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United States Government | Department of Energy

memorandum

Idaho Operations Office
West Valley Project Office

DATE: April 15, 1992

SUBJECT: Summary of the Investigation of Fissile Material Accumulation in the Liquid Waste Treatment System (LWTS)

TO: T. W. McIntosh, EM-343
Project Manager for West Valley

Attached for your information is a report which summarizes the investigation and resolution of the fissile material accumulation in the LWTS. The report presents background information, details the technical review and conclusions, discusses chemical cleaning and the final condition of the system.

If you have any questions, please call Alan Yeazel of my staff at FTS 473-4780.

W. Stephen Ketola

for T. J. Rowland, Director
West Valley Project Office

Attachment: Report

cc: G. C. Comfort, NRC-HQ (w/att)
J. Roth, NRC, Region 1 (w/att)
J. L. Lyle, DOE-ID (w/att)
J. Psaras, DOE-HQ (w/att)
F. L. Piciulo, NYSERDA (w/att)

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West Valley
Nuclear Services Company
Incorporated

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MS-W

April 1, 1992

Mr. T. J. Rowland, Director
West Valley Project Office
U.S. Department of Energy
MS-DOE
P.O. Box 191
West Valley, New York 14171-0191

Dear Mr. Rowland:

Attention: J. A. Yeazel

SUBJECT: Summary of the Investigation of Fissile Accumulation in the Liquid Waste Treatment System (LWTS)

Transmitted for your information is a report (Attachment A) which presents the results of the investigation of fissile material accumulation in the Liquid Waste Treatment System (LWTS). The report details the technical review and conclusions, and discusses chemical cleaning and final condition of the systems.

During November 1990 it was observed that an increase in the concentration of plutonium in the liquid in the high-level waste (HLW) Tank 8D-2 had caused material to accumulate downstream, presumably in the LWTS. WVNS performed an extensive review of this situation and commissioned several teams of independent outside experts to assist in the final resolution. It was first established that there was no safety question nor was there a criticality concern because of the small quantities of Plutonium and Uranium involved; it was further concluded that this processing phenomenon was not an Unreviewed Safety Question (USQ). A nitric acid cleaning was performed on the tanks, pipes, and evaporator in the LWTS to collect the fissile material and clean the system. The acid cleaning was successful in removing the majority of fissile material as shown by chemical analysis of the cleaning solution.

The acid cleaning was effective in removing 251.8 grams of fissile plutonium from the starting fissile plutonium inventory of 291 grams. The difference, 39.2 grams, serves as the starting inventory for continued processing. Analysis of the LWTS influent and effluent flow streams will be used as process controls on accumulation in the future. This, in addition to controls on STS pH and the use of Ti-Treated Zeolite will assure that recurrence of this phenomenon is prevented.

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Mr. T. J. Rowland

If there are any questions in this matter, please contact the undersigned at 4504 or G. A. Smith at extension 4325.

Sincerely,

A. J. Howell

A. J. Howell, Manager
Operations Technical Support
West Valley Nuclear Service Co., Inc.

DA:92:0057

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Attachment A - Report on Investigation and Resolution of Fissile Accumulation in the Liquid Waste Treatment System (LWTS)

Summary of Investigation and Resolution of Fissile Accumulation in the Liquid Waste Treatment System (LWTS).

G. A. Smith
A. J. Howell
R. F. Gessner

BACKGROUND

The West Valley Demonstration Project (WVDP) is a cleanup effort which is actively removing liquid high-level nuclear waste from an underground tank, extracting radioactive cesium from the liquid using an ion-exchange system and stabilizing the resulting low-level waste (LLW) in an NRC-endorsed cement waste form. This process takes place in the Integrated Radwaste Treatment System (IRTS). In May 1988, the tank contained approximately 560,000 gallons of liquid high-level nuclear waste containing about 39 weight percent total dissolved solids (TDS) left from the first commercial spent fuel reprocessing operation in the United States. Since May 1988, WVDP has successfully processed over 420,000 gallons of high-level radioactive waste, resulting in 10,394 cement drums with an average surface radiation reading of 35 mR/hr.

