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LIQUID WASTE TREATMENT SYSTEM
FINAL REPORT

Topical Report

By
M. N. Baker
H. M. Houston

June, 1999

Work Performed Under Contract No. DE-AC24-81NE44139

Prepared by
West Valley Nuclear Services Co.
10282 Rock Springs Road
West Valley, NY 14171-9799

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Prepared for
U.S. Department of Energy
Assistant Secretary for Nuclear Energy

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ABSTRACT

Pretreatment of high-level liquid radioactive waste (HLW) at the West Valley Demonstration Project (WVDP) involved three distinct processing operations: decontamination of liquid HLW in the Supernatant Treatment System (STS); volume reduction of decontaminated liquid in the Liquid Waste Treatment System (LWTS); and encapsulation of resulting concentrates into an approved cement waste form in the Cement Solidification System (CSS). Together, these systems and operations made up the Integrated Radwaste Treatment System (IRTS).

The IRTS was used to pretreat more than two million liters of HLW over seven years of operation, resulting in the production of 19,877 drums of cement-encapsulated waste. Campaigns were run to process three chemically different HLW liquids during this operating period: supernatant, plutonium/uranium extraction process (PUREX) sludge wash liquid, and PUREX/thorium extraction process (THOREX) sludge wash liquid. This report discusses the volume reduction of decontaminated supernatant in the LWTS during IRTS operations and processing events that took place during the final supernatant processing campaign.

EXECUTIVE SUMMARY

Reducing the amount of liquid high-level radioactive waste (HLW) that needed to be vitrified at the West Valley Demonstration Project (WVDP) was critical to ensuring efficient vitrification of the HLW. A series of pretreatment systems, known as the Integrated Radwaste Treatment System (IRTS), was developed for this purpose.

The main IRTS systems were the Supernatant Treatment System (STS), Liquid Waste Treatment System (LWTS), and Cement Solidification System (CSS). During IRTS operations, supernatant and sludge wash liquids were pumped from Tank 8D-2, decontaminated through ion-exchange in the STS, and held in an existing storage tank (8D-3), until transfer to the evaporator feed tank in the LWTS. From the evaporator feed tank, decontaminated liquids were pumped to the LWTS evaporator for volume reduction, with resulting concentrates being transferred to the CSS for encapsulation in an approved cement waste form. Water from the evaporation process was decontaminated through ion-exchange, sampled, and then recycled or released to the environment as appropriate.

Since the completion of HLW pretreatment, the STS has continued to be used for decontaminating water decanted from Tank 8D-2 or 8D-1. The LWTS has continued to be used to volume-reduce this water for recycling or release.

1.0 INTRODUCTION

The Liquid Waste Treatment System (LWTS) is used to volume-reduce decontaminated liquids through evaporation. A brief description of LWTS subsystems and components is given in "Integrated Radwaste Treatment System Lessons Learned from 2½ Years of Operation" [DOE/NE/44139-68].¹

During Integrated Radwaste Treatment System (IRTS) operations, the LWTS was used to reduce decontaminated supernatant and sludge wash liquids to a minimum volume by evaporation. Volume-reduced concentrates were then transferred to the Cement Solidification System (CSS) for encapsulation in cement. Volume reduction of decontaminated supernatant began with the start of IRTS operations in May 1988, and continued until January 1991. The system was then used to volume reduce sludge wash liquids from April 1992 until May 1995.

The LWTS continues to perform its design function by concentrating water decanted from either Tank 8D-2 or 8D-1. Decontaminated water is sampled and then released to the environment. Concentrated liquids are returned to Tank 8D-2 for processing in the Vitrification Facility. This report focuses on the operation of the LWTS during supernatant processing, and describes events that occurred during the final supernatant campaign.

2.0 LIQUID WASTE TREATMENT SYSTEM OPERATION

The LWTS reduces the volume of decontaminated liquids through evaporation. When supernatant processing operations were taking place, decontaminated liquids that had been processed through ion-exchange columns in the Supernatant Treatment System (STS) were held in an existing storage tank (8D-3) until this tank was nearly full. Decontaminated waste liquids were pumped to the evaporator feed tank (5D-15B), then into the evaporator for volume reduction.

