

The environmental impacts of constructing and operating facilities for these alternative technologies are being identified and evaluated in this *Salt Processing Alternatives Supplemental Environmental Impact Statement* (SEIS) (DOE 1998a, 1999).

Need for ITP Replacement

Benzene generated during the ITP process results from the decomposition of tetraphenylborate (TPB), which is used to separate soluble radioactive cesium from the HLW salt solution. The cesium is precipitated as an insoluble solid that can be filtered from the waste solution. Under certain conditions the tetraphenylborate is subject to a radiolytic and catalytic decomposition that forms benzene and allows the separated cesium to return to the salt solution. Benzene is a toxic, flammable, and potentially explosive organic substance that must be safely controlled. The redissolution of cesium as a result of tetraphenylborate decomposition must be curtailed to achieve the required decontamination of the salt solution.

Tetraphenylborate decomposition is catalyzed by certain metals in the radioactive waste, notably the fission product palladium. The extent and rate of tetraphenylborate decomposition is affected by the chemical form of the catalyst, and increases with time of exposure to and temperature of the catalyst. Controlled release of benzene from the salt solution, as required to mitigate potential benzene hazards, is promoted by agitation or stirring. Flammability is controlled by maintaining a nitrogen gas cover that excludes oxygen above concentrations that could cause benzene combustion.

The ITP facilities were unsuitable to control tetraphenylborate decomposition and benzene generation because:

- Large volumes and long cycle times allowed excessive tetraphenylborate decomposition before the precipitate could be separated by filtration from the salt solution.
- Adequate temperature control was not possible in the large tank.
- Agitation by slurry pumps produced insufficient mixing.
- Purge of the nitrogen gas cover was inadequate because the large tank was not adaptable to positive pressure or secondary confinement.

These limitations were assessed against requirements for safely processing the large inventory of HLW salt within the time projected for completion of sludge processing in the DWPF. Based on this assessment, DOE concluded that the ITP process could not achieve safety and production requirements for the high-level radioactive waste system.

A.2 Current HLW System Configuration

The SRS HLW system was developed to receive and store radioactive wastes in a safe and environmentally sound manner and to convert these wastes into forms suitable for final disposal (DOE 1994). A schematic of the process is shown in Figure A-3 (WSRC 1998b). As planned, sludge components and the highly radioactive soluble constituents recovered from the salt components of the wastes would be immobilized in DWPF as borosilicate glass contained in stainless steel canisters for disposal in a monitored geologic repository. Low activity salt solutions would be immobilized in cementitious form (saltstone) for disposal in onsite vaults. Secondary products from these operations, including mercury derived from sludge processing and benzene released during salt processing operations, would be recovered for appropriate disposition (recycling or destruction). Miscellaneous radioactive and hazardous process wastes would be incorporated into the SRS waste management system for disposal.

A.3 Processes and Facilities

A.3.1 HLW STORAGE AND EVAPORATION

HLW from SRS chemical processing operations is received in the F- and H-Area Tank Farms as an aqueous slurry of insoluble sludge and soluble salts in alkaline solution. The tank farms concentrate (by evaporation of excess water) and store these wastes, pending further processing in other facilities. The sludge component of the alkaline wastes settles to the bottom of the storage tank, and the salt solution is decanted and concentrated by evaporation, leaving a solid saltcake and a concentrated supernatant. Evaporation reduces the volume and mobility of the wastes, enhancing long-term storage. The water driven off by evaporation is processed through the Effluent Treatment Facility (ETF) for decontamination before release to an onsite stream. No water is released from ETF to a stream unless it meets all regulatory criteria.

A.3.2 EXTENDED SLUDGE WASHING

The insoluble sludges accumulated in the tanks are hydraulically slurred and transferred to tank farm facilities for washing with inhibited water to remove soluble salts entrained in the sludge. (Inhibited water contains low concentrations of sodium nitrite and sodium hydroxide to inhibit corrosion of the steel waste tanks.) To reduce the quantity of glass waste formed, sludge with high levels of aluminum is treated with caustic (3 to 5 molar sodium hydroxide) to convert aluminum hydroxide to soluble sodium aluminate, which is washed from the sludge along with other soluble salts. The wash solutions are concentrated by evaporation and returned to the waste tanks as salt waste components. The washed sludge is transferred to DWPF for conversion to the borosilicate glass waste form.

