

200
11/3/97 JS①

DOE/NE/44139-82

**THOREX PROCESSING AND ZEOLITE TRANSFER FOR
HIGH-LEVEL WASTE STREAM PROCESSING BLENDING**

Topical Report

By
S. Kelly, Jr.
D. C. Meess

July, 1997

MASTER

Work Performed Under Contract No. DE-AC24-81 NE 44139

Prepared by
West Valley Nuclear Services Company, Inc.
P.O. Box 191
West Valley, New York 14171-0191

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

**THOREX PROCESSING AND ZEOLITE TRANSFER FOR
HIGH-LEVEL WASTE STREAM PROCESSING BLENDING**

Topical Report

By
S. Kelly, Jr.
D. C. Meess

July, 1997

Work Performed Under Contract No. DE-AC24-81 NE 44139

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

MASTER

Prepared by
West Valley Nuclear Services Company, Inc.
P.O. Box 191
West Valley, New York 14171-0191

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ng

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

TABLE OF CONTENTS

| <u>Section</u> | <u>Page</u> |
|--|-------------|
| LIST OF FIGURES | iv |
| LIST OF TABLES | v |
| ABSTRACT | vii |
| 1.0 INTRODUCTION | 1 |
| 2.0 SUPERNATANT PROCESSING | 4 |
| 3.0 SLUDGE WASHING | 6 |
| 3.1 Sludge Wash No. 1 and Processing | 6 |
| 3.2 Sludge Wash No. 2 and Processing | 8 |
| 3.3 THOREX Transfer and Neutralization | 8 |
| 3.4 THOREX/PUREX Wash Processing | 8 |
| 3.5 Zeolite Mobilization and Transfer | 9 |
| 4.0 SUMMARY AND CONCLUSIONS | 14 |
| 5.0 REFERENCES | 17 |
| LIST OF ACRONYMS | 18 |

LIST OF FIGURES

| <u>Figure</u> | | <u>Page</u> |
|---------------|--|-------------|
| 1 | Integrated Radwaste Treatment System | 5 |
| 2 | Simplified Supernatant Treatment System Flow Diagram | 7 |
| 3 | Planar View of Tank Structure | 10 |
| 4 | Percent Zeolite Removed Versus Transfer Number | 12 |
| 5 | Cumulative % of Zeolite Removed | 13 |

LIST OF TABLES

| <u>Table</u> | | <u>Page</u> |
|--------------|--|-------------|
| 1 | Chemical Composition of PUREX Supernatant | 1 |
| 2 | Major Radionuclide Composition of PUREX Supernatant (as of 7/1/86) | 2 |
| 3 | Chemical Composition of THOREX Liquid | 2 |
| 4 | Major Radionuclide Composition of THOREX Liquid (as of 7/87) | 3 |
| 5 | Zeolite Transfer Summary | |
| | Amounts of Initial Zeolite Transferred | 11 |
| 6 | Integrated Radwaste Treatment System | |
| | Processing Totals | 15 |
| 7 | Projected Composition of Blended HLW Supernatant | 15 |

ABSTRACT

The West Valley Demonstration Project (WVDP) completed the pretreatment of the high-level radioactive waste (HLW) prior to the start of waste vitrification. The HLW originated from the two million liters of plutonium/uranium extraction (PUREX) and thorium extraction (THOREX) wastes remaining from Nuclear Fuel Services' (NFS) commercial nuclear fuel reprocessing operations at the Western New York Nuclear Service Center (WNYNSC) from 1966 to 1972. The pretreatment process and subsequent vitrification of the HLW were authorized by Congress in 1980 by passage of the WVDP Act. This gave the U.S. Department of Energy (DOE) the responsibility to conduct a HLW management project at the WNYNSC to among other things, demonstrate the ability to stabilize the HLW stored on the site from prior reprocessing operations and propose viable decontamination and decommissioning techniques.

HLW pretreatment operations, utilizing the existing facilities to the maximum extent practical, were conducted to separate the radioactive portion of the waste from the salts found in the waste in order to minimize the quantity of vitrified waste that will have to be produced. The pretreatment process removed cesium as well as other radionuclides from the liquid wastes and captured these radioactive materials onto silica-based molecular sieves (zeolites). The decontaminated salt solutions were volume-reduced and then mixed with portland cement and other admixtures. Nineteen thousand eight hundred and seventy-seven 270-liter square drums were filled with the cement-wastes produced from the pretreatment process. These drums are being stored in a shielded facility on the site until their final disposition is determined.

Over 6.4 million liters of liquid HLW were processed through the pretreatment system. PUREX supernatant was processed first, followed by two PUREX sludge wash solutions. A third wash of PUREX/THOREX sludge was then processed after the neutralized THOREX waste was mixed with the PUREX waste. Approximately 6.6 million curies of radioactive cesium-137 (Cs-137) in the HLW liquid were removed and retained on 65,300 kg of zeolites. With pretreatment complete, the zeolite material has been mobilized, size-reduced (ground), and blended with the PUREX and THOREX sludges in a single feed tank that will supply the HLW slurry to the Vitrification Facility.

1.0 INTRODUCTION

The PUREX waste was generated from reprocessing 640 metric tons of uranium oxide fuel to recover both uranium and plutonium. Sodium hydroxide was added to neutralize this acidic waste for safe storage in a 2.8 million liter, vaulted, underground carbon steel, single-shell storage tank, designated Tank 8D-2. Neutralization and concentration of the tank's contents caused insoluble hydroxides and other salts, notably sodium sulfate (Na_2SO_4), to precipitate out of the liquid supernatant and form sludge layers in the bottom of Tank 8D-2. Both hard and soft sludge layers were found to exist through sampling programs.¹ Prior to the initiation of the HLW pretreatment, approximately 100,000 kg of sludge (Sp. Gr. = 3.3) and two million liters of supernatant (Sp. Gr. = 1.32) were contained in Tank 8D-2. The major chemical and radionuclide constituents are listed in tables 1 and 2, respectively.