The LWTS evaporator is made up of two parts: a "flooded" design reboiler that has an integral steam bundle, and a vapor body with a condenser mounted at the top. Steam enters at the top of the steam bundle. Cold liquid from the vapor body enters near the bottom, and flows through the tubes of the steam bundle, setting up a thermosyphon effect. Vapor separates from liquid in the vapor body, which holds about 800 gallons of boiling liquid. Saturated vapor flows upward, past three sets of bubble trays, and through a mist eliminator, which removes entrained liquid from the saturated vapor. In the falling film-type condenser, cooling water in the outside of the tubes condenses the vapor into liquid. This liquid then flows, as a thin film, down the inside of the tubes.

Resulting concentrates can be transferred for further waste processing, or recycled back to Tank 8D-2. The resulting water, cooled in the evaporator condenser, is routed through a zeolite ion-exchange column, sampled and released to the environment.

Figure 2.2.
Liquid Waste Treatment Evaporator

Figure 2.3.
Liquid Waste Treatment System Reboiler and Condenser

The LWTS was designed to achieve a maximum evaporator feed rate of 12 gallons per minute (gpm). It was scheduled to process 10 gpm during IRTS operations to allow for sampling, valve manipulations, and steam variables. This a permitted transfer of 10,000-gallon batches of decontaminated liquid a day, at a transfer rate of 25 gpm. Transfers took from six to eight hours, allowing sufficient time to evaporate a batch before the next transfer.

Concentrates, at up to 41 wt. % total dissolved solid (TDS), were formed by evaporating decontaminated supernatant and sludge wash liquids. These concentrates were withdrawn by the concentrates storage pump, and cooled in the concentrates cooler, a single-pass, shell-and-tube heat exchanger. After cooling, concentrates were sent to one of two concentrates storage tanks (5D-15A1 or 5D-15A2), and then fed downstream to the CSS for encapsulation in cement.

2.1 Supernatant Volume Reduction

During supernatant processing campaigns, raw supernatant liquid was fed from Tank 8D-2 to the STS as samples were being taken for process control and analysis. After removing cesium (Cs-137) and strontium (Sr-90) from the supernatant by processing it through the ion-exchange columns mounted in Tank 8D-1, decontaminated supernatant was collected in 8D-3. Samples were taken from 8D-3 to ensure that dose rates remained below shielding design limits for downstream systems and equipment. Batches of approximately 40,000 liters of decontaminated liquid were then pumped to the LWTS evaporator feed tank (5D-15B) and sampled. These samples provided the first process control samples for the LWTS and CSS, and ensured that CSS dose rates remained well within design limits.

Concentrates held in the concentrate storage tanks (5D-15A1 and 5D-15A2) were sampled for process control of the cement recipe. Using these samples, a full radionuclide analysis was done for waste classification of cement drums. These samples were used for trending analysis of process data. The site's Analytical and Process Chemistry (A&PC) Laboratory performed these analyses. Once sampled, no new concentrates were added to the storage tanks.

2.2 Evaporation and Material Accumulation

Timing of IRTS operations was such that when a batch of decontaminated liquid was boiled down, a new batch of dilute, decontaminated liquid was available for evaporation. The volume reduction process was repeated throughout the course of one week. The following week, concentrates were solidified in the CSS.

Determining concentrations of uranium (U) and plutonium (Pu) in Tank 8D-2 was part of the routine review done to monitor long-term tank chemistry throughout supernatant processing. During the last supernatant processing campaign (Campaign 21), a review showed a slow increase in U and Pu concentration over the last two years of IRTS operation. Matching increases in U and Pu concentration took place in the evaporator feed tank during the same time period.

A review of U and Pu concentrations in the LWTS and the concentrates storage tanks (5D-15A1 and 5D-15A2) revealed an anomaly: feed concentrations for fissile isotopes U and Pu did not agree with product concentrations after boildown. For example, if the Pu concentration for 5D-15B was $8 \text{ E } 3 \text{ } \mu\text{Ci/mL}$ at 10 wt.% solids, the concentrated product at 40 wt.% solids should have been $32 \text{ E } 3 \text{ } \mu\text{Ci/mL}$ (4:1 increase). Results did not show this expected concentration. In part, this error was related to the fact that feed liquid was being fed to the evaporator as the feed tank sample was being analyzed.

