

"The President shall submit to the Committees on Armed Services of the Senate and of the House of Representatives not later than June 30, 1983, a report which sets forth his plans for the permanent disposal of high-level and transuranic wastes resulting from atomic energy defense activities".

According to the Atomic Energy Act of 1954, as amended, and the Department of Energy Organization Act, responsibility for radioactive waste and byproducts generated by DOE's nuclear activities belongs to the Secretary of the Department of Energy. The flow of materials and the resulting waste from the atomic energy defense activities addressed in P.L. 97-90 are illustrated in Figure E-1.

Defense high-level waste (HLW) and defense transuranic (TRU) waste are in interim storage at three sites, namely: at the Savannah River Plant, in South Carolina; at the Hanford Reservation, in Washington; and at the Idaho National Engineering Laboratory, in Idaho. Defense TRU waste is also in interim storage at the Oak Ridge National Laboratory, in Tennessee; at the Los Alamos National Laboratory, in New Mexico; and at the Nevada Test Site, in Nevada. (Figure E-2).

This document describes a workable approach for the permanent disposal of high-level and transuranic waste from atomic energy defense activities. The plan does not address the disposal of "suspect" waste which has been conservatively considered to be high-level or transuranic waste but which can be shown to be low-level waste. This material will be processed and disposed of in accordance with low-level waste practices.

The primary goal of this program is to utilize or dispose of high-level and transuranic waste routinely, safely, and effectively. This goal will include the disposal...
### MAJOR MILESTONES AND COSTS FOR PERMANENT DISPOSAL OF DEFENSE HIGH-LEVEL WASTE

#### Savannah River Plant (SRP)
High-level waste from this site is readily retrievable and will be sent off-site for disposal in a geologic repository. Processing for disposal will begin at this site before the other two because it contains 75 percent of DOE's tanked waste radioactivity and because environmental factors are less favorable than at the other two sites. Savannah River Plant waste will be immobilized in the Defense Waste Processing Facility (DWPF) (Figure E-4) beginning in 1989.**

#### Hanford Reservation
Hanford's high-level waste tanks are isolated from the water table and contain much less radioactivity than tanks at the Savannah River Plant. Immobilization of new and readily retrievable high-level waste will begin about 1990 after sufficient experience is available from Savannah River's vitrification process.

**All years shown in this plan are fiscal years.
High-Level Waste Characterization

- ICPP High-Level Waste is unique to the DOE reprocessing complex
  - Acidic solution, HF and HNO₃
  - Contains the spent fuel cladding material (Zr, Al) plus radionuclides
  - Contains additives to prevent criticality, Stabilize dissolver products and reduce corrosion (B, Cd, Aluminum Nitrate)
  - Routinely calcined and stored as solid

- Savannah River/Hanford/West Valley Wastes
  - Stored as liquid in basic form, Al(OH)₃ and NaOH
  - Consists of sludge, supernatant and salt cake
Source of Chemicals in ICPP High Level Wastes

- Dissolver: HF, HNO₃, Cd-B Poison
- Extraction: F, Al, Zr, Cd-B
- U Product
- Off Gas
- Calciner
- Calcined Waste

Waste, wt%

- Al₂O₃: 7
- ZrO₂: 19
- CaF₂: 43
- CaO: 12
- Cd,B Oxide: 9
- Na,K Oxide: 6
- Other: 4
- Total: 100

* HLLW is acidic
  HNO₃ and complexed HF solution
GLASS-CERAMIC PROCESS

Calcine from NWCF and retrieval
Calcine mixing
Calcine degassing
Calcine-blending
Vacuum pump
Calcine particle sizing
Evacuation and can sealing
Can delivery system
Can filling and compacting
Glass ceramic additive
Glass ceramic formation and decontamination
Canister sealing and decontamination
To temporary storage and shipping
Can filler
Canister loading
Canister from delivery system
# Idaho HLW Immobilization Program

Canisters of Immobilized HLW

<table>
<thead>
<tr>
<th></th>
<th>Existing Calcine</th>
<th>Existing NA-HLLW</th>
<th>Future NA-HLLW</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>4970</td>
<td>3315</td>
<td>1325</td>
<td>9615</td>
</tr>
<tr>
<td>Glass-Ceramic /</td>
<td>1950</td>
<td>1300</td>
<td>520</td>
<td>3770</td>
</tr>
<tr>
<td>Calcine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass /</td>
<td>450</td>
<td>300</td>
<td>120</td>
<td>870</td>
</tr>
<tr>
<td>Pyrochemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass / Ceramic /</td>
<td>170</td>
<td>115</td>
<td>45</td>
<td>330</td>
</tr>
<tr>
<td>Pyrochemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conceptual ICPP HLW Immobilization Processes
Relative Volumes
Comparative Volumes of Alternative ICPP Waste Forms