On November 14, 1990, the IRTS was placed in standby because on-going sampling and testing associated with completing the liquid high-level waste treatment indicated that dilution of the supernatant caused dissolution of fissile material out of the sludge which has formed beneath the liquid. Sample analysis of the liquid reflected very slowly increasing concentration of fissile material. Associated with this concentration increase was some small accumulation of fissile material in the IRTS components downstream of the Supernatant Treatment System (STS). The accumulated fissile material and all solution concentrations were significantly below the site's criticality operation safety requirements, and no operations occurred outside any site safety limit or limiting condition for operations. However, the IRTS was placed in standby while a full assessment was completed to assure a thorough understanding of this phenomenon and an occurrence report (Reference 1) was issued.

A strategic plan (Reference 2) was issued to the West Valley Project Office (WVPO) on December 17, 1990. The plan was set up with three major goals to be completed before the resumption of IRTS Operations could commence.

1. Characterize changes in Tank 8D-2 supernatant and the distribution of fissile materials across the IRTS.

2. Make a decision as to the need to access the evaporator internals.

3. Provide an assessment of this situation to determine if it was an Unreviewed Safety Question (USQ).

INVESTIGATION

A. Characterization of Liquid

WVNS characterized the changes in the Tank 8D-2 supernatant and the distribution of fissile materials across the IRTS. The focus of this step of the investigation was two-fold. One was to determine the exact changes that had occurred within Tank 8D-2 during 2 1/2 years of processing the liquid; and second, to determine the consequences of these changes throughout the IRTS. This work was initiated with extensive sampling (Figure 1) across the IRTS systems.

Samples were taken and analyzed for uranium, plutonium, total dissolved solids (TDS), and density. A plutonium chemistry expert from Westinghouse Savannah River was brought to WVNS to perform an independent review of the method used at WVNS for plutonium analysis. The results from analysis of Tank 8D-2 supernatant were compared to supernatant sample results from sampling performed prior to IRTS start-up in May 1988. The samples indicate the plutonium concentration of the liquid in Tank 8D-2 increased from 7.52 E-02 µCi/mL at 39.5 Wt% TDS to 11.4 E-02 µCi/mL at 23 Wt% TDS. These data were the first indication that the chemistry of 8D-2 had changed. H. P. Holcomb agreed with the method used at WVNS for plutonium analysis and with the results obtained, detailed in his report (Reference 3).

B. Sampling Components of LWTS

One of the first aspects of our study was to determine what effects, if any, were caused by the increase in plutonium concentration in Tank 8D-2. The intense sampling plan was continued to sample upstream and downstream of all major process equipment throughout the IRTS. The sample points used are outlined in Figure 1. The results from this sampling determined that the evaporator and tanks in the Liquid Waste Treatment System (LWTS) were accumulating fissile material.

C. Evaporation Test

A controlled full-scale test of the LWTS was conducted. Decontaminated supernatant was analyzed for plutonium before and after evaporation (from 8.86 Wt% TDS to 41.03 Wt% TDS). The actual gross alpha in the concentrates of the evaporator was 1.35 E-01 uCi/ml as compared to the calculated expected value of 7.83 E-01 uCi/ml (Reference 4).

A lab scale boil-down test of evaporator feed material was initiated to further check the theory that fissile material was being deposited in the evaporator. This test further confirmed the results given above.

D. Testing Cemented Drums

As a final check, and to assess whether excess fissile material had carried thru the evaporator to the Cement Solidification System (CSS) waste form, five drums were sampled to determine the amount of fissile material in the cement product. One drum produced in 1988 was compared to four drums produced in 1990. The results of this testing indicate that there was no unexpected increases of fissile plutonium in the CSS waste form from 1988 to 1990. The data are listed in Table 1 (Reference 5).

An evaluation was made to assess how much plutonium and uranium salts had deposited in the LWTS tanks and piping. This was accomplished by performing mass balance calculations across the LWTS. For plutonium, gross alpha (one way of estimating plutonium) data were available for every evaporator feed tank and every evaporator concentrates tank that had been processed through the evaporator. This led to an estimate of 359± 100 grams of total plutonium in the evaporator (Reference 6). For uranium only one data point existed for uranium across the evaporator. This data point led to an estimate of 26 Kg of total uranium in the evaporator (Reference 7).