Although the actual quantity of the increase in alpha activity was quite small, taken together and multiplied by thousands of gallons, the increase amounted to several kilograms of U and Pu. After calculating the increase in alpha activity across the LWTS evaporator, it was necessary to determine, if possible, exactly where material was accumulating. The potential existed for material to form "bathtub rings" in one of the tanks, or to accumulate in the LWTS evaporator. It also was possible for material to accumulate in low-velocity areas in pump piping, or in the pumps themselves.

Normally, samples were drawn from a limited number of locations because few areas were easily accessible. Sampling work was complicated by the fact that the LWTS is an all-welded system. Several approaches were considered, including cutting a hole in the evaporator, then welding a patch over it, and welding on a clean-out hatch. Bringing in a suitably trained welder was considered because American Society of Mechanical Engineers (ASME) Boiler Code stamped vessels require a qualified weld method and welder. Other methods were also considered concurrently.

The pumps were selected as sample locations because they had flanges and could be opened for sampling. Several work orders were prepared to obtain samples from these locations. A material balance calculated across the LWTS evaporator (i.e., activity $\times$ gallons, minus 5D-15A1/A2 alpha activity $\times$ gallons) confirmed a small increase in alpha activity across the evaporator. Further investigation also showed that alpha activity in Tank 8D-2 supernatant had been slowly increasing.

3.0 FISSILE MATERIAL ACCUMULATION ASSESSMENT

Accumulation of fissile material is a primary concern at any radiological waste treatment facility. Although material and solution concentrations were significantly below safety requirements, the IRTS was placed in standby, and a peer review group was formed to evaluate the situation. This group focused on multiple aspects of material accumulation including:

- Reasonableness of fissile material accumulation estimates;
- Mechanisms for accumulation;
- Disposition of the LWTS evaporator for IRTS restart; and
- Existence of an Unreviewed Safety Question Determination (USQD), according to the definition given in DOE Order 5480.1B.

The peer review group included scientists from several areas of nuclear expertise, including a Pu Chemist from Westinghouse Savannah River, Co., and two criticality experts from the DOE's Oak Ridge Facility. They used various methods to determine the concentration, geometry (shape), and mass of material accumulated in the LWTS evaporator. Chemically, Pu and U are drawn to titanium. The stainless steel sections of the reboiler heat transfer surfaces were either titanium, or titanium clad. It was important to determine how these materials collected, and whether they had collected in a sphere in the evaporator reboiler or as a thin film on the reboiler's surfaces. Using available data, the peer review group was able to quantify the amount of Pu and U, in grams, that had accumulated in the evaporator and reboiler.

3.1 Plutonium Estimate and Uncertainty

Daily samples of Tank 8D-2 liquids were taken from the STS feed tank (D-001) during each processing week throughout IRTS operations. A conversion ratio for curies of alpha-emitting plutonium to grams of plutonium was computed based on the high-level waste (HLW) characterization done for Tank 8D-2, allowing for decay.² It was 3.68 grams of total Pu per curie of alpha-emitting Pu. The equations used to compute the grams of Pu that accumulated in the evaporator were:

$$\alpha \text{ Pu}_i [\mu\text{Ci/mL}] = \frac{(\text{Measure } \alpha \text{ Pu}_i) \times (\text{calculated wt.\% out}) \times (\text{density out})}{(\text{calculated wt.\% inlet}) \times (\text{density inlet})}$$

$$\text{Calculated wt.\% out} = [\text{density out} - 1] / 0.00475]^{-0.8726}$$

$$\text{Calculated wt.\% inlet} = [(\text{density inlet} - 1) / 0.00475]^{-0.8726}$$

$$\text{Delta} = \alpha \text{ Pu}_i [\mu\text{Ci/mL}] - \text{Measure } \alpha \text{ Pu}_o [\mu\text{Ci/mL}]$$

$$\alpha \text{ Pu} [\text{Ci}] = 3.68 \times \text{Delta} \times \text{Volume of Concentrates}$$

Two major types of measurement errors were considered: error in density and error in alpha Pu activity concentrations. These measuring uncertainties were judged to dominate the total uncertainty. The generic governing equation of uncertainty is created by partial derivatives of the Pu calculation. The fully developed equation is quite extensive and, therefore, not presented here.