A.3.3 SALT PROCESSING

In the salt processing operations, as originally projected, saltcake in the waste tanks would be redissolved and combined with concentrated supernatant, and the resulting salt solution transferred hydraulically to the ITP facilities. ITP was to be conducted in a large waste tank; tetraphenylborate would be added to the salt solution to coprecipitate radioactive cesium (along with essentially nonradioactive potassium) as an insoluble solid, and a slurry of the particulate solid monosodium titanate would be added to react with residual strontium and actinides by a sorption process. The resulting precipitate solids would be concentrated in the tank and separated by cross-flow filtration before being transferred to DWPF for melting into a glass waste form, along with sludge components of the waste. (Cross-flow filtration is a process in which the solid slurry is passed through porous membrane tubes under pressure to force the salt solution into a surrounding vessel and concentrate the solids in the slurry.) The low activity salt solution recovered by filtration would be immobilized in onsite vaults as saltstone.

A.3.4 DWPF GLASS PROCESSING

If the ITP process were operational, sludge and salt precipitate solids would be transferred as aqueous slurries to DWPF for conversion in a glass melter to the glass waste form. Currently, only sludge is being vitrified at DWPF.

In DWPF, the sludge slurry is acidified and treated chemically to extract mercury before the sludge is sent to the glass melter. The recovered mercury is stored for future disposal. If ITP operated for salt processing, the precipitate slurry would be treated in DWPF, using a hydrolysis process to decompose the tetraphenylborate solids. The hydrolysis reaction would produce an aqueous solution of inorganic salts including the radioactive cesium, several organic products (principally benzene), boric acid, and residual titanate solids. The benzene would be distilled from the mixture, washed, and collected for disposal. To avoid potential explosion hazards from benzene, the tetraphenylborate precipitate would be processed in a carbon dioxide atmosphere. The aqueous residues of the precipitate hydrolysis process would be mixed with sludge and glass frit as feed for the DWPF melter. Molten glass would be poured into stainless steel canisters about 2 feet in diameter by 10 feet long, suitable for interim onsite storage and permanent disposal in a monitored geologic repository. | TC

Storage of Recycle DWPF Wastes

DWPF operations produce large volumes of recycle wastes, mostly water, returned to the HLW storage tanks. Without a salt processing technology in place, the DWPF sludge-only operation will increase the volume of waste that must be stored in the HLW tanks. Management of existing tank space and equipment would allow DOE to continue sludge-only vitrification in DWPF until about 2010, the projected time for startup of salt processing plant operations (text box page 2-2).

Tank space management would include some or all of the following activities intended to reduce storage requirements in the HLW tanks (WSRC 1999a):

- Continue to evaporate liquid waste in the tanks
- Convert ITP processing tanks 49 and 50 to HLW storage
- Reduce DWPF low-level waste streams sent to the tank farms
- Implement several activities to gain small incremental volumes
- As 2010 approaches, reduce the available emergency space in the tank farms while maintaining the minimum emergency space required by the Authorization Basis.

A.3.5 SALTSTONE PROCESSING

The low activity salt solution from the ITP process would be mixed with a blend of cement, flyash, and slag in the Saltstone Manufacturing and Disposal Facility to produce a grout suitable for disposal in onsite vaults. The grout would be poured into the vaults to solidify into large saltstone monoliths.

As originally designed, the saltstone vaults are near-surface concrete containment structures that serve as forms for the cast saltstone and provide a diffusion barrier to the environment (Wilhite 1986; Wilhite et al. 1989). The vaults, 300 feet in length, 200 feet wide, and about 25 feet high, with 1.5-foot-thick sidewalls, a 2.5-foot base and a 1.5-foot cover, are sized to contain approximately 1.4 million cubic feet (40,000 m³) of saltstone within six subdivided cells of the vault. During decommissioning, clay caps would be placed over the vaults, with drainage systems installed between the caps to reduce the volume of rainwater infiltrating the disposal site.

The grout composition and the vault design were specified to minimize the release rate

of waste components into the surrounding environment (Langton 1988; Wilhite 1986). Performance criteria imposed on the saltstone vaults required that groundwater quality at the disposal site meet drinking water standards. Performance modeling, validated by field tests, demonstrated the capability of the saltstone vaults to meet these standards (Martin Marietta 1992).