Table 1. Chemical Composition of PUREX Supernatant

| Constituent | % Solids (Wet Basis) |
|--------------------------|----------------------|
| NaNO_3 | 21.10 |
| NaNO_2 | 10.90 |
| Na_2SO_4 | 2.67 |
| NaHCO_3 | 1.49 |
| KNO_3 | 1.27 |
| Na_2CO_3 | 0.88 |
| NaOH | 0.61 |
| Others | 0.61 |
| Total | 39.53 |

Table 2. Major Radionuclide Composition of PUREX Supernatant (as of 7-1-86)

| Radionuclide | Activity (Ci) |
|--------------|---------------|
| Cs-137 | 7.43E+06 |
| Ba-137m | 6.98E+06 |
| Cs-134 | 1.94E+04 |
| Sr-90 | 2.96E+03 |
| Y-90 | 1.60E+03 |
| Tc-99 | 1.60E+03 |
| Pu-241 | 1.58E+03 |

THOREX waste liquid was produced by reprocessing one core of mixed uranium-thorium fuel from the Indian Point No. 1 Nuclear Plant. This acidic HLW was stored in a 50,000 liter, vaulted, underground, stainless steel, single-shell storage tank, identified as Tank 8D-4. Approximately 31,000 liters (Sp. Gr. = 1.84) of this waste, having the chemical composition shown in table 3 and the major radionuclide content presented in table 4, were present at the beginning of HLW pretreatment.

Table 3. Chemical Composition of THOREX Liquid

| Constituent | Weight Percent (Wet Basis) |
|-----------------------------------|----------------------------|
| Th(NO ₃) ₄ | 34.3 |
| Fe(NO ₃) ₃ | 9.1 |
| Al(NO ₃) ₃ | 5.6 |
| Cr(NO ₃) ₃ | 2.1 |
| NaNO ₃ | 1.9 |
| Ni(NO ₃) ₂ | 0.85 |
| H ₃ BO ₃ | 0.77 |
| Ca(NO ₃) ₂ | 0.57 |
| KNO ₃ | 0.51 |
| Other | 1.6 |
| Total | 57.3 |

Table 4. Major Radionuclide Composition of THOREX Liquid (as of 7/87)

| Radionuclide | Activity (Ci) |
|--------------|---------------|
| Cs-137 | 4.90E+05* |
| Ba-137m | 4.63E+05* |
| Sr-90 | 4.08E+05* |
| Y-90 | 4.08E+05* |
| Pm-147 | 9.11E+03 |
| Sm-151 | 4.78E+03 |
| Eu-154 | 3.40E+03* |
| Ni-63 | 2.51E+03* |
| Co-60 | 1.61E+03* |
| Pu-238 | 1.04E+03* |
| Pu-241 | 8.50E+02 |
| Eu-155 | 8.44E+02 |
| Fe-55 | 5.63E+02 |
| Cs-134 | 3.10E+02 |
| Sb-125 | 2.89E+02 |
| Am-241 | 2.41E+02 |
| Tc-99 | 1.47E+02* |

* 1993 WVNS analyses; all others from Ref. 1.

2.0 SUPERNATANT PROCESSING

The Integrated Radwaste Treatment System (IRTS) was operated from May, 1988 until November, 1990 processing 2.34 million liters of PUREX supernatant having cesium-137 concentrations ranging from 1,100 to 2,800 $\mu\text{Ci/ml}$. Approximately 5.20 million curies of cesium-137 were removed from this liquid at a decontamination effectiveness of greater than 99% and adsorbed on 42,500 kg of UOP IONSIV^R IE-96 zeolite, which was stored under liquid in Tank 8D-1. The decontaminated supernatant, concentrated to a nominal 40% Total Dissolved Solids (TDS), was solidified using a cement-based recipe into 10,393 270-liter square drums. The total cesium-137 activity in these drums totalled 302 curies. Through various test programs, this cement-waste has been shown to meet all U.S. Nuclear Regulatory Commission (NRC) requirements for a stabilized, low-level radioactive waste form.² Additional test programs also demonstrated that heavy metals contained in the liquid waste; primarily barium, cadmium, chromium, mercury, and selenium; are immobilized so that the solid waste is classified under Resource Conservation and Recovery Act (RCRA) regulations as nonhazardous. These drums are currently stored on site in the Drum Cell (DC). Figure 1 is a graphic representation of the IRTS high-level waste pretreatment process.