Figure 3.1. LWTS Cylindrical Deposition Model

Figure 3.2. LWTS Hemispherical Deposition Model

Multiplication rates were calculated for homogeneous fuel concentrations in two geometries: cylinders and hemispheres. Hemispherical source geometries (not considered to be realistic), were evaluated to determine the most reactive radius. This would have been a hemisphere center located on the axis, at the base of a cylinder used to model the reboiler.

Likewise, cylindrical source geometries were evaluated to determine the most reactive cylinder height. This would have occurred while holding the cylinder diameter at 4' 0", the diameter of the reboiler tank.

Using the most conservative estimates for fuel source mass and source geometry, results showed that the evaporator was subcritical.

3.2 Criticality Evaluation

After the best estimates of U and Pu had been determined, and agreed with by the United States Department of Energy (DOE) Ohio Field Office West Valley Demonstration Project (OH/WVDP) Technical Review Group (TRG), calculations were done to evaluate criticality risks in the evaporator

The Safety Analysis Report (SAR) prepared for the LWTS included a table that gave fissile concentration limits for both U and Pu. However, these limits assumed that all U and Pu would be held in solution. No limits had been established for fissile materials that might precipitate, or settle at the bottom of vessels holding solution (i.e., tanks). Therefore, to be conservative, the criticality analysts assumed that all of the U and Pu was in the heel of the evaporator reboiler, most likely settled in a cylindrically shaped mass.

Multiplication rates were calculated for homogeneous fuel concentrations in two geometries: cylinders and hemispheres. Hemispherical source geometries (not considered to be realistic), were evaluated to determine the most reactive radius. This would have been a hemisphere center located on the axis, at the base of a cylinder used to model the reboiler.

3.3 Plutonium Solubility

Approximately 600,000 gallons of liquid HLW were scheduled for pretreatment when IRTS operations began. The first phase of pretreatment involved decontaminating 8D-2 supernatant. One part of supernatant was diluted with two parts of water before transferring it to the STS to be decontaminated. About 40 gallons per minute (gpm) of supernatant were removed from Tank 8D-2, with two gpm of this volume being transferred on for further processing. About 38 gpm were recycled back to 8D-2. Initially, the supernatant had 39 wt.% total dissolved solids (TDS). Dilution reduced this weight percentage to 24 wt.% TDS by the time the last campaign had started. To achieve successful cement processing, decontaminated supernatant was evaporated back to 37 to 41 wt.% TDS before being encapsulated in cement in the CSS.

Initially, the supernatant had a concentration of about 5% sodium hydroxide (NaOH). Some NaOH was added to the waste processing solutions before being recycled back to 8D-2 to maintain tank integrity. As IRTS operations progressed, returning various waste solutions to 8D-2 lowered the tank pH to about 10. In addition, operating the floating suction arm of the supernatant removal pump disturbed the sludge layer, especially as the level in the tank was lowered. Research shows that the solubility of Pu in caustic solutions is a function of pH, with the lowest solubility at 12 to 13 pH. Solubility is also related to reduced oxidation (REDOX) potential. Consequently, disturbing the sludge layer in a lower pH environment increased the solubility of Pu in the supernatant by a factor of four. Later sampling confirmed that the concentration of Pu in 8D-2 had increased by a factor of two.

3.4 Unresolved Safety Question Evaluation

Any proposed change or modification to an operating system may affect the safety limits (i.e., safety envelope), approved for that system. According to DOE Orders 5480.1B and 5480.5, a number of factors must be considered when evaluating the significance of a proposed physical or administrative change to an operating system, and its potential for causing an unresolved safety question.

First, it is necessary to determine if the proposed change will increase the risk from a hazard beyond that previously analyzed and reviewed. Increased risk could result from a variety of changes, including: operating characteristics (i.e., speed, temperature, or pressure); increases in the quantity of hazardous materials; changes in design features; or administrative changes.

Re-analysis of the bounding accident scenarios established in the Safety Analysis Reports for the STS and LWTS (WVNS-SAR-004 and WVNS-SAR-005), showed that accumulation of U and Pu in the evaporator were within approved safety limits given in these documents. On this basis, all other accident scenarios that had been analyzed also remained within the approved safety envelope. Therefore, the increase in fissile material did not constitute an increase in risk from hazards beyond those previously analyzed.

