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Office of River Protection
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04-TPD-025

FEB 27 2004

Mr. Michael A. Wilson, Program Manager
Nuclear Waste Program
State of Washington
Department of Ecology
1315 W. Fourth Avenue
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RECEIVED
FEB 26 2004
EDMC

Dear Mr. Wilson:

COMPLETION OF HANFORD FEDERAL FACILITY AGREEMENT AND CONSENT ORDER (HFFACO) TARGET DATE M-45-05L-T01 AND PARTIAL COMPLETION OF TARGET DATE M-45-05M-T01.

This is to advise you that the U.S. Department of Energy (DOE), Office of River Protection (ORP) has completed target date M-45-05L-T01, "Complete full scale C-106 waste retrieval," and partially completed target date M-45-05M-T01, "Submit C-106 waste retrieval results, analysis of residual waste(s), and (if appropriate) request for exception to the criteria pursuant to agreement Appendix H."

Regarding target date M-45-05L-T01, full scale retrieval of Tank 241-C-106 was completed on December 31, 2003. The retrieval campaign began in August 2003 and deployed two retrieval technologies, oxalic acid dissolution and modified sluicing, to retrieve as much waste as technically possible, with a remaining residual of no more than 360 cubic feet (ft^3), in accordance with the criteria in the HFFACO M-45 milestones.

During the retrieval campaign, a total of six batches of oxalic acid were added to Tank 241-C-106 to dissolve the solid waste sludge in the tank, and four sluicing operations were performed to physically break up the solids and remove the resultant slurry. The limit of technology for oxalic acid dissolution was attained with the sixth batch when the pH of the solution reached a steady state short of the expected acid depletion end point, indicating the exposed waste had fully reacted with the acid. The sluicing efficiency, in terms of volume of solids removed per volume of sluicing water added, steadily decreased from 8% for the first sluicing to 0.3% for the last sluicing, indicating the limit of the technology for sluicing was also reached.

Regarding target date M-45-05M-T01, the waste retrieval results are provided below. The analysis of residual results will be provided to the State of Washington Department of Ecology (Ecology) in April 2004. A request for exception to the HFFACO retrieval criteria of 360 ft^3 pursuant to Appendix H is not necessary because the criteria were met.

The residual waste volume was calculated by the Computer-Aided Design (CAD) modeling method specified in "Tank 241-C-106 Component Closure Action Data Quality Objectives (DQO)", RPP-13889, Revision 1. The volume of residual waste was determined to be 359.0 ft^3, including 336.9 ft^3 of solids in the bottom of the tank, 4.8 ft^3 of solids contained with in abandoned

M-045-05L-T01 M-045-05M-T01

equipment (pipes, hoses, and suction floats) inside the tank, and 17.3 ft^3 of solids remaining on the stiffener rings inside the tank.

A pool of liquid with a volume of 11.3 ft^3 was also present at the center of the bottom of the tank. The liquid is residual sluicing water left in the tank heel that is inaccessible to the retrieval pump. However, this liquid was not included in the final residual waste volume because it is qualitatively different from the residual solids and contributes negligible risk in comparison to the solids.

In addition to the CAD modeling method, the residual waste volume was also determined by a waste immersion method using Enraf level detection instrumentation. In January 2004, after the last sluicing operation, water was added to Tank 241-C-106 until the entire waste residue in the tank was submerged. The water in Tank 241-C-106 was then transferred to Tank 241-AN-106. Based on the Enraf readings for 241-C-106 before the transfer and Enraf readings for 241-AN-106 after the transfer, the transferred volume was determined to be 364 ft^3, which compares favorably with the CAD modeling volume determination.

The results of the waste immersion method are consistent with and support the CAD modeling method. Also, the waste immersion method is typically more accurate than the CAD modeling method. For these reasons, ORP will seek to incorporate it into DQO documents for future retrievals, with Ecology's agreement.

ORP will provide Ecology a complete project report for the C-106 waste retrieval in April 2004 in accordance with the requirements in HFFACO Milestone M-45-05H. The project report will also include the residual waste analysis to complete the reporting requirements of target date M-45-05M-T01. Attached is a preliminary report that includes a summary of retrieval technology performance and the residual volume determination.

If you have any questions, please contact me, or your staff may contact Roger A. Quintero, Tank Farms Programs and Projects Division, (509) 373-0421.

Sincerely,

Roy J. Schepens
Manager

TPD: RAQ

Attachment

cc:
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ATTACHMENT
04-TPD-025

RPP-20110, Rev. 0
Retrieval Data Report for Tank 241-C-106

(23 pages total including coversheet)

Retrieval Data Report for Tank 241-C-106

Terry L. Sams

Richland, WA 99352
U.S. Department of Energy Contract DE-AC27-99RL14047

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Abstract: This report is a summary of the C-106 Retrieval Campaign Report and the Calculation for the Post-Retrieval Volume Determination for Tank 241-C-106. This report was transmitted to the Office of River Protection to be submitted to the Washington Department of Ecology.