RESOLUTION AND RECOVERY

A. Expert Reviews

The extensive sampling plan suggested that the LWTS evaporation (volume reduction) operations were causing the fissile salts to accumulate. The next step was to determine the best and safest way to recover from this processing phenomena. To this end two separate engineering evaluations were made. The first was a plan to gain access to the evaporator internals by pulling the reboiler tube bundle. A survey of the evaporator and the surrounding area, (Reference 8), showed a general area dose of 50 to 100 mR/hr and a 2 R/hr hot spot on the evaporator reboiler. Based on this survey, the in-cell location of the evaporator, and the knowledge that the removal of the evaporator reboiler steam chest would be a labor intensive process, accessing the evaporator was not the preferred method for ALARA reasons.

The second engineering assessment was to develop a method to chemically clean the evaporator with nitric acid. Off-site experts H. P. Holcomb from Savannah River and R. A. Corbett from Corrosion Testing Laboratories Inc. were enlisted to help with the determination of the parameters to be used during the acid cleaning. Holcomb, a plutonium chemist, suggested that as a minimum 1 molar nitric acid should be used to remove the scale (Reference 9). Corbett, a titanium corrosion expert, after examining the design data of the evaporator, suggested the nitric acid not exceed 2 molar (Reference 10).

B. Unreviewed Safety Question (USQ) Review

Using the knowledge of the processing pheno[illegible] that had occurred in the LWTS, WVNS conducted an investigation to determi[illegible] there was an USQ with respect to this event.

DOE order 5480.1B "Environment Safety and Health Program for Department of Energy Operations" states "a proposed change, test, or experiment shall be deemed to involve an unreviewed safety question if: (1) The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety evaluated previously by safety analysis will be significantly increased or (2) A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

WVNS convened a peer review panel of plutonium and criticality experts from Savannah River Plant and Oak Ridge National Laboratory. This panel consisted of H. P. Holcomb, H. Dyer, and C. Parks. Their task was to evaluate the evidence and advise WVNS on the USQ issue, review the pertinent Safety Analysis Reports for the IRTS, investigative data and analysis with respect to criticality issues, and summarize their findings in written reports (References 9, 11). With respect to the USQ issue, the group agreed that even with continued processing of the supernatant a criticality could not have occurred in the evaporator. The Peer Review Panel concluded that no USQ existed.

The information concerning the fissile accumulation in the LWTS evaporator was also presented to the WVPO Independent Review Group. The minutes (Reference 12) of that meeting state "that the Independent Review Group agreed with the review process for IRTS and concluded there is no unreviewed safety question."

Based on the assessment provided by the Peer Review Panel, the Independent Review Group and the evidence accumulated during the investigation, WVNS concluded that there was not an USQ associated with the accumulation of fissile material in the LWTS evaporator, components (Reference 13). The West Valley Project Office (WVPO), following an independent review, and the Office of Health Physics and Industrial Hygiene (EH-41) concurred with this conclusion (Reference 14,15). DOE-HQ-EM-343 also agreed that there was not a USQ in the approval letter for resumption of IRTS Operations (Reference 16).

C. Clean out of Fissile Material

It was determined that nitric acid should be used to chemically clean the LWTS and SIP 91-03 (Reference 17) was issued. During the cleaning the evaporator was run in reflux, meaning all distillates were returned to the main liquid pool in the evaporator. Basically, the acid cleaning solution was allowed to simmer in the evaporator while samples of the liquid were taken to track the effectiveness of the cleaning. Three separate acid flushes of the evaporator took place during August 1991. The acid strengths used during these flushes were 1-2 Normal Nitric Acid with 1 g/L Boron added for additional criticality safety.

Figure 2 summarizes the mass of fissile plutonium and fissile uranium that were removed from the LWTS during the acid cleaning evolutions. The total plutonium and uranium removed from the LWTS amounts to 310.5 grams total Pu (251.8 grams fissile Pu) and 12.12 kg total (212 grams fissile U)(figure 2). Also, as a conservative step WVNS in conjunction with the WVPO and the NRC, shipped four samples from the evaporator cleaning solution to New Brunswick Laboratory (NBL) for independent Uranium and Plutonium Analyses. NBL analytical results, agreed with WVNS analytical results, within approximately 2 percent for both uranium and plutonium (Reference 18).