After it was clearly established that the accumulation of U and Pu did not increase risk from hazards beyond those previously analyzed, it was necessary to determine if there had been any reduction in reliability of hardware, components, or equipment important to safety for which credit had been taken for the reduction or control of criticality. Since neither the STS nor LWTS had such items, no unresolved safety question existed on this basis.

The third factor considered involves introduction of a new hazard. Analyses of hazards documented in WVNS-SAR-004 and WVNS-SAR-005 were based on processing supernatant with U and Pu. An increase in the concentration of U and Pu in the STS feed and accumulation in the LWTS evaporator did not constitute the introduction of a new hazard.

The fourth factor considered concerns application of new regulations. Application of new regulations had not been promulgated that were pertinent to the operation of the STS or LWTS. Thus, accumulation of U and Pu did not constitute an unresolved safety question on this basis.

The fifth and final factor considered involves receipt of new information that indicates an increased hazard associated with an existing operation. Process streams in the STS and LWTS were routinely sampled and analyzed in accordance with approved run plans. Trending analysis done on these samples established that an increase in fissile material concentration in the STS feed and LWTS evaporator had occurred. Although this did constitute receipt of new information, it did not result in the identification of an increased hazard associated with operation of either system. Both systems were designed to operate within shielded containment equipped with ventilation systems. These ventilation systems were capable of mitigating hazards associated with processing liquid radioactive waste that contained fissile material. An increase in the concentration of fissile material in the waste stream, therefore, did not constitute an increase in hazards associated with processing it.

Based on evaluation of these criteria, the review group established to assess accumulation of U and Pu in the LWTS evaporator concluded that the occurrence of an event was not possible, that the probability of criticality was zero, and that an unresolved safety question did not exist.

4.0 RECOVERY OPERATIONS

4.1 Extraction Cell Entry

Most of the LWTS processing equipment is installed in an area referred to as Extraction Cell #3 (XC-3). This equipment includes the evaporator, reboiler, condenser, distillate surge tank, concentrates cooler, distillate (ion-exchange) polishing column, and spent resin tank cooler. In addition, a substantial quantity of process piping is located in XC-3. The cell itself measures approximately 15' x 21' x 57' high. Access to the cell is through a shield door located at the lowest level of the cell.

Once radioactive operations began, cell entry was complicated by the possibility of airborne contamination from leaks. Large quantities of concentrated radioactive liquids, with undetermined dose rates, made cell entry difficult. No plans existed for routine cell entry. Scaffolding had been installed during LWTS construction and testing, but did not provide access to all components.

To minimize risk to the greatest extent practical, all equipment in the evaporator subsystem was thoroughly flushed and drained to reduce the inventory of radioactive liquids in the equipment. In addition, the steam supply to the evaporator reboiler was shut off, and the system allowed to cool.

A controlled ventilation tent, permanently installed in the Cell Access Aisle at the entrance to the cell, was used as the entry point. With proper preparation and suit-up, the door to XC-3 was carefully unsealed. Experience gained with IRTS repairs allowed cell entry to proceed with confidence.

A gamma radiation detector was used to determine dose rates as inspectors from Radiation and Safety, and Engineering groups entered the cell. Survey of the evaporator and its peripheral equipment showed dose rates of 1R/hr, with a 2 R/hr hot spot on the bottom of the reboiler. Dose rates on the sides of the reboiler ranged from 200 mR/hr near the bottom, to 450mR/hr at the top. The evaporator vapor body/separator showed dose rates from 200 mR/hr on the bottom to 100 mR/hr on the side.

4.2 Material Removal

After entry into XC-3 was made to evaluate conditions in the evaporator, a group of on-site and off-site experts met to determine a method that could be used to chemically clean the evaporator with no "hands on" work required within the evaporator itself.

The group recommended that a nitric acid wash solution be used to chemically clean the evaporator, followed by flushing with demineralized water. A Pu chemist from Westinghouse Savannah River Company (H. P. Holcomb), recommended using a nitric acid wash solution with 1 Molar concentration. A titanium corrosion expert from Corrosion Testing Laboratories (R. A. Corbett), examined the physical structure of the evaporator.