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RETRIEVAL DATA REPORT FOR TANK 241-C-106

T. L. Sams
CH2M HILL Hanford, Inc.

Date Published
February 2004

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EXECUTIVE SUMMARY

This report describes the single-shell tank 241-C-106 (C-106) retrieval campaign performance summary, post-retrieval waste volume determination, and a basis for the conclusions. This report also describes the performance of two retrieval technologies for the full scale waste retrieval of C-106 and includes data to support completion of retrieval. Post-retrieval waste volume calculations provide an independent verification and comparison of the volume measurements obtained during the retrieval campaign. Modified sluicing and acid dissolution were the technologies deployed to remove the waste remaining in the tank and at completion had removed 2,771 gallons or 370 cubic feet. The final volume of 370 cubic feet included approximately 11 cubic feet of liquid waste. At the beginning of modified sluicing, the percent waste entrained in the waste slurry pumped from C-106 was approximately 8 percent solids. At termination of sluicing operations, the percent of waste entrained in the slurry had decreased to less than 0.3 percent solids. At less than 2 percent of waste removed for each additional batch of acid and at 0.3 percent of entrained waste in sluicing operations, the efficacy of these two technologies to remove waste had reached a level of performance that did not justify continued operation.

The volume determination used during retrieval operations was obtained by two methods; material mass balance calculations using a flow totalizer and waste immersion using Enraf[1] level detection. The in-process material mass balance calculations using flow totalizers indicated 2,584 gallons of waste removed (345 cubic feet), and waste immersion measurements of waste indicated 2,722 gallons of waste removed (364 cubic feet) (see Table ES-1). The final waste volume determination of topographical modeling using the video camera/CAD Modeling System was independent of the in-process measurements and confirmed mass flow and Enraf level volume estimates. The video camera/CAD Modeling System provided the final waste volume calculation of 370 cubic feet remaining in the tank. The final volume was calculated at 80 percent and 95 percent confidence levels and resulted in errors of plus or minus 18 percent and 27 percent, respectively.

The final interim data report for C-106 (delivered at a later date) will include information regarding residual tank waste characterization, Waste Management Area C post retrieval risk assessment, a feasibility study of available retrieval technologies with associated detailed cost estimates, actions to refine and develop tank waste retrieval technologies, and recommendations for further action.

[1] Enraf is a trademark of Enraf-Nonius, N.V. Verenigde Instrumentenfabrieken, Enraf-Nonius Corporation Netherlands, Rontegenweg 1, Delft, Netherlands.

Table ES-1. Tank 241-C-106 Waste Volume Summary.

Volume measurement technologies	Waste volume	
	gal	ft^3
Waste immersion	2,722	364
Material mass balance	2,584	345
Video camera/CAD Modeling System[a]	2,771	370

Note:

[a] Post-retrieval waste volume calculation.

Note: The waste volume on the stiffener rings that was calculated by the Video Camera/CAD Modeling System included approximately 17.3 ft^3 of the total volume of waste remaining in the tank. This waste volume was not included in the waste measurements of either waste immersion using Enraf measurements or material mass balance using the flow totalizer data.

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LIST OF TERMS

ATG	Advanced Technology Gauge
C-106	single-shell tank 241-C-106
CAD	computer-aided design
CCMS	CAD Modeling System
DQO	data quality objective
gpm	gallons per minute
HFFACO	*Hanford Federal Facility Agreement and Consent Order*

1.0 INTRODUCTION

This report describes the single-shell tank 241-C-106 (C-106) retrieval campaign performance summary and post-retrieval waste volume determination. This report also describes the performance of two retrieval technologies for the full scale waste retrieval of C-106 and includes data to support completion of retrieval. Post-retrieval waste volume calculations provided an independent verification and comparison of the volume measurements obtained during the retrieval campaign. The volume determination during retrieval operations was obtained by material mass balance calculations and waste immersion using liquid level detection. The final waste volume determination of topographical modeling using the video camera/CAD Modeling System (CCMS) was independent of the in-process measurements and was calculated at 80% and 95% confidence levels.

The final interim closure data report for C-106 (delivered at a later date) will include information regarding residual tank waste characterization, an updated Waste Management Area C risk assessment based on residual waste characterization of C-106, a feasibility study of available retrieval technologies with associated detailed cost estimates, actions to refine and develop tank waste retrieval technologies, and recommendations for further action.

1.1 PURPOSE

Full scale C-106 waste retrieval will remove existing residual tank waste remaining after past retrieval campaigns to criteria that would allow for interim tank closure. To achieve this goal, retrieval operations deployed retrieval technologies to meet the criteria of the *Hanford Federal Facility Agreement and Consent Order* (HFFACO) (Ecology et al. 1989) Milestone M-45-00. This defined an end state for interim tank closure that required the selected retrieval technology to remove as much waste from the tank as is technically possible and to leave no more than 360 ft^3 of residual waste in the tank.

The engineering data of the two retrieval technologies provided for an estimate of the waste volume remaining in C-106 and provided the basis for concluding that the technical limits of a modified sluicing/acid dissolution process had been met. This was indicated during retrieval operations by waste recoveries of less than 2% per acid batch processed, less than 0.3% of entrained solids by sluicing, the presence of unreacted acid in the last oxalic acid bath addition and an observed declining trend of waste removed for each technology. At this point of diminishing returns, the retrieval of waste was terminated.

The waste volume during retrieval operations was documented by waste immersion using the Enraf[1] level detection measurements and material mass balance calculations using a flow

[1] Enraf is a trademark of Enraf-Nonius, N.V. Verenigde Instrumentenfabrieken, Enraf-Nonius Corporation Netherlands, Rontegenweg 1, Delft, Netherlands.

totalizer. The post-retrieval waste volume measurements were documented by a CCMS. The CAD topographic modeling was developed and qualified by testing to establish a final volume of waste remaining in the tank at the completion of retrieval operations and to verify and compare with the waste immersion and material mass balance volume calculations.