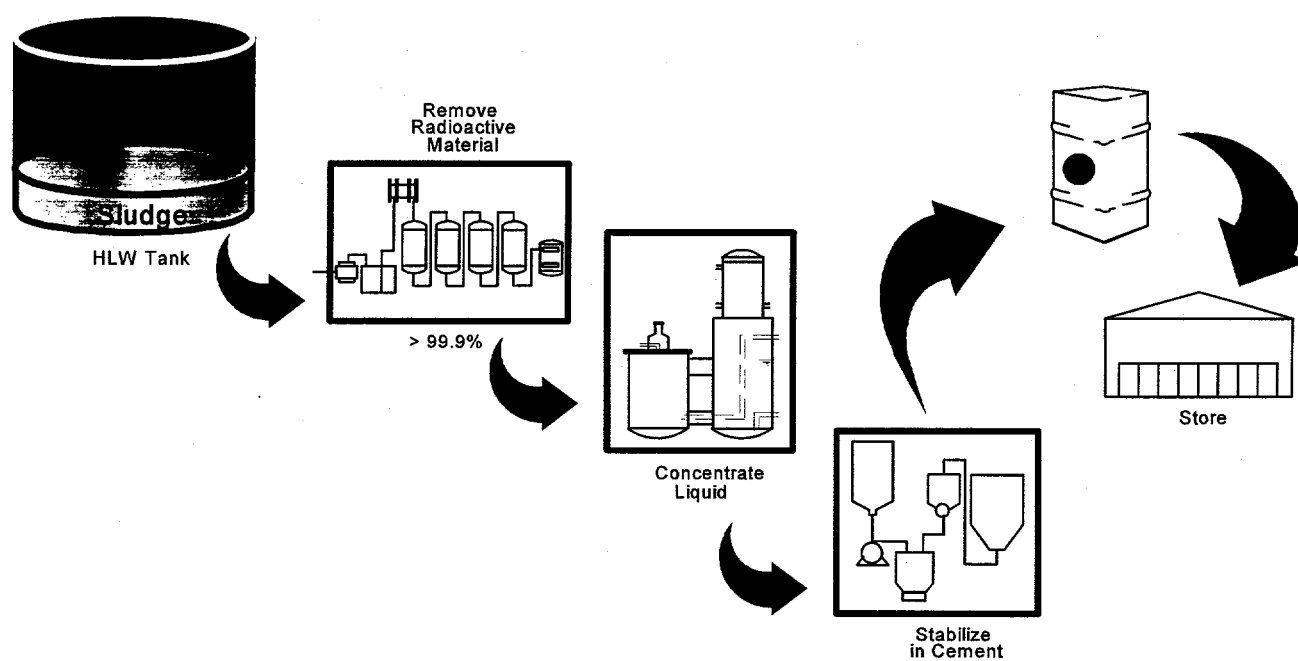


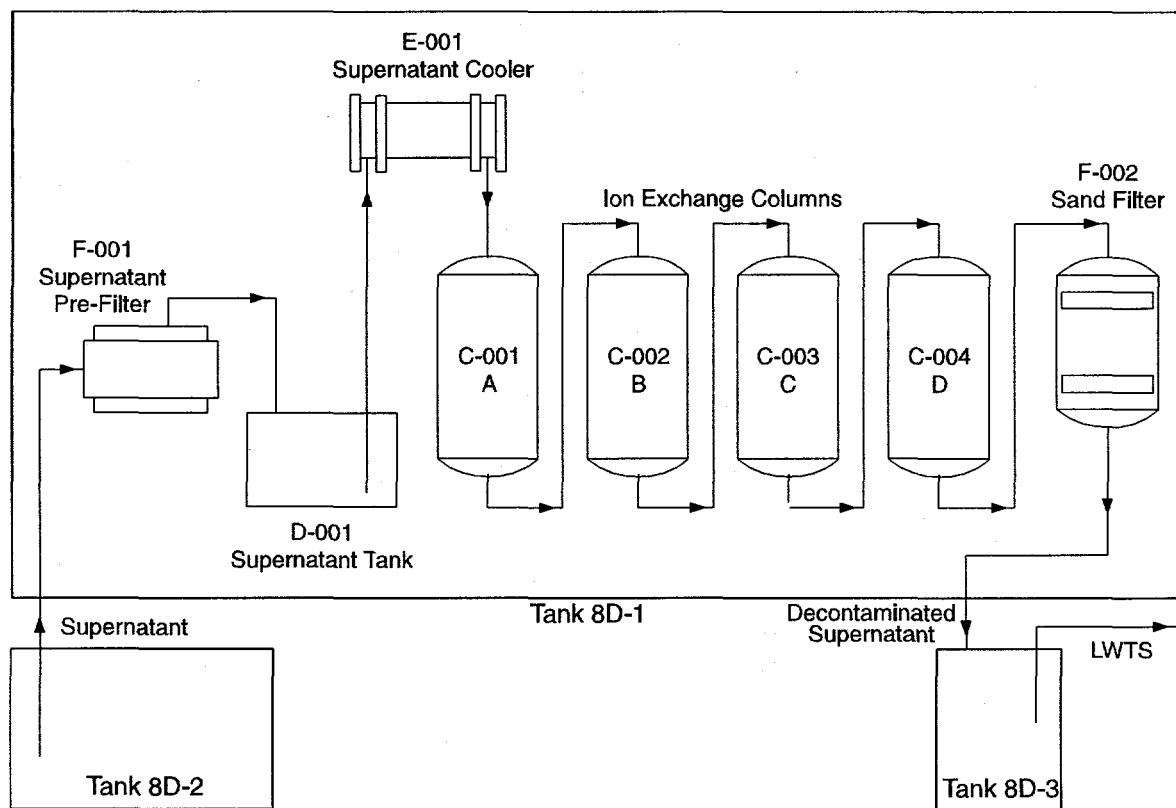
Figure 1. Integrated Radwaste Treatment System

3.0 SLUDGE WASHING

After completing laboratory simulation tests, preparations, and operational readiness reviews; both internal and DOE/NRC; the PUREX sludge in Tank 8D-2 was washed from October, 1991 to January, 1992. Washing consisted of adding a sodium hydroxide solution and additional water to increase the alkalinity of the liquid waste from an indicated pH of 10 to a pH of 12.5. This was done in conjunction with sequential operation and lowering of the five 150-hp mobilization pumps in the HLW tank to thoroughly mix the contents. This washing process dissolved the hard layer of sludge present in the tank, solubilized the sulfate and other undissolved salts present in the sludge, and mixed the interstitial liquid trapped in the sludge with the wash solution. The alkalinity increase precipitated the plutonium and uranium compounds formed so that these concentrations in the sludge wash were reduced by factors of 10 and 20, respectively. This was desirable since much more of these long-lived radionuclides would be vitrified with the sludge and not carried through to the cement-waste product.

