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WASTE MANAGEMENT PROGRAM TECHNICAL PROGRESS REPORT

APRIL - JUNE, 1983

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E. I. du Pont de Nemours & Co.
Savannah River Plant and Laboratory
Aiken, SC 29808

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ABSTRACT

This quarterly report provides current information on operations and development programs for the management of radioactive wastes from operation of the Savannah River Plant. The studies on environmental and safety assessments, process and equipment development, TRU waste, and low-level waste are a part of the Long-Term Waste Management Technology Program. The following studies are reported for the SR Interim Waste Operations Program: surveillance and maintenance, waste concentration, low-level effluent waste, tank replacement/waste transfer, and solid waste storage and related activities.

FOREWORD

This quarterly report provides information on the current status of plant operations and research and development programs for the management of radioactive wastes at the Savannah River Plant. These efforts are funded by the Office of Nuclear Waste Management of the U.S. Department of Energy.

This technical progress report consists of two general sections: Long-Term Waste Management Technology and SR Interim Waste Operations.

Long-Term Waste Management Technology is currently planned to solidify high-level waste and ship the contained wastes to a Federal repository.

In the reference design process for high-level waste, the salt will be dissolved, and the resulting solution will be used to slurry the sludges from the tanks where they are currently stored. The salt solution will be separated from the sludge by centrifugation. More than 99% of the ^{137}Cs and residual ^{90}Sr will be removed from the salt solution by ion exchange. The remaining liquid will be evaporated to salt cake (mostly sodium nitrate) that contains only a small fraction of the total biologically hazardous radioactive material. The ^{137}Cs and ^{90}Sr will be eluted from the ion exchange resin and combined with the sludge (containing most of the ^{90}Sr and ^{239}Pu). The combined eluate and sludge will be incorporated into borosilicate glass and shipped to a Federal repository.

The Defense Waste Processing Facility (DWPF) is being designed to incorporate the Savannah River Plant (SRP) defense waste into borosilicate glass according to the reference design process.

The current operational status for the liquid waste treatment and storage facilities at the SRP is reported for this quarter. The research and development program in support of interim tank storage of liquid and crystallized plant waste comprises: (1) analysis of the present tank system; (2) development of improved processes and equipment; (3) corrosion studies; and (4) analysis of environmental effects.

A concurrent program is developing technology for long-term management of these wastes. Because the long-term plan includes solidification and temporary storage in a retrievable storage facility, interim treatments must permit retrieval of the waste and incorporation into a high-integrity form. The SRP waste management program requires that all sludge be removed from waste tanks before tank retirement.

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HIGHLIGHTS

LONG-TERM WASTE MANAGEMENT TECHNOLOGY

Preparation of environmental safety documentation continued in support of construction and operation of the Defense Waste Processing Facility. (Page 17)

All chapters and appendices of the Strategy Recommendations Document have been drafted. A review of most drafted sections has been completed. (Page 18)

Removal of technetium (Tc-99) during decontamination of SRP high-level waste salt has been considered as a means for lowering residual radioactivity levels of the salt prior to disposal by saltstone burial. (Page 19)

The 8800-hour test cesium chloride capsule was completed and opened at ORNL to visually examine the inner capsule for pitting (Page 34)

Two waste forms, glass and ceramic, may be suitable candidates to immobilize liquid Fluorinel waste to result in a reduced volume of final waste. A preliminary investigation of the conditions required to produce these waste forms has been completed. (Page 35)

The Fourth Semiannual Workshop on the Leaching Mechanisms of Defense High-Level Waste Forms was held at the Materials Research Laboratory on the campus of Pennsylvania State University. (Page 39)

The theoretical melter performance of Frit 165 waste is examined and compared with that of Frit 131 waste and assesses the suitability of Frit 165 waste for use in the DWPF melter. (Page 42)

The large slurry-fed melter was fed premelted black frit to obtain a melt rate equal to that of the larger DWPF melter. This was necessary to simulate the pouring conditions of the DWPF melter to gain knowledge of canister filling, sealing, and decontamination processes. (Page 58)

An energy balance has been performed on the large slurry-fed melter not only to optimize the slurry-fed melting process but also to determine differences in melter operation with different glass compositions. (Page 71)

Flow rate measurements will be required for both liquid and slurry feed streams in the DWPF. The slurry feed streams have been anticipated to be the most difficult feed streams to monitor for flow rate due to their abrasivity, variable rheology, and high solids content. Additional conditions for DWPF flowmeter applications are discussed. (Page 88)

Large quantities of both formic acid and nitric acid will be routinely handled in the DWPF. A basis was established to assure that the facility design precludes the uncontrolled mixing of these two acids. Technical data concerning formic/nitric acid chemistry and an assessment of the justification for the present design bases is presented. (Page 105)

The small cylindrical melter-2 (SCM-2) was successfully restarted using a graphite slurry. This startup method is being evaluated as a possible backup procedure in the event lid heaters fail. (Page 111)

The mechanisms by which radioactive contamination would be bonded to a DWPF canister surface are being investigated. The canister decontamination process for the DWPF, air-injected slurry blasting, was selected on the basis of its ability to remove contamination bonded to the canister by the most severe temperature conditions expected. (Page 121)

Two contaminated water processing facilities are being proposed, one for F Area and one for H Area. The facilities are to treat both canyon cooling water and waste farm storm runoff in the event of an accidental radioactive release. (Page 127)

The full-scale precipitation test facility was designed and built at the engineering test facility in support of the salt decontamination demonstration taking place in Tank 48H. The facility uses a precipitation process to remove radionuclides from waste supernate. (Page 131)

Sodium tetraphenylborate and sodium titanate have been demonstrated as two reagents which can decontaminate high-level radioactive liquid waste containing cesium, strontium, and plutonium. (Page 133)

The procurement, preparation, and quality control of the reagents for the in-tank salt processing demonstration are summarized. (Page 134)

A process has been described for removing technetium by adsorption on the strong base ion exchange resin (Dowex® 1-X8). (Page 139)

A method that was recently developed to determine Tc-99 in DWPF decontaminated supernate solutions is described. (Page 152)

A preliminary Technical Data Summary describes a reference process for solid transuranic wastes. (Page 165)

A full-scale incineration process for Savannah River Plant low-level beta-gamma combustible waste was demonstrated at the Savannah River Laboratory using nonradioactive wastes. (Page 183)

The Solvent Waste Incineration Facility for Testing (SWIFT) burned 1520 gallons of nonradioactive solvents in four campaign runs. These tests were to develop and demonstrate an effective method for permanently disposing of 150,000 gallons of spent Purex solvent that is stored in underground tanks in the burial ground and the 2000 gallons generated annually. (Page 190)

The Du Pont Engineering Services Division was contacted to perform a relief analysis of the Solid/Solvent Waste Incinerator Facility for Testing and to recommend a method of explosion protection. The investigation for each component of the facility is summarized and alternatives for explosion protection for the system are suggested. (Page 207)

Gas samples were taken during SWIFT incinerator operation to determine the composition of the exhaust and ensure that emissions met state standards. Stack sampling data were also used to measure the efficiency of the neutralization and fixation process of chlorine and phosphorus. (Page 210)

A process to solidify beta-gamma incinerator ash in concrete, called ashcrete, is envisioned to be included in the Phase II and Phase III demonstration of the beta-gamma incinerator. The overall scope of the ashcrete program is to: (1) specify process equipment, (2) install and test the process equipment at TNX, and (3) to relocate the process equipment to the beta-gamma incinerator site in H Area. (Page 217)

Results from analyses of 88 groundwater wells in or near the 643-G and 643-7G low-level, radioactive waste burial grounds show a general decrease in the concentration of mercury from last year. (Page 222)

The low-level solid radioactive waste expected to be generated by the new Naval Reactor Fuel Materials Facility is described and the compatibility of this waste with the proposed greater confinement disposal facility is assessed. (Page 227)

A capillary barrier to reduce rainwater infiltration into the proposed saltcrete landfill is described. (Page 234)

Saltcrete buried in a landfill in the unsaturated zone will be leached by two mechanisms. One is a mechanism controlled by the diffusion of salts out of saltcrete. The second is dissolution and removal of salts from the saltcrete by permeating water and has been studied during the past two years because of its potential to dominate salt releases from saltcrete. (Page 243)

The calculated values for the F- and H-Area ^{85}Kr emissions for the period October 1982 through January 1983 have been received from the Environmental Analysis and Planning Division. (Page 247)

Design progress for the DWPF is proceeding satisfactorily. At the end of the quarter, the design is estimated to be about 30% complete. Actual construction of the DWPF is expected to begin in early FY-1984 with some early site work planned for late FY-1983. Revisions to the melter off-gas system resulted in an estimated eight-week delay in the project with mechanical completion currently anticipated for January 1988. (Page 249)

SAVANNAH RIVER INTERIM WASTE OPERATIONS

Ultrasonic thickness measurements by the Equipment Engineering Department have detected pitting in some of the waste tank purge condenser shells. (Page 259)

Radiolytic decay heat removal from Tank 39H was calculated based upon May 10 conditions and was in good agreement with the heat generation rate calculated from TAFI (computer program). (Page 260)

The F-Area seepage basins continue to exhibit low seepage rates. (Page 261)

Coordination of SRP and SRL groups in activities related to the permanent closure of the SRL earthen seepage basins continued during the second quarter of CY-1983. (Page 262)

An extensive investigation program is under way to study the current disposition of the old TNX basin (Building 904-76G). (Page 263)

All radioactive releases to the F-Area seepage basins during February, March, and April were below the monthly and prorated year-to-date release guides. (Page 263)

All radioactive releases to the H-Area seepage basins in February and March were below the monthly and prorated year-to-date release guides. However, during April the monthly release guide for ^{124}Sb and ^{125}Sb was slightly exceeded. (Page 263)

Mercury released to the H-Area seepage basins decreased from six pounds in February to two pounds in March and April, respectively. (Page 264)

The Waste Processing Technology Division began process development work for the contaminated water control facilities in March. (Page 264)

Construction of the new Nonradioactive Hazardous Waste Interim Storage Facility, Building 709-G, was completed in April. (Page 266)

A National Environmental Protection Act checklist was completed for the nonradioactive hazardous waste landfill in April. (Page 266)

Groundwater studies were initiated in April at the Silverton Road waste site and the CMP pits to determine the extent of chlorinated organic contamination. (Page 268)

Interstitial salt solution in Tank 10H indicates both nitrate and corrosion inhibitor concentrations were outside technical standard limits. (Page 268)

The salt decontamination demonstration was completed on April 14 with the end of the third precipitate wash. (Page 269)

Waste Management and Du Pont Engineering Department representatives met in April to revise the scope of work for long-term salt processing. (Page 272)

Construction of the annulus cleaning demonstration facility was completed in April. (Page 274)

Initial TNX run-in of the three slurry pumps for Tank 17F was conducted in April. Construction installed the three slurry pumps and the telescoping transfer pump in Tank 17F during June. (Page 274)

A design review for extended sludge processing was held in May with representatives of Waste Management and the Du Pont Engineering Department. (Page 275)

Advanced authorization for $300,000 was received in April to begin procurement of the TRU waste assay system. (Page 276)

Section II of the Inventory Workoff Plan Draft document was completed in April and submitted to DOE/ALO and TWSO on schedule. (Page 276)

The WIPP Review Committee met with Waste Management Technology personnel in June to review comments on the Savannah River Certification Plan for Newly Generated, Contact Handled TRU Waste. (Page 277)

SRL and Waste Management continue to develop the process design to install the Plutonium-238 Waste Incinerator. (Page 277)

In January, a four-hour test was conducted on the Shirco incinerator in Dallas, TX, to evaluate the design for potential application to the Plutonium-238 Waste Incinerator. (Page 278)

Construction of the Beta-Gamma Incinerator Facility is 80 to 85% complete. (Page 279)

SRL is developing the ashcrete process to solidify ash from the Beta-Gamma Incinerator, and the design for this process is 90% complete. (Page 280)

A request for technical assistance for $875,000 was written and approved in June for Waste Disposal Technology to develop, procure, and test the ashcrete process. (Page 281)

LONG-TERM WASTE MANAGEMENT TECHNOLOGY

HIGH-LEVEL WASTE TECHNOLOGY

Environmental and Safety Assessments (SRL)

Environmental Monitoring During DWPF Construction (SRL)

The first of a series of quarterly reports has been issued summarizing water quality data obtained by the Savannah River Plant (SRP) and the Savannah River Ecology Laboratory (SREL) from ten sampling stations surrounding the DWPF site and downstream on Upper Three Runs Creek. Data presently being acquired should provide a good backlog of background information before major construction activity anticipated about October.

Du Pont Construction completed the installation of the four small "refuge ponds" proposed by SREL as a research project to determine the effectiveness of new, small, simple depressions in providing substitute habitat.

Environmental and Safety Assessments (SRL)

Preparation of environmental safety documentation continued in support of construction and operation of the Defense Waste Processing Facility (DWPF). The first revision status letter for the DWPF Preliminary Safety Analysis (PSA) was transmitted to DOE-SR on April 29. None of the items reported require immediate revision of the PSA. The items requiring future revision include Subsurface Hydrology, DOE-SR comments on Fire Protection, changes in Facility Design (Chapter 5), and comments on the PSA from Arthur D. Little, Inc.

Saltcrete Lysimeter Test (SRL)

An Environmental Evaluation Impact Analysis was issued on the planned Tank 24H Saltcrete Lysimeter Test. The analysis concludes that the environmental effects of constructing and operating the saltcrete lysimeters would be insignificant. Final disposition of the lysimeters will depend upon results of the lysimeter test (expected to begin in July 1983) and was not included in the analysis.

Environmental and Safety Assessments (ICPP)

Alternative Strategies for Disposal of ICPP-HLW (ICPP)

All chapters and appendices of the Strategy Recommendation Document have been drafted. A review of most drafted sections has been completed by ENICO and DOE-ID personnel. Comments from this review are being resolved and will be included in the draft for final review of the document. This document evaluates alternative strategies using the following criteria:

- technology: status and development required;
- cost: including cost of development, design/construction, operation, transportation/disposal, and decommissioning;
- risk: including worker and population risk;
- regulatory: including the proposed regulations; draft DOE Order 5820, EPA 40 CFR 191, and NRC 10 CFR 60; and
- legislation/policy: including the Nuclear Waste Policy Act of 1982 and the Defense Waste Management Plan.

The regulatory and legislation/policy criteria were found to be the most important in the evaluation, while technology, cost, and risk criteria were not as important at this stage of the evaluation process. The alternative strategies are tentatively ranked as:

1. Alternative 6. Immobilize Liquid Waste and Dispose Offsite; Delay Decision on Stored Calcine.
2. Alternative 3. Immobilize Waste and Dispose Onsite.
3. Alternative 2. Immobilize Waste and Dispose Offsite.
4. Alternative 1. Calcine Waste and Dispose Offsite.
5. Alternative 4. Separate Actinides, Immobilize, and Dispose Offsite; Dispose of Actinide-Depleted Calcine Onsite.
6. Alternative 5. Calcine Waste; After 100 to 500 yr, Immobilize and Dispose Offsite.

A camera-ready draft of the Recommendation Document will be completed by the end of the fiscal year.

A study evaluating feasibilities to reduce the volume of ICPP to be disposed at an offsite repository has been initiated. Volume reduction options being evaluated include: 1) improved waste forms, 2) Na waste stream separation and treatment as LLW, 3) reducing additives to calcine waste, 4) modified head-end processes to reduce "inerts", 5) separate Np and/or Pu as a saleable byproduct, 6) removal of "inerts" from the waste, and 7) removal of actinides. These options are being evaluated as ways to reduce waste volumes to 500 canisters per year. The options being evaluated are based on technology, availability, conceptual flowsheets, plant impacts, facility needs, and research and development needs.

The Integrated Data Base document was reviewed at the request of ORNL. Sections reviewed were waste volume inventories and fuel inventories at the ICPP. Comments were provided to ORNL.

Other Support (SRL)

Criteria and Costs for Technetium-99 Recovery from High-Level Waste Salt

Removal of technetium (Tc-99) during decontamination of SRP high-level waste salt has been considered as a means for lowering residual radioactivity levels of the salt prior to disposal by saltstone burial. Technetium-99, half-life 2.1 x 10^5 y, is the major long-lived radionuclide remaining in the salt after in-tank processing to reduce Cs-137 and Sr-90 by precipitation-adsorption methods.[1] The Tc-99, present as pertechnetate ion with high solubility in water and little potential for retardation in soil, might contribute to the long-term radiological hazard of salt disposal. Separation of Tc-99 from the salt during decontamination would reduce this hazard and make the radionuclide available for beneficial use.[2] [3]

Review of regulatory criteria for disposal of the decontaminated salt by onsite burial without Tc-99 removal indicates that predicted chemical and radionuclide releases from the new "saltstone" form are below EPA drinking water limits, as well as NRC limits for low-level waste disposal. Separation of Tc-99 from the decontaminated salt is, therefore, not required to meet waste management regulations and must be justified by beneficial use rather than environmental considerations.

Projected processes for Tc-99 removal by ion exchange would reduce Tc-99 content of decontaminated salt solution by a factor of 10 or more. With further concentration and conversion to final form, up to about 900 kg of separated Tc-99 could be produced for beneficial use. Evaluation of projected capital and operating expenditures indicate the unit cost of Tc-99 recovery would be about $150/g, three times the current ORNL price of $55/g.[2]

Alternatives for final disposal of the Tc-99, if recovered from salt, include long-term storage for eventual beneficial use and final disposal along with other high-level waste in DWPF-processed glass waste forms. Costs are minimized in these cases by processing the recovered Tc-99 to a concentrated product form.

Reference Salt Disposal Plan

In the reference plan for salt disposal, the salt in high-level waste tanks is decontaminated by in-tank precipitation of Cs-137 as tetraphenylborate and adsorption of residual Sr-90 and plutonium on sodium titanate.[4] The solids, separated from the salt solution by crossflow filtration, are accumulated in the tank. These solids, which contain most of the radioactivity in the salt, are removed as a slurry, treated to either decompose or recover the tetraphenylborate, and fed to the DWPF glass melter. The filtered salt solution, which could be further decontaminated by removal of Tc-99 using ion exchange methods, is processed to solid form by mixing with concrete for onsite burial.[1] About 100 million gallons of salt supernate must be processed to work-off SRP waste inventory expected to be accumulated through the year 2001. At a processing rate of 10 gpm reduced to 5 gpm after 10 years, this inventory will be processed in about 30 years. The lower rate after 10 years is established by the availability of waste salt aged 15 years to allow Ru-106 decay.

For final disposal, the decontaminated salt will be buried as concrete monoliths in landfill trenches constructed to meet applicable criteria for chemical and low-level radioactive waste disposal.[1 5 6] The concrete monoliths, each typically 125 ft long, 25 ft thick, and 15 to 40 ft in width, will occupy an onsite area of about 100 acres. The monoliths will be located at least 3 meters above the historic water tables at the site and be covered with at least 5 meters of soil overburden.[1]

Two concrete forms, designated "saltcrete" and "saltstone", have been developed for the waste salt disposal.* The original

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* Compositions of concrete forms are as follows:

	Original Saltcrete	New Saltstone
Cement	51.1 wt %	22.8 wt %
Salt	15.5	12.1
Water	33.0	25.7
Pozzolith	0.4	0.2
Soil	-	39.2

saltcrete form contained only cement (and Pozzolith additive) mixed with salt solution.[5 6] The new saltstone form, which was developed for lower water permeability (5×10^{-10} cm/sec) than the original saltcrete form (10^{-7} cm/sec), contains soil components as well as cement and salt solution.[1 6] Landfill modeling studies have shown that burial trenches for the original saltcrete must be lined and capped with low permeability (10^{-9} cm/sec) clay barriers to maintain chemical (nitrate/nitrite) releases within acceptable limits. Development of the new saltstone form with reduced permeability eliminates the need for clay liners in the burial trenches by reducing nitrate/nitrite releases to below drinking water standards. Use of a clay cap to inhibit ingress of water into the monolith would further reduce chemical (and radionuclide) releases to the groundwater.