The three-dimensional CCMS was the volume measurement method prescribed by the approved *Tank 241-C-106 Component Closure Action Data Quality Objectives* (DQO) (RPP-13889) document and the final approved method used to determine the post-retrieval waste volume. The accuracy and precision of the three techniques was quantifiable and is discussed in this report. The material mass balance process calculations were used primarily to track operational efficiencies of waste removal and to account for potential leakage of waste during transfer operations. Waste transfer system configuration and equipment accuracy was adequate to track waste slurry flow rates and in-tank waste level measurements as required by administrative procedures, but was not used for final calculations of waste volumes. The waste volume measurement uncertainties introduced by the transfer dynamics, varying waste forms, and waste geometries did not support the more rigorous requirements for final waste volume accuracy. These uncertainties are discussed in Section 2.3.1.

1.2 PRE-RETRIEVAL CONDITIONS

C-106 is a 530,000-gal single-shell tank that has been used to store mixed radioactive waste since its construction in 1947. To address a high-heat safety issue, the majority of waste stored in C-106 was successfully retrieved and transferred to double-shell tank AY-102 in 1998 and 1999 (Project W-320). However, approximately 36,000 gal of solid and liquid waste remained (RPP-12547, *Tank 241-C-106 Residual Liquids and Solids Volume Calculation*). Therefore, as part of the initial retrieval campaign preparation, 18,000 gal of liquid was pumped from C-106 to tank AY-102 in April 2003. The final retrieval campaign was initiated on August 7, 2003 with the addition of the first batch of oxalic acid, to retrieve the remaining solid waste to the goals established in the HFFACO Milestone M-45-00.

2.0 RETRIEVAL/VOLUME MEASUREMENT TECHNOLOGIES

2.1 RETRIEVAL TECHNOLOGIES

The sluicing campaigns of 1998 and 1999 removed most of the waste sludge from C-106, but did not remove the solid material in the tank, which were characterized as a cobble-like, stable agglomeration with varying dimensions up to 6 in. in size (RPP-13707, *Process Control Plan for Tank 241-C-106 Closure*). The acid dissolution and modified sluicing technologies were selected to remove the remaining waste to less than 360 ft^3 or to the limits of the selected technology, which ever is less. Acid dissolution reflects the use of oxalic acid to dissolve solids. Oxalic acid has historically been used at Hanford and other U.S. Department of Energy sites to decontaminate tanks and equipment. The phrase "modified sluicing" is used to reflect various

performance enhancing sluicing improvements that have been instituted since the 1999 retrieval effort. The combination of the two methods was designed to maximize removal of the present waste.

Through experience gained operating Savannah River Site facilities, such as the Defense Waste Processing Facility and tank farm evaporators, the effectiveness of oxalic acid to remove contamination on waste processing equipment was well known (WSRC-TR-2003-00401, *Waste Tank Heel Chemical Cleaning Summary*). As a result of studies performed at the Savannah River Site, the addition of oxalic acid was proposed to enhance the removal of the remaining waste in C-106. The Savannah River studies also referenced a variety of tests that were conducted using oxalic acid and determined that up to 70% volume of sludge could be dissolved with the oxalic acid process. In that study oxalic acid generally dissolved a larger percentage of sludge than other chemical agents or combinations of reactants. The Savannah River study also revealed that longer contact time, in addition to higher solution-to-sludge volume ratios, did not result in significant gains in waste dissolution. As was corroborated in laboratory testing at Hanford, the Savannah River testing of oxalic acid dissolution resulted in identification of hematite and boehmite in the insoluble sludge residue. The oxalic acid process was subsequently tested and its performance to dissolve waste was validated in laboratory testing at Hanford (RPP-16462, *Process Control Plan for Tank 241-C-106 Acid Dissolution*).

Laboratory-scale testing of acid-dissolution (using a sample of the C-106 waste) was performed to determine the effectiveness for dissolving the waste. This laboratory testing demonstrated that nearly 70% of the waste solids dissolved in oxalic acid (RPP-17158, *Laboratory Testing of Oxalic Acid Dissolution of Tank 241-C-106 Sludge*). To validate this technology, laboratory tests were conducted in two phases. The first phase examined whether significant sludge dissolution was feasible. The second phase optimized the amount of oxalic acid required and examined operating impacts such as the amount and type of gas generated and the impact on the double-shell receiver tank.

The first phase of testing showed that 50% to 70% of the sludge by weight could be dissolved in oxalic acid or in a mixture of oxalic acid and nitric acid. The mixture of both oxalic and nitric acids was only slightly more effective in dissolving the sludge than oxalic acid alone. Nitric acid would cause measurable oxidation of tank surfaces and therefore was not considered suitable for tank waste retrieval.

In the second phase, sludge was dissolved over a period of 18 days with the result that the reaction time to dissolve waste mass per day was effectively equivalent each day for the duration of the test. During the test, 68% of the water-washed sludge dissolved and the amount of sludge dissolved was nearly equivalent regardless of whether the volume of acid was added in a single batch or in three smaller batches. The acid dissolution reaction produced primarily carbon dioxide, and additional testing further indicated that mixing of the acid leachate with simulated tank AN-106 supernatant liquid produced large volumes of easily-compacted smaller solid material. The smaller compactable solids were determined to be insoluble residues that contained hematite, gibbsite, boehmite, and manganese oxalate.

