

OBU-SWE-2003-00047

April 2, 2003

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MANAGING LOW-LEVEL WASTE PUREX SOLVENT SOLUTIONS DISCARDED FROM THE CANYONS (OBU-SWE-2003-00037)

Attached is the subject "white paper" that describes how we manage low-level waste PUREX solvent solutions. After a comparison with DOE Order 435.1 "Radioactive Waste Management" requirements and guidance as well as referenced statutes and requirements, the paper confirms that discarded PUREX solvent is low-level waste.

PUREX solvent is used as a material in process during canyon operations. PUREX solvent is recovered, washed, and recycled independently of other canyon systems. When discarded from the canyon, the PUREX solvent is stored in low-level waste (LLW) tanks pending treatment and disposal. Discarded PUREX solvent has been historically managed as LLW and documentation is consistent on that point. For example, PUREX solvent is stored in mixed LLW or LLW tanks, has been incinerated in the Consolidated Incineration Facility as a mixed LLW under RCRA permit, tanks that previously stored PUREX solvent were closed in the old burial ground as LLW, and PUREX solvent is listed in the Site Treatment Plan as a mixed LLW.

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MANAGING LOW-LEVEL WASTE PUREX SOLVENT SOLUTIONS DISCARDED FROM THE CANYONS

March 14, 2003

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Managing Low-Level Waste PUREX Solvent Solutions Discarded from the Canyons

Summary

Canyon solvent solutions have been, and still are, used in the SRS Reprocessing Facilities (Building 221-F and 221-H Canyons) as a chemical solvent to perform classical chemical engineering unit operations called solvent extraction. Solvent extraction is used to separate selected constituents from complex chemical solutions in order to recover them as product. Over the years, different materials have been recovered in F- and H-Canyons for different reasons (such as Pu-239, Pu-238, U-238, U-235, Np-237, Cf-252).

During the solvent extraction separation process, several chemicals have been used to effect the unit operations. The primary chemicals are:

- Nitric acid for dissolving spent fuel from the SRS reactors (the feed stream to solvent extraction), as the salting agent for the extraction process, and dilute nitric acid is used to strip, or back extract, product from solvent,
- Tributyl phosphate (TBP) as an organic extractant for the solvent extraction process,
- And, n-paraffin (similar to kerosene) used as an organic diluent for the higher viscosity and higher density TBP to allow reasonable aqueous/organic separation during processing, as well as to limit actinide concentrations in solvent for criticality safety purposes.
- Tributyl phosphate and n-paraffin is traditionally referred to as PUREX solvent, Plutonium and URanium EXtraction solvent.

PUREX solvent is introduced into the canyons solely for the solvent extraction processes in the canyons. Solvent degrades over time due to acid attack and radiolysis. The primary degradation products, dibutyl phosphate and monobutyl phosphate, effect the extraction performance of the solvent and therefore must be removed. For removal of these degradation products, a solvent recovery cycle is used that consists of a carbonate wash cycle followed by a nitric acid adjustment. Solvent is continuously washed during processing to maintain solvent quality and continuously reused.

There is a point where solvent is no longer efficient in performance of its solvent extraction function and is removed from F- or H-Canyon and stored for treatment and disposal as a low-level waste (LLW). Sluicing of some of the stored solvent when transferring between storage tanks using water has resulted in an aqueous layer in the

storage tanks. The aqueous layer will pick up some of the chemicals and radionuclides from the organic solvent by diffusion across the interface. This separate aqueous layer can be separated by decanting from the organic to provide different treatment options for the organic phase and aqueous LLW liquids.

Why Solvent is a LLW

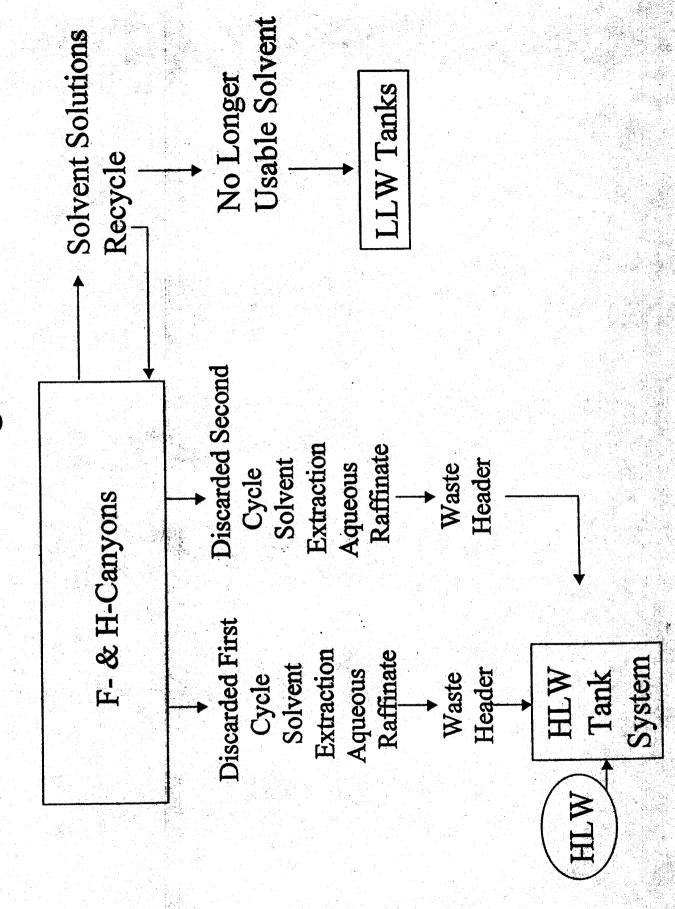
Canyon processing consists of dissolving spent nuclear fuel and transferring those solutions to the solvent extraction unit operation. The main solvent extraction cycles are called first cycle of solvent extraction and second cycles of solvent extraction.