Technetium Recovery

Technetium-99 is the major remaining long-lived radionuclide in decontaminated salt which has been aged 15 years from reactor discharge. Chemical composition of the decontaminated salt solution is shown in Table 1, and radionuclide content of the salt after in-tank decontamination is given in Table 2.[1 6] Technetium recovery by ion exchange methods would reduce the Tc-99 concentrations in the decontaminated salt by a factor of 10 or more. The total quantity of Tc-99 in the salt component of SRP high-level waste is estimated to be about 1000 kg (1.68×10^4 Ci).

In the Tc-99 removal process,[7] the caustic salt solution is passed through a resin column using ion exchange technology. The technetium is adsorbed as pertechnetate ion on a strong-base anion exchange resin [Dowex 1-X8® (Dow Chemical Co.) or equivalent] with typically about 150 column volumes (CV) producing breakthrough at flow rates of 15 CV/hr. Resin loaded to technetium breakthrough would either be stored as such for an interim time or further processed to a form appropriate for beneficial use.

In a representative process for preparation of a final form, the Tc-99 would be eluted from the caustic-rinsed resin using 4 to 6M HNO_3 and the nitric acid evaporated from the recovered product by batch distillation. After neutralization, the Tc-99 could either be concentrated on a weak-base anion resin and eluted at relatively high concentrations in caustic solution, or converted to a solid oxide by resin calcination. The product solution or oxide would be stored for shipment as such or for further processing to final form.

TABLE 1

Chemical Composition of Decontaminated Salt Solution

Component	Composition, wt %
H_2O	68.0
$NaNO_3$	15.6
$NaNO_2$	3.9
NaOH	4.2
Na_2CO_3	1.7
$NaAl(OH)_4$	3.6
Na_2SO_4	1.9
NaF	0.06
NaCl	0.12
Na_2SiO_3	0.04
Na_2CrO_4	0.05
NaHgO(OH)	1.7×10^{-6}
$NaAg(OH)_2$	1.4×10^{-7}
Na_2MoO_4	0.008
KNO_3	8.6×10^{-6}
$CaSO_4$	2.5×10^{-4}
$Na_2C_2O_4$	0.31
Na_3PO_4	0.13
NH_4NO_3	6.7×10^{-6}
$Na[B(C_6H_5)_4]$	0.06
Other Salts	0.20

TABLE 2

Concentrations of Major Radionuclides in Decontaminated Salt

Isotope ($T_{1/2}$, yr)	Concentration, nCi/g*
H-3 (12.3)	40
C-14 (5730)	0.03
Co-60 (5.3)	0.7
Sr-90 (29)	3
Y-90** (3.1 hr)	3
Tc-99 (2.1×10^5)	100
Ru-106 (1.0)	100
Rh-106** (2.2 hr)	100
Sb-125 (2.7)	30
I-129 (1.7×10^7)	0.7†
Cs-137 (30.2)	70
Ba-137m** (2.5 min)	60
Pm-147 (2.6)	10
Sm-151 (93)	7
Eu-154 (8.2)	3
Eu-155 (4.76)	1
All TRU	0.8

* 15 years after reactor discharge of fuel.

** Daughter of preceding radionuclide.

† Upper limit established by calculational methods. Actual concentration expected lower.

Regulatory Criteria

The reference process for salt disposal by burial in solid form originated as a chemical and low-level radioactive waste disposal procedure, designed to meet regulations for such waste disposal by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC). The NRC regulations applicable to the radionuclide content of decontaminated salt require (1) protection of the general public from release of radioactivity to the environment, (2) protection of individuals from inadvertent intrusion after institutional controls on the disposal site are removed, and (3) protection of occupational workers during site operations.[7] The first requirement limits radioactive materials released to the environment in groundwater, surface water, air, soil, plants, and animals to concentrations that would not result in annual doses to individuals of the general public exceeding 25 mrem whole body, 75 mrem thyroid, and 25 mrem any other organ. Effort must be made to maintain releases of radioactivity to the general environment as low as reasonably achievable. Compliance with this requirement for decontaminated salt disposal requires a pathway analysis of radioactivity transport to the environment and dose-to-man evaluations considered in a later section.

Compliance with the second requirement, e.g., inadvertent intruder protection, is demonstrated by comparison of radionuclide concentrations in the waste form with limiting concentrations for wastes in categories designated Classes A, B, and C. Radionuclide limits for each category are specified so as to prevent annual radiation exposures to an inadvertent intruder greater than 500 mrem. Class A (segregated) wastes can contain possibly unstabilized material with radionuclides limited to concentrations ensuring intruder protection within the required 100 year time of institutional site control. Class B waste must be treated so as to be structurally stable for 300 years. Class C intruder waste must be structurally stable and also provided with special protection against inadvertent intrusion (by deeper burial or other barrier) for 500 years. Comparison of the radionuclide content of decontaminated salt with the waste classification limits is shown in Table 3 for long-lived and short-lived radioactivities.[6] The radionuclide content of the salt in saltstone forms is less than the limiting concentrations for all three waste categories. The saltstone form is considered to provide the stabilization needed for Class B waste, and the depth of burial of the saltstone monoliths should provide the protection against inadvertent intrusion specified for Class C waste.

Compliance with the third NRC requirement, operational exposures within prescribed limits, 5 rem/yr for restricted (controlled) areas and 0.5 rem/yr for unrestricted areas, is

TABLE 3

Comparison of Radionuclide Concentrations in Saltstone with NRC Low-Level Waste Disposal Categories

	Concentration in Saltcrete, µCi/cc	Concentration Limit, µCi/cc		
A. Long-Lived Activities		Class A		
C-14	1×10^{-5}	0.8		
Ni-59	2×10^{-7}	22 (in activated metal)		
Tc-99	0.04*	0.3		
I-129	0.002	0.008		
TRU (except Pu-241)	0.0002	0.019 (equiv. to 10 nCi/g)		
Pu-241	4×10^{-5}	665 (equiv. to 350 nCi/g)		
B. Short-Lived Activities		Class A	Class B	Class C
Any, half-life <5 yr	0.09	700	**	**
H-3	0.01	40	**	**
Co-60	2×10^{-4}	700	**	**
Ni-63	2×10^{-5}	3.5	70	700
Sr-90	0.002	0.04	150	7000
Cs-137	0.04	1	44	4600

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* Tc-99 removal would reduce concentration to 10% of value shown.

** No limit.

assured by existing DOE rules and site practices. The DOE occupational exposure limit for controlled areas is 5 rem/yr, reduced to 3 rem/yr by site practice. The saltcrete burial operation has been designed to maintain occupational exposures below 1 rem/yr in conformance to DOE and site specifications for new facilities.

Control of chemical hazards of waste disposal is guided by Environmental Protection Agency (EPA) and SC Department of Health and Environmental Control (SCDHEC) regulations for chemical waste dumps.[8-11] These regulations require that concentrations of chemical contaminants in groundwaters at waste site boundaries not exceed limits specified in *National Interim Primary Drinking Water Regulations*.[12] The constituent of primary concern in decontaminated salt is nitrate/nitrite and its prescribed limit (as nitrogen) is 3.5 mg/L.[1] Solid wastes that could potentially contaminate groundwaters beyond such a limit must be disposed of in landfills meeting specified requirements, including protective (low permeability) clay caps and liners and effluent monitoring systems.

Release of salt from the waste forms is the key factor in the control of chemical contamination of groundwater. Salt release can occur by two processes (1) dissolution by infiltrating rainwater penetrating the protective clay cap and permeating through the waste form and (2) leaching by diffusion to waste form surfaces. Quantities of salt released by these mechanisms have been determined by computer modeling and field tests are in progress to guide the design of the saltcrete landfill. For the saltcrete form, with a measured permeability of about 10^{-7} cm/sec, the permeation mechanism dominates the salt release process. Modeling studies show that drinking water standards for nitrate/nitrite could be met only by surrounding the saltcrete blocks of this form with low permeability (10^{-9} cm/sec) clay caps and liners. For the saltstone form with a measured permeability of less than 5×10^{-10} cm/sec, the drinking water standards can be met without clay caps or liners, with nitrate/nitrite in the groundwater reduced to 0.5 ppm Na. Provision of a clay cap as currently projected would further reduce nitrate/nitrite in groundwater to 0.03 ppm N. Release of nitrate/nitrite from the saltstone form is thus well below drinking water limits, as are other chemical contaminants concurrently released by the permeation mechanism.

Contamination of groundwater by the diffusion mechanism is predicted to be similarly small. Laboratory leach rates of 10^{-5} g/cm^2 for saltstone forms in distilled water, reduced by a factor of typically 50 to take into account the limited amount of water in contact with the saltstone block in the unsaturated soil of a landfill trench, yield nitrate/nitrite concentrations of about 0.002 ppm N in groundwater under the landfill. Predicted concentrations of chemical (and radionuclide) contaminants released by both permeation and diffusion mechanisms into groundwater are summarized in Table 4. None of the contaminant concentrations exceed drinking water limits. Field tests of prototype landfills in progress are designed to verify these predicted values.

Neither NRC regulations for disposal of low-level radioactive waste nor EPA regulations for disposal of chemical wastes directly restrict radionuclide releases to groundwater, although the EPA drinking water standards limit radionuclides in public drinking water supplies. The NRC regulations do, however, specify limits (previously cited) on radiation exposure to the general public resulting from release of radioactive material to the environment. Such limits apply over all exposure pathways, including consumption of foodchain products, which in some scenarios could produce higher exposures than drinking water. In a representative foodchain scenario, the saltstone disposal site is assumed to revert to general agricultural use following a period of institutional control. Individuals inhabiting a nearby farm could ingest Tc-99 by consumption of foodchain products using water in the vicinity of the disposal site for crop irrigation as well as drinking water. Radiation exposures from Tc-99 are compared with drinking water exposures in Table 5. The exposures are expressed as 50-year dose commitments resulting from chronic 1-year intakes of water and the several foodchain products; for Tc-99 with a short biological half-life (48 to 60 hours), the 50-year dose commitment approximates an annual dose.[13] Exposures projected in both cases are well below the prescribed NRC public exposure limits for several water sources. Drinking water sources include near-surface wells utilizing groundwater at the disposal site, as well as more distant tributary streams and the Savannah River, since chemical contaminants as well as radionuclide concentrations in the groundwater (Table 4) are below EPA drinking water limits. Water sources for crop irrigation are limited to tributary streams and the Savannah River.

Near-surface wells utilizing groundwater at the disposal site are assumed unsuitable because of restricted flow, and deep wells that would be suitable for crop irrigation would contain much lower concentrations of released radionuclides.

It is concluded from the foregoing analysis that disposal of the decontaminated salt by burial using the new saltstone form would be acceptable without Tc-99 removal. Incremental costs of Tc-99 recovery from the SRP high-level waste salt should therefore be allocated exclusively to its use as a beneficial waste byproduct.

TABLE 4

Comparison of Chemical and Radionuclide Releases from New Saltstone Forms with Drinking Water Standards

Element, unit	Concentration in Saltstone	Permeation Controlled Release	Diffusion Controlled Release	Total Groundwater Content	Drinking Water Standards*	Concentration in McQueen's Branch**	Concentration in Upper Three Runs Creek at F Road***	Concentration in Upper Three Runs Creek at the Savannah River (Plant Boundary)†
N, ppm	11,200	0.03	0.02	0.05	3.2	$4\text{x}10^{-3}$	$6\text{x}10^{-5}$	$3\text{x}10^{-5}$
Fe, ppm	90	$2\text{x}10^{-4}$	$2\text{x}10^{-4}$	$4\text{x}10^{-4}$	1.4	$3\text{x}10^{-5}$	$4\text{x}10^{-7}$	$2\text{x}10^{-7}$
Cr, ppm	50	$1\text{x}10^{-4}$	$1\text{x}10^{-4}$	$2\text{x}10^{-4}$	0.05	$2\text{x}10^{-5}$	$2\text{x}10^{-7}$	$1\text{x}10^{-7}$
Hg, ppm	0.004	$1\text{x}10^{-8}$	$1\text{x}10^{-8}$	$2\text{x}10^{-8}$	0.002	$2\text{x}10^{-11}$	$2\text{x}10^{-9}$	$1\text{x}10^{-11}$
Ag, ppm	0.0003	$8\text{x}10^{-10}$	$6\text{x}10^{-10}$	$1.4\text{x}10^{-9}$	0.05	$1.2\text{x}10^{-10}$	$1.5\text{x}10^{-12}$	$9\text{x}10^{-13}$
C_6H_6, ppm	180††	$5\text{x}10^{-4}$	$4\text{x}10^{-4}$	$9\text{x}10^{-4}$	0.35†††	$8\text{x}10^{-5}$	$1\text{x}10^{-6}$	$6\text{x}10^{-7}$
^{90}Sr, pCi/L	$3\text{x}10^{5}$	0.9	0.7	1.6	8	0.14	$1.8\text{x}10^{-3}$	$1.1\text{x}10^{-3}$
^{99}Tc, pCi/L	$2\text{x}10^{7}$¶	50	40	90	900	8	0.1	0.06
^{129}I, pCi/L	$1\text{x}10^{5}$	0.3	0.3	0.6	1	0.05	$7\text{x}10^{-4}$	$4\text{x}10^{-4}$
^{137}Cs, pCi/L	$1\text{x}10^{7}$	35	29	64	200	5	$7\text{x}10^{-2}$	$4\text{x}10^{-2}$

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* EPA 570/9-76-003, National Interim Primary Drinking Water Regulations.

** Based on measured flow rate of 2 cfs.

*** Based on measured flow rate of 150 cfs.

† Based on measured flow rate of 270 cfs.

†† Potentially available from decomposition of $NaB(C_6H_5)_4$.

††† EPA suggested no adverse response limit.

¶ Does not include Tc removal.

TABLE 5

Drinking Water and Foodchain Projection of Tc-99 Radiation Exposures for Saltstone in Clay-Capped Landfill*,**

A. Drinking Water Exposures

Source of Water	50-yr Dose Commitment from Chronic 1-yr Intake (mrem/person)		
	Whole Body	Thyroid	Stomach Wall
Groundwater	0.003	0.5	0.9
Tributary Stream	$3x10^{-5}$	$3x10^{-3}$	$8x10^{-3}$
Savannah River	$9x10^{-8}$	$9x10^{-6}$	$2x10^{-5}$

B. Foodchain Exposures

	50-yr Dose Commitment from Chronic 1-yr Intake (mrem/person)		
	Whole Body	Thyroid	Stomach Wall
Tributary Stream	0.003	0.3	0.6
Savannah River	$1x10^{-5}$	$2x10^{-3}$	$3x10^{-3}$

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* Adapted from Tables 3 and 4 using 90 pCi/L Tc-99 release to groundwater. Exposure scenarios assume ingestion of radionuclide by consumption of (A) drinking water only and (B) drinking water, fish, crops, cow's milk, and meat produced using contaminated water source for crop irrigation.

** Annual NRC exposure limits 25 mrem whole body, 75 mrem thyroid, and 25 mrem any other organ (stomach wall).

Costs of Tc-99 Recovery

Technetium-99 would be recovered for beneficial uses by processing the relatively low-activity decontaminated salt in a minimum-shielded facility located near the waste tank salt decontamination complex. A process flowsheet is shown in Figure 1, with stages at which the recovered Tc-99 could be processed for final disposal indicated. Capital costs for the Tc-99 separation facility, developed from high-spot estimates prepared by the Du Pont Engineering Department (ED), total $13 million.[6] Equipment for further concentration of Tc-99 solution (reduced in volume by a factor of 10 or more) and for conversion to final form are estimated to add $11 million to thse capital costs. Operating costs for the Tc-99 recovery and finishing operations are estimated at $3 million/yr, including $1 million/yr for chemical supplies (ion exchange resin).

Unit costs for recovery of Tc-99 calculated by standard discounting procedures for pricing of Government services are given in Table 6. The discounting procedures are based on full recovery of Government expenditures, assuming a 10% discount rate over the 30-year time period required for SRP salt waste processing. The unit recovery cost for Tc-99 is about $150/g. This exceeds the quoted ORNL price of $55/g for Tc-99 in the small quantities currently available.

Final Disposal Options

Separation of Tc-99 for beneficial use presumes final disposition by offsite shipment to potential users. In the event that a substantial demand for the product did not materialize, alternative methods for disposal of the product must be developed. Three general approaches are considered potentially practical:

1. *Discontinued product recovery, with unrecovered Tc-99 going* into saltstone as a constituent of the decontaminated salt. Costs would be limited to those for abandonment and decomissioning of the Tc-99 separations facility, assuming loss of revenue from Tc-99 sales offset by reduced costs of waste processing for Tc-99 recovery.