2.2 RETRIEVAL OPERATIONS

Several modes of operation were used for the retrieval operation of C-106:

- Oxalic acid was added in discrete and accurately measured batches to C-106 through the mixer-eductor or the pump drop leg
- Acid was recirculated with the mixer eductor, followed by removal of the acid using the retrieval pump
- Water was continuously added to C-106 (between 85 and 350 gpm) through one of the two sluicers to mobilize and redistribute, as well as to remove solids, with subsequent or concurrent removal by the retrieval pump.

The oxalic acid dissolution process leached additional waste constituents directly from the sludge and also reacted with carbonates in the waste to increase solid waste porosity. Both the loss of carbonates and the agitation of the waste increased the surface area of solids and therefore the amount of surface sites available for leaching waste constituents during subsequent sluicing and acid dissolution events.

During acid dissolution, operations were performed using oxalic acid with a concentration of 0.9 molar. A mixer-eductor was used to recirculate the oxalic acid in C-106. The acid dissolution reaction for each acid batch reached steady state (i.e., reaction complete) after an average of seven days. After the acid reaction reached steady state, dissolved wastes were transferred via a pump to tank AN-106 at a controlled rate using a near surface buried or aboveground hose-in-hose transfer line. The mixer-eductor was removed after the fifth batch of oxalic acid was added to the tank. The mixer-eductor was replaced with a second sluicer that was placed in riser R-7.

Recirculation of the oxalic acid batches was no longer possible after removal of the mixer eductor following the fifth acid batch. However, good contact between the waste and acid was realized without recirculation as most of the waste had been leveled into a thin layer, allowing the majority of the waste to be submerged in acid.

The sluicing technology utilized a hydraulic process that deployed an articulated high-pressure water head that physically broke-up sludge, entrained solids and soluble waste, and moved the resultant slurry to the retrieval pump intake. Sluicing in this campaign was initiated after the third acid batch and used after each subsequent oxalic acid batch to remove additional waste.

2.3 WASTE VOLUME MEASUREMENT TECHNOLOGIES

The amount of waste resident in C-106 was determined by three methods. Material mass balance and waste immersion calculations were complementary techniques used during retrieval operations and after completion of retrieval, the CCMS was used as an independent method to establish the final waste volume based on approved DQO. In addition to the waste on the bottom

of the tank, the CCMS effort provided estimates of residual waste remaining on the tank wall and stiffener rings and waste contained in equipment identified as abandoned in the tank. The CCMS is described in detail in Section 2.3.3.

2.3.1 Material Mass Balance

Administrative controls (HNF-SD-WM-TSR-006, *Tank Farms Technical Safety Requirements*) required that a material balance be performed during all waste transfers to account for all liquid and solid waste bounded within the system. The data requirements for performing the material balance included the flow and time, flow totalizer at C-106 during transfers out, levels of C-106 and tank AN-106, normal transfer material balances, the volume of acid put into the tank, the amount of water added, and the volume of caustic rinse.

The C-106 liquid surface was expected to exhibit a slight negative trend during monitoring periods because of evaporative losses. In addition, the waste was expected to effervesce (offgas) due to the acid reaction with carbonates with the effect of a slight loss of mass. The oxalic acid dissolution process therefore introduced inherent inaccuracies in the material mass balance calculations that although minimal, were not easily measured. For example, the amount of offgas could not be measured with the effect that the material balance could be inaccurate by a small percentage of the total sludge left in the tank. Additionally, solids changed volume as they were dissolved in the acid and although the mass remained constant, the volume and level could have been affected. Eventually some of the oxalates produced by the acid reacting with waste solids and had the potential of forming insoluble oxalate solids. The acid was neutralized when pumped to tank AN-106 and the dissolved solids re-precipitated as different chemical compounds. The oxalic acid was neutralized into insoluble sodium oxalate, so additional solids that were not present in C-106 were being created.

2.3.2 Waste Immersion Technology

Waste immersion required filling C-106 with a known volume of liquid to a tank level that covered the waste. This volume of liquid was compared to the known volume of tank geometry corresponding to the level of liquid in the tank. The difference described the volume of waste in the tank. The Enraf level detectors were used to determine the liquid level that provided input to the volume calculation. Level changes were measured using the Enraf Series 854 Advanced Technology Gauge (ATG). The Series 854 ATG is widely used throughout industry and specifically in the Hanford tank farms for primary tank waste surface level measurements. It uses the principle of buoyancy to track level changes within each tank. A displacer is suspended from a thin wire and lowered into the tank until the instrument load cell detects a loss in weight resulting from the displacer contacting a liquid or solid surface. The Enraf system maintains a weight that is a fraction less than the true weight of the displacer, such that the displacer is primarily suspended from the wire and only slightly supported by the surface medium. The instrument tracks the position of the displacer and continuously reports the level of the encountered liquid or solid.

The instrument is capable of an absolute accuracy of ± 0.04 in. at 100 ft, and a repeatability of ± 0.004 in. under ideal conditions, (vendor specification). Hanford uses the top of a ball valve as the primary depth reference, but because the calibration surface is not flat this practice introduces a potential calibration error of ± 0.10 in. Therefore, the applicable accuracy is ± 0.10 in. based on the rounded ball valve calibration. And although the true precision (repeatability) of the gauge is ± 0.004 in., Hanford only reads the gauge to two decimal places. As a result, the applicable precision for Hanford applications is ± 0.01 in.

