Hanford Waste Encapsulation: Strontium and Cesium

R.R. Jackson

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Atlantic Richfield Hanford Company
Richland, Washington 99352

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HANFORD WASTE ENCAPSULATION: STRONTIUM AND CESIUM

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Waste Fractionization and Encapsulation Process Engineering
Engineering
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ABSTRACT

The strontium and cesium fractions separated from high radiation level wastes at Hanford are converted to the solid strontium fluoride and cesium chloride salts, doubly encapsulated, and stored underwater in the Waste Encapsulation and Storage Facility (WESF). A capsule contains approximately 70,000 curies of $^{137}$Cs or 70,000 to 140,000 curies of $^{90}$Sr. Materials for fabrication of process equipment and capsules must withstand a combination of corrosive chemicals, high radiation dosages and frequently, elevated temperatures. The two metals selected for capsules, Hastelloy C-276 for strontium fluoride and 316-L stainless steel for cesium chloride, are adequate for prolonged containment. Additional materials studies are being done both for licensing strontium fluoride as source material and for second generation process equipment.
A goal of the Waste Management Program at Hanford is solidification of the present high radiation level liquid waste stored in underground tanks. One requirement in achieving that goal is quantitative removal of the long-lived, high heat producing fission products, $^{90}\text{Sr}$ and $^{137}\text{Cs}$, from the liquid and sludges in the storage tanks. Separation processes have been in operation since 1967 for the treatment of these stored wastes. To assure isolation and prolonged containment of the resultant purified products, a new plant, the Waste Encapsulation and Storage Facility (WESF), was built. Here the isotopes, $^{90}\text{Sr}$ and $^{137}\text{Cs}$, are doubly encapsulated and stored in cooled water basins. The Facility began hot operation in September 1974.

The Waste Encapsulation flowsheets$^{1,2,3}$ as shown in Figure 1 are relatively simple. The strontium feed solution is approximately 0.35 molar strontium nitrate (varying between 0.09 and 0.17 molar $^{90}\text{Sr}$). It may contain up to 0.1 molar nitric acid. The predominate impurity is sodium (approximately 3 molar). The batch size is set up by optimum strontium fluoride cake filtration, which is normally 4,500 grams containing from 110,000 to 225,000 curies of fission product strontium. The fission product to total strontium ratio varies on a campaign basis due to variations in age of feed and trace quantities of cold strontium in cold chemicals used in separations facilities. Strontium fluoride is precipitated by the addition of sodium fluoride powder after pH adjustment to assure a basic solution. Filtration is performed by vacuum transfer through four parallel sintered metal filters. These filters, of 316-L stainless steel,
**FIGURE 1**

**WASTE ENCAPSULATION**
have a mean pore size of five microns to ten microns. After filtration, a cake wash of about 30 cake volumes is performed. Product loss via the combined filtrate and wash waste is about 0.1 to 0.3 percent. The filter cakes, after self-drying, are dumped into Inconel X furnace boats. The strontium fluoride cake is dried at 1100 °C for approximately eight hours in a resistance furnace which utilizes silicon carbide heating elements. Algomeration of the strontium fluoride occurs during drying due to traces of residual sodium nitrate. Hence, a cake crushing step is required prior to incremental compaction into the inner or Hastelloy C-276 capsule tube. Using a pneumatic operated jack hammer to load the strontium fluoride powder, 65 to 70 percent of theoretical density can be achieved. Helium gas is introduced into the capsules, the lid is tack welded to the tube, and a circumferential weld is performed by pulsed fusion welding (tungsten-inert gas (TIG) welding). The capsule is placed in a vacuum chamber and a conventional helium leak test performed. The inner capsule is transported to the decontamination cell and cleaned to an essentially non-smearable contamination level. It is placed into an outer, 316-L stainless steel capsule which is welded shut, again using a TIG welding process. The outer assembly final weld is examined with conventional ultrasonic scanning apparatus to assure weld penetration is greater than or equal to 75 percent of tube wall thickness (277 millimeters).

The cesium feed stock is an alkaline solution of cesium carbonate approximately 2.5 molar cesium (of which 48 percent is $^{137}$Cs). The predominate impurity is sodium. The solution is titrated with 12 molar
hydrochloric acid to a pH end point of three-to-four. The cesium chloride solution is vacuum transferred to the evaporator-melter, which is an induction heated vessel of approximately 75-liter capacity. The solution is evaporated to dryness and the resulting cake of salt melted (at approximately 640 °C). Through an electrically heated tube the cesium chloride melt is vacuum transferred to the casting assembly, which consists of an insulated electrically heated head against which nine inner cesium capsules seal. A normal melt transfer fills approximately seven capsules. The capsules are then handled identically to the strontium capsules, with the single exception that cesium chloride is encapsulated in a 316-L stainless steel inner as well as outer capsule.

The capsule assemblies are stored in pools under 13 feet of water. The water is continuously treated by anion-cation exchange to maintain high purity. The chloride content is maintained less than one part per million (ppm). The total metallic ion content is maintained at less than five ppm.