After the completion of the acid cleaning at LWTS, an extensive flushing of all possible acid exposed pipes, pumps and vessels was done. This flush was intended to return the cleaned LWTS and all of its equipment to a processing ready condition. Finally, a survey of the evaporator and associated vessels was performed after the acid cleaning. This survey showed that the general radiation field surrounding the evaporator was reduced from 50 to 100 mR/hr to 0.5 mR/hr, and hot spots were reduced from approximately 2 R/hr to less than 1.5 mR/hr (see figure 3).

D. Process Control for Processing

To lower the concentrations of uranium and plutonium in the liquid in Tank 8D-2, twenty percent sodium hydroxide (caustic) was added to elevate the pH. Testing performed at WVNS indicated that at an elevated pH the uranium and plutonium concentrations in the liquid would decrease. Table 2 shows Tank 8D-2 sample data from before and after the addition of caustic to the tank. This addition reduced plutonium concentration level in the liquid 15 times and the uranium concentration level 17 times. Additionally as part of sludge washing titanium treated zeolite will be used in the Supernatant Treatment System (STS) would further reduce the level of plutonium in the liquid.

Process control procedures to monitor fissile material distributions throughout the IRTS, TR-IRTS-11 and OSR-IRTS-12 (Reference 19, 20), have been developed to monitor the volume of Tank 8D-2 liquid that flows through the titanium treated column in the STS and track the accumulation of fissile material in the LWTS evaporator. Both of these documents use extensive sampling plans to track volumes processed and fissile accumulation. These documents also include safe limits for a) total volumes processed, and b) fissile accumulation in the respective areas.

The baseline or initial inventory of fissile material in the LWTS was established as part of the process control. WVNS conservative estimates for plutonium and uranium in the LWTS were reported to be 359 grams total plutonium (291 grams fissile) and 26 kilograms total uranium (455 grams fissile). Subtracting the grams of fissile material removed from the LWTS from the estimated grams of fissile material yields the following values: approximately 39.2 grams of fissile plutonium and 243 grams of fissile uranium. These values will be used as the initial inventory of fissile material in the evaporator per TR-IRTS-11.

SUMMARY

WVNS characterized the changes in the Tank 8D-2 Supernatant and the distribution of the fissile materials across the IRTS. This characterization determined that the evaporator and tanks in the Liquid Waste Treatment System (LWTS) were accumulating fissile material. An engineering analysis developed a method to chemically clean the LWTS with nitric acid. This chemical cleaning was effective in removing 251.8 grams of fissile plutonium from the starting fissile plutonium inventory of 291 grams. Additionally, using the knowledge of the processing phenomena that had occurred in the IRTS, WVNS conducted an investigation that determined there was no USQ with respect to this event. The investigation that took place here was an excellent example of cooperation throughout the entire DOE system. WVNS received input and help from the DOE WVPO and DOE ID field offices and from several other DOE sites in the form of technical and peer review groups.

REFERENCES

1. Occurrence Report WVNS-90-0026, LWTS-90-0001, "Significant Curtailment of Operations by WVNS to Perform an Investigation of a Processing Phenomenon", dated 11/14/90.

2. Letter WD:90:1317, T. J. Rowland from J. C. Cwynar, "Strategic Plan for Investigation of Fissile Material Accumulation in the Integrated Radwaste Treatment System (IRTS), dated December 17, 1990.

3. Letter NMP-STL-90-0044, P. J. Valenti from H. P. Holcomb (Savannah River Company), "Trip Report - Visit to West Valley Demonstration Project to Discuss Plutonium Chemistry Associated with Integrated Radwaste Treatment System (IRTS), December 3-6, 1990", dated December 10, 1990.

4. WVNS analytical request forms 910087 and 9100106.

5. Memo DC:91:0023, P. S. Klanian from J. C. Cwynar, "Confirm Waste Classification of CSS Drums Final Report", dated April 11, 1991.

6. Memo CJ:91:0047, P. J. Valenti from J. L. Mahoney, "Best Estimate and Uncertainty of Pu in the LWTS Evaporator", dated May 28, 1991.