2.3.3 Video Camera/CAD Modeling System

The CCMS documents the calculation of the post-retrieval residual waste volume in the bottom of the tank and was included in the DQOs. Also included in the CCMS analysis are estimates of the residual waste remaining on the tank wall, the stiffener rings, and in equipment abandoned in the tank. Waste volume was determined by a topographic model based on information obtained from video observations and observations of still video. To support these calculations, an in-tank video of C-106 was taken on February 4, 2004. The camera was located in riser R-14 and at heights of 25, 15, and 8 ft above the bottom of the tank.

2.3.3.1 CCMS Error Determination. RPP-18744, *Results of the Video Camera/CAD Modeling System Test*, contain the calculations for the estimate of percentage error in calculating waste volume using the CCMS method. Mock-up tests at the Cold Test Facility were performed to provide data for estimating the percentage error following the approved RPP-17663, *Test Plan for the Video Camera/CAD Modeling System*. The approved test plan calls for an 80% confidence level for the error used in conjunction with the CCMS for the final residual volume estimate of solid waste. This error was determined to be 18%, at the 80% confidence level, for the total volume. The error calculated at the 95% confidence level is 27% and was calculated using the same methods as for the 80% confidence level in RPP-18744.

2.3.3.2 CCMS Tank Bottom Waste Volume Calculations. The volume of the residual waste in the bottom of C-106 was determined using the CCMS with the AutoCAD Land Development Desktop Release 2i software. The AutoCAD Land Development Desktop is being used by the CCMS to determine waste volumes remaining in a waste storage tank by calculating the volume within the three-dimensional coordinates of a series of points, which are identified on the waste surface. The waste surface point coordinates are determined using observations from a video camera imaging system in conjunction with known tank geometry and available tank and waste information. The tank bottom dimensionally is an inverted dome (dished bottom) with a spherical segment base radius of approximately 33.74 ft. The dished bottom center is 12 in. deep and has a volume of approximately 13,380 gal. Internal tank dimensions are documented in HNF-5267, *Waste Retrieval Sluicing System Campaign Number 3 Solids Volume Transferred Calculation.*

AutoCAD Land Development Desktop was also used to model the residual waste configurations on the surface of various tank components and to determine these volumes. Using the software, a digital terrain model was built with the information obtained from viewing a video recording and still photographs taken from the video (RPP-19866, *Calculation for the Post-Retrieval Waste Volume Determination for Tank 241-C-106*).

2.3.3.3 CCMS In-tank Equipment Waste Volume Calculations. The amount of residual waste in the equipment in C-106 was determined by using the in-tank video and tank information to determine the equipment remaining in the tank. Video evaluation was also used to estimate the dimensions of hoses and pipes in the tank and this information, including equipment drawings, was used to estimate the volume of waste in the equipment. The calculations for the residual waste volume in the equipment are provided in RPP-19866, Appendix B.

2.3.3.4 CCMS Stiffener Ring Waste Volume Calculations. The four stiffener rings are structural members welded to the side of the interior tank wall. The stiffeners were observed to have the heaviest amount of crusted waste on the bottom ring closest to the bottom of the tank. The accumulated waste dissipated as the rings graduated up the wall with the top ring having no observed waste. The amount of waste on the stiffener rings was estimated by visually estimating the size of any waste clumps and by visual examination of still video to determine if a waste film was present. Based on the observations, an average waste thickness was estimated for each stiffener ring and used for the calculation to determine waste volume (RPP-19866).

2.3.3.5 CCMS Tank Wall Waste Volume Calculations. Based on the lack of video evidence of waste on the tank side wall, the volume of waste on this surface was estimated to be zero. Only a small amount of waste was observed on the tank wall, and because it appeared to be the result of the sluicing of the stiffener rings, the volume of that waste was included as part of the stiffener ring calculation. No other waste was observed on the tank wall.

2.4 RETRIEVAL PERFORMANCE

Several methods were used to evaluate the removal of waste during retrieval operations. The purpose was to evaluate the combined effectiveness of modified sluicing and acid dissolution to remove waste from the tank to the limits of these two technologies. During retrieval operation, material balance and Enraf measurements were conducted to determine when the retrieval technologies would reach the point of diminishing returns. Material balances were maintained to estimate the volume increase in tank AN-106 relative to the volume of material added to C-106. The volume increase in tank AN-106 was compared to the inputs into C-106 and provided an estimate of the waste removed from C-106. Carefully measured volumes of both oxalic acid and water were added to C-106. The volume of acid or water pumped from C-106 also was carefully measured. The difference between the volume pumped to tank AN-106 and the volume of acid and water added also provided an estimate of waste removed for each operation.

Waste volume estimates were established using waste immersion. Before the start of retrieval operations, an estimate of the volume of waste remaining in C-106 was made and a known volume of water was added to the tank and verified by a liquid level measurement. By this method, the amount of waste left in the tank prior to the start of this retrieval was estimated to be approximately 18,000 gal, most of which were solids.

After the last sluicing operation, the volume of waste left in C-106 was estimated by submerging all the waste in the tank (to a known tank geometry and volume) and subsequently measuring the volume of liquid transferred from the tank. The difference between the known volume that submerged the waste and the transferred volume was the estimate of the remaining waste. The

amount of waste removed per unit batch was tracked to determine the effective completion of the acid reaction and to determine an endpoint of diminishing returns for the selected technology.