Together, the group reviewed the risks associated with acid washing, including processing risks, and waste form questions. Waste form questions were evaluated because LWTS concentrates were produced from alkaline, not acidic, liquids, and therefore could adversely affect the final cement waste form. The final recommendation included careful consideration of:

- How much acid to use, and at what concentration;
- When the acid should be neutralized;
- How flushes should be done;
- How many washes and flushes were needed; and
- How adequate removal should be confirmed.

The chemical compatibility of all existing LWTS components also was evaluated, including pumps, hoses, valves, fittings, and equipment purchased for acid washing.

Using a nitric acid wash solution with no more than 2 Molar concentration was recommended to maintain the integrity of the evaporator's physical structure. Following this recommendation, the evaporator was cleaned with three nitric acid washes with up to 2 Molar concentration, and six rinses using demineralized water. Although fissile isotopes were at a safe concentration, and U was diluted 50 to one with nonfissile isotopes of U, boron was added to the cleaning solution as a neutron poison to increase the safety margin against criticality.

Washing, sampling, and rinsing were relatively straightforward operations. A chemical handling area was set up in the Lower Extraction Aisle (LXA). Concentrated nitric acid was added to the demineralized water in evaporator feed tank (5D-15B), then to the evaporator. Running in "reflux" mode, the solution was boiled, with the condensate dropping back into the vessel to provide continuous cleaning. Samples were taken continuously. Several rinses and flushes were performed to ensure that as much Pu and U had been removed as possible. Some samples were sent to an off-site laboratory to confirm the A&PC Lab results.

Samples were taken after each wash to determine its effectiveness. Examination of results from the first wash suggested that a second wash was needed. Results from the second wash again suggested that a third wash was needed. All wash solutions and rinses were returned to Tank 8D-2 for eventual vitrification. The amounts of Pu and U removed from the LWTS evaporator and tanks are shown in Table 4.1.

Table 4.1 - Pu and U Removal

	Plutonium		Uranium	
	<i>Total Pu</i>	<i>Fissile Pu</i>	<i>Total U</i>	<i>Fissile U</i>
<i>Estimated Total Present</i>	359± 100	291.1	26,000	455
<i>Total Removed</i>	310.5	251.8	12,120	211.8
<i>Estimated Remaining</i>	39.3		234	
<i>Limiting Condition for Restart</i>	450		1,886	

It should be noted that the remaining inventory of fissile Pu (Pu-239 and Pu-241) contained in the evaporator deposits was estimated to be 39.3 grams. This was less than 10% of the 450 grams of fissile Pu specified as the Limiting Condition for Operation (LCO) for restarting IRTS operations. In addition, the remaining inventory of fissile U (U-233 and U-235) contained in evaporator deposits was estimated to be 243 grams. This is less than 13% of the limit of 1,886 grams of fissile U specified as a LCO for restarting IRTS operations.

4.3 Gasket Replacement

Steady increases in XC-3 sump levels were observed shortly after acid washing the evaporator. Personnel entry into the cell revealed a slow leak at the evaporator's vapor body/condenser joint. It is important to note that the gasket at the top of the evaporator reboiler had been replaced during LWTS construction. Replacement of the reboiler gasket was quite easy. The reboiler steam bundle was raised by using a gantry crane in the Extraction Chemical Room (XCR) above the cell. This crane was in place for cell decommissioning and subsequent construction work. After hot operations began, it was no longer available for use in XC-3.

Three separate entries were made into XC-3 to inspect the area. General inspection was done during the first entry to determine overall conditions. A second entry was made to assess radiation protection requirements. An industrial safety engineer also participated in this entry to evaluate the status and condition of scaffolding in the cell. Safety inspection showed that scaffolding left in the cell from construction was missing some vertical supports. Scaffold planks wired to supports with carbon steel wire had rusted, and needed to be replaced before repairs began. Hand rails and toe boards could not be added because the area was so congested. Safety harnesses and lanyards were, therefore, required for actual repair work. Temporary lighting also was needed.

The final entry was made by the cognizant engineer and maintenance foreman. They took a series of measurements to determine the cause of the leak, and evaluated the contributing factors. A number of observations were made during this entry.