3.1 Sludge Wash No. 1 and Processing

Sludge wash No. 1 processing through the IRTS began in April, 1992 and finished in May, 1994. Over 1.55 million liters of the sludge wash No. 1 solution containing 910,000 curies of cesium-137, with concentrations between 520 and 850 $\mu\text{Ci/ml}$, were decontaminated using UOP IONSIV[®] IE-96 and TIE-96 zeolites. The TIE-96 zeolite was developed jointly by Battelle Pacific Northwest National Laboratory (PNNL), UOP, and West Valley Nuclear Services Co., Inc. (WVNS), with its first commercial use at the WVDP during sludge wash No. 1 processing through the Supernatant Treatment System (STS) (figure 2). In addition to cesium, the TIE-96 zeolite removes plutonium and strontium, with typical decontamination factors of 10 to 100. By using this new zeolite, the amounts of these long-lived radionuclides that are solidified in cement-waste are minimized and the quantities vitrified are maximized. Six thousand five hundred kilograms of the TIE-96 zeolite and 4,900 kg of IE-96 zeolite were used during sludge wash No. 1 processing. The cesium activity passing through into the cement-waste was 201 curies.



STS_FLOW.CDR

Figure 2. Simplified Supernatant Treatment System Flow Diagram

Two new stabilized cement-waste forms were developed to solidify the new waste stream to newly revised NRC stability requirements. Portland Type V cement was used in one of the waste forms, instead of the Type I cement, to resist the impact of the increased sulfate content in the sludge wash and to increase the waste concentration from a nominal 20 wt% TDS to 30 wt% TDS. Seven thousand two hundred and eighty 270-liter square drums of cement-waste were produced from the decontaminated sludge wash No. 1 concentrate: 4,160 with Type I and 3,120 with Type V portland cement. Both waste forms were developed to meet applicable U.S. Environmental Protection Agency (EPA) and New York State Department of Environmental Conservation (NYSDEC) regulations for immobilization of heavy metals, and the updated stability requirements contained in the 1991 NRC Branch Technical Position on Waste Form. The sludge wash cement-waste that was produced meets 10 CFR 61 criteria for a Class A low-level waste due to three factors: (1) precipitation of the plutonium in the alkaline sludge wash, (2) plutonium and strontium removal provided by the TIE-96 zeolite and, (3) the slightly lower waste concentration employed to adequately produce a stabilized cement waste containing the much higher sulfate levels which also limited precipitation of solids in the Liquid Waste Treatment System (LWTS) evaporator.

3.2 Sludge Wash No. 2 and Processing

A second sludge wash of the PUREX sludge was performed during May and June, 1994 to further reduce the amount of sulfates in the HLW prior to vitrification. As with the first sludge wash, sodium hydroxide and water were added to Tank 8D-2 while the mobilization pumps mixed the contents of the tank. Following the second wash, the wash solution was again processed through the IRTS from June to August, 1994. Approximately 1.35 million liters of wash No. 2 solution, containing 126,000 curies of cesium-137 at a concentration of 100 $\mu\text{Ci/ml}$, were decontaminated in the STS with both types of UOP zeolites used earlier. Only 1,600 kg of zeolite were used during this processing. The cesium activity passing into the 750 drums of cement-waste produced from the decontaminated sludge wash concentrate was limited to 21 curies. All drums meet 10 CFR 61 criteria for Class A Low-level Waste (LLW).

3.3 THOREX Transfer and Neutralization

Following the completion of sludge washing, final preparations were made to complete the installation of the HLW transfer system which links all three HLW tanks and the Vitrification Facility together with double-contained piping run in underground concrete trenches and pits. Vertical, turbine-type transfer pumps were installed in Tanks 8D-1, 8D-2, and 8D-4. Readiness assessments for the THOREX transfer and neutralization, THOREX-wash processing, and zeolite transfer were conducted by both WVNS and DOE, with oversight by the NRC. Tank 8D-2 was prepared for the acidic THOREX addition during November and December, 1994 by increasing its alkalinity with sodium hydroxide to a pH of approximately 13. Corrosion probes and a NO_x monitor were employed to monitor and limit tank corrosion during the THOREX addition. Dilution air was also added into the HLW tank vapor region to minimize corrosion during the transfers.

The acidic THOREX was transferred from Tank 8D-4 to Tank 8D-2 and neutralized during January, 1995. The THOREX was brought over in three separate transfers. A first transfer of 18,000 liters, a second transfer of 38,600 liters of THOREX with water added to reduce its corrosion potential in Tank 8D-2, and a third transfer of 21,100 liters of a second THOREX dilution. In total, 98% of the THOREX waste was removed from Tank 8D-4 with the remainder left in the tank heel. The NO_x monitor and corrosion probes in Tank 8D-2 indicated no significant increase in corrosion rate during the neutralization process. Following neutralization, sodium nitrite was added to Tank 8D-2 to minimize pitting corrosion that could result from the large amount of nitrates in the THOREX.

3.4 THOREX/PUREX Wash Processing

After mixing the following contents of Tank 8D-2: washed PUREX sludge, sludge wash, THOREX precipitates, and THOREX solubles; the liquid THOREX/PUREX wash was processed through the IRTS. From January to May, 1995, 1.19 million liters of the THOREX/PUREX wash solution, containing 300,000 curies of cesium-137 at a 250 $\mu\text{Ci/ml}$ concentration, were decontaminated using 1,600 kg of UOP IE-96 and 1,600 kg of TIE-96 zeolite. The decontaminated THOREX/PUREX wash was concentrated to 20 to 29 wt% TDS in preparation for solidification in Type V cement.

Waste form stability tests were performed on the new Type V portland cement-waste form for the THOREX/PUREX wash. Test data indicated that the waste form immobilizes the heavy metals; specifically barium, cadmium, chromium, mercury, selenium, and silver; so that the waste is classified as RCRA-

nonhazardous. Additional qualification tests were performed to demonstrate that the resulting cement-waste meets NRC requirements for LLW stability. Actual post-production waste analyses indicated that nearly all of the drums of solidified THOREX/PUREX wash meet 10 CFR 61 criteria for Class A LLW. This is attributed again to the effectiveness of the alkaline wash of Tank 8D-2 to precipitate plutonium and the adsorption capability of the UOP TIE-96 zeolite in removing strontium and plutonium from the wash solution, in addition to cesium removal. One thousand four hundred fifty-one 270-liter drums containing 46 curies of cesium-137 were produced from the decontaminated THOREX/PUREX wash concentrates, bringing the total number of drums stored on site in the Drum Cell to 19,877.