Waste samples were taken to evaluate the waste inventory per volume of waste and to identify the contaminants of concern. Material mass balance and liquid level Enraf readings were used to document the efficacy of waste removal and ultimately the performance of both the modified sluicing and oxalic acid waste dissolution technologies.

2.5 CAMPAIGN CHRONOLOGY

The chronology for the retrieval operations in C-106 is shown below.

- About 187,000 gal of waste were removed from C-106 during the retrieval operation in 1998 and 1999. At that time 62,000 gal of residual waste were left in the tank which included an estimated 5,200 gal of solids.
- About 18,000 gal of residual supernatant was pumped from the tank, starting April 1, 2003. Evaporation of water reduced the volume that was left following the end of sluicing in 1999 to about 36,000 gal.
- The sluicer in riser R-3 was used to level the solids and rinse soluble constituents. Approximately 37,000 gal of sluicing liquid was pumped, starting June 9, 2003. Starting waste volume was determined.
- The first oxalic acid batch was added, starting August 7, 2003.
- The second oxalic acid batch was added, starting August 27, 2003.
- The third oxalic acid batch was added, starting September 16, 2003.
- To prepare for sluicing, the pump was replaced and the new pump tested, starting October 3, 2003.
- The first modified sluicing operation was conducted, starting October 14, 2003.
- The fourth oxalic acid batch was added, starting October 20, 2003.
- The second modified sluicing operation was conducted, starting October 28, 2003.
- The fifth oxalic acid batch was added, starting October 30, 2003.
- To allow for additional spray head coverage, the mixer-eductor was replaced by the second sluicer, starting November 6, 2003.
- The third modified sluicing operation was conducted, starting December 4, 2003.
- The sixth oxalic acid batch was added, starting December 14, 2003.

- The fourth modified sluicing operation was conducted, starting December 28, 2003.

The results of material balance calculations are shown in Table 1. The starting waste volume was determined by waste immersion calculations and video review. The ending volume is the preliminary estimate from the volume increases in tank AN-106 and material mass balance calculations.

Table 1. Material Balance Calculations for Oxalic Acid and Sluicing Batches in 2003.

Date	Oxalic acid added (gal) [a]	Water including sluice water added (gal)[b]	Estimated waste removed (gal)[c]	Waste remaining (estimated from transfer balances) (gal)	Waste remaining (estimated from transfer balances) (ft^3)
Start	--	--	--	18,000	2,406
August 7	15,803	579	1,441	16,559	2,214
August 27	25,957	1,343	2,131[d]	14,428	1,929
September 16	31,686	1,021	4,727[d]	9,701	1,297
October 14	--	56,160	4,873	4,828	645
October 20	31,772	1,960	~2,597[d]	7,425	993
October 28	--	46,472	1,607	5,818	778
October 30	15,632	908	80	5,738	767
December 4	--	59,228	857	4,881	653
December 14	21,169	315	547	4,334	579
December 28	--	83,501	217	4,117	550
Total	142,019	251,487	13,883	--	--

Notes:

[a] Acid was added in measured batches.

[b] Water additions are based on metered inputs.

[c] Waste removed is calculated by subtracting inputs (acid or water added) from the volume change in tank AN-106 as measured by Enraf.

[d] The estimate of waste removed is dependent on the liquid heel remaining from the previous batch. The liquid heel volumes varied significantly for some of the September and October batches. Two different pumps were involved in these operations.

~ = approximately.

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2.6 RESULTS

2.6.1 Acid Dissolution

To ensure all waste was subject to an acid reaction, the sludge was leveled with sluice water before the initial addition of acid. The estimated 18,000 gal of waste left in the tank prior to retrieval were equivalent to a layer that averages about 6.5 in. across the bottom of the 75-ft diameter tank. After oxalic acid was added, the waste was soaked to allow the waste digestion process to complete (acid reaction stabilized). During the soak period, the acid pool was agitated to facilitate the acid-waste reaction. After completion of the soak period, the retrieval pump was used to remove the solution from the tank.

A summary of the material balance of the acid batches is presented in Table 2. The material balance for the acid batches was recorded to determine the approximate volume of waste that was transferred with each batch. The extended contact time for acid batch #5 resulted from additional field activities to remove the mixer-eductor and to install the second sluicer. It was not included in the average of seven days for an acid bath to reach steady state.

The pH of the acid in C-106 was monitored during the last acid batch. The pH of the solution showed a gradual increase in the first six days and then showed no increase (steady state) during the rest of the contact period. The increase in pH indicates that acid reacted with the waste heel. The average pH over the last four days was approximately 0.79, but never reached the expected acid depletion endpoint (a pH of about 1.5), indicating that the exposed waste was fully reacted, i.e., the limits of this technology had been reached.

The waste recoveries of less than 2% per acid batch processed and the presence of unreacted acid in the last oxalic acid bath addition combined with an observed declining trend of waste removed for each technology indicated a limit of this technology to remove addition waste from C-106.

Table 2. Material Balance Estimates for Oxalic Acid Additions to C-106.