Some characteristics of the strontium and cesium capsules are shown in Figure 2. The entire assembly is approximately 50 centimeters in length and six centimeters in diameter. Approximately 70,000 curies of $^{137}$Cs or 70,000 to 140,000 curies of $^{90}$Sr are loaded per capsule; the strontium varies depending upon the feed isotopic composition. The heat output, not shown, is in the neighborhood of 300 watts per cesium capsule and varies between 400 and 900 watts for a strontium capsule. Capsule dosimeter measurements were performed with the following results:
### WASTE CAPSULES

#### PER CENT of THEORETICAL DENSITY

<table>
<thead>
<tr>
<th>Form</th>
<th>Loading</th>
<th>Total Void Space of Capsule</th>
<th>Temperature Air</th>
<th>Temperature Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium Fluoride</td>
<td>Compacted Powder 150 KCl (Max.)</td>
<td></td>
<td>68°C Center Line</td>
<td>71°C Center Line</td>
</tr>
<tr>
<td>Cesium Chloride</td>
<td>Melt-Cast</td>
<td>70 KCl</td>
<td>45°C Center Line</td>
<td>58°C Center Line</td>
</tr>
</tbody>
</table>

#### REMOTE GAS TUNGSTEN ARC WELD

- HELIUM LEAK CHECKED
- REMOTE GAS TUNGSTEN ARC WELD
- ULTRASONIC TESTED (UT)

#### MATERIALS

<table>
<thead>
<tr>
<th>Capsule</th>
<th>Inner</th>
<th>Outer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium Fluoride</td>
<td>Hastelloy C-276</td>
<td>Stainless Steel 316-L</td>
</tr>
<tr>
<td>Cesium Chloride</td>
<td>Stainless Steel 316-L</td>
<td>Stainless Steel 316-L</td>
</tr>
</tbody>
</table>

#### Thickness

- **Total Thickness**
- **Outside Diameter**
- **Total Length**
- **Total Cap Thickness**

#### Dimensions

- **NOTE**: All dimensions are in cm.
Both product forms, strontium and cesium, contain approximately four to six weight percent impurities. Typical metallic impurities are:

<table>
<thead>
<tr>
<th>Strontium Fluoride (Weight Percent)</th>
<th>Cesium Chloride (Weight Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na 2.2</td>
<td>Na 0.2</td>
</tr>
<tr>
<td>Al 0.3</td>
<td>Al 0.1</td>
</tr>
<tr>
<td>Ca 0.5</td>
<td>Mg 0.1</td>
</tr>
<tr>
<td>Mg 0.5</td>
<td>K 0.6</td>
</tr>
<tr>
<td>Ba 0.9</td>
<td>Ni 0.2</td>
</tr>
<tr>
<td>Fe 0.4</td>
<td>Fe 0.2</td>
</tr>
<tr>
<td>Cr 0.4</td>
<td>Cr 0.1</td>
</tr>
<tr>
<td>Zr 1.6</td>
<td>Si 0.1</td>
</tr>
</tbody>
</table>

A typical cesium capsule assembly (inner capsule contained in outer) and a typical cesium inner capsule, both containing non-radioactive cesium chloride, were subjected to the specified tests required for licensing as "Special Form Material."(4) No capsule failures or loss of capsule contents
occurred during or as a consequence of the tests. Slight end cap and weld distortion resulted from the drop test. The tests indicate that the cesium inner capsule suffices by itself to satisfy the licensing requirements.

Capsule selection material was based on salt compatibility at elevated temperatures, commercial availability, and ease of fabrication and welding.\(^5\) Compatibility tests were performed with both non-radioactive and radioactive compounds. Due to time limitations imposed by program requirements, the tests were short-term; three year maximum duration for non-radioactive compounds and one year maximum duration for radioactive compounds. All tests were conducted at elevated temperatures. The subsequent extrapolations of corrosion results (Figures 3, 4, and 5) are based on data obtained at 400 °C. This results in a substantial margin of safety in that 400 °C represents the maximum metal-salt interface temperature.\(^5\) The interface temperature will be less than 400 °C for most of the storage period.

For cesium containment, 316-L stainless steel proved most suitable. As shown in Figure 3, corrosion resistance is satisfactory.

Hastelloy C-276 was selected for strontium fluoride packaging. Figure 4 illustrates the projected corrosion rate over the capsule storage period. Both tungsten and titanium-zirconium-molybdenum (TZM) alloys possess better resistance to strontium fluoride attack at elevated temperatures. However, neither material is readily available or suitable for the
FIGURE 3

ESTIMATED LONG-TERM ATTACK OF 316-L STAINLESS STEEL by CESIUM CHLORIDE
FIGURE 4

ESTIMATED LONG-TERM ATTACK of HASTELLOY C by STRONTIUM FLUORIDE
present welders. Haynes 25 is somewhat more corrosion-resistant than Hastelloy C-276 as shown in Figure 5. However, availability and ease of fabrication and welding favored the selection of Hastelloy C-276.