2. Long-term storage of all or part of the recovered Tc-99 inventory. Storage of Tc-99 at high concentration in alkaline solution or in solid form, as a potential national asset until employed for research or practical application should entail no major environmental or economic penalty. This disposal option would, in general, require processing to the concentrated product form since long-term storage of the strong-base anion exchange resin without further concentration would entail

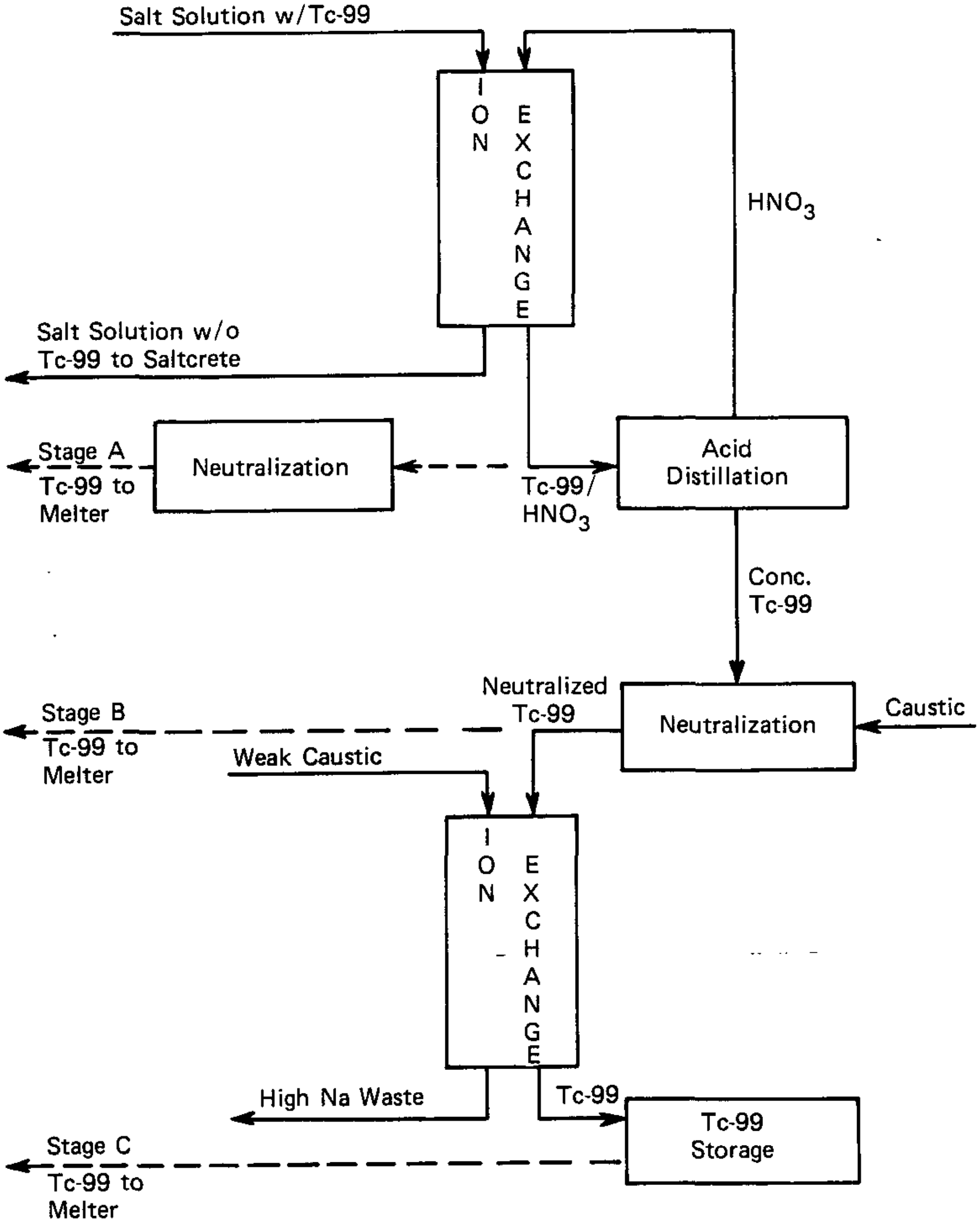

FIGURE 1. Tc-99 Recovery Process

TABLE 6

Projection of Technetium-99 Recovery Costs
(All Costs in Million 1983 Dollars, Discount Rate 10%)

Year	Capital Cost	Operating Cost	Total Cost	Product Recovered, kg	Discount Factor	Discounted Cost	Discounted Product, kg
1983					1.000		
1984					0.909		
1985	3.0		3.0		0.826	2.48	
1986	13.0		13.0		0.751	9.77	
1987	8.0		8.0		0.683	5.46	
1988		3.0	3.0	45	0.621	1.86	27.9
1989		3.0	3.0	45	0.565	1.69	25.4
1990		3.0	3.0	45	0.513	1.54	23.1
1991		3.0	3.0	45	0.467	1.40	21.0
1992		3.0	3.0	45	0.424	1.27	19.1
1993		3.0	3.0	45	0.386	1.16	17.2
1994		3.0	3.0	45	0.351	1.05	15.8
1995		3.0	3.0	45	0.319	0.96	14.3
1996		3.0	3.0	45	0.290	0.87	13.0
1997		3.0	3.0	45	0.263	0.79	11.8
1998		3.0	3.0	22.5	0.240	0.72	5.4
1999		3.0	3.0	22.5	0.218	0.65	4.9
2000		3.0	3.0	22.5	0.198	0.59	4.5
2001		3.0	3.0	22.5	0.180	0.54	4.0
2002		3.0	3.0	22.5	0.164	0.49	3.7
2003		3.0	3.0	22.5	0.149	0.45	3.3
2004		3.0	3.0	22.5	0.135	0.41	3.0
2005		3.0	3.0	22.5	0.123	0.37	2.8
2006		3.0	3.0	22.5	0.112	0.34	2.5
2007		3.0	3.0	22.5	0.102	0.30	2.3
2008		3.0	3.0	22.5	0.092	0.28	2.1
2009		3.0	3.0	22.5	0.084	0.25	1.9
2010		3.0	3.0	22.5	0.076	0.23	1.7
2011		3.0	3.0	22.5	0.069	0.21	1.6
2012		3.0	3.0	22.5	0.063	0.19	1.4
2013		3.0	3.0	22.5	0.057	0.17	1.3
2014		3.0	3.0	22.5	0.053	0.15	1.2
2015		3.0	3.0	22.5	0.049	0.14	1.1
2016		3.0	3.0	22.5	0.044	0.13	1.0
2017		3.0	3.0	22.5	0.040	0.12	0.9
Total	24.0	90.0	114.0	900		37.02	239.3

Levelized unit cost = Discounted cost/Discounted product = $154.72

additional expenditure for resin supply and storage capability. The total quantity of Tc-99 recovered from SRP waste salt processing could be contained at about 1 g/L concentration of 0.1M NaOH solution in a 25,000-gal tank, or as a solid oxide in smaller capacity facilities.

3. Vitrification in glass for disposal as high-level waste. This option, originally envisioned as the ultimate disposal mode for all of the Tc-99 recovered from decontaminated salt, is available for any part of the inventory not ultimately used for other purposes. Disposal in glass form in a geologic repository along with other high-level wastes reduces environmental impacts to the minimum potentially available, assuming technology for introduction of the Tc-99 into the glass melting furnace without excessive off-gassing could be developed. Systems costs of such Tc-99 disposal would depend on the process stage at which the product is committed to vitrification and would be minimized by charging the Tc-99 to the glass furnace in final, high-concentration form. At earlier process stages, the alkaline product solutions would contain very large quantities of sodium as sodium nitrate or hydroxide, which would be concurrently incorporated as a nonradioactive constituent in the glass. The resultant quantities of glass expressed as number of high-level waste canisters for repository emplacement are shown in Table 7. Product recovered from the strong-base resin by nitric acid elution and directly neutralized for melter feed (Stage A) would require 30,000 canisters, three times the number of canisters projected for other SRP high-level waste disposal.[14] Additional processing to reduce sodium content of melter feed by nitric acid distillation prior to neutralization (Stage B) would decrease the total number of canisters required to about 500. Further concentration by ion exchange on a weak-base resin to the concentrated solution form suitable for long-term storage (or alternative conversion to solid form) would decrease the number of canisters required for final Tc-99 disposal to less than 10.

TABLE 7

Number of DWPF Canisters Required for Disposal of Recovered Technetium-99

Disposal Stage	Na/Tc-99 Ratio, M	No. of Canisters
A	32,000	30,000
B	540	500
C	10	9

In Situ Storage or Disposal

Cesium Capsule Corrosion Studies (RHO)

The 8800-hour test cesium chloride (CsCl) capsule was completed and shipped to ORNL where it was opened to visually examine the inner capsule for pitting conditions.

An arcing problem on the electropolisher was identified in Waste Encapsulation and appeared to be the likely cause of the staining and pitting observed on the 4400-hour test CsCl capsules.

Testing of the unusual surface conditions on the outside of the PNL 4400-hour corrosion test of the CsCl capsule was initiated by ORNL. Testing included metallography and photography of the pits with incremental grinding through a cross section, scanning electron microscopy and microprobe for elemental analysis.

Micrographs of the samples from the 2200-hour capsule were received at PNL. The micrographs were reviewed and compared with earlier results for the baseline zero-time capsules. Destructive analysis of the 8800-hour test capsule was initiated by ORNL. Testing on this capsule is complete.

Micrographs of samples from the 4400-hour test capsules were reviewed at PNL. Comparison of micrographs from zero-time, 2200- and 4400-hour samples showed that corrosion attack was occurring at the 316L stainless steel-cesium chloride interface. There appears to be approximately 10 to 12 mils attack in the worst-case 4400-hour sample.

Waste Tank Corrosion Studies (RHO)

The corrosion testing program continued at PNL. The program is investigating the relationships of corrosion rates to the following variables:

1.	Time	(3 time periods)
2.	Temperature	(5 to 6 temperatures)
3.	Steel Type	(2 steel types)
4.	Steel Condition	(2 conditions, stressed and unstressed)
5.	Waste Type	(3 general waste types)
6.	Waste Composition	(up to 7 components per waste type)

Of the sixteen reports scheduled for completion during the two-year corrosion program, two were produced this quarter. Those were:

1) The eight-month Low Temperature Customer Waste Test Report, March 1983.

2) The twelve-month Low Temperature Customer Waste Test Report, May 31, 1983.

The corrosion rates for the eight- and twelve-month customer waste tests were generally low. Most rates were below 1 mpy and often less than 0.7 mpy. However, there were dilute solutions, which were low in hydroxide and nitrite that gave corrosion rates in the range of 1 to 4 mpy. No cracking of the test coupons was evident in either test, although some cracking was reported earlier in the four-month tests.

The interim report on the low-temperature double-shell slurry tests is being cleared by PNL management. The report provides prediction equations for temperatures below 100°C. Within the composition range tested, all corrosion rates were below 1 mpy.

The final low-temperature test, eight-month future Purex waste, was completed on June 4, 1983, and the report is on schedule for an August 1, 1983 release.

The high-temperature tests for solutions containing complexants were started on June 1, 1983. Pressure vessels were fabricated and tested to alleviate the foaming problem observed with complexant-containing solutions in previous tests. A set of four-month high-temperature tests was completed for future Purex and double-shell slurry mixtures without complexant.

Testing continued on the in-tank corrosion probe. Measurement of the iron released to the solution suggests a corrosion rate of 0.04 mpy. The lower detection limit of the probe is 0.5 mpy. The solution has been replaced by a solution which showed higher corrosion rates at the test temperature.

Waste Form Development and Characterization

Waste Form Studies (ICPP)

Two waste forms, glass and ceramic, may be suitable candidates to immobilize liquid Fluorinel waste to result in a reduced volume of final waste. A preliminary investigation of the conditions required to produce these waste forms has been completed.

A solution representative of the waste produced by the Fluorinel fuel dissolution process was used for the investigations. Composition of this simulated waste is given in Table 8.

TABLE 8

Composition of Simulated Liquid Fluorinel Waste Used in Waste Form Evaluation Studies

Zr	0.52M	B	0.33M
Al	0.52M	Cd	0.13M
F^-	4.10M	$SO_4^=$	0.07M
NO_3^-	2.12M	NH_4	0.06M

Ceramic Waste Form

The composition of reactants required to prepare a high waste loading (72 wt % waste) ceramic product based on forming the crystalline phases of magnetoplumbite, zirconolite, and fluorite are given in Table 9. A ceramic product with such a composition at a theoretical density of 3.8 g/cm^3 could result in an overall HLW volume reduction of 68%.

TABLE 9

Composition of Reactants to Prepare the Ceramic Product

Reactant	Amount
Simulated Liquid Fluorinel Waste	350 mL
$CaNO_3$	89.9 g
TiO_2	24.0 g
Mixed Rare Earth Oxides	0.5 g

Reactants were combined and evaporated to dryness and ignited at 500°C. After ignition the residue was blended with a low temperature cellulose binder and a zinc stearate lubricant. Next, this mixture was cold pressed at 20,000 psi and sintered in atmospheric conditions at 1200°C for four hours to densify and crystallize the ceramic product. The composition used will result in a 72 wt % loading of the equivalent calcined waste.

The product of the test run at the above conditions has the properties given in Table 10.

TABLE 10

Properties of Ceramic Product Prepared from Liquid Simulated Fluorinel Waste

Phases Observed*,**	Product Density, g/cc	Response to Soxhlet Leach Test (loss rate in g/m^2d)†	
$CaTiO_3$ (Perovskite)			
ZrO_2	3.0		
CaF_2 (Fluorite)		Cs	<1.5
		Al	12.9
		B	14.4
		Zr	0.05

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* Phase assemblage expected: magnetoplumbite, zirconolite, fluorite

** Phases identified by x-ray diffraction analysis (XRD)

† Normalized elemental leach rates

The results obtained indicate that with the relatively simple techniques of cold pressing and sintering in atmospheric conditions only partial product crystallization can be attained. Cadmium, an important constituent of the waste solution, did not form a detectable crystalline phase as determined through the application of x-ray diffraction analysis

The product properties obtained under the test conditions of this investigation indicate that further densification during sintering is required to produce a product of maximum theoretical density. Such conditions can be obtained by sintering the reactants in an inert or reducing atmosphere inside a hot isostatic press.

Glass Waste Form

This study was performed to investigate the conditions required to vitrify liquid simulated Fluorinel waste to a glass product after approximately 90% of the fluorides have been volatilized, resulting in an overall HLW volume reduction of approximately 52%. Frit 127, Table 11, was chosen for this purpose because of its proven success to vitrify zirconia calcine which is of cationic composition similar to that of liquid Fluorinel waste.

TABLE 11

Composition of Formula 127 Glass Frit Used to Vitrify Fluorinel Waste

Component	Mole Percent	Weight Percent
SiO_2	67.6	70.3
Na_2O	11.9	12.8
Li_2O	11.9	6.2
B_2O_3	7.1	8.5
CuO	1.5	2.1

Frit components, and calcium to retain 10% of the fluoride in the waste, to flux the glass melt, were combined with a volume of simulated liquid Fluorinel waste to result in a glass product of 33 wt % waste loading. This mixture was evaporated to dryness at 150°C and then ignited at 750°C for 5 hours to convert the residue, except calcium fluoride, to oxides. Past studies of zirconia calcine vitrification by Frit 127 have demonstrated that a melt temperature of 1100°C for at least three hours is required to vitrify calcine containing 100% of the fluorides at a loading of 33 wt %. The present studies indicate that some fluoride must be retained to flux the melt. Additional time may be required to vitrify the simulated liquid Fluorinel waste containing only 10% of the fluoride because it is more refractory than the calcine waste. Thus, to investigate the preparation requirements of converting simulated liquid Fluorinel waste to a glass, a two-level factorial design experiment of two variables was performed. The experimental matrix is given in Table 12. Four tests in which the two independent variables are changed as shown in Table 12 are required in this experiment. Independent variables used were vitrification time and amount of fluorine remaining in the melt to flux the glass. Conditions held constant were waste loading (33 wt %), melt temperature (110°C), and the previtrification preparation steps discussed above. The response to the test was the amount of vitrification in the test product.

TABLE 12

Factorial Design Experiment Matrix for Fluorinel Waste Glass Preparation

	Independent Variables	
Test No.	X_1 Melt Time, hr	X_2 Fluorine Complexed in Melt, %
1	3	5
2	20	5
3	3	20
4	20	20

Products of the tests run at the above conditions have properties given in Table 13. The results indicate that at 1100°C and a waste loading of 33 wt %, vitrification is promoted by the retention of larger quantities of fluoride in the melt and by longer melt times, such as shown in test Number 4.

The product properties obtained under the test conditions of this investigation indicate that studies of melt time and fluoride retention are needed. The effects of increased waste loading on vitrification extent should also be studied.

Conclusions

The results of preliminary laboratory-scale scoping studies indicate that a high waste loading glass or ceramic product can be produced from simulated Fluorinel liquid waste. A maximum HLW volume reduction which could be attained is 68% for the ceramic product and 52% for the glass product. Further densification tests using the HIP are required to form a ceramic product at a theoretical density. Further tests with glass melts are required to establish practical glasses for liquid Fluorinel wastes by volatilizing fluorides.

Leaching Mechanism Program (MCC)

The Fourth Semiannual Workshop on the Leaching Mechanisms of Defense High-Level Waste Forms was held at the Materials Research Laboratory on the campus of Pennsylvania State University on June 20, 1983. Each of the Leaching Mechanism program participants made an approximately 30-minute presentation on their progress in the last 6 months. SRL personnel also made a presentation on

TABLE 13

Properties of Products from Factorial Design Glass Formation Experiment

Test Number	Product Appearance	Relative Viscosity*	Response to Soxhlet Leach Test** (leach rate in g/m^2-d) Total Mass Loss	Cs	Zr	B	Cd	X-Ray Diffraction Analysis
1	Opaque Inhomogeneous	2	1.27	1.50	0.21	15.10	1.03	Amorphous with minor $ZrSiO_4$, CaF_2, metallic Al
2	Partial Vitrification	4	1.51	1.40	0.12	20.70	1.30	Amorphous with minor $ZrSiO_4$
3	Opaque Inhomogeneous	2	1.17	0.78	0.18	9.60	0.61	Mostly amorphous with minor metallic Al
4	Complete Vitrification	3-4	1.60	0.97	0.15	35.4	0.84	Mostly amorphous with minor metallic Al

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* Visual observation: 2 = 75-150 poise, 3 = 150-300 poise, and 4 = 300-400 poise.

** 72-hour test with distilled H_2O at 95°C.

the related leaching activities being carried on in support of the DWPF. Following the workshops, a 1-1/2 day steering committee meeting was held. More in-depth discussions of experimental results were carried on at the closed workshop, and important decisions were made on future activities. Two of the most important decisions were:

- Closer interaction between the PROTOCOL modeling activity and the experimentalists will be forced by having the experimentalists participate in onsite run-throughs with the computer at LLNL.
- A long lead time in which to edit and refine the final report of the Leaching Mechanisms program will be assured by having the authors each prepare a finished draft of their section(s) by October 31, 1983. The goal is to have a draft of the final report ready for peer review about 9 months before it will actually be issued. This will give ample time to accommodate all comments that are received on the draft.

A large amount of optimization work was done on PROTOCOL at LLNL, shortening the routine and condensing the output, in preparation for the massive number of computations scheduled for the near future. A new approach to developing a waste-glass-leaching-specific thermochemical data base for PROTOCOL is also being investigated at LLNL. This approach does not require that the solubility be controlled by known crystalline, stoichiometric phases; instead the chemical composition of the solid phase can be assembled at any point in the computation by summing the formulas and masses of the component oxides, based on the bond energies involved and solution analyses.

Leach Testing of SRL Waste Forms (MCC)

All one-year data have been collected for the MCC-1 and MCC-4 test method experiments. The data base is quite large. Data from SRL-131 glass and Synroc-D were collected at two temperatures (MCC-1 and -4), four leachants for MCC-1, three leachants for MCC-4, and two flow rates for MCC-4. In the MCC-1 test, cation, anion (nonbrine), uranium, and inorganic/organic carbon analyses have been performed on 424 liquid leachates. The 182 and 364 day samples were filtered which increases the sample load at each sample time by a factor of three. These were included in the 424 total sample load.

In the MCC-4 test, 42 leachates were monitored on a weekly basis. To date, 2184 flow rate measurements have been made. Duplicate specimens have been used in this test. These have yielded 336 leachates which have been analyzed for anions (nonbrine), cations, uranium, and inorganic/organic carbon.

Preparation of MCC-D2 and MCC-D3 data packaes for presentation to the MRB continues. Both are MCC-1 leach test data and are in the final stages of preparation. Combined with the MCC-D1 data package already submitted to the MRB, the new data packages will lead to MCC-1 leach data on three different materials being considered for publication in the Handbook as follows:

MCC-D1	PNL 76-68 glass
MCC-D2	SRL-131 glass; Synroc-D
MCC-D3	SRL-131 glass

Process and Equipment Development

Theoretical Behavior of Frit 165 + TDS-3A Simulation Waste in a Continuous, Slurry-Fed Cylindrical, Joule-Heated Melter

Waste glass made with Frit 165 is more durable than waste glass made with Frit 131. Frit 165 is also known to produce a more viscous glass melt than Frit 131. Therefore, the feasibility of producing waste glass with Frit 165 needs to be evaluated. Several campaigns using Frit 165 slurry feed have been run in the PNL and LSFM melters. Melt rates observed during these campaigns were lower than melt rates observed using Frit 131 slurry feed under similar or identical operating conditions. This section examines and compares the theoretical melter performance of Frit 165 waste with that of Frit 131 waste and assesses the suitability of Frit 165 waste for use in the DWPF melter.