7. Memo CJ:91:0082, P. J. Valenti from J. L. Mahoney, "Best Estimate of U in the LWTS Evaporator", dated September 23, 1991.

8. Survey Form No. 18633 dated November 2?, 1990.

9. Letter NMP-STL-91-0004, P. J. Valenti from H. P. Holcomb (Savannah River Co.), "Trip Report - Visit to West Valley Demonstration Project to Serve on Peer Review Panel to Evaluate Findings, Status, and Path Forward for Integrated Radwaste Treatment System (IRTS), February 13-14, 1991", dated February 20, 1991.

10. Letter CTL REF #07196, P. J. Valenti from R. A. Corbett (Corrosion Testing Laboratories, Inc.), "Chemical Cleaning of Titanium Liquid Waste Treatment System (LWTS) Evaporator", dated March 20, 1991.

11. Letter OW:91:0011, P. J. Valenti from Oak Ridge National Laboratory, "Visit to West Valley Demonstration Project to Discuss Criticality Safety Concerns Associated with Fissile Material Accumulation in the Integrated Radwaste Treatment System Evaporator, February 13-14, 1991", dated March 19, 1991.

12. "Draft Minutes of WVNS Technical Review Group (TRG) Meeting of February 19-20, 1991". S. J. Szalinski to G. Oertel dated February 22, 1991.

13. Letter WD:91:0324, T. J. Rowland from J. C. Cwynar, "Conclusion on Fissile Material Accumulation in the IRTS Evaporator", dated March 22, 1991.

14. Letter DW:91:0426, J. J. Buggy from T. J. Rowland, "WVPO Decision on Unreviewed Safety Question Issue", dated June 20, 1991.

15. Memo to T. W. McIntosh from D. M. Rohrer, "Review of Documentation Related to the Resumption of Operations for the Integrated Radwaste Treatment System (IRTS) at the West Valley Demonstration Project (WVDP)", dated September 17, 1991.

16. Letter J. E. Lytle to T. J. Rowland, approval level for resumption of IRTS Operations for the purpose of High-Level Waste sludge washing, dated February 18, 1992.

17. WVNS SIP 91-03, Rev. 0, "Operation of the LWTS High TDS Evaporator (31017) to Chemically Clean Accumulated Scale Deposits and Return Cleaning Solutions to 8D-2 Tank", dated February 1991.

18. Letter AY:012:92-0390:92:08, W. G. Poulson from T. J. Rowland, "Final Results of Analysis on Waste Evaporator Acid Wash", dated February 27, 1992.

19. TR-IRTS-11, Rev. 0, "Fissile Material Mass Balance Across the LWTS Evaporator", dated August 1991.

20. CSR-IRTS-12, Rev. 0, "Supernatant Treatment System Feed Requirements", dated January 16, 1992.

TABLE 1
Sample Results Showing No Unexpected
Fissile Plutonium in CSS Waste Form.

	Drum Production Date		Activi ty (from drum)
Drum #72830 Radionuclide	7/20/88	Gross Alpha	1.71 E-02
		Total Pu	1.90 E-02
		Pu-241	1.48 E-01
Drum #81912 Radionuclide	11/1/90	Gross Alpha	1.77 E-02
		Total Pu	2.82 E-02
		Pu-241	2.48 E-01
Drum #80949 Radionuclide	10/29/90	Gross Alpha	2.66 E-02
		Total Pu	2.67 E-02
		Pu-241	2.77 E-01
Drum #79816 Radionuclide	7/16/90	Gross Alpha	1.30 E-02
		Total Pu	1.87 E-02
		Pu-241	1.39 E-01
Drum #79953 Radionuclide	7/16/90	Gross Alpha	2.51 E-02
		Total Pu	1.66 E-02
		Pu-241	1.36 E-01

TABLE 2
Tank 8D-2 Sample Results Show Decrease in
Total Uranium and Alpha Plutonium Concentrations.