A.4 Salt Processing Alternatives

Facility capabilities have been demonstrated and all waste processing operations for the SRS HLW management system are currently operational, with the exception of ITP processing and related late wash of the precipitate. In December 1995, DOE determined that the ITP process was generating benzene at higher rates than expected and operational testing was suspended in March 1996. Benzene is a flammable product of the decomposition of tetraphenylborate added to precipitate cesium from the salt solution. The excess benzene resulted from the decomposition of tetraphenylborate in the processing tank, allowing redissolution of the precipitate before it could be separated by filtration. In concurrence with a Defense Nuclear Facilities Safety Board recommendation, chemical studies were initiated that would better explain the underlying mechanisms for benzene generation and release during the tetraphenylborate precipitation process. These studies demonstrated that the process to remove cesium from the salt solution, as then configured, could not achieve production goals and meet safety requirements for processing the salt wastes.

In early 1998, DOE directed Westinghouse Savannah River Company (WSRC) to initiate a program for evaluation of alternative salt processing technologies. A High-Level Waste Salt Processing Systems Engineering Team (SET) was chartered to identify technologies to replace the ITP process, evaluate the technologies, and recommend a selected technology or technologies to convert the HLW salt solution (supernatant plus dissolved saltcake) to waste forms that could meet regulatory requirements. The SET was composed of WSRC employees with technical support from universities, several na-

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tional laboratories, independent consultants, and the DOE complex.

The initial screening of approximately 140 salt processing technologies options identified 18 for further evaluation. The 18 technologies, grouped by general category (WSRC 1998c), were:

Crystallization

Fractional Crystallization – DWPF Vitrification

Electrochemical Separation

Electrochemical Separation and Destruction – DWPF Vitrification

Ion Exchange

Elutable Ion Exchange – DWPF Vitrification

Acid Side Ion Exchange – DWPF Vitrification

Crystalline Silicotitanate Ion Exchange – DWPF Vitrification

Crystalline Silicotitanate Ion Exchange – New Facility Vitrification

Crystalline Silicotitanate Ion Exchange – Ceramic Waste Form

Zeolite Ion Exchange – DWPF Vitrification

Precipitation

Potassium Removal followed by Tetraphenylborate Precipitation – DWPF Vitrification

Reduced Temperature ITP – DWPF Vitrification

Catalyst Removal ITP – DWPF Vitrification

ITP with Enhanced Safety Features – DWPF Vitrification

Small Tank Tetraphenylborate Precipitation – DWPF Vitrification

Solvent Extraction

Caustic Side Solvent Extraction – DWPF Vitrification

Acid Side Solvent Extraction – DWPF Vitrification

Vitrification

Direct Vitrification

Supernatant Separation – DWPF Vitrification

Direct Disposal of Cesium in Grout – DWPF Vitrification

A.4.1 SCREENING

The SET employed a phased approach, as summarized in Figure A-4. In Phase I, approximately 140 possible technology options were identified to replace ITP, and meet safety and production requirements. Each option was evaluated against a set of screening criteria that established minimum requirements. This initial screening reduced the original 140 options to 18 technologies that were selected for further evaluation.

During Phase II of the technology selection process, the SET performed a preliminary technical and programmatic risk assessment for each of the 18 technologies to establish a short list for in-depth analysis. As part of the Phase II analysis, the SET evaluated preliminary material balances, cycle times, and impacts to the HLW system for each of the 18 technologies. A technical document (WSRC 1998d) provides supporting data and the results of this assessment, which narrowed the list of 18 technologies to four:

- Small Tank Tetraphenylborate Precipitation (Small Tank Precipitation)
- Crystalline Silicotitanate (non-elutable) Ion Exchange (Ion Exchange)
- Caustic Side Solvent Extraction (Solvent Extraction)
- Direct Disposal (of cesium) in Grout (Direct Disposal in Grout).

Phase III of the process evaluated the final four technologies in still greater detail, including life-cycle cost estimates and schedule assessments (WSRC 1998b). Some of the uncertainties and assumptions in the Phase II efforts were resolved in Phase III by additional research, literature review, calculations, and experiments. The facility components of the technologies, such as tanks and transport systems, were described in greater detail. Equipment sizing was refined and used to develop pre-conceptual facility layouts and process flow configurations. The layouts were used to develop project schedules and life-cycle cost estimates. This analysis is docu-

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