The theoretical melt behavior of Frit 131* waste glasses has been determined in an earlier study. The theory developed for predicting melt rate models the melt behavior of a slurry-fed, joule-heated, cylindrical glass melter. Definitions of independent and dependent variables used in the model along with their nominal ranges are shown in Table 14. Physical properties and composition data for Frit 165 waste glass are listed in Tables 15 through 17.

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* All glasses in this study contain TDS-3A simulated waste, unless indicated otherwise.

TABLE 14

Variables Used in Melt Rate Theory

Independent Variables

R_f = feedpile radius, 0.50-4.0 ft

T_w = average melter plenum temperature, 300-1200°C

T_g = molten glass temperature, 1150°C

f_s = weight fraction of solids in slurry, 0.30-0.60

blt = thermal boundary layer thickness in the molten glass beneath the feedpile, 0.5-4.0 inches

Dependent Variables

h_c = total height of the crust, inches

h_{cb} = height of crust below melt line, inches

W_{co} = melt rate, lb/hr

W_w = water removal rate, lb/hr

Φ = mass flux of glass, lb/hr-ft^2

W_{sl} = slurry feed rate, lb/hr

Q_m = joule heat to feedpile, kW

Q_{rad} = radiant energy to feedpile, kW

RETC	- radiant energy to crust expressed as a percent of the total incident energy to the crust.
HCTCB	- heat conduction to crust bottom expressed as a percent of the total incident energy to the crust.
HCTS	- heat conduction to crust side expressed as a percent of the total incident energy to the crust.
HCFCTS	- heat conduction from crust to slurry expressed as a percent of the total energy lost from the crust.
ERFGMC	- energy required for glass melting in the crust expressed as a percent of the total energy lost from the crust.

TABLE 15

Measured Viscosities of Frit 165 Glasses

W-Al		TDS-3A		W-Fe	
Temp, °C	Poise	Temp, °C	Poise	Temp, °C	Poise
1169	150	1164	60	1166	33
1120	240	1115	88	1116	43
1074	380	1067	140	1069	62
1024	660	1020	240	1020	98
976	1200	973	390	973	160
925	2200	923	830	923	290
878	4600	876	1900	875	620
830	1100	827	4900	825	1400

TABLE 16

Densities of SRP Waste Glasses

Temp, °C	131 TDS-3A, g/cm^3	131 High-Fe, g/cm^3	131 High-Al, g/cm^3	165 TDS-3A, g/cm^3	165 High-Fe, g/cm^3	165 High-Al, g/cm^3
20	2.75	2.82	2.60	2.76	2.94	2.67
100	2.743	2.813	1.593	2.753	2.933	2.663
200	2.745	2.804	2.585	2.745	2.923	2.655
300	2.726	2.795	2.577	2.736	2.914	2.646
400	2.718	2.786	2.569	2.728	2.905	2.638
500	2.68	2.75	2.537	2.680	2.867	2.605
600	2.64	2.701	2.516	2.65	2.816	2.584
700	2.60	2.651	2.495	2.61	2.764	2.562
800	2.56	2.602	2.474	2.57	2.713	2.541
900	2.52	2.552	2.453	2.53	2.663	2.519
1000	2.48	2.503	2.432	2.49	2.610	2.497
1025	2.47	2.498	2.426	2.48	2.604	2.491
1050	2.465	2.493	2.42	2.47	2.599	2.485
1075	2.452	2.486	2.445	2.465	2.592	2.511
1100	2.45	2.48	2.407	2.46	2.586	2.472
1125	2.443	2.475	2.401	2.452	2.580	2.466
1150	2.436	2.47	2.395	2.445	2.575	2.459
1175	2.429	2.465	2.489	2.438	2.57	2.453
1200	2.422	2.46	2.383	2.431	2.71	2.447

TABLE 17

Calculated Specific Heats of Frit 165 Glasses, cal/g-°C

Temp, °C	Mean Heat 165 TDS-3A	True Heat 165 TDS-3A	Mean Heat High-Fe	True Heat High-Fe	Mean Heat High-Al	True Heat High-Al
20	0.198	0.204	0.198	0.204	0.196	0.202
100	0.218	0.240	0.219	0.243	0.216	0.217
200	0.237	0.272	0.240	0.278	0.235	0.269
300	0.253	0.295	0.257	0.302	0.250	0.291
400	0.266	0.312	0.270	0.320	0.263	0.308
500	0.276	0.325	0.282	0.334	0.273	0.321
600	0.285	0.334	0.292	0.344	0.282	0.330
700	0.293	0.342	0.300	0.353	0.289	0.338
800	0.299	0.349	0.307	0.359	0.296	0.344
900	0.305	0.354	0.313	0.365	0.302	0.349
950	0.308	0.356	0.316	0.367	0.304	0.352
1000	0.310	0.358	0.318	0.370	0.307	0.354
1025	0.311	0.359	0.320	0.371	0.308	0.355
1050	0.313	0.360	0.321	0.372	0.309	0.355
1075	0.314	0.361	0.322	0.372	0.310	0.356
1100	0.315	0.362	0.323	0.373	0.311	0.357
1125	0.316	0.362	0.324	0.374	0.312	0.358
1150	0.317	0.363	0.325	0.375	0.313	0.359
1175	0.319	0.364	0.326	0.376	0.314	0.359
1200	0.319	0.365	0.328	0.377	0.315	0.360
1250	0.321	0.366	0.30	0.378	0.317	0.361
1300	0.322	0.367	0.331	0.379	0.319	0.363

The most critical assumption used in the computations was the estimated temperature at the interface of the cold cap and bulk glass. A 5% change in cold-cap bottom temperature results in a 20% change in computed glass melt rate. Temperature profile data for LSFM-6 and LSFM-7 indicate the cold-cap bottom temperature for normal Frit 165 waste glass production to be about 1000°C. Using cold-cap bottom temperature of 1000°C produced theoretical melt rates in close agreement with preliminary melt rates obtained from LSFM-7. A cold-cap bottom temperature of 1000°C was assumed for all Frit 165 simulated waste theoretical calculations.

Figures 2-11 graphically represent the melt behavior of Frit 165 simulated waste at a constant weight percent solids of $f_s = 0.40$ and a constant thermal boundary layer thickness of 2.0 inches. These two constraints were chosen so that Figures 2-11 would best represent melter and feed conditions presently encountered in the slurry-fed melter program of the DWPF.

The melt rate of Frit 165 waste glass is highly sensitive to the average plenum temperature. Figure 2 suggests that the melt rate is a strong function of feedpile radius and plenum temperature. However, an analysis of the melt flux (melt rate per square foot of melt surface area, based on a 100% conversion from feed to glass) for the same conditions (Figure 3) indicates that feedpile radius is not as important to melt rate as suggested in Figure 2. Figures 4 and 5 show the slurry feed and water removal rates encountered operating under the melter conditions shown in Figures 2 and 3. Based on the data presented in Figure 3, a melt flux of 8 to 11 lb/hr-ft^2 would be predicted for the DWPF melter using Frit 165 and an 850°C plenum temperature.

Energy is supplied to the feedpile by convective heat transfer from the glass melt beneath the cold cap bottom, by radiant heat transfer from lid heaters placed in the plenum space above the feedpile and by heat conducted to the sides of the feedpile. Figures 6-8 describe the effects of plenum temperature and feedpile radius on the distribution of energy incident to the feedpile. As the plenum temperature rises, the contribution of radiant energy to the feedpile increases while the contribution to convective heat transfer decreases. Figure 9 indicates that the total crust thickness changes with plenum temperature, which will directly affect heat transfer from the bulk glass to the feedpile. Figures 10 and 11 show quantitative power requirements for melt rates achieved in Figures 2 and 3.

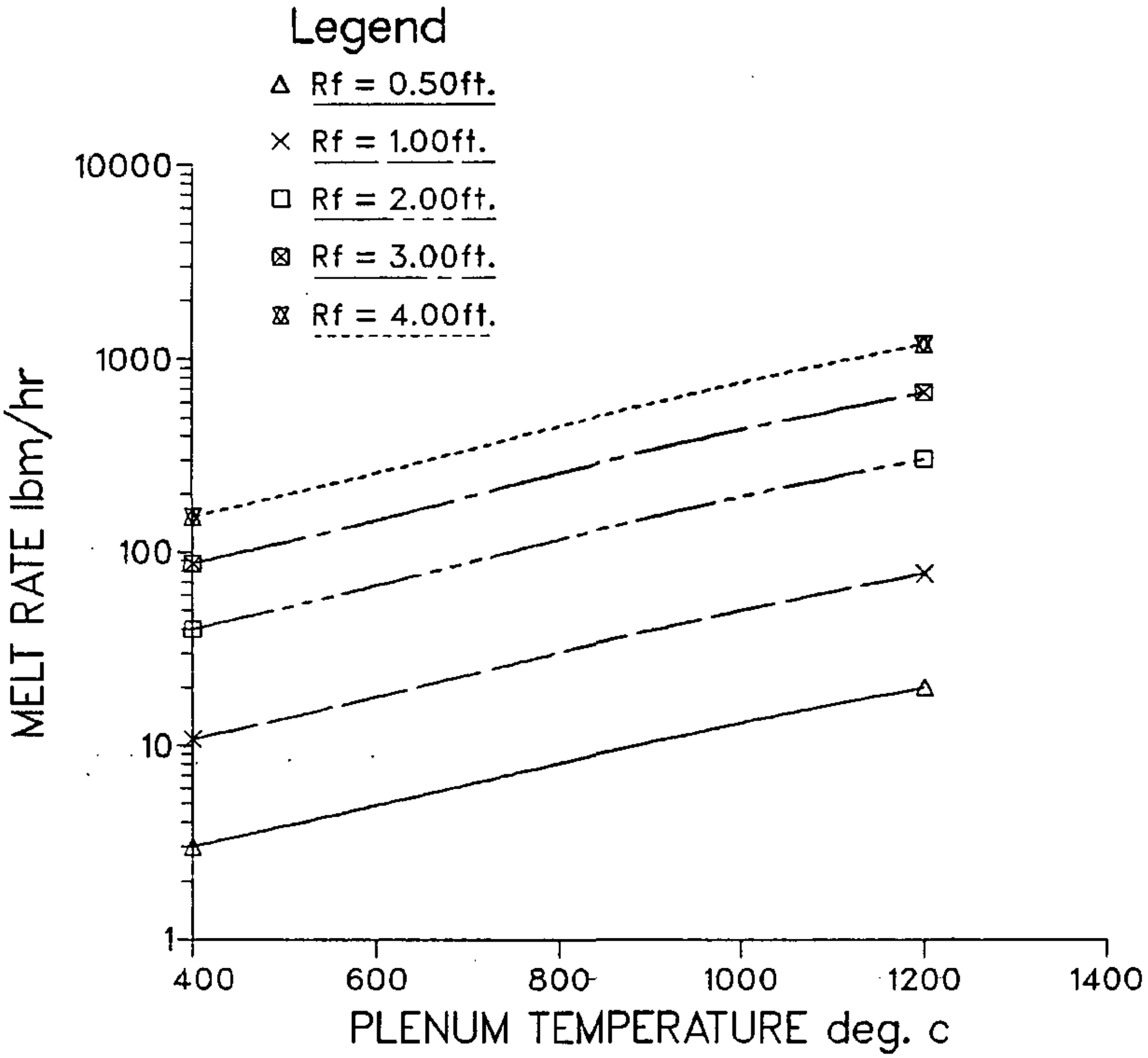

FIGURE 2. Melt Rate vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

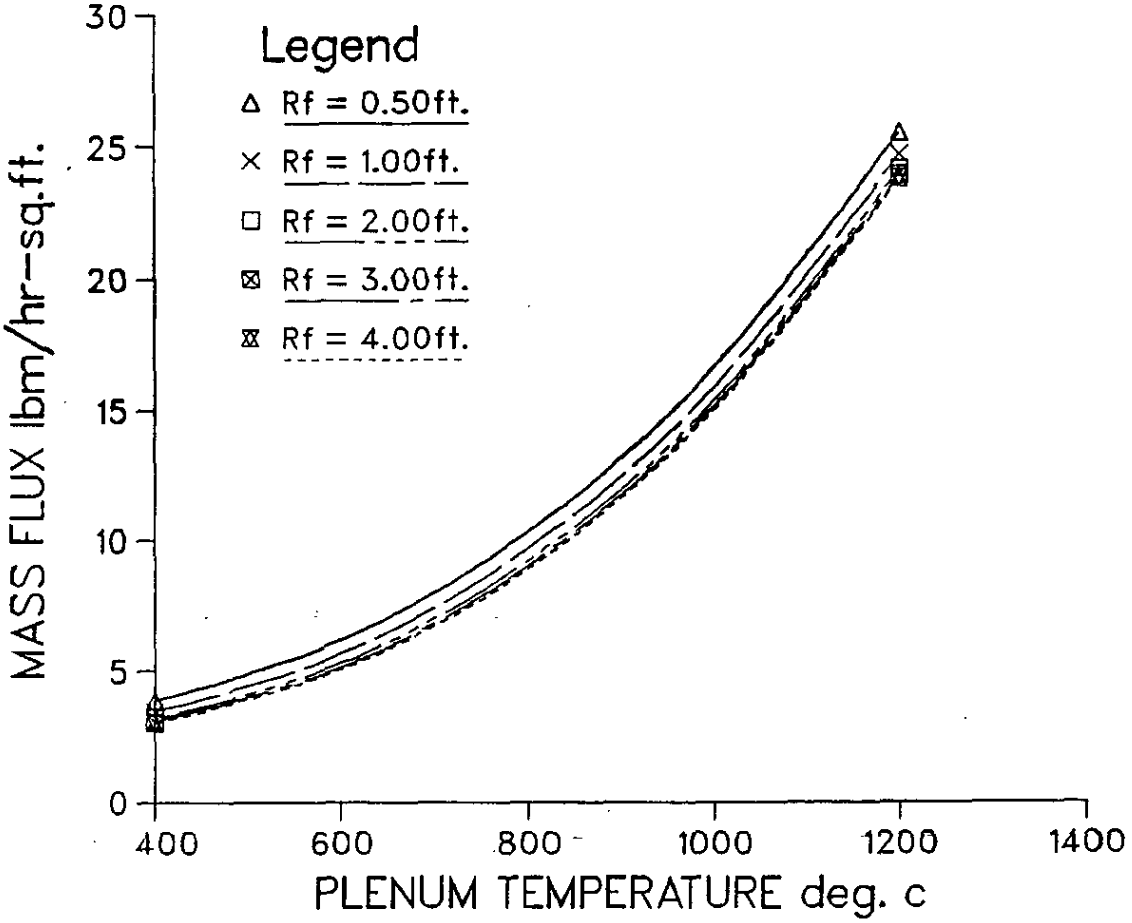

FIGURE 3. Mass Flux vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

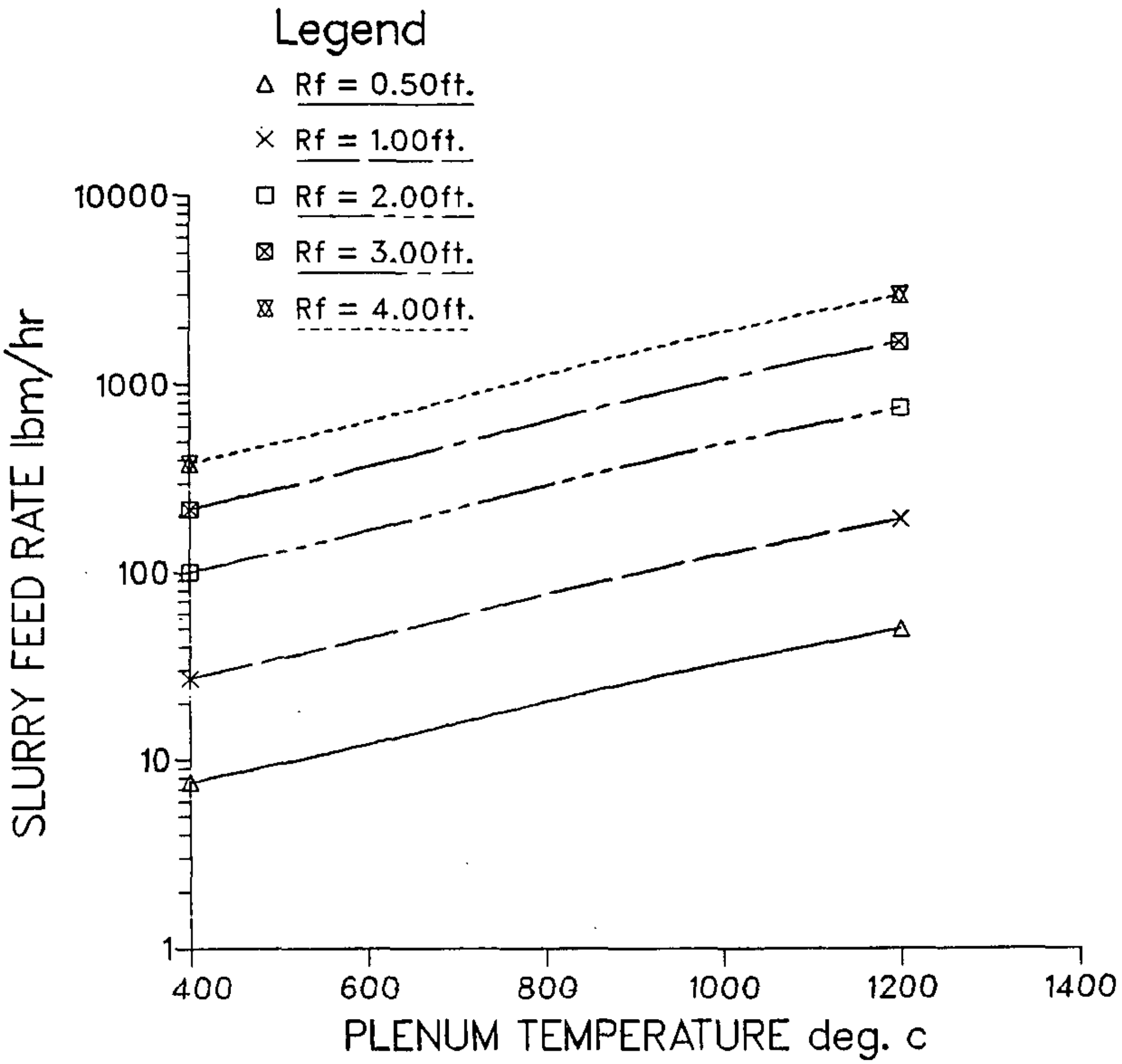

FIGURE 4. Slurry Feed Rate vs. Plenum Temperature
for Varying Feedpile Radius
Frit 165 + TDS-3A