At present long-term strontium fluoride is under study as part of the program to license $^{90}\text{SrF}_2$ for heat source applications. Compatibility at elevated temperatures (800 °C to 1100 °C) is being defined for tungsten, TZM, Haynes 25 and Hastelloy C-276. Some additional insights have resulted, specifically indications of the influence of various impurities on chemical attack and microstructure alterations. It has been found that the presence of strontium oxide results in severe chemical attack on both nickel and cobalt based alloys. Fluorides of multivalent cations, such as iron, (from corrosion of process equipment) also adversely affect compatibility.

As part of the long-term compatibility studies, seven encapsulated kilograms of WESF product of $^{90}\text{SrF}_2$ have been delivered to Battelle-Pacific Northwest Laboratories for use in the licensing program. Two production capsules have been placed in insulated overpacks in-cell at WESF for short-term storage at elevated temperatures. It is planned to section one capsule after six months and one after 12 months for metallographic examination of the Hastelloy C-276 capsule tube wall. Also, the long-term product surveillance program at WESF will involve periodic reworking of pre-selected capsules in order that the capsule tube may be subjected to metallographic examination to gauge the extent, if any, of chemical attack and alterations of the metal microstructure.
FIGURE 5

ESTIMATED LONG-TERM ATTACK of HAYNES 25 by STRONTIUM FLUORIDE
A number of key process steps involve a combination of corrosive chemicals, elevated temperatures and high radiation dosages culminating in severe attack on process equipment. The three most notable are strontium fluoride precipitation, strontium fluoride drying, and cesium chloride evaporation, melting and melt casting. Equipment is protected primarily by control of process parameters coupled with judicious selection of materials of fabrication.\(^7\)

The fluoride precipitation and digestion step is performed in an alkaline condition, with the pH controlled at about 8.5. Fluoride corrosion of the 316-L tank becomes pronounced at a pH of less than six.

Strontium fluoride drying takes place at 1100 °C. The metal boats containing the fluoride powder are severely attacked despite an inert atmosphere of argon. This attack is compounded by the techniques required to remove the dried powder from the boats. At present, Inconel 690 and Inconel X seem to provide the best service. A number of other alloys have been and are being tested, including ceramics, but none so far perform as well.

The rate of attack of molten cesium chloride on 18:18:2 stainless steel as a function of temperature is as follows:\(^8\).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Corrosion Rate (mm/mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.02</td>
</tr>
<tr>
<td>800</td>
<td>0.07</td>
</tr>
<tr>
<td>900</td>
<td>0.25</td>
</tr>
<tr>
<td>1000</td>
<td>0.46</td>
</tr>
</tbody>
</table>
However, increasing the corrosion product chloride content of the melt has a profound affect on the rate of chemical attack. Chemical attack on 18:18:2 was measured at 700 °C for varied concentrations of a "corrosion product" mix, consisting of 70 percent iron chloride, 20 percent chromium chloride and ten percent nickel chloride. The results were:

<table>
<thead>
<tr>
<th>Corrosion Product Content (Weight Percent)</th>
<th>Rate of Attack (mm/mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>8.1</td>
</tr>
<tr>
<td>0.25</td>
<td>30.0</td>
</tr>
<tr>
<td>1.0</td>
<td>36.0</td>
</tr>
</tbody>
</table>

A test performed at 1000 °C with five weight percent corrosion product chlorides in the melt resulted in catastrophic attack and embrittlement of the 18:18:2 stainless steel coupon.

The temperature differential between this point and the cesium chloride melting point is adequate, however, for control in the low corrosion zone. At present, more advanced cesium equipment is designed to eliminate vacuum melt transfers. Hastelloy G has been selected as the material of fabrication. Multimelt (20 percent nickel, 20 percent cobalt and 20 percent chromium) would also prove satisfactory for this service.

Evaluation and selection of materials for both fission product containment and for process equipment fabrication have been and will continue to be a major concern at the Waste Encapsulation and Storage Facility. Improving WESF productivity requires continued improvement of existing hardware, as well as investigation and testing of new processes and equipment.
Equipment reliability at WESF is often a direct function of the adequacy of materials chosen or available for fabrication of the part or assembly. Examples of current studies along these lines were cited above.

The program to license strontium fluoride for source applications, if successful, will require increased process flexibility to meet the various packaging requirements posed by potential applications.

REFERENCES


6. BNWL-1967, November 1975, H. T. Fullam, "The Containment of $^{90}$SrF$_2$ at 800 to 1100 °C - Preliminary Results."

7. ARH-1600 (Unclassified), April 5, 1974, L. M. Knights, "Specifications and Standards for Waste Processing and Encapsulation Plant."

8. Letter, January 8, 1975, R. F. Maness to J. D. Moore, "Corrosiveness of Molten Cesium Chloride."