Acidic solutions from dissolved fuel are transferred to first cycle and contacted with solvent to effect separation of the product materials into the solvent. These product materials may be moved forward to subsequent cycles for further processing. The acidic solution from the first cycle solvent extraction from which the majority of the product materials have been extracted is referred to as raffinate.

In the canyon first cycle solvent extraction process, the majority of the highly radioactive fission products from dissolved spent nuclear fuel exit the solvent extraction process in this raffinate stream. The raffinate stream can undergo further processing for removal of additional desirable products before final discard from the canyon processes. When the raffinate stream is finally discarded, the acidic stream is neutralized for storage in carbon steel waste tanks. Because the raffinate stream being discarded had its source directly from the reprocessing of spent nuclear fuel and contains the highly radioactive fission products, the stream, when discarded, is defined as high-level waste. Subsequent solvent extraction cycles also produce a raffinate stream that, when discarded, is defined as high-level waste even though this stream does not normally contain the same high concentration of highly radioactive fission products as the first cycle raffinate stream.

Note: In the discussion above, the PUREX solvent is not part of the discarded raffinate streams that are HLW. PUREX solvent is recovered, washed, and recycled independently of the HLW system. When PUREX solvent is removed because it is no longer useful, it is managed as LLW during storage, treatment and disposal.

Diagrams



Regulatory Definitions

The first legal definition of HLW was established in 1970 by the Atomic Energy Commission (AEC) defined in 10CFR50 Appendix F as:

"...those aqueous wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, in a facility for reprocessing irradiated reactor fuel."

The Nuclear Regulatory Commission (NRC) defined HLW in 10CFR 60 as:

"....(1) Irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated waste from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated fuel, and (3) solids into which such liquid wastes have been converted."

The Nuclear Waste Policy Act (NWPA) of 1982 defined HLW as:

"...(a) The highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and (b) other highly radioactive material that the Commission, consistent with existing law, determines by rule requires permanent isolation."

The Department of Energy (DOE) Order 435.1 definition of HLW is similar to the NWPA of 1982 except for the reference to the "Commission" and is follows:

"High-level waste is the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations, and other highly radioactive material that is determined, consistent with existing law, to require permanent isolation."

Discussion:

PUREX solvent does not meet the definition of high-level waste. Since PUREX solvent is not "highly radioactive waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing...," it is clear that PUREX solvent is LLW. In fact, PUREX solvent is not liquid waste produced directly in reprocessing. As described above, PUREX solvent is a material used in the solvent extraction unit operation in the canyons to allow reprocessing, and is continuously recycled and reused as long as its extraction performance is maintained. Spent PUREX solvent is removed from the canyon as a low-level waste and never combined with HLW. Spent solvent is low in radionuclide content. The solvent used in reprocessing activities is selected for its ability to selectively extract actinide elements (product materials) from

the highly radioactive fission products in spent nuclear fuel. Degraded solvent does retain some radioactive material content due to the selectivity of the solvent degradation products for certain elements. Any solvent discarded is managed as a low-level waste, as is any other aqueous material that may contact the solvent. A case in point is the water decanted from the discarded LLW solvent that had previously been used for transfer of solvent between LLW storage tanks.

Conclusion

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The definitions contained in the regulations and DOE orders define LLW, transuranic (TRU) and HLW.

Low-level waste is any nuclear waste not defined as HLW or TRU. According to DOE Order 435.1, transuranic waste is radioactive waste containing more than 100 nano curies of alpha emitting transuranic isotopes per gram of waste, with half-lives greater than 20 years. PUREX solvent is relatively low in TRU concentration, therefore, it is not TRU waste.

PUREX solvent consists of chemical material used in the canyons as an extractant to remove selected materials in the process in order to recover products such as plutonium or uranium. The PUREX solvent is removed from the canyon process and stored in LLW tanks after it is recycled several times through a washing step to improve its efficiency. The removal of PUREX solvent from the canyons takes place in a system completely separate from other systems and dedicated to PUREX solvent.

High-level waste is defined as "highly radioactive waste material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing..." In the canyon first and second cycle solvent extraction process, the highly radioactive fission products from dissolved spent nuclear fuel exit the process as a raffinate stream, is neutralized, and transferred to HLW carbon steel storage tanks. This raffinate stream when discarded to the HLW tanks becomes HLW. As stated above, PUREX solvent is not part of the discarded raffinate stream that becomes HLW. The PUREX solvent exits the process facility as LLW in an entirely separate processing system. Therefore, PUREX solvent is not waste produced directly in reprocessing, nor is it highly radioactive. In fact, PUREX solvent is relatively low in radionuclide content.

PUREX solvent does not meet the definition of TRU waste or high-level waste.

Therefore, PUREX solvent is LLW and shall be managed according to LLW DOE orders and applicable regulations.