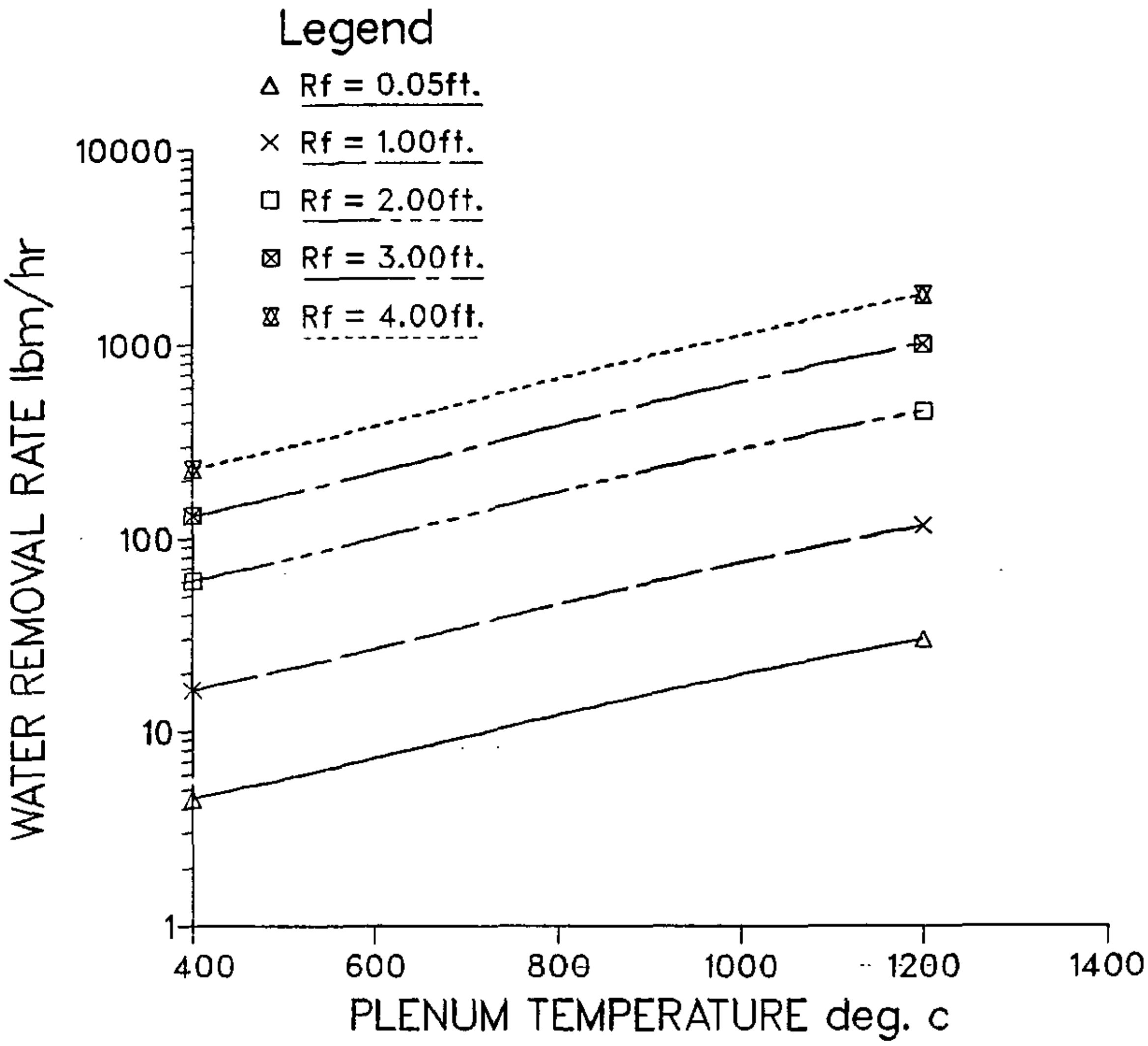

FIGURE 5. Water Removal Rate vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

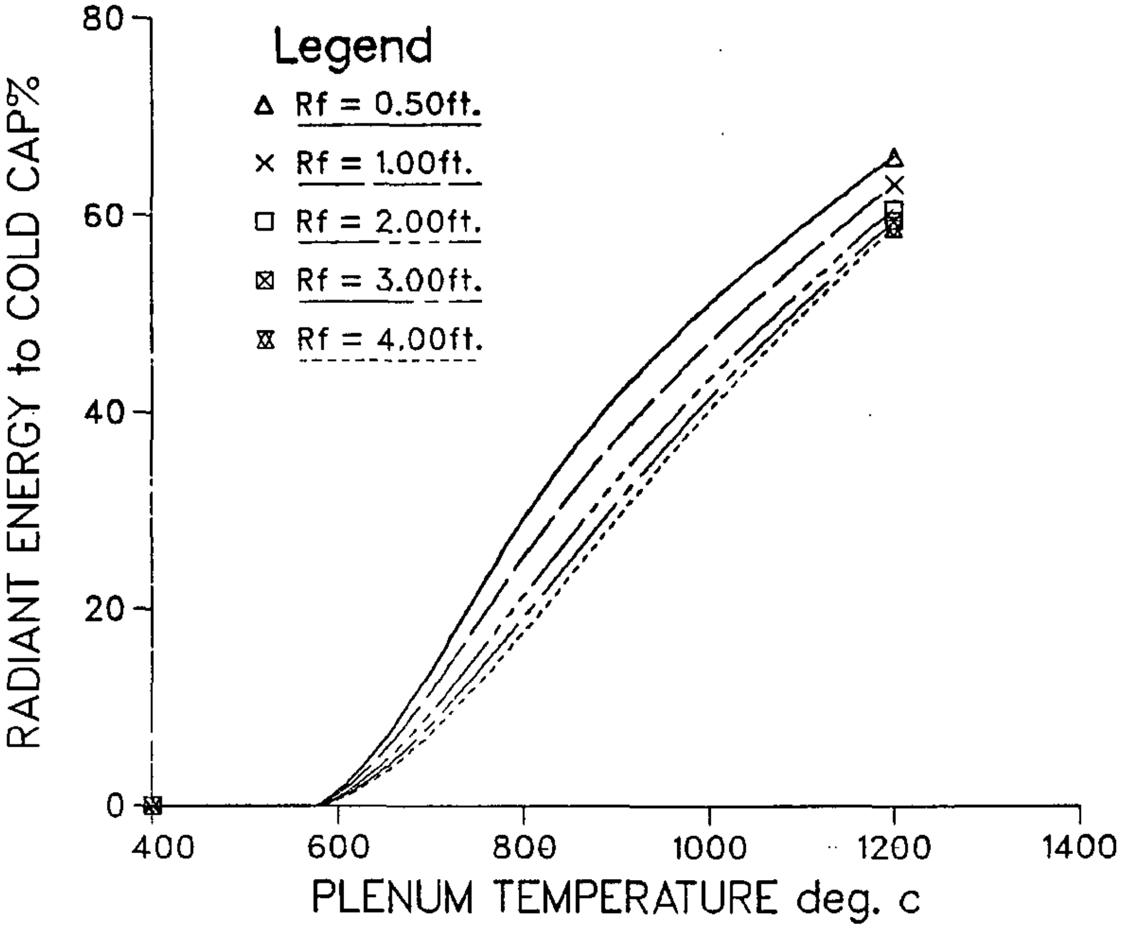

FIGURE 6. Radiant Energy to Feedpile vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

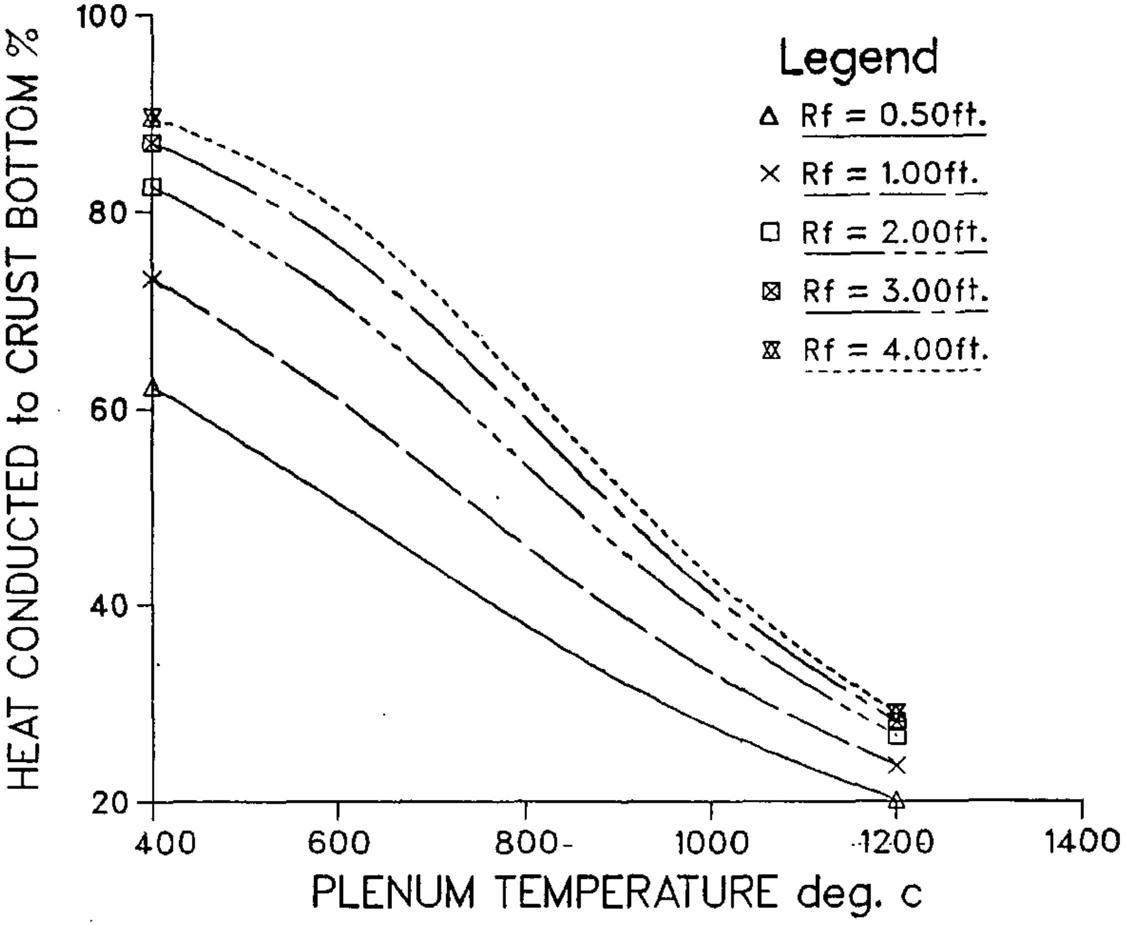

FIGURE 7. Heat Conducted to Crust Bottom vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

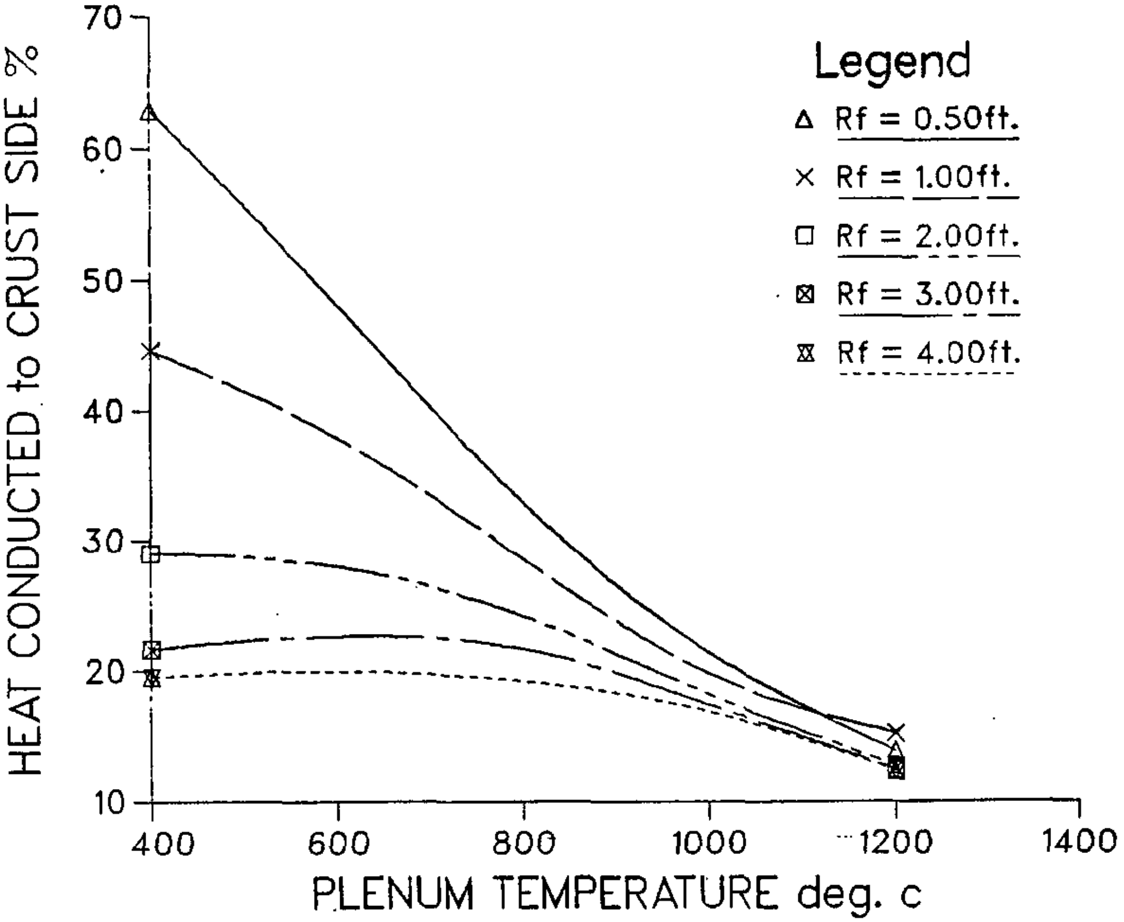

FIGURE 8. Heat Conducted to Crust Side vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

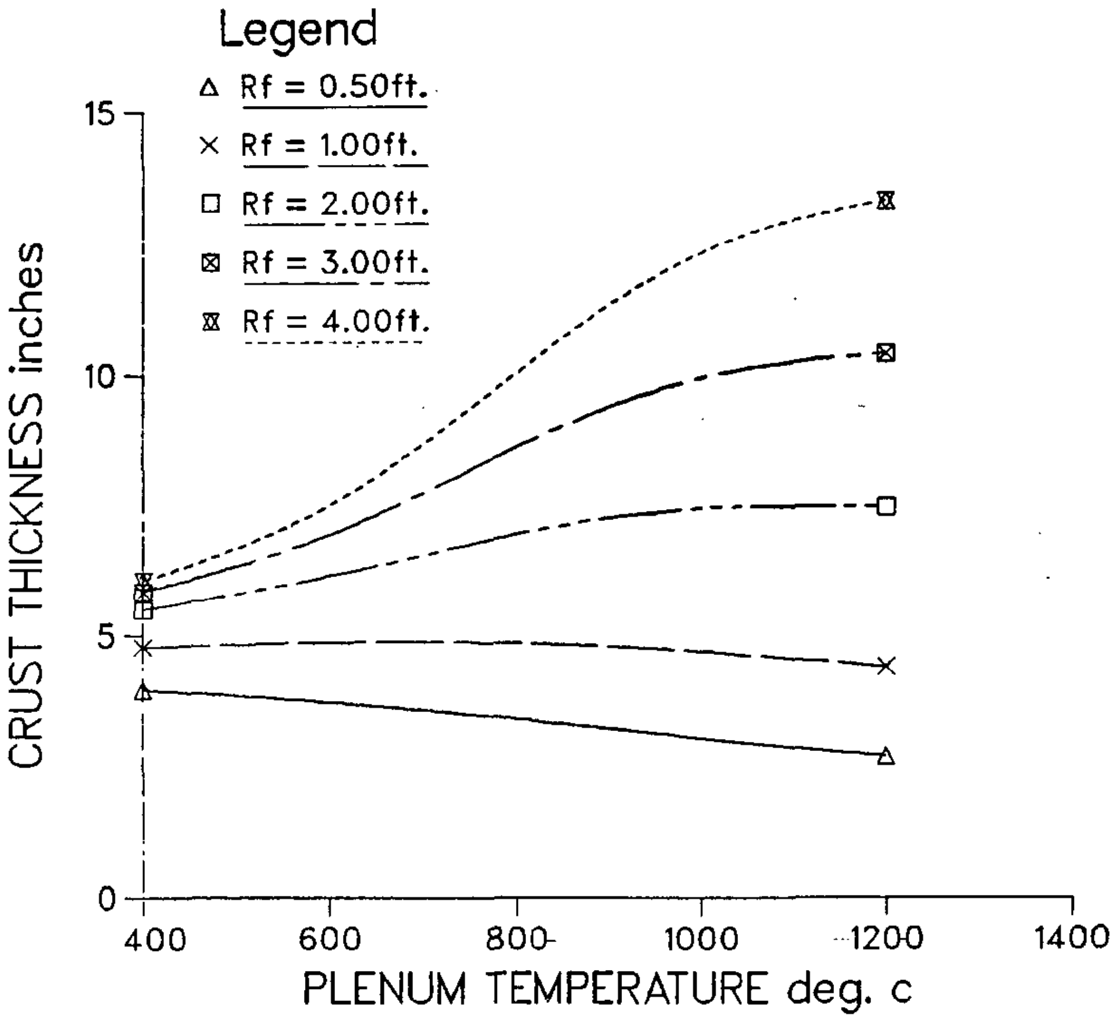

FIGURE 9. Crust Thickness vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

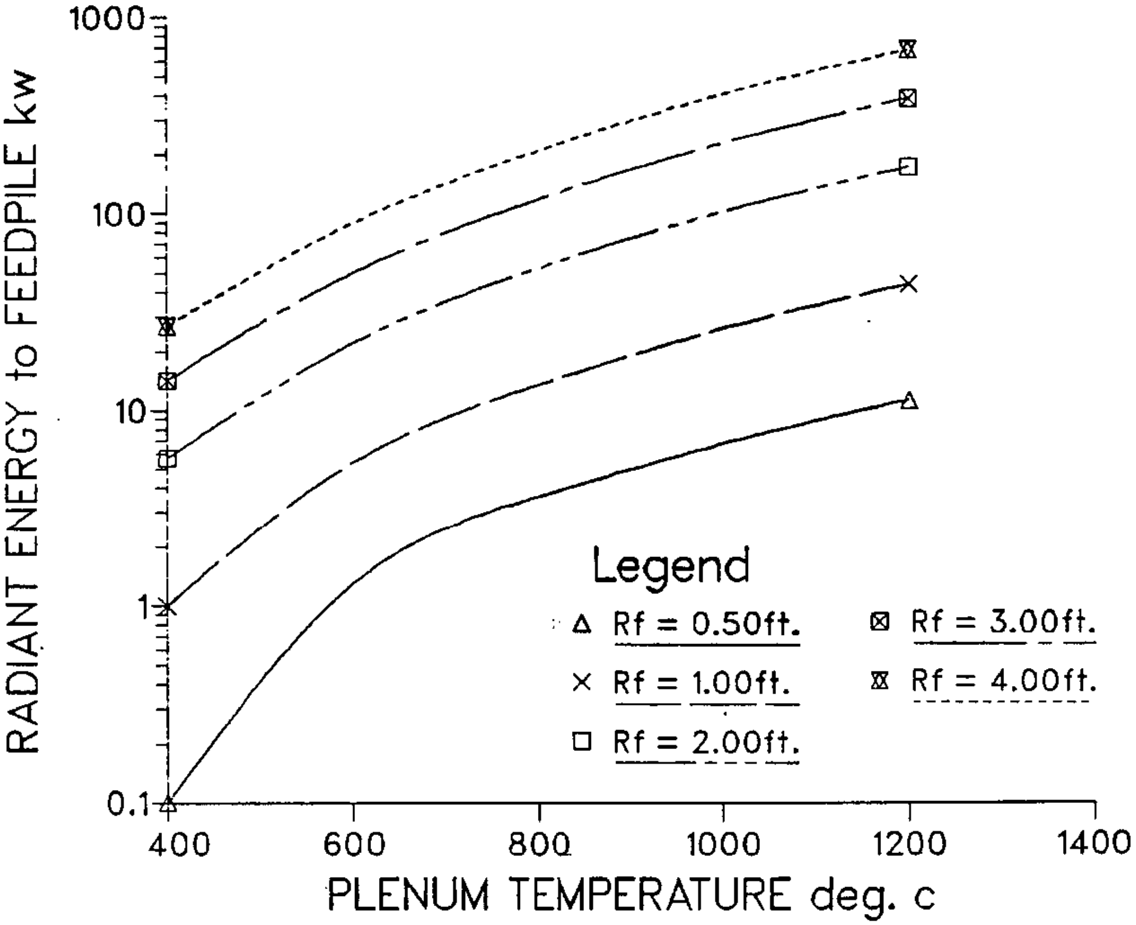

FIGURE 10. Radiant Energy to Feedpile from Lid vs. Plenum Temperature for Varying Feedpile Radius
Frit 165 + TDS-3A