3.5 Zeolite Mobilization and Transfer

The last major pretreatment operation at the WVDP ran from July, 1995 to January, 1996. The 65,300 kg of zeolite stored in spare HLW Tank 8D-1 have been mobilized with five 150-hp mixing pumps installed in the tank. Once fluidized, the zeolite slurry was pumped from Tank 8D-1 through an in-line grinder that size-reduced the 20 to 50 mesh (840 to 300 microns) zeolite size to approximately 50 microns or less before the slurry was added into Tank 8D-2 and mixed with the PUREX and THOREX sludge. Once a zeolite transfer was completed, Tank 8D-2 liquid was then decanted back to Tank 8D-1 to aid in mobilizing and transferring the next batch of zeolite slurry to Tank 8D-2. The 16 zeolite transfers have been accomplished with an estimated removal of 85 to 93% of the original zeolite stored in Tank 8D-1. To accomplish this, over 14 million liters of zeolite slurry have been transferred from Tank 8D-1 to Tank 8D-2. The amount of zeolite transferred has been estimated by the use of radiation probes placed along the transfer piping within the trench, and confirmed by video inspections of the heel remaining in Tank 8D-1. The amount of zeolite removed from Tank 8D-1 greatly exceeds the required quantity to begin HLW vitrification. Additional flushes of Tank 8D-1 are scheduled to be performed in parallel with HLW vitrification to further remove zeolite from the tank heel. These additional flushes will require more intricate manipulations of the mobilization and transfer pumps due to the structural interferences of the tank bottom (figure 3).