Acid batch	Volume of acid added (gal)	Volume of water added (gal)	Volume transferred to tank AN-106 (gal)	Volume increase (gal)	Approximate duration of acid contact (days)
1	15,803	579	17,829	1,441	12
2	25,957	1,343	29,431	2,131[a]	5
3	31,686	1,021	37,434	4,727[a]	5
4	31,772	1,960	31,135	~2,597[a]	6
5	15,632	908	16,620	80	35[b]
6	21,169	315	22,031	547	9

Notes:

[a] The estimate of waste removed is dependent on the liquid heel remaining from the previous batch. The liquid heel volumes varied significantly for some of the September and October batches. Two different pumps were involved in these operations.

[b] The Mixer–eductor was removed and the 2nd sluicer added leading to this extended soak of 35 days.

~ = approximately.

2.6.2 Modified Sluicing

The equipment configuration of the single sluicing nozzle reached the limit of operational effectiveness to retrieve solid waste after the fourth acid dissolution cycle and second sluicing retrieval. The sluicer nozzle located in riser R-3 was no longer effective in moving solids from the far side of the tank to the pump, which was in the middle of the tank. Additionally, sluicing created piles of solids against the tank walls in the location of the tank circumference farthest from the sluicer toward the opposite wall. The motive force of the sluicer nozzle at this configuration was not able to move the remaining waste.

In response to this diminished performance, a second sluicer nozzle was installed in the tank in riser R-7 and the second sluicer was used to break up the remaining waste piles. Following this sluicing action, oxalic acid was added for a sixth time to dissolve the additional waste. The residual waste volume represents the quantity remaining after sluicing following the sixth oxalic acid addition.

Table 3 contains the material balance of the sluicing operations. The material balance for the sluicing operations was recorded to determine the approximate volume of waste that was transferred with each batch. A sluicing efficiency based on percent solids in the slurry was calculated as a measure of the technology performance. The gradual decrease from 8% solids in sluicing operation number 1 to 0.3% in sluicing operation number 4 shows that the limits of technology (modified sluicing) had been reached.

Table 3. Material Balance Estimates for Sluice Water Additions to C-106.

Sluice Operation	Volume of water added (gal)	Volume transferred to tank AN-106 (gal)	Volume increase (gal)	Approximate efficiency, estimated volume percent solids
1	56,160	61,033	4,873	8
2	46,472	48,079	1,607	3.3
3	59,228	60,085	857	1.4
4	83,501	83,718	217	0.3

The average sluicing efficiency in the first sluicing operation was about 8% entrained solids by volume. The amount of entrained solids removed was estimated from the volume increase in tank AN-106 as compared to the volume of water used to sluice the waste in C-106. The retrieval efficiency in subsequent batches was declining and was calculated at 3.3%, 1.4%, and 0.3%. At the completion of the last retrieval the metal bottom of the tank had been exposed throughout the circumference of the tank. The exception was the solids near the tank wall that were out of reach of the nozzle motive force or in the shadow of the sluicing equipment. Additionally, some pieces or piles of debris remained in place because they were too large to mobilize by sluicing or were too large to enter the pump intake.

It should be noted that the efficiency calculations are affected by the amount of solids left in the pump heel volume. If the pump heel included all solid waste before sluicing and no solid waste existed after sluicing, the waste solid volume would be changed by as much as 800 gal. For example, during the fourth sluicing operation, the maximum amount of solids removed could have been as much as 272 gal plus 800 gal resulting in 1,072 gal. The efficiency for this example would have been about 1.3%. Since a significant amount of water is always left in the pump heel before and after sluicing, the actual efficiency would have been closer to the efficiency calculated in Table 3.

2.6.3 In Process Waste Volume Measurement

The water in the C-106 was pumped to tank AN-106 on January 20, 2004, and based on the tank AN-106 Enraf liquid level readings, the volume transferred was 39,332 gal. The difference between the volume measured in C-106 and the transferred volume describes the estimated volume remaining in C-106, which was about 2,722 gal (364 ft^3).

The volume of water transferred to tank AN-106 was also measured by a flow totalizer that indicated 39,470 gal. The estimated volume remaining in C-106 based on the flow totalizer readings were approximately 2,584 gal (345 ft^3). The subsequent video examination of the tank bottom after water removal showed a small liquid heel surrounding the pump near the center of the tank. The remaining solids were thinly distributed around the bottom of the tank and solids are visible in the liquid heel.

2.6.4 CCMS Waste Volume Determination

2.6.4.1 Summary of Results. The total volume of post-retrieval residual waste in C-106 and the waste volumes associated with the various waste components are given in Table 4 and were calculated by the CCMS. The total post-retrieval waste volume in C-106 is estimated to be 370+67/-63 ft^3 (2,771+499/-471 gal). This estimate using the CCMS method is in agreement with the waste immersion using the Enraf level measurements (364 ft^3) and the material mass balance using the flow totalizer (345 ft^3). The waste volume included in equipment remaining in the tank adds approximately 5 ft^3 to the total, while the waste volume on the stiffener rings comprises about 5% (approximately 17.3 ft^3) of the total volume of waste remaining in the tank.

Table 4. Tank 241-C-106 Total Waste Volume and Component Waste Volumes.

Component	Waste volume			Estimated error (%)
	m^3	ft^3	gal	
In the bottom (dish) of the tank (solids and liquids)	9.861	348.19	2,605	±18
In equipment in the tank	0.137	4.84	36	+0/-25
On the stiffener rings	0.490	17.30	129	+18/-0
On the tank wall	0	0	0	n/a
Total	10.488	370.33	2,771	+18/-17

Note:
n/a = not applicable.
Sum of gallons does not equal total gallons because of rounding.