	Before Caustic Addition	After Caustic Addition
Date	10/28/91	11/14/91
Lab Log Number	9102073	9102216
pH	9.98	12.6
Total U	197 Ug/g	11.6 Ug/g
Alpha Pu	.238 uCi/ml	.0171 uCi/ml

FIGURE 1
FISSILE ACCUMULATION INVESTIGATION
SAMPLE POINTS

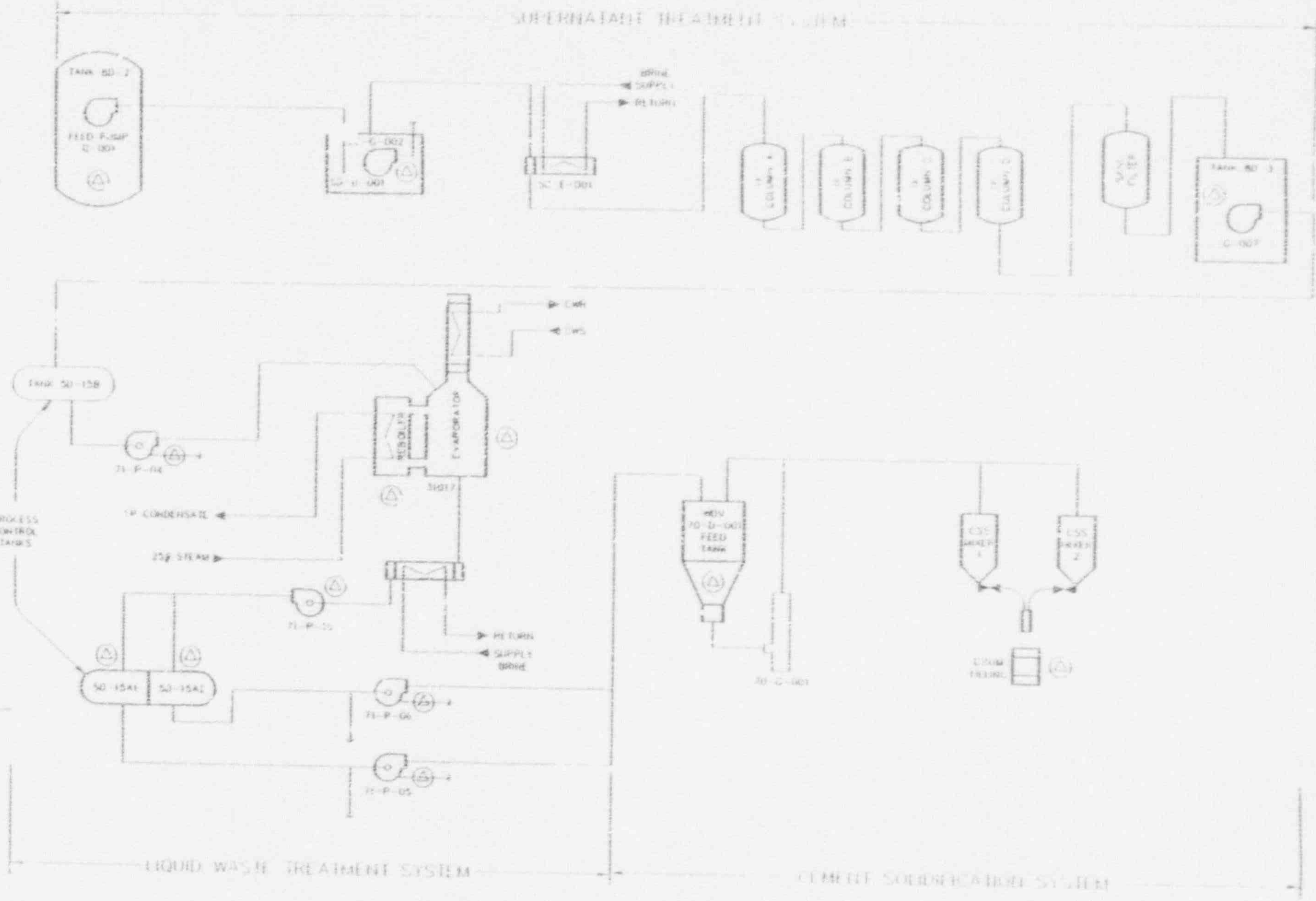

Figure 2