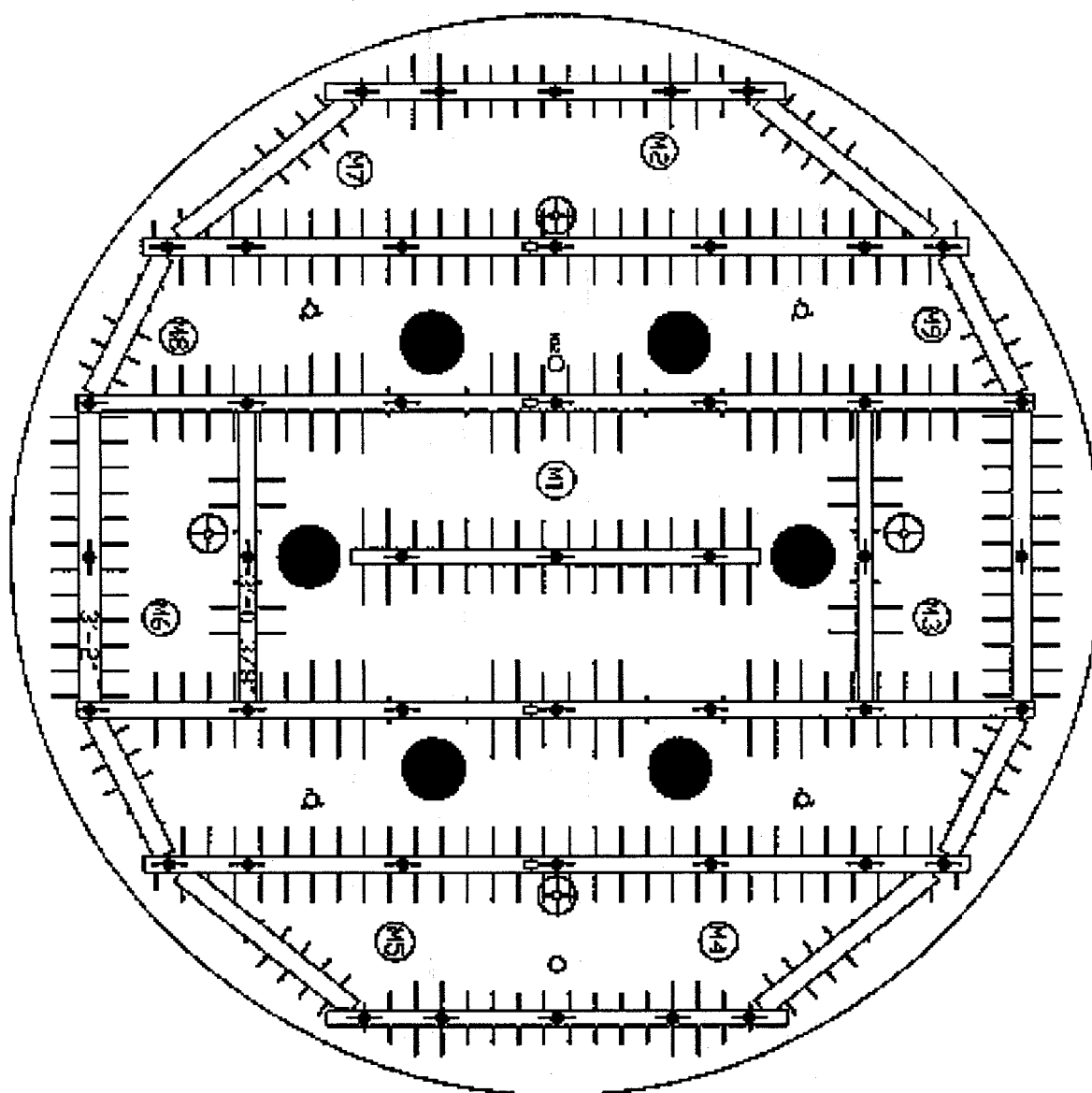


Figure 3. Planar View of Tank Structure

Table 5. Zeolite Transfer Summary

| Amounts of Initial Zeolite Transferred* | | | |
|--|---------------------------|----------------------|---------------------|
| Transfer # | Volume of Transfer | Incremental** | Cumulative** |
| | (gallons) | % | % |
| 1 | 126,400 | 27.1 | 27.1 |
| 2 | 131,900 | 3.4 | 30.5 |
| 3 | 104,600 | 2.1 | 32.6 |
| 4 | 77,800 | 2.1 | 34.7 |
| 5 | 139,200 | 5.5 | 40.2 |
| 6 | 221,800 | 4.6 | 44.8 |
| 7 | 201,800 | 5.4 | 50.2 |
| 8 | 310,400 | 5.7 | 56.0 |
| 9 | 429,700 | 6.6 | 62.6 |
| 10 | 209,500 | 3.0 | 65.6 |
| 11 | 360,000 | 10.4 | 76.1 |
| 12 | 242,600 | 3.4 | 79.5 |
| 13 | 333,700 | 5.6 | 85.1 |
| 14 | 505,200 | 2.5 | 87.6 |
| 15 | 394,600 | 3.4 | 91.0 |
| 16 | 318,900 | 2.0 | 93.0 |

* Based on radiation probe with 1.15 R/hr per Ci/L.