The gasket itself had pushed out about one sixth of the way around the circumference of the condenser flange, and there was crusting near the gasket. Measurements were taken to determine how much the flanges had separated. Although spacing between the flanges was uniform, flange thickness varied. Overall thickness of both flanges varied by three sixteenths of an inch. Nuts on the six studs holding the separator and condenser flanges together were loose, and could be turned by hand. Threads on the studs still had a lubricant coating on them, later identified as molybdenum disulfide. The nuts turned freely on the studs. Tightness of the nuts holding the reboiler flange in place also were checked. It was estimated that it took 50 to 60 ft. lbs. of torque to loosen the two nuts that were checked. Drawings indicated that the nuts should have been torqued to 500 ft. lbs. Retorquing these bolts was necessary after gasket repairs were completed.

The loose flange bolts, gasket "blow-out", and crusted material near the gasket suggested several interesting processing events. The loose flange bolts indicated that the flanges had been working during operation (i.e., supporting loading and unloading, including thermal-induced loading). However, gasket "blow-out" suggested that the condenser had been operating under positive pressure instead of negative pressure during operation. There were a number of potential causes.

Carry over of solids from the liquid pool could have created positive pressure. Excessive steam rates or high liquid levels were potential contributing factors. A plugged demister pad also could have created pressurization. Although the demister pad was washed routinely with demineralized water, the pad could have become clogged by using excessive steam rates. Crusted material near the gasket suggested carry over of material past the bubble trays. Poor disengagement in the bubble cap tray (i.e., failure to "knock" out liquid particles) may have caused pressurization.

Carry over of solids, and therefore radioactivity, into the demister pad would have been evidenced by increased radioactivity in the condensate. Under proper operation, no credit for a decontamination factor across the demister pad was taken because the saturated vapor passing through the demister should have been free of solids, and therefore radioactivity. Samples taken during evaporator restart showed normal activity in the condensate, with no evidence of carry over.

Temporary instrumentation was added to this area of the separator/condenser as a corrective action. With up to two inches of accumulated water each, the three bubble trays should have indicated a pressure drop of approximately six inches during normal operation. Pressure readings taken every four hours after the evaporator was returned to service showed pressure drops from 4 to 6.5 inches of water pressure differential.

After gasket replacement and repairs were completed, and the evaporator was returned to service, visual examination of the gasket showed no further leakage.

4.4 Resumption of IRTS Operations

The IRTS resumed operations with two new technical requirements (TRs) in place. The first technical requirement, TR-IRTS-10, required sampling of the STS feed immediately upstream and downstream of each ion-exchange column. This requirement was put into place to track the deposition of U and Pu on the titanium-coated zeolite (TIE-96™). The second technical requirement, TR-IRTS-11, required sampling of each batch of decontaminated liquid in the evaporator feed tank (5D-15B), and the corresponding batch in the concentrate tanks (5D-15A1 and 5D-15A2) to track the accumulation of U and Pu in the evaporator. Mass inventories were limited to 450 grams of fissile Pu and 1,500 grams of fissile U. A record of all batches and sample results, translated to accumulation, is maintained for the duration of vitrification operations. Calculations also were performed to evaluate concentration and geometry to ensure that criticality would not occur in ion-exchange columns.

5.0 RECIPE DEVELOPMENT

5.1 Processing Changes

The basic sludge wash process involved adding a liquid solution, specifically demineralized water and sodium hydroxide, to Tank 8D-2, and then blending the tank's contents by mixing the sludge layer with liquid additions. During supernatant processing, small batches of process liquids, including supernatant and flush water, were recycled to 8D-2. These liquids contained sodium hydroxide that had been added to Tanks 8D-2 and 8D-1 for corrosion control. Returning process liquids to 8D-2 was chemically similar to the sludge wash process. Liquid recycling had, in effect, started the sludge wash process.

5.2 Sludge Wash Chemistry

Preparations for the sludge washing phase of high-level waste (HLW) pretreatment had started before the LWTS was placed in standby. Testing done at Battelle Pacific Northwest National Lab (PNNL) showed that titanium-coated zeolite (TIE-96™) was effective in extracting traces of Pu, Sr-90, and Cs-137 from samples of sludge wash liquid taken from Tank 8D-2. Interruption of supernatant processing during evaporator cleaning and recovery offered the opportunity to begin sludge wash cement recipe development. It was made a priority, starting with a complete laboratory test program.