2.6.4.2 Estimate of Waste in Bottom of Tank. Table 5 shows the volumes of solids and liquids estimated by the CCMS. The waste is uniformly spread out over the bottom of the tank with several raised areas of solids observed and the majority of the raised areas are located on the northeast side of the tank near the tank wall. Additionally, a kidney-shaped pool of liquid

extends northeast from around the bottom of the center of the tank. The determination of the uncertainty associated with the CCMS method is discussed in RPP-19866. The error is estimated to be ±18% or ±63 ft^3 (±469 gal) at an 80% confidence level per RPP-13889. The error determined at the 95% confidence level is 27% and was calculated using the same methods as for the 80% confidence level in RPP-18744.

Table 5. Tank 241-C-106 Waste Volume in Tank Bottom.

Component	Waste volume		
	m^3	ft^3	gal
Solid phase	9.541	336.89	2,521
Supernatant phase	0.320	11.30	85
Total	9.861	348.19	2,605

2.6.4.3 Estimate of Waste Volume in Equipment. Potential waste-containing equipment remaining in the tank included three transfer pumps, three suction floats, and various lengths of hoses and pipes. Two of the transfer pumps are known to contain no waste because they were flushed and drained. The volume in the third pump was assumed to be negligible since it was drained after its last use. Therefore these components are not included in Table 6.

Using the upper and lower estimates made for hose lengths and diameters, the volume of waste contained in the equipment remaining in C-106 is estimated to range from 4.7 ft^3 (35 gal) to 4.8 ft^3 (36 gal). Table 6 provides the breakdown, by component, for the upper estimate and these volumes were calculated assuming that the waste holding portions of this equipment was full of waste. However, the suction floats were positioned on the bottom of the tank with their openings facing downward and thus may contain little or no waste. Therefore, the estimated error for the waste volume in the equipment is +0/-1.21 ft^3 (+0/-9 gal).

Table 6. Tank 241-C-106 Waste Volume in Equipment in Tank.

Component	Quantity	Total waste volume		
		m^3	ft^3	gal
Suction floats	3	0.034	1.21	9
3-in. hoses	2	0.032	1.13	8
4-in. pipes	2	0.069	2.42	18
Hose attached to thermocouple tree	1	0.002	0.08	1
Total		0.137	4.84	36

2.6.4.4 Estimate of Waste on Stiffener Rings. The waste volume remaining on the stiffener rings is estimated to be 17.3 ft^3 (129 gal) and volumes for each ring are provided in Table 7. No

waste was observed in the video on the top ring which is also above the maximum design waste level and therefore the volume is estimated to be 0 ft^3. Estimates for the lower rings are based on best estimates of the average waste thickness on each ring ($^3/_8$ in., ¾ in., and 1 in. for stiffener rings #2, #3, and #4, respectively. The error associated with the thickness is estimated to be $+^3/_8$ in. and –0 in., resulting in a volume error of +3/-0 ft^3 (+23/-0 gal).

Table 7. Tank 241-C-106 Waste Volume on Stiffener Rings.

Component	Waste Volume		
	m^3	ft^3	gal
Stiffener ring #1 (top)	0	0	0
Stiffener ring #2	0.086	3.05	23
Stiffener ring #3	0.173	6.11	46
Stiffener ring #4 (bottom)	0.231	8.14	61
Total	0.490	17.30	129

Note:
Sum of gallons does not equal total gallons because of rounding.

2.6.4.5 Estimates of Waste on Tank Wall. The tank wall was estimated to have no waste on its surface. Only a small amount of waste was observed on the tank wall, and because it appeared to be the result of the sluicing of the stiffener rings, the volume of that waste was included as part of the stiffener ring calculation. No other waste was observed on the tank wall.

2.7 CONCLUSIONS

The objective of this retrieval was to remove tank waste to the limits of the retrieval technologies selected and to leave no more than 360 ft^3 of residual waste in the tank. The performance data of the two retrieval technologies tracked the efficacy of the technologies to remove waste, provided an estimate of the waste volume remaining in C-106, and provided the basis for concluding that the technical limits of a modified sluicing/acid dissolution process had been met. The technical limits of modified sluicing and acid dissolution were indicated by a declining trend of waste recovery resulting in 0.3% solids being recovered in the last sluicing operation and an unreacted oxalic acid in the last acid batch. The process data indicate that limits of technology for both the modified sluicing and oxalic acid technologies have been reached

The above discussion demonstrates three key points to conclude that the modified sluicing/acid dissolution process reached the technological limits to remove waste. The waste that was capable of acid dissolution as described in the process control plan has fully reacted based on the steady state pH readings recorded for the acid batches; the waste that can be mobilized to the pump intake by sluicing has been moved to within the influence of the pump and retrieved as evidenced by the video; and the pump was operated until loss of suction occurred, which indicates the limit of the pump to remove waste at the lowest level of pump suction.

The waste volume remaining after retrieval completion has been documented by a number of methods that included prior to completion, waste immersion and material mass balance calculations. At retrieval completion a CCMS calculation was performed to determine the remaining waste volume. The CAD modeling of solid and liquid waste was developed and qualified by testing to establish a final volume of waste remaining in the tank at the completion of retrieval operations and to verify and compare with the waste immersion estimate via Enraf level readings and material mass balance volume calculations.

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