** Based on final Tank 8D-2 visual inspection; percentages shown may be 10% higher than actuals.

ZEOLITE REMOVAL from TANK

8D-1

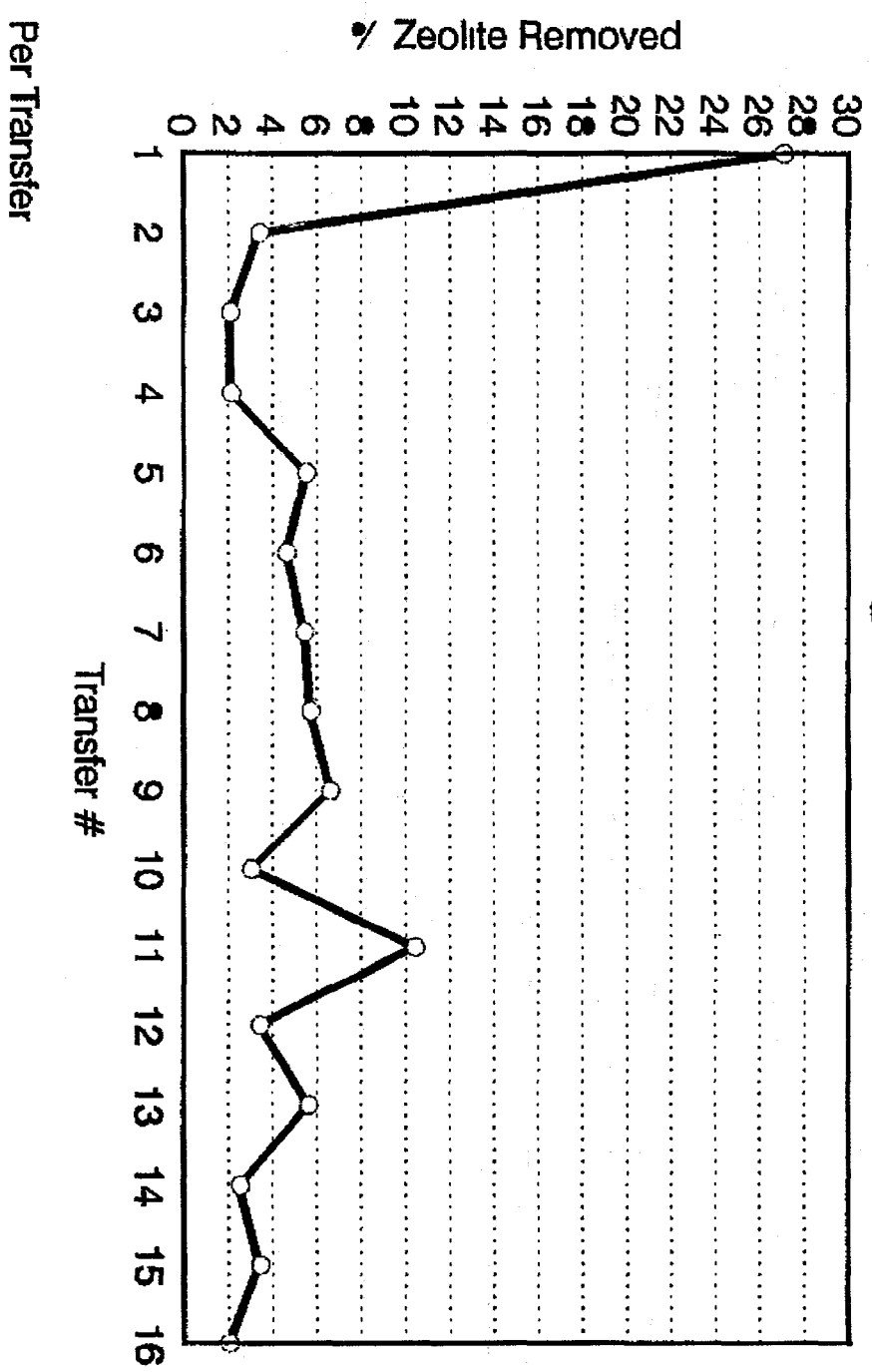


Figure 4. Percent Zeolite Removed Versus Transfer Number

ZEOLITE REMOVAL from TANK

8D-1

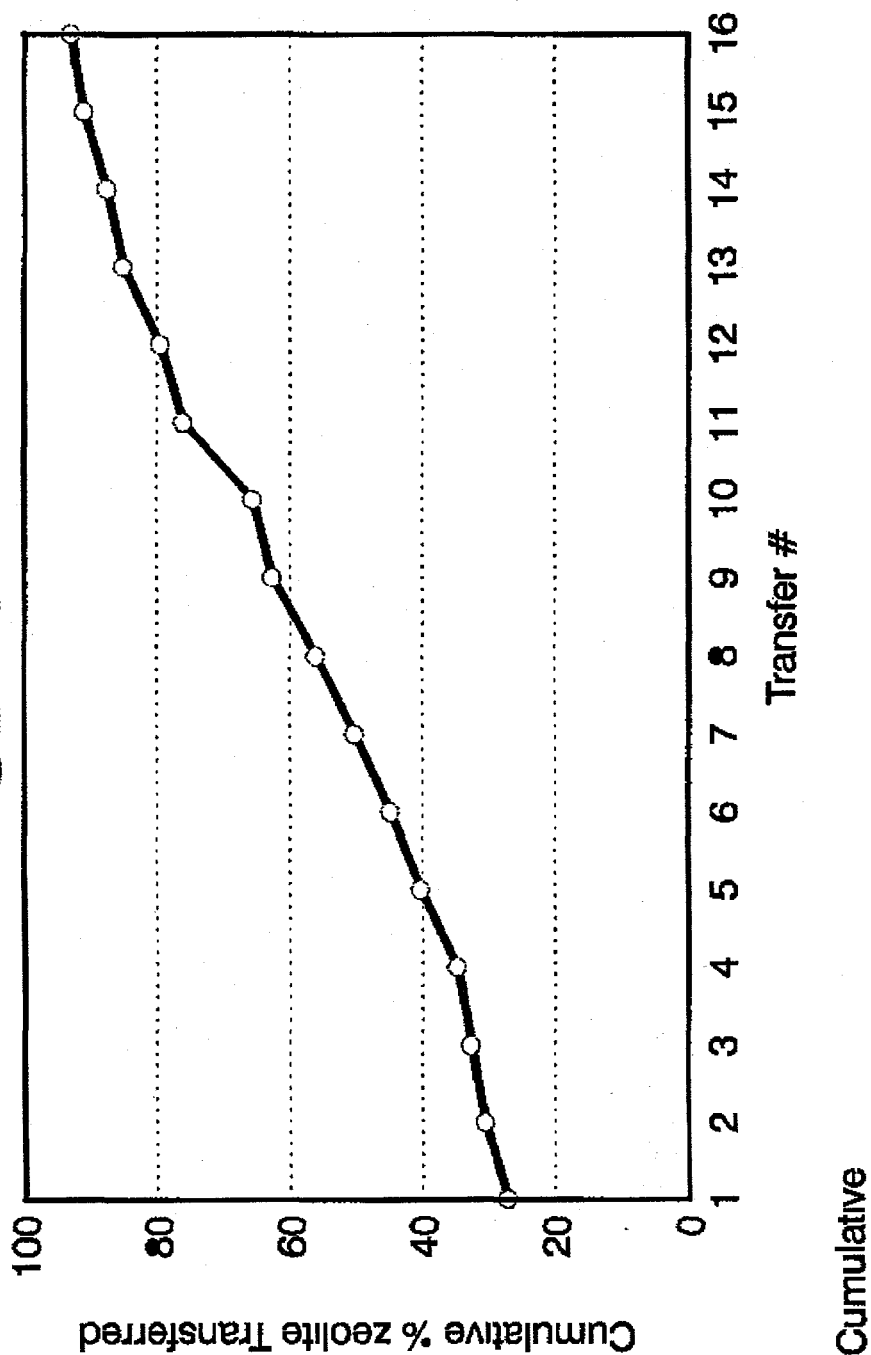


Figure 5. Cumulative % of Zeolite Removed

4.0 SUMMARY AND CONCLUSIONS

The WVDP has completed its high-level radioactive waste pretreatment program that was begun in 1988. The pretreatment process consisted of four distinct phases: PUREX supernatant processing, sludge washing, THOREX waste neutralization and washing, and zeolite mobilization and transfer. Pretreatment of the HLW was specified to separate the majority of the radioactive species from the nonradioactive salts, specifically those of sulfate, in order to increase the stability of the glass and reduce the total volume of HLW glass produced.

The pretreatment process for the first three phases was similar. The HLW supernatant from the PUREX waste, sludge washing, and neutralized THOREX waste was processed through the STS where the cesium-137, and later the plutonium and strontium-90 radionuclides, were adsorbed onto the zeolite. This system effectively removed these radionuclides, thereby providing decontamination factors of at least 1,000 for cesium-137 and approximately 10 to 100 for plutonium and strontium-90. The spent zeolite was stored in a spare HLW tank until later in the pretreatment process. The resulting decontaminated salt solutions were then volume-reduced by a steam-fed evaporator in the LWTS. The concentrated, radioactive mixed waste was blended with portland cements and special additives in the Cement Solidification System (CSS) that employed high-shear cement mixers. Specially constructed 270-liter square drums were filled with the cement-waste that met the NRC stabilization criteria for Class B and C LLW, as well as the EPA Toxicity Characteristic Leaching Procedure (TCLP) requirements for heavy metals. Nineteen thousand eight hundred seventy-seven drums of four different stabilized cement-waste recipes; each meeting 10 CFR 61 criteria for Class A, B, or C LLW; have been produced and are currently stored in the remotely operated DC awaiting final disposition. Table 5 presents IRTS processing totals.

Table 6. Integrated Radwaste Treatment System Processing Totals

| Processing Operation | Volume Processed (thousand liters) | Cesium-137 Activity Removed (Ci) | Zeolite Used (kg) | Cement Drums Produced | Measured Cesium-137 Activity in Cement Waste (Ci) |
|----------------------|------------------------------------|----------------------------------|-------------------|-----------------------|---|
| PUREX Supernatant | 2,340 | 5,300,000 | 45,100* | 10,393 | 302 |
| Sludge Wash #1 | 1,550 | 910,000 | 11,400 | 7,279 | 201 |
| Sludge Wash #2 | 1,350 | 130,000 | 1,600 | 754 | 21 |
| PUREX/THOREX Wash | 1,190 | 300,000 | 4,900 | 1,451 | 46 |
| Totals | 6,430 | 6,640,000 | 65,300 | 19,877 | 570 |

* 2,600 kg from nonradioactive start-up testing

The last pretreatment phase consisted of mobilizing approximately 85 to 93% of the 63,300 kg of zeolite stored under water in the spare HLW tank, size-reducing the particles from the original 570 micron size (20 to 50 mesh) to approximately 50 microns or less, and transferring the slurry into the original HLW tank containing the washed sludges. The size-reduced zeolites have been blended with the sludges to form a homogenous HLW feed for the Vitrification Facility. The projected composition of the resulting HLW liquid phase is shown in table 7.