The test program got underway using a four-column, laboratory-scale simulation of the STS, including water-cooled column that duplicated the in-line STS chiller. A glass test column was set up in the A&PC Hot Cells for testing, using actual sludge wash liquid drawn from 8D-2.

Tests were done at three different pH levels, with three different dilutions, and three different temperatures to simulate the full range of anticipated operations conditions. A small quantity of TIE-96™ (i.e., titanium-coated zeolite) was ordered from the manufacturer to use for testing before full-scale production began. Later, tests were duplicated using a test set-up with one column of TIE-96™ and three columns of IE-96™ (i.e., uncoated zeolite). Decontaminations factors (DFs) were satisfactory for Cs-137, Pu, and Sr-90.

5.3 Sludge Wash Operations

Sludge wash operations began with mixing settled PUREX sludge with the supernatant liquid in 8D-2. The purpose of sludge washing was to displace interstitial salts and dissolve sodium sulfate salts in the sludge. Sodium hydroxide (NaOH), in the form of a 20% solution, was added to 8D-2 to raise the pH from 10 to more than 12.5 to suppress the solubility of Pu during actual washing. To support sludge wash operations, the STS was configured to use one ion-exchange column containing titanium-coated zeolite (TIE-96™) to retain Pu as well as Cs-137.

6.0 CONCLUSION

After all actions and issues related to the accumulation of fissile material that took place during the final supernatant processing campaign were resolved, IRTS operations resumed and the first PUREX sludge wash campaign was started. This campaign was part of a series of nine processing campaigns that involved processing three sludge washes. Except for minor corrections in evaporator setpoints for density that were needed for automatic operations, and upstream dilution adjustments, these campaigns were completed without incident. A single THOREX wash campaign was performed after these campaigns were completed. The THOREX wash campaign and processing results are described in DOE/NE/44139-82.³

Careful, pro-active attention to changing upstream conditions and the downstream cement waste form resulted in satisfactory LWTS performance throughout IRTS operations. Experience gained during IRTS operations continues to be applied as the LWTS concentrates water decanted from Tank 8D-2 or 8D-1. Concentrated liquids resulting from volume reduction in the LWTS evaporator are returned to 8D-2 or 8D-1 for processing in the Vitrification Facility, while water resulting from volume reduction is decontaminated through ion-exchange, sampled, and either recycled or released to the environment. Successful operation of the LWTS remains essential to HLW treatment at the WVDP.

REFERENCES

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2. L. E. Rykken, "High-Level Waste Characterization at West Valley, Report of Work Performed 1982–1985" [DOE/NE/44139-14], June 1986.
3. S. Kelly Jr., D. C. Meess, "THOREX Processing and Zeolite Transfer for High-Level Waste Stream Processing Blending," [DOE/NE/44139-82], 1997.

ACRONYMS

A & PC	Analytical and Process Chemistry
ASME	American Society of Mechanical Engineers
CSS	Cement Solidification System
DF	Decontamination Factor
DOE	United States Department of Energy
HLW	High-level Waste
IE-96™	Uncoated Zeolite
IRTS	Integrated Radwaste Treatment System
LCO	Limiting Condition for Operation
LLW	Low-level Waste
LWTS	Liquid Waste Treatment System
LXA	Lower Extraction Aisle
NaOH	Sodium Hydroxide
OH/WVPO	Ohio Field Office West Valley Demonstration Project
PNNL	Battelle Pacific Northwest National Lab
Pu	Plutonium
PUREX	Plutonium/Uranium Extraction
REDOX	Reduced oxidation
SAR	Safety Analysis Report
STS	Supernatant Treatment System
TIE-96™	Titanium-coated zeolite
TDS	Total Dissolved Solids
THOREX	Thorium Extraction
TR	Technical Requirement

ACRONYMS (cont.)

TRG	Technical Review Group
U	Uranium
USQD	Unresolved Safety Question Determination
XC-3	Extraction Cell #3
XCR	Extraction Chemical Room
WVDP	West Valley Demonstration Project

DOE/NE/44139-88

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