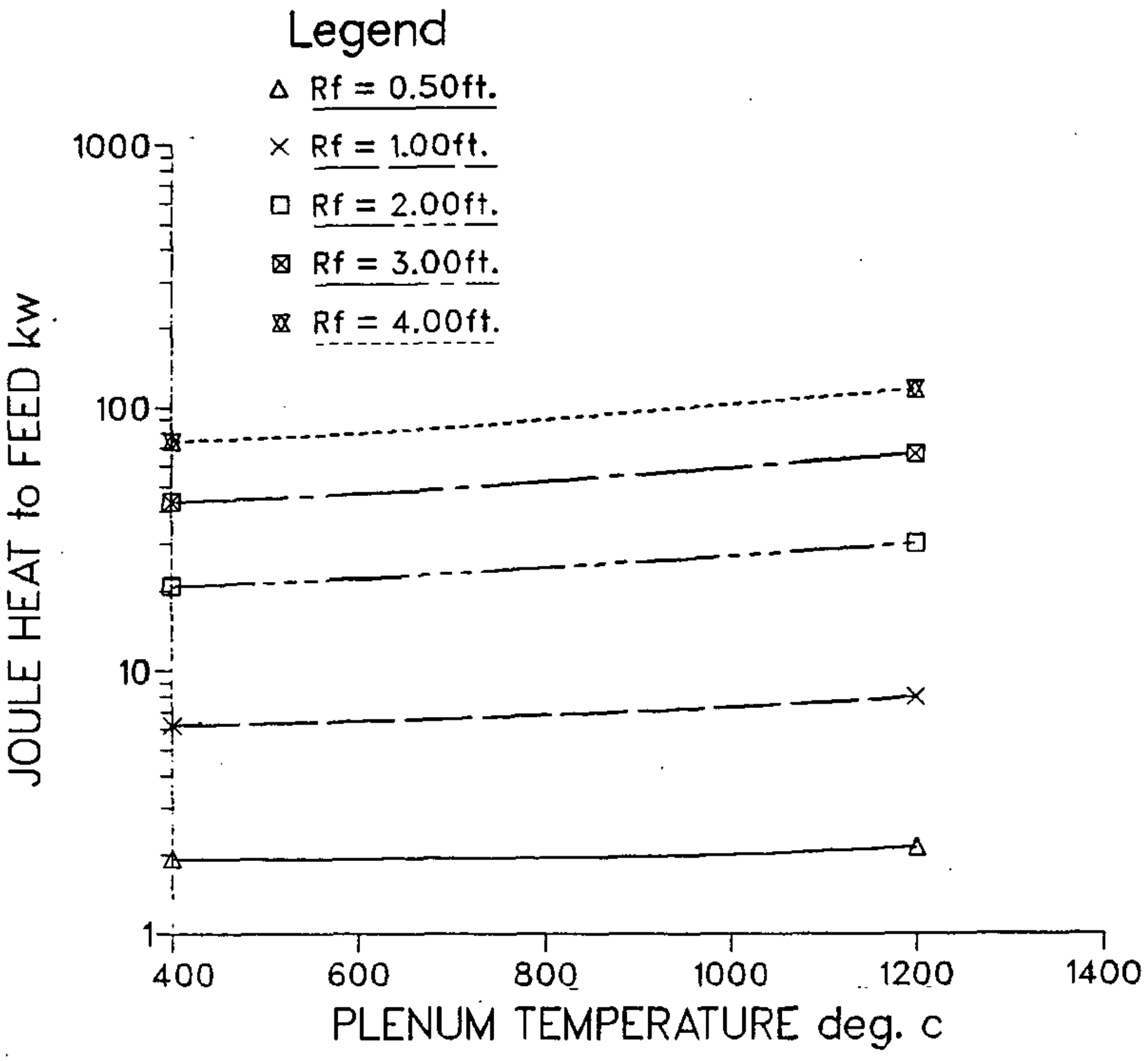

FIGURE 11. Joule Heat to Feedpile vs. Plenum Temperature for Varying Feedpile Radius Frit 165 + TDS-3A

At plenum temperatures above 800°C, the mass flux for Frit 165 simulated waste is relatively insensitive to changes in boundary layer thickness (Figure 12). An 8X increase in bounding layer thickness will result in a decrease in melt flux of only 10 to 15%. The mass flux for Frit 165 simulated waste is more responsive to changes in solids weight fraction (Figure 13) than to changes in boundary layer thickness.

Figures 14, 15, and 16 compare the melt behavior of Frit 211, Frit 131, and Frit 165 glasses. Frit 165 and Frit 131 glasses show a similar mass flux at plenum temperatures above 900°C. However, Frit 165 glass has a 10 to 20% lower mass flux than Frit 131 glass at plenum temperatures below 900°C. Lid heat requirements for Frit 165 glass are greater than that for Frit 131 glass. Joule heat supplied to the feedpile is consistently lower for Frit 165 glass. The most likely cause for the observed differences in power requirements is the higher viscosity of Frit 165 waste compared to Frit 131 waste. This causes the temperature at the bottom of the feedpile to increase from about 850°C for Frit 131 + TDS-3A waste to about 1000°C for Frit 165 + TDS-3 waste. This in turn increases the energy requirements of the glass in the feedpile, decreases heat transfer from the glass to the feedpile, and thus lowers the melt rate.

Frit 131 simulated waste is easier to melt than Frit 165 simulated waste. Frit 131 simulated waste uses less lid heat and offers 10 to 20% higher melt rates at expected DWPF melter plenum temperatures (<850°C). Theoretically, the DWPF melter should attain melt rates of 8 to 11 lb/hr-ft^2 with Frit 165 slurry feed (depending on feedpile radius) at this plenum temperature.

LSFM Dry Feeding Campaign

During the month of March 1983, the Large Slurry-Fed Melter (LSFM) was fed premelted black frit to obtain a melt rate equal to that of the larger DWPF melter. This campaign was necessary to simulate the pouring conditions of the DWPF melter to gain knowledge of the canister filling, sealing, and decontamination processes. The campaign began February 28 and ended March 29 after filling 17 canisters under reference conditions with Frit 165 simulated waste glass.

The dry feed campaign's primary function was to fill canisters under DWPF conditions to provide information for the canister development program. To accomplish this, the LWFM feed system was altered to provide the capability of feeding a premelted frit of composition similar to Frit 165 simulated waste glass (black frit). By feeding dry frit, instead of slurry, the LSFM was capable of obtaining a melt rate equal to that of a DWPF melter.

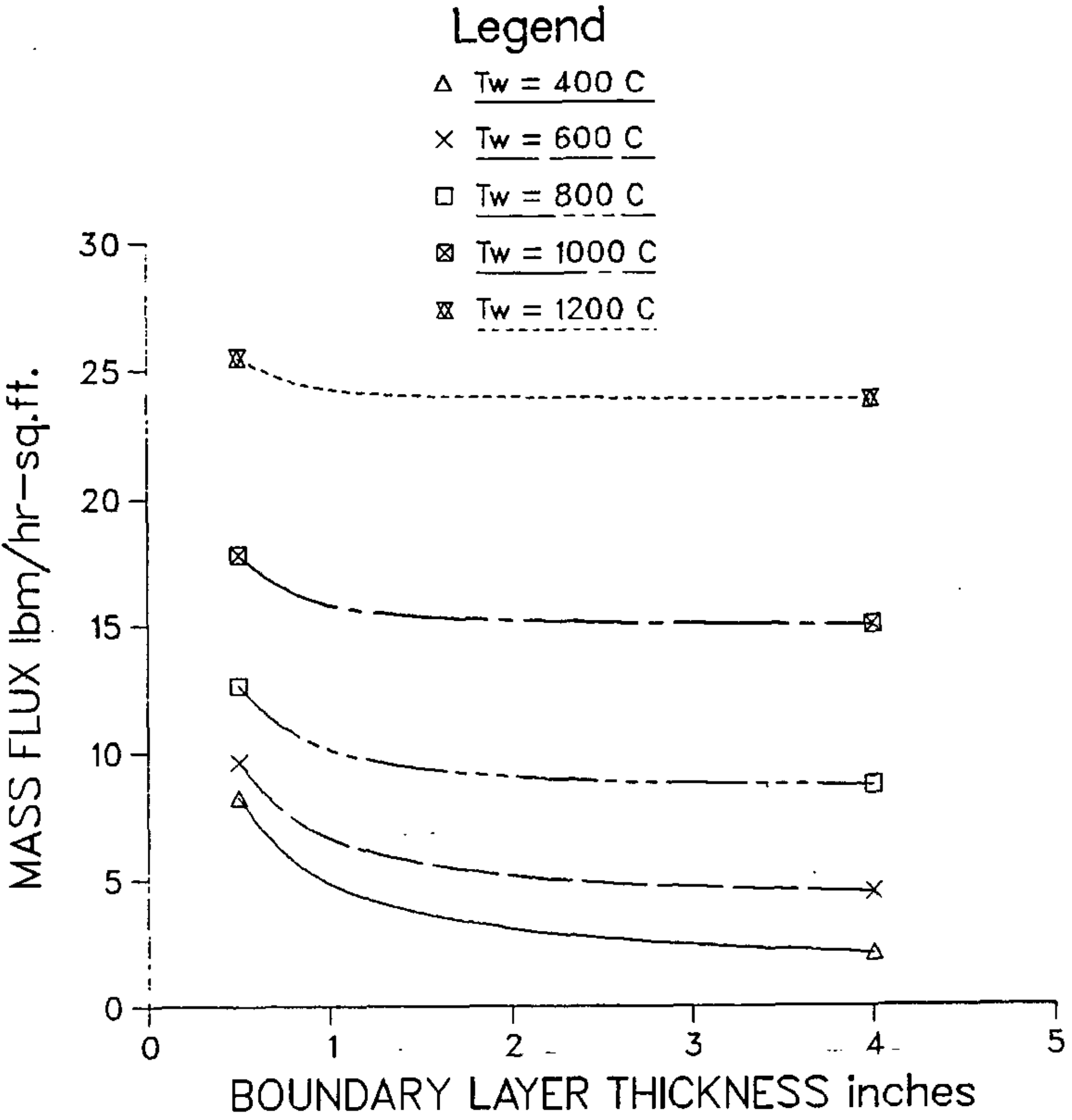

FIGURE 12. Mass Flux vs. Boundary Layer Thickness
for Varying Plenum Temperature
Rf = 3.0 ft

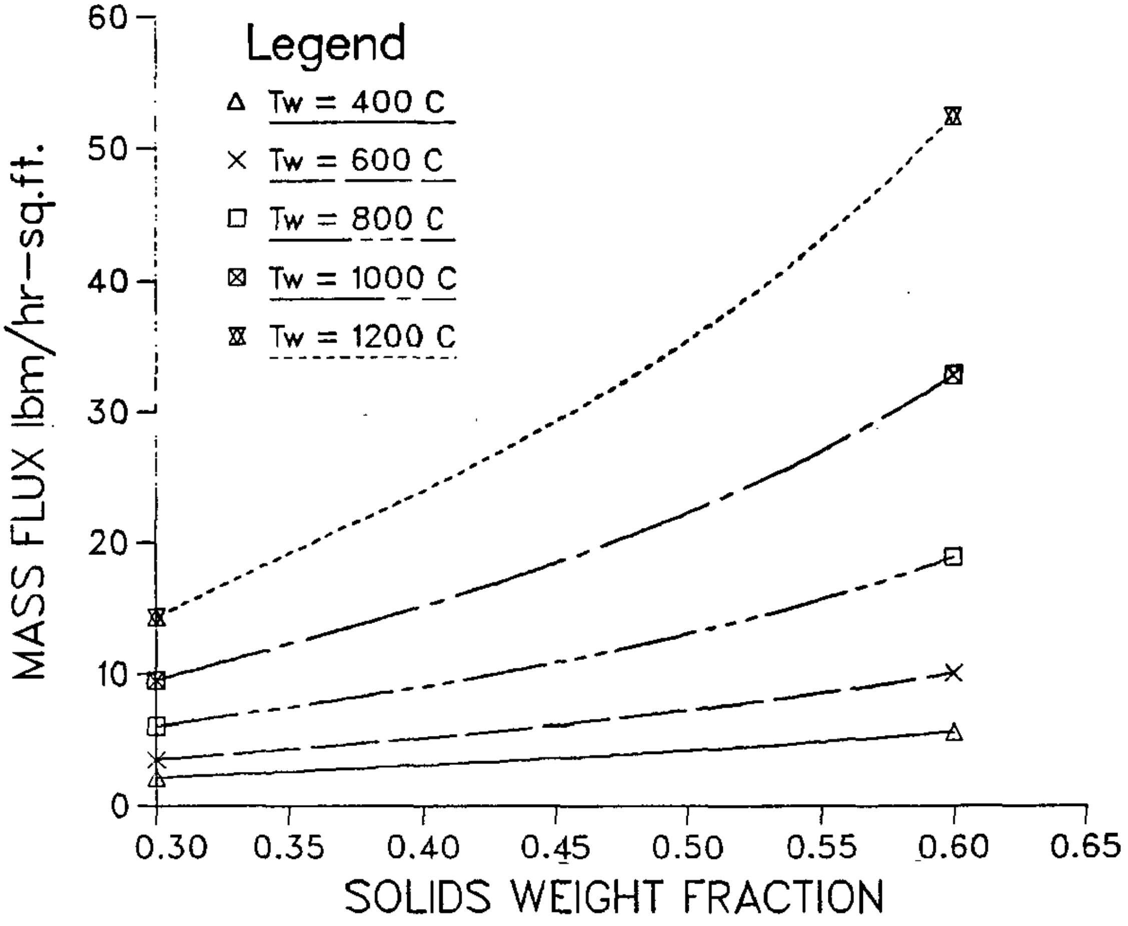

FIGURE 13. Mass Flux vs. Solids Weight Fraction for Varying Plenum Temperature
Rf = 3.0 ft

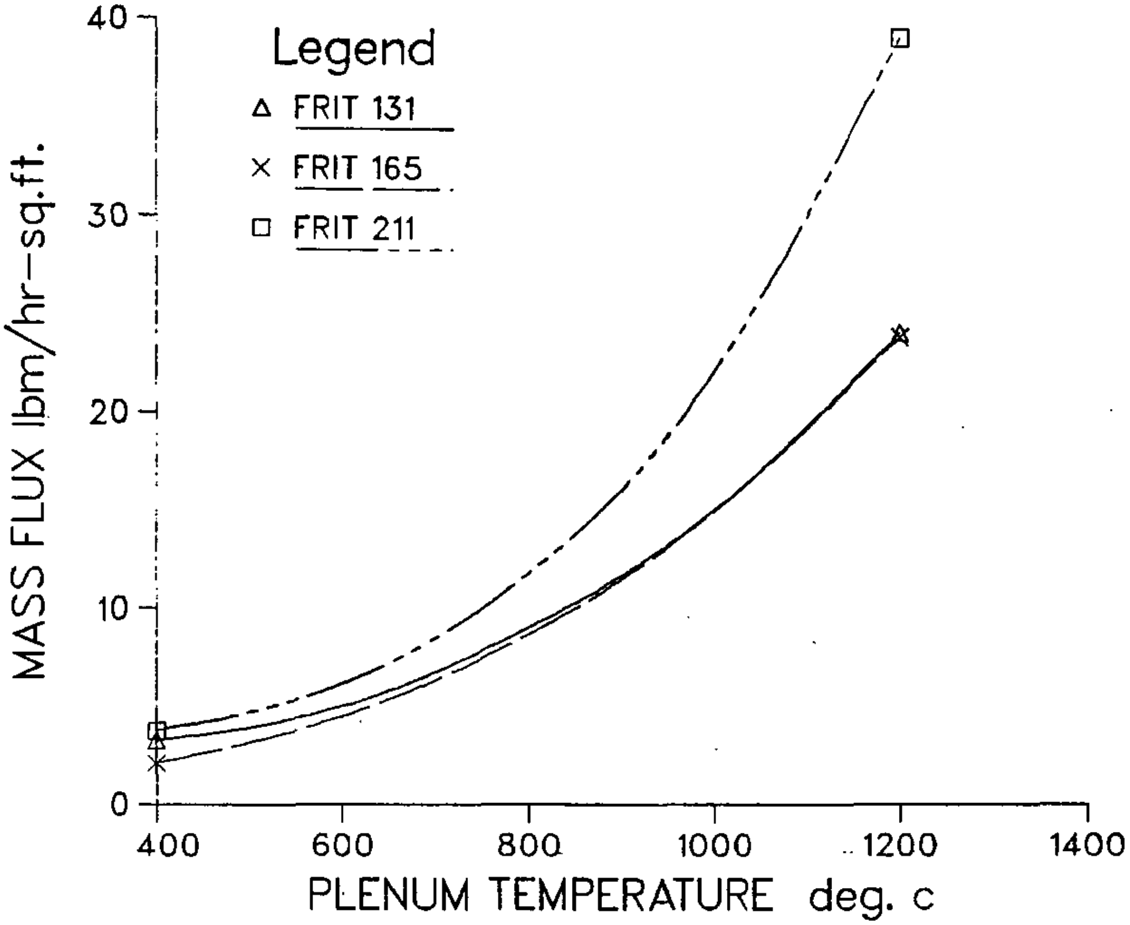

FIGURE 14. Comparison of Melt Rate Performance for Frit 165, Frit 131, and Frit 211 Glasses Rf = 3.0 ft, fs = 0.5, blt = 4.0 in.