Flow Diagram for Cleaning Evaporator and Fissile Collection

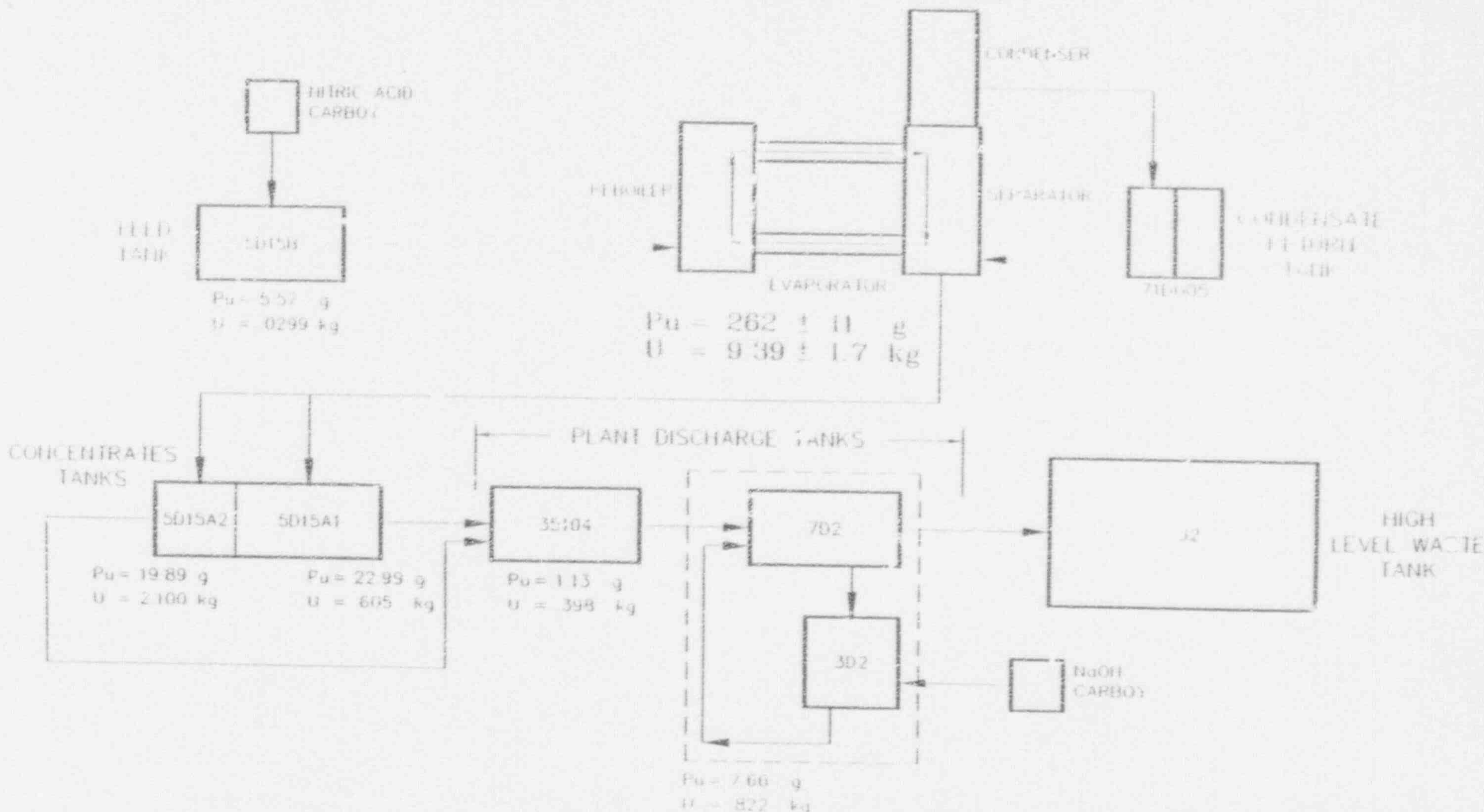

Figure 3

Acid Cleaning Substantially Reduces Radiation in LWTS

Radiation Survey Results		
Location	Before (mR/hr)	After (mR/hr)
1	2000	1.3
2	450	.4
3	200	.2
4	100	.2
5	1000	.5
6	50-100	.3