- Liquid Waste (50)
- Calcine (10)
- Glass (15)
- Ceramic (5)
Pyrochemical Treatment of HLW Calcine

Calcine Solids Storage

Multi-Purpose Reaction Vessel

Condenser

Electrorefining Cell

Fission Product & Actinide Alloy

Low-Level Waste

Fluoride Salts
Alumina, Zirconia

Calcine

Metall Reagent
(Possibly Ca)

Densification

Immobilization

OR

IMMOBILIZATION

Melter

OR

Class Additives

Waste Canisters
Pyroprocessing of HLW Calcine

- Heating and distillation of volatile species
- Separation of ZrO$_2$, Al$_2$O$_3$, CaF$_2$, CaO from radioactive and hazardous components.
- Reduction and electrorefining can then be performed on the remaining material.
Calcine Pyroprocessing Issues

- Must demonstrate initial separation
- Not demonstrated on large scale in radioactive environment.
- May reduce HLW volume by factor of 7 for existing calcine.
- LLW volume will be about volume of original calcine.
ICPP HLW Calcine Disposal Program Plan

Criteria Development
Evaluate Candidate Processes for Component & Subsystem Testing
Laboratory Testing
Component/Subsystem Testing
Cold Integrated Testing in Multifunction Pilot Plant Facility
Hot Demonstration Testing
Design & Construction of Full Scale Plant
Full Scale Plant Operation

Fiscal Year
WASTE IMMOBILIZATION FACILITY INTEGRATION


TECHNOLOGY R & D
- Development of Alternative Disposal Options
- Feasibility Studies
- Unit Operation Development
- Waste Form Development
- Independent Review of Development Program
- Technology Status Reports

ICPP Expansion EIS and ROD
- Environmental Impact Statement for Full-Scale IWIF and Technology Selection
- Address Candidate Technologies for DT & E Testing

ENVIRONMENTAL DOCUMENTATION
- NEPA
- RCRA
- NESHAP
- PSD/PTC
- PSAR/FSAR

PERMITS
- Design Criteria RCTA, NESHAP, PSD/PTC, PSAR/FSAR

IDAHO WASTE IMMOBILIZATION FACILITY (IWIF)
- IMIF DESIGN
- CONSTRUCTION
- Full Scale Hot Operations

DT & E: PROCESS VERIFICATION TESTING

Transportation and Repository Disposal

INTERIM STORAGE

WINCO
Idaho National Engineering Laboratory
HLW Technical Development and Process Verification

FY-1991 Major Accomplishments

- Pilot-plant mock-up units fabricated to test feasibility of particle sizing, calcine blending, and solids flow valves.
- Glass-ceramic forms prepared, leach-tested, and characterized for glass and crystalline microstructure showed leaching similar to acceptable HLW glass.
- Glass prepared from neutralized HLW liquid did not have acceptable waste loadings.
- Milestone reports on BDAT vitrification and glass-ceramic, including flowsheets issued:
  - Vitrification not cost effective because of large HLW volume.
  - Unit operations identified for pilot-plant testing.
- Proposal developed for new high-risk, large payback pyrochemical treatment of calcine.
**Idaho HLW Immobilization Program**

**Leach Rates of Candidate HLW Forms**

**Normalized MCC-1 Leach Rate at 90%, g/m²-day**

<table>
<thead>
<tr>
<th>Material</th>
<th>Boron</th>
<th>Silicon</th>
<th>Sodium</th>
<th>Total Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-Ceramic</td>
<td>0.08</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>(70 wt% Calcine)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>0.5</td>
<td>0.8</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>(33 wt% Calcine)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.13. Representative chemical composition of current and future HLW liquid at ICPP