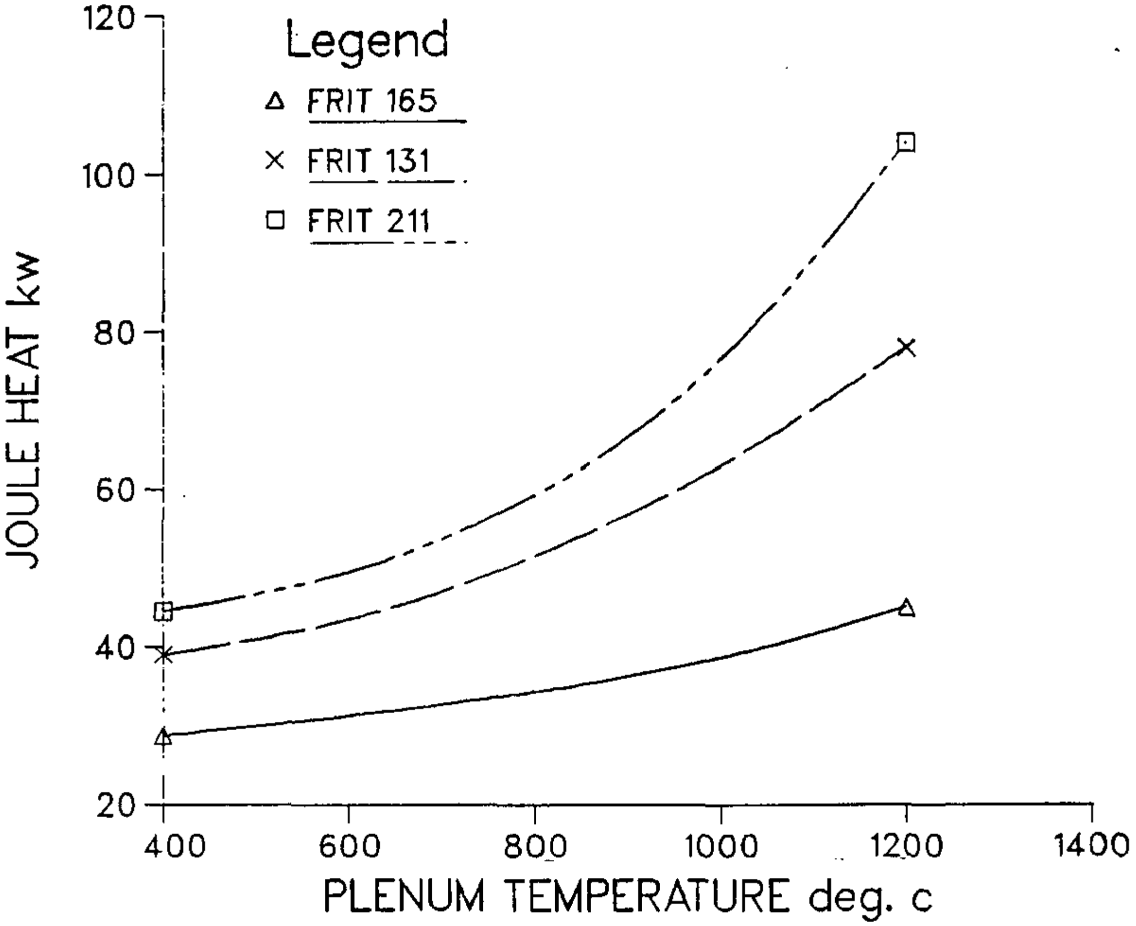

FIGURE 15. Comparison of Frit 165, Frit 131, and Frit 211 Glasses by Joule Heat vs. Plenum Temperature Rf = 3.0 ft, fs = 0.4, blt = 4.0 in.

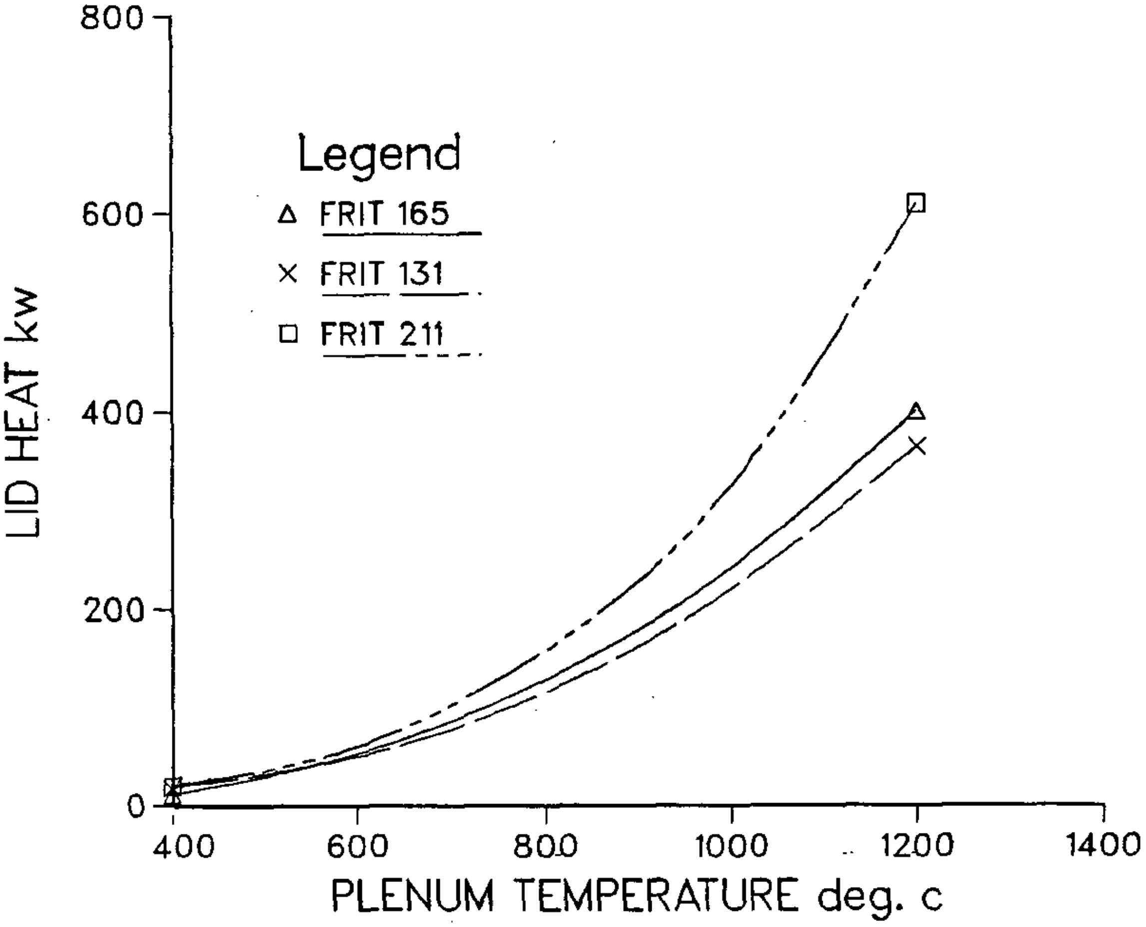

FIGURE 16. Comparison of Frit 165, Frit 131, and Frit 211 Glasses by Lid Heat vs. Plenum Temperature Rf = 3.0 ft, fs = 0.4, blt = 4.0 in.

Feed Summary

The black frit used in the campaign was purchased from two frit vendors (Mobay and Ferro) and consisted of a Frit 165 simulated waste glass. The composition was derived by combining the waste oxides of simulation 3 with Frit 165 in a 28/72 oxide to frit ratio.

Table 18 shows the goal composition and the composition of each frit vendor and the frit size for each vendor as received. A goal for both batches was -80 mesh. The Mobay black frit was considerably finer than the Ferro black frit.

Although chemically the two frits were similar, physical differences existed, most probably a result of the frit packaging. The Ferro frit was shipped in 500-pound drums which were tightly sealed with a lid gasket. Contrarily, the Mobay frit was shipped in 400-pound drums lined with plastic, but containing a poor metal-to-metal drum seal with no lid gasket. In addition, the Mobay drums were old and rusty, and generally appeared in much poorer condition than the Ferro drums. As a result of these differences, all Ferro frit drums contained dry material, whereas the Mobay drums contained moist and lumpy frit. In some cases the Mobay frit had become "cemented" together in large chunks. Most often, the frit near the top of the drum was in the worst condition. In addition, the condition of the Mobay frit varied considerably from drum to drum.

Both batches of frit were stored onplant for a considerable length of time before being fed in the dry feed campaign. The delivery date for the Mobay frit was 8-6-82, while the Ferro frit was approximately 2 weeks later. A portion of both was stored outside beneath a tarp. Whereas the condition of the Ferro frit was independent of storage location, the Mobay frit was somewhat affected. Mobay drums stored outside were in slightly worse condition than the drums stored inside. However, the important point is that adequate drum sealing can prevent poor frit condition, regardless of the storage location.

Feed System

As a result of the difference in frit condition, feeding difficulties were encountered with the Mobay frit. The feed system used during this campaign was originally used to feed the in-can melter during its dry feeding campaigns. The system was adapted for the LSFM and is shown in Figure 17.

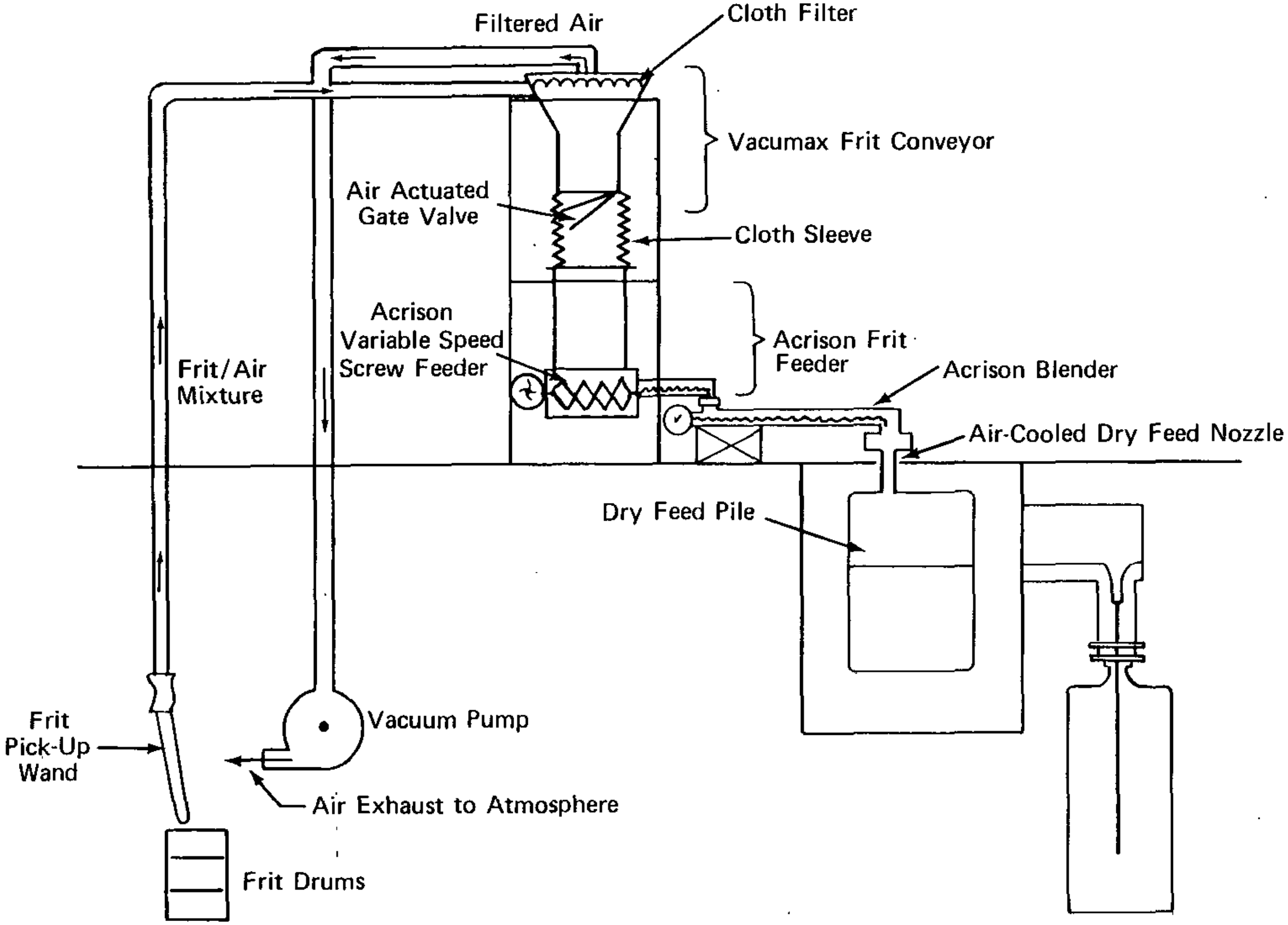

FIGURE 17. LSFM Dry Feed System

TABLE 18

Black Frit Composition

Component	Goal	Mobay	Ferro
SiO_2	54.7	55.4	54.1
Fe_2O_3	11.2	11.3	12.3
Na_2O	10.9	10.4	10.3
B_2O_3	7.2	7.2	6.8
Li_2O	5.0	4.8	4.7
Al_2O_3	4.3	4.2	4.1
MnO_2	2.5	2.1	2.9
CaO	1.3	1.1	1.5
NiO	0.9	0.9	0.9
MgO	0.7	0.7	0.8
ZrO_2	0.7	0.9	1.2
F		0.14	0.06
Cl		Nil	0.05
P_b		Nil	0.05
K_2O		0.14	
TiO_2		0.23	
BaO		0.07	
ZnO		0.05	

Black Frit Screen Analysis

Mesh	Mobay, wt %	Ferro, wt %
+80	0	2
-800 +200	4	50
-200 +325		23
-325	96	25

The system uses a vacuum frit conveyor to transfer the frit from ground level to the melter level. The frit conveyor is coupled to a screw feed and operates automatically to convey frit to maintain an adequate amount in the feeder hopper. The feeder is the device which actually determines the feed rate to the melter by its variable speed motor. In addition, the screw feeder is equipped with a secondary, screw-like, device which mixes the frit near the bottom of the feeder hopper to eliminate frit bridging.

The feeder was designed for feeding fine ground frit. During operation of this campaign the frit feeder was operated at maximum speed to maintain the desired feed rate of 240 lb/hr. To adapt this feed system to the LSFM, a blender (simply a larger screw feeder) was installed to transfer frit from the feed to the melter. The feed then entered the melter through an air-cooled feed nozzle.

During the campaign the feed system operated well when dry frit was fed. The Ferro frit was fed while filling the first eight canisters (31,000 pounds). During the ninth canister the Ferro frit supply was exhausted and the Mobay black frit was fed for the final 2000 pounds of the canister fill. Immediately, the feed rate to the melter dropped off although the frit feeder was operating at maximum speed. Evidently, the moist Mobay frit fed at a slower rate in the frit feeder. This was probably caused by frit bridging in the feeder hopper and also because the moist frit seems to contain a significant amount of void volume as a result of its lumpiness. To maintain the desired feed rate of 240 lb/hr, the feed system was supplemented by manually feeding a desired amount of frit every half hour. It is interesting to note that the feed rate (from the frit feeder) varied from dum to drum with the Mobay frit. Thus, the amount of frit added manually varied from drum to drum so that an average pour rate of 240 lb/hr was maintained. Whereas the Ferro frit fed at 240 lb/hr through the feed system, the Mobay frit only fed at a rate of 120 to 200 lb/hr. The final 8 canisters were all filled by supplementing manual feeding with the dry feed system.

Melter Operation

Melter conditions for this campaign were similar to those on past slurry-fed runs. They included even power skewing on the main electrodes, a bulk glass temperature of 1150°C, and a plenum temperature of 800 to 850°C. Air sparging bubblers were not used.

Canisters were filled on a daily basis, lasting about 6 hours. The melter was then returned to idle conditions until the next canister fill began, usually the following day. As a result, steady-state melter operation was never achieved. (Normally, 48 to 72 hours are required to reach steady state). Near the end of each canister fill the main electrode power requirements averaged 50 to 60 kilowatts, and the lid heat power requirements averaged 55 kilowatts. For comparison, power inputs for Frit 165 feeds while slurry feed (LSFM-6, 7, 8), ranged from 52 to 60 kilowatts on the main electrode and 75 to 100 kilowatts for lid heat.

Thus, the main electrode energy, or joule heat, is very similar for both slurry feeding and dry feeding, indicating similar bulk glass heat transfer for the two feeding modes. The amount of lid heat was different between the two because of the extra energy needed to evaporate water in the slurry. Keep in mind that steady-state conditions were not reached during the dry feeding campaign and, thus, the results are of only limited value.

As expected, the feedpile for dry feeding was much different than slurry feeding. While slurry flows and covers the entire melt surface in a relatively thin layer, dry frit tends to pile up directly beneath the feed entry. During this campaign, feeding 240 lb/hr, the feedpile height reached 12 inches or more while the melt surface coverage appeared to be only 50 to 60 percent of the total 12-square-foot surface area. Thus, it appears that the LSFM can maintain a 20 lb/hr-ft^2 melt flux while feeding Frit 165 black frit.

For all canisters, DWPF pouring conditions were simulated by maintaining a melter pour spout temperature of 1050°C. The goal pour rate was 240 lb/hr. Table 19 summarizes each canister filled in the dry feeding campaign. Most canisters were filled to 3900 pounds although the reference weight is 3260 pounds. A combination of two factors account for the difference. First, the canister nozzle has been shortened which increases the canister volume. Secondly, the density of Frit 165 waste glass was measured at 169 lb/ft^3 which is about 10% higher than the value measured for previous glasses. The combination of these two factors required a glass fill of 3900 pounds while still maintaining a 3.7-cubic-foot freeboard within the canister.

Canisters 6 and 9 were filled at slightly lower pour rates. During Canister 6, melter power was lost three times because of a faulty circuit breaker. As a result, the average pour rate for that can was only 217 lb/hr. In addition, the canister load cells (weight reading) were reading incorrectly, and this resulted in filling the canister to 4400 pounds (500 pounds more than desired). The load cell problem was traced to a cover guard which displaced part of the canister weight. This exemplifies the need for a canister level detection device in the DWPF to prevent canister overfills. Load cells alone are not sufficient.

TABLE 19

LSFM Dry Feed Campaign

Can No.	Date Filled	Identification	Pour Rate, lb/hr	Glass Wt, lb
1	2/28	CS-1	248	3,307
2	3/2	MS-15	250	3,499
3	3/4	MS-14	254	3,900
4	3/7	MS-21	240	3,917
5	3/8	MS-11	240	3,900
6	3/11	UF-25	217	4,400
7	3/14	UF-26	242	3,959
8	3/15	MS-22	237	3,895
9	3/17	Ti	208	3,750
10	3/18	MS-12	241	3,891
11	3/21	MS-17	254	3,751
12	3/22	UF-24	233	3,918
13	3/23	UF-29	240	3,900
14	3/24	UF-27	232	3,829
15	3/25	UF-28	235	3,901
16	3/28	MS-23	243	3,950
17	3/29	CS-2	239	3,265
				64,932

The Canister 9 filling occurred during the transition from the dry Ferro frit to the moist Mobay frit. The average pour rate for this can is lower because of feeding problems with the Mobay frit. By the end of the canister fill, the problem was resolved by supplementing manual feeding. All remaining canisters were filled near the desired rate of 240 lb/hr.