Table 7. Projected Composition of Blended HLW Supernatant

| Constituent | Wt% (Dry Basis) | Characteristic | Value |
|-------------------------------|-----------------|------------------|----------------|
| Na | 35 | Alkalinity | 0.05 Molar |
| NO ₂ | 33 | pH | 10.5 |
| NO ₃ | 11 | TDS | 2.0 wt% |
| TIC | 3.6 | Specific Gravity | 1.013 |
| SO ₄ ⁻² | 1.4 | Cs-137 | 50 µCi/ml |
| TOC | <0.23 | Alpha-Pu | 0.00025 µCi/ml |
| Total U | 0.12 | Gross Alpha | 0.4 µCi/ml |
| Ca | 0.039 | Gross Beta | 50 µCi/ml |
| Al | 0.025 | Sr-90 | 0.1 µCi/ml |
| | | Tc-99 | 0.03 µCi/ml |

Many challenges presented themselves during the pretreatment of the HLW that led to the development of major technical innovations, including:

- Development of cement-wastes that met increasingly more stringent stabilization requirements.
- First use of square drums to minimize the size of the Drum Cell.
- Design, fabrication, and use of specialized remote tooling to repair process equipment within HLW tanks where radiation fields range over 1,000 R/hr.
- Development, commercialization, and use of the UOP IONSIV[®] TIE-96 zeolite that removes plutonium and strontium, as well as cesium. This allowed production of a LLW cement-waste having much lower concentrations of these radionuclides.
- The use of fully remote drum handling and bar code tracking systems in the CSS and Drum Cell.
- Safely neutralizing the acidic THOREX waste in the primary carbon steel HLW tank using in-tank corrosion probes and a NO_x analyzer to monitor the process and ensure minimal corrosion.
- Increasing the capacity of the existing Drum Cell from 19,877 to 21,200 drums by modifying hardware and software systems.
- Removal of the zeolite from the spare HLW tank after up to seven years of storage in an alkaline environment.
- Assessing and subsequently rotating the supernatant removal pump to allow more volume to be removed during the sludge wash process and effectively eliminating the need for a fourth sludge wash.
- Acid wash the LWTS evaporator to remove accumulated radionuclides and returning the high-activity wash solution to the high-level waste tank.

Through innovative engineering and disciplined pretreatment operations, these and other challenges have been met and solutions achieved. Over 6.6 million curies of cesium-137 were removed from the HLW liquid and adsorbed onto the zeolite. The original two million liters of PUREX waste and 31,000 liters of THOREX waste have been processed to produce a slurry of approximately 1.1 million liters that contains washed sludge and size-reduced zeolite. The decontaminated salt solutions produced 19,877 cement drums, collectively containing a measured 570 curies, for an average cesium removal efficiency of over 99.99%.

- The WVDP pretreatment program has been completed and the accomplishments over the last seven years illustrate that HLW processing can be safely and successfully managed. In addition, the pretreatment processing is a success in that the WVDP cement-wastes have met commercial NRC stabilization requirements, and the heavy metals in the wastes have been immobilized below EPA and NYSDEC TCLP limits, producing RCRA-nonhazardous wastes.

5.0 REFERENCES

L. E. Rykken, High-Level Waste Characterization at West Valley, Topical Report DOE/NE44139-14, June, 1986.

C. W. McVay, J. R. Stimmel and S. Marchetti, Cement Waste Form Qualification Report-WVDP PUREX Decontaminated Supernatant, Topical Report DOE/NE/44139-49, August, 1988.

D. K. Ploetz and I. M. Leonard, Supernatant Treatment System Design Through Testing, Topical Report DOE/NE/44139-47, December, 1988.

M. N. Baker, W. E. Mateer, G. H. Metzler, S. R. Reeves, and D. J. Rickettson, Design and Construction of the Low-Level Liquid Waste Treatment System, Topical Report DOE/NE/44139-56, March, 1989.

R. G. Jezek, Low-Level Waste Cement Solidification Design, Installation, and Start-up, Topical Report DOE/NE/44139-50, August, 1988.

B. Landau, A. F. Russillo, D. E. Frank, and D. H. Garland, The Design, Construction, and Operation of the Integrated Radwaste Treatment System (IRTS) Drum Cell, Topical Report DOE/NE/44139-52, December, 1989.

LIST OF ACRONYMS

| | |
|--------|--|
| CSS | Cement Solidification System |
| DC | Drum Cell |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| HLW | High-level Radioactive Waste |
| IRTS | Integrated Radwaste Treatment System |
| LLW | Low-level Radioactive Waste |
| LWTS | Liquid Waste Treatment System |
| NFS | Nuclear Fuel Services |
| NRC | U.S. Nuclear Regulatory Commission |
| NYSDEC | New York State Department of Environmental Conservation |
| PNNL | Pacific Northwest National Laboratory |
| PUREX | Plutonium Uranium Extraction |
| RCRA | Resource Conservation and Recovery Act (1976), as amended and applicable New York Hazardous Waste Regulations |
| STS | Supernatant Treatment System |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TDS | Total Dissolved Solids |
| THOREX | Thorium Extraction |
| WNYNSC | Western New York Nuclear Services Center |
| WVDP | West Valley Demonstration Project |
| WVNS | West Valley Nuclear Services Company, Inc. |