<table>
<thead>
<tr>
<th>Component</th>
<th>Zirconium fluoride</th>
<th>Sodium bearing</th>
<th>Nonfluoride</th>
<th>Fluoride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.3</td>
<td>0.8-1.6</td>
<td>1.51</td>
<td>0.742</td>
</tr>
<tr>
<td>B</td>
<td>0.15</td>
<td>0.005-0.01</td>
<td>0.003</td>
<td>0.241</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>0.03-0.2</td>
<td>0.27</td>
<td>-</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>-</td>
<td>0.06-0.1</td>
<td>0.023</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>-</td>
<td>1.42</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>0.036</td>
<td>0.0007</td>
</tr>
<tr>
<td>F⁻</td>
<td>3.4</td>
<td>0.005-0.06</td>
<td>0.032</td>
<td>5.99</td>
</tr>
<tr>
<td>Fe</td>
<td>0.04</td>
<td>0.05-0.09</td>
<td>0.19</td>
<td>0.023</td>
</tr>
<tr>
<td>H²</td>
<td>1.12</td>
<td>0.03-0.15</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>K</td>
<td>1.12</td>
<td>0.03-0.15</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
<td>-</td>
<td>0.062</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>0.048</td>
<td>0.0004</td>
</tr>
<tr>
<td>Na</td>
<td>0.12</td>
<td>2.1-4.0</td>
<td>1.31</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>0.016</td>
<td>0.0049</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>13.7</td>
<td>19.4-23.3</td>
<td>23.1</td>
<td>11.47</td>
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<tr>
<td>SO₄²⁻</td>
<td>-</td>
<td>0.33-0.5</td>
<td>0.65</td>
<td>1.52</td>
</tr>
<tr>
<td>Zr</td>
<td>2.47</td>
<td>-</td>
<td>-</td>
<td>3.89</td>
</tr>
<tr>
<td>H₂O</td>
<td>76.6</td>
<td>76.6-69.2</td>
<td>70.9</td>
<td>76.0</td>
</tr>
</tbody>
</table>

Density, g/ml. 1.2 1.2-1.3 1.2 1.2

Table 2.14. Representative chemical composition of current and future HLW calcine at ICPE*

<table>
<thead>
<tr>
<th>Component</th>
<th>Alumina</th>
<th>Zirconium fluoride</th>
<th>Zirconium-sodium blend</th>
<th>Stainless steel sulfate</th>
<th>Fluorine-sodium blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>82.0-95.0</td>
<td>13.0-17.0</td>
<td>10.0-16.0</td>
<td>4.4</td>
<td>0.5-7.5</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{SO}_4)_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>81.0</td>
<td>-</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>0.5-2.0</td>
<td>3.0-4.0</td>
<td>2.0-3.0</td>
<td>-</td>
<td>3.0-3.2</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>-</td>
<td>2.0-4.0</td>
<td>13.0-17.0</td>
<td>-</td>
<td>3.3-3.6</td>
</tr>
<tr>
<td>$\text{CaF}_2$</td>
<td>-</td>
<td>50.0-56.0</td>
<td>33.0-39.0</td>
<td>-</td>
<td>46.0-49.0</td>
</tr>
<tr>
<td>$\text{Cd}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>6.0-8.5</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>1.3</td>
<td>-</td>
<td>6.0-8.0</td>
<td>-</td>
<td>10.0-13.0</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0</td>
<td>0.02-0.03</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>5.0-9.0</td>
<td>0.5-2.0</td>
<td>7.0-9.0</td>
<td>-</td>
<td>10.0-17.0</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>-</td>
<td>21.0-27.0</td>
<td>16.0-19.0</td>
<td>-</td>
<td>10.0-20.0</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.5-1.5</td>
<td>0.5-1.5</td>
<td>0.5-1.5</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>Fission products and actinides</td>
<td>0.2-1.0</td>
<td>0.2-1.0</td>
<td>0.2-1.0</td>
<td>0.2-1.0</td>
<td>0.2-1.0</td>
</tr>
<tr>
<td>Density, g/mL</td>
<td>1.1</td>
<td>1.4</td>
<td>1.6</td>
<td>1.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Liquid (10^6 Ci)</th>
<th>Calcine (10^6 Ci)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90Sr</td>
<td>1.738</td>
<td>13.139</td>
</tr>
<tr>
<td>90Y</td>
<td>1.738</td>
<td>13.139</td>
</tr>
<tr>
<td>106Ru</td>
<td>0.024</td>
<td>0.010</td>
</tr>
<tr>
<td>106Rh</td>
<td>0.024</td>
<td>0.010</td>
</tr>
<tr>
<td>134Cs</td>
<td>0.107</td>
<td>0.192</td>
</tr>
<tr>
<td>137Cs</td>
<td>1.901</td>
<td>14.512</td>
</tr>
<tr>
<td>137mBa</td>
<td>1.798</td>
<td>13.728</td>
</tr>
<tr>
<td>144Ce</td>
<td>0.067</td>
<td>0.040</td>
</tr>
<tr>
<td>144Pr</td>
<td>0.067</td>
<td>0.040</td>
</tr>
<tr>
<td>147Pm</td>
<td>0.000</td>
<td>0.0790</td>
</tr>
<tr>
<td>154Eu</td>
<td>0.023</td>
<td>0.093</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>7.487</strong></td>
<td><strong>55.603</strong></td>
</tr>
</tbody>
</table>

**Specific activity, Ci/L**

0.88

15.9

^aTaken from ref. 3. Curies as of December 31, 1990. Similar values for actinide nuclides are not available.