Over the entire campaign, seventeen canisters were filled with 64,932 pounds of glass. All canisters were reference 24-inch-diameter cans fabricated from stainless steel (14), carbon steel (2), or titanium. A few of the canisters were insulated with one or two inches of Kaowool® (Babcock and Wilcox Co.) insulation. During filling, these canisters expanded in length by as much as 1-1/2 inches. Without insulation, the canister thermal expansion during filling was much less noticeable (probably 1/2 inch).

LSFM Total Glass Production

Since startup in January 1982, the LSFM has operated for over 14 months. During that time, eight separate slurry-fed campaigns have been completed in addition to a dry feed flushing (to Frit 165 glass), dry feeder checkout, and this dry feed campaign. Including all of these, the LSFM has produced over 107 tons of simulated waste glass while feeding a total of 86 days (Table 20). The LSFM has surpassed both the total operating time (13 months) and the total glass production (74 tons) of the 1941 melter.

TABLE 20

LSFM Glass Production

Run	Date	Length, days	Frit Type	Glass, lb
LSFM-1	2/82	2	131	2,750
LSFM-2	3/82	4	131	4,600
LSFM-3	4/82	5	131	9,600
LSFM-4	5/82	5	131	11,000
LSFM-5	6/82	14	131	35,005
Dry Feed Flushing	9/82	3	165	11,147
LSFM-6	9/82	11	165	19,190
LSFM-7	11/82	10	165	17,622
Dry Feed Checkout	1/83	10	165	2,774
LSFM-8	1/83	10	165	23,315
LSFM-8A	2/83	4	165	9,253
Dry Feed Campaign	3/83	17	165	64,932
Miscellaneous				
		86		214,282

214,282 = 107.1 tons

Energy Balance on the Large Slurry-Fed Melter, Runs 5-8

Energy balances are important to identify heat losses and optimize process parameters for any process. Specifically, for a joule-heated glass melter, an energy balance can be used to determine power requirements and power distribution within the melter. An energy balance has been performed on the large slurry-fed melter (LSFM), not only to optimize the slurry-fed melting process, but also to determine differences in melter operation with different glass compositions. This report includes energy balance calculations for LSFM Runs 5-8, including melter operation with both Frit 131 and Frit 165 slurry feeds.

An analysis of the results of energy balances on the LSFM for Runs 5-8 show that:

- One-half of the energy supplied b the LSFM lid heaters is lost to air inleakage into the melter plenum.
- Heat transfer from the melt pool (joule-heat) to the cold cap with the Frit 165 glass composition (without bubbler) is 43% less than Frit 131 glass.
- With the use of air sparging bubblers in the LSFM, heat transfer from the melt pool to the cold for Frit 165 glass is equal to that for Frit 131 glass without bubblers.
- The high air inleakage (850 lb/hr) reported during LSFM Run 6 was not caused by extra inleakage in the melter plenum. An energy balance shows that the air inleakage into the melter plenum was similar to that of all other runs (~400 lb/hr).
- The TDS air inleakage rate of 20 lb/hr seems overly optimistic. A more realistic minimum of 100 lb/hr should be used for the DWPF melter.

Discussion

LSFM Runs 5-8 were slurry-fed melter runs lasting 10 or 15 days in which steady-state conditions were reached. During each run a melter plenum temperature of 800°C was used along with a bulk glass temperature of 1150°C. Slurry feeds consisted of both Frit 131 and Frit 165 feeds using the simulation 2 formated waste composition.

Heat energy is supplied to the LSFM by two main electrode pairs, one riser electrode pair, 4 pour trough heaters, one pour spout heater, and 12 lid heaters. Figure 18 shows the approximate location of each heat source within the melter. Only the main

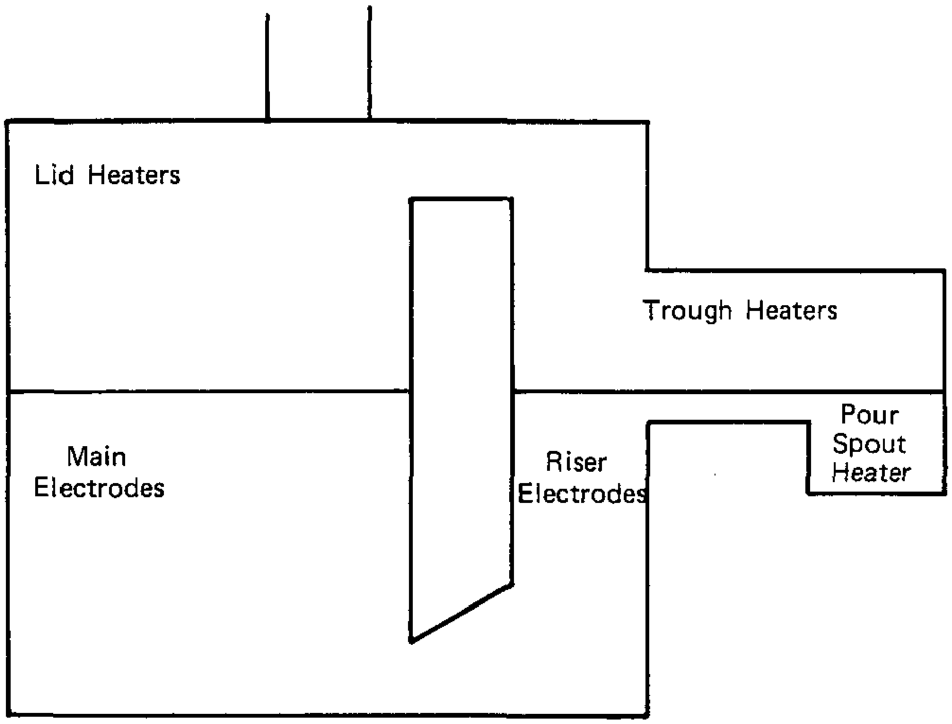

FIGURE 18. Melter Heat Input

electrodes and riser electrodes extend into the molten glass. The other heaters are used either to supplement melting or aid in pouring the molten glass at a desired temperature.

Heat losses leave the melter in a variety of manners. First, conductive heat losses continually escape from the melter shell due to the temperature differential between the inside of the melter and the ambient conditions on the outside of the melter. Second, the melter is equipped with an off-gas system which continually draws hot vapors from within the melter plenum. During run conditions the vapors consist of two main fractions; steam from the incoming slurry feed and air from air inleakage points within the melter plenum. In addition, there is a small amount of calcination gases which form during melting of slurry solids and are also drawn off. Third, a glass pour stream (usually 1050°C) leaves the melter in direct proportion to the amount of incoming slurry being fed and melted. Figure 19 shows the approximate location of each heat loss. In the figure, the conductive heat losses are divided into that fraction which escapes below the melt line and that fraction which escapes above. This was done only to make computations easier. The heat transfer coefficients and conductive energy losses for the LSFM were obtained from the Design Basis of the LSFM. The values amount fo 22.8 kW below the melt line and 8.8 kW above the melt line.

With different flows (slurry, off-gas vapors, molten glass) entering and leaving the melter, an energy balance must also include a mass balance. Figure 20 shows where components enter and leave the melter. Those entering include the incoming slurry feed and also any air inleakage into the melter plenum. Leaving streams include only the molten glass pour stream and the off-gas vapors. Under steady-state conditions the slurry feed rate, glass pour rate, and the amount of steam and calcination gases are directly proportional to one another based on the solids loading of the feed and also the solids to glass conversion factor. On all LSFM runs thus far the solids to glass conversion has been very consistent, and for all calculations in this report a value of 0.90 is used.

This means that for each 100 pounds of slurry solids fed, 90 pounds of glass and 10 pounds of calcination gases are produced. For the LSFM runs considered in this report the solids loading of the slurry feed has varied, but for each run the average value is given in Table 21.

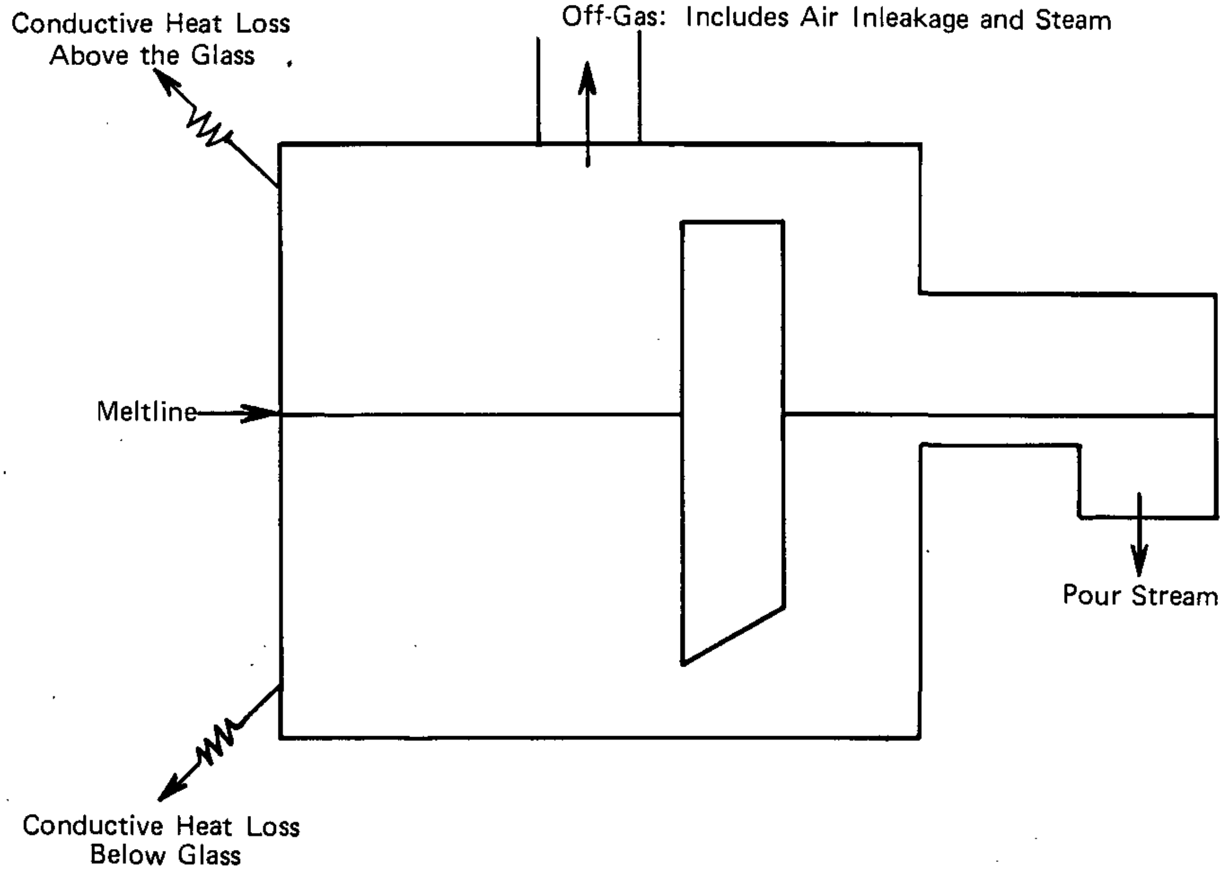

FIGURE 19. Melter Heat Losses

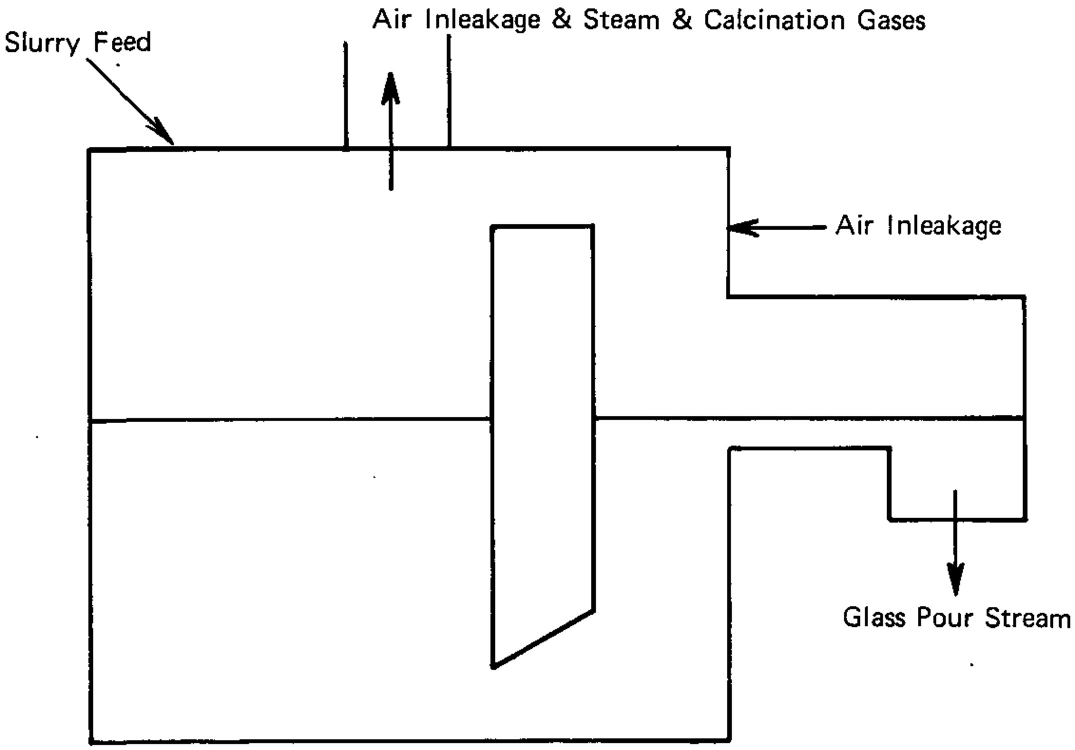

FIGURE 20. Mass Balance

TABLE 21

Solids Loading for LSFM Runs

Run No.	Wt % Solids	Frit Type Used
5	45	131
6	45	165
7	41	165
8	45	165

Figure 21 shows energy inputs and mass flows both entering and leaving the melter for LSFM Run 5. The energy balance is taken around the entire melter (dotted line). For this run and all other runs considered, the values for mass flows and energy inputs were obtained during periods of steady-state operation with the melter operating at near maximum capacity (85 to 95% cold-cap coverage). In addition, the amount of lid heat reported in LSFM run summaries has been reduced by 10% due to the power loss caused by the lid heater power controllers. To calculate the heat input necessary to change from slurry at 25°C to molten glass (pouring at 1050°C) and steam and calcination gases (both at 800°C), the heat capacity of glass and the enthalpy change of water at 25°C to steam at 800°C were used. The heat capacity of the calcination gases was considered to be equal to that of air. Although there is an exothermic reaction which occurs during melting, the energy generated is small compared to the energy losses in the melter, and thus, the heat of reaction of melting was assumed to be zero.

Enthalpy changes used in calculations for each run is listed in Table 22. Table 23 gives the power inputs for each run, while Table 24 gives mass flows. Table 25 gives the enthalpy difference for slurry to glass, steam, and calcination gases, in addition to air inleakage (25 to 800°C).

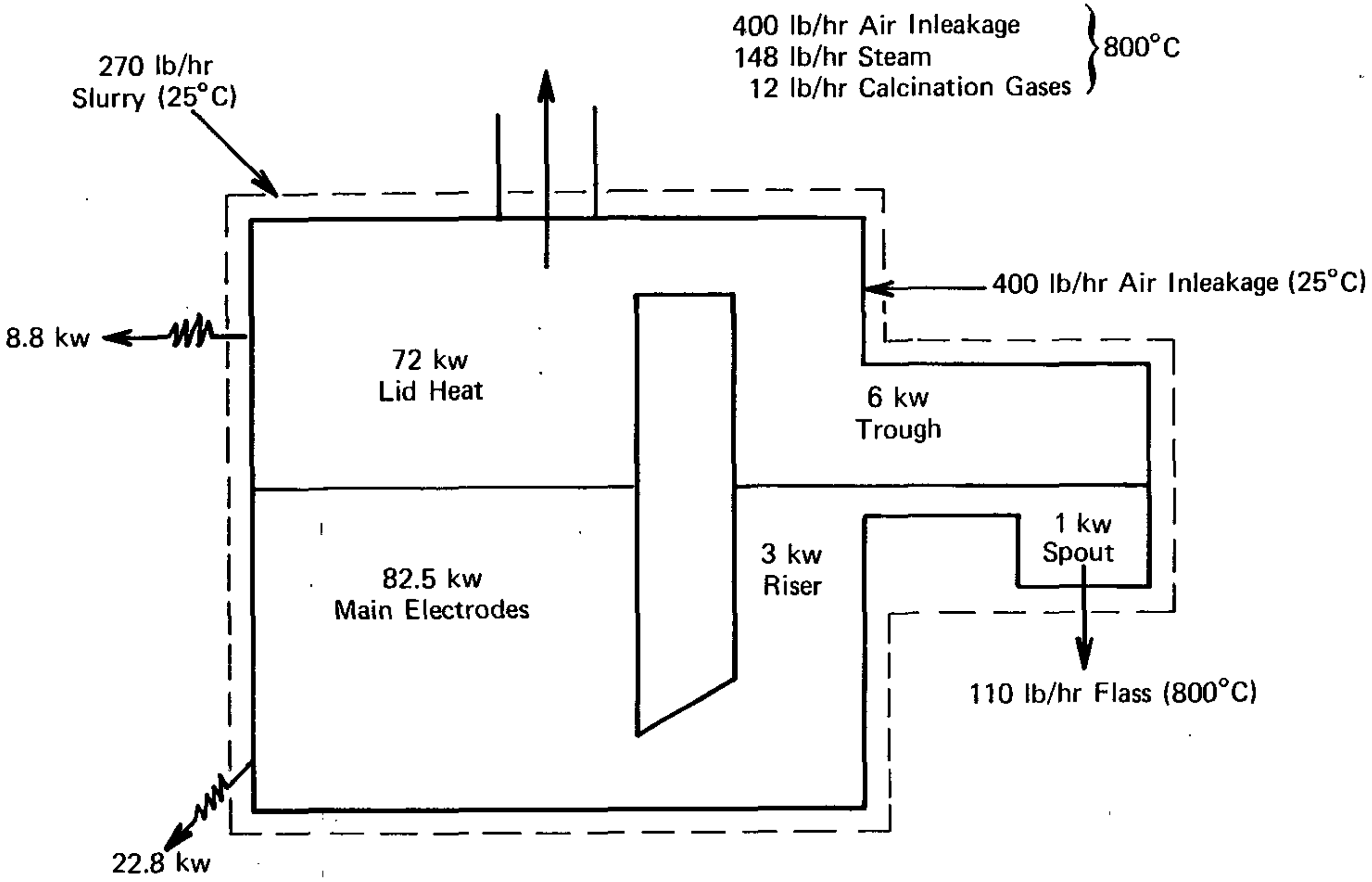

FIGURE 21. LSFM-5 Energy Balance

TABLE 22

Enthalpy Changes

Heat loss to air inleakage (25 -- 800°C) = 0.11 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (air)}}$

Heat loss to steam [water (25°C) -- Steam 800°C] = 0.52 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (steam)}}$

Heat loss to glass

[slurry solids (25°C) -- glass (800°C)] = 0.12 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (glass)}}$ (Run 5)

[slurry solids (25°C) -- glass (1050°C)] = 0.15 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (glass)}}$ (Runs 6-8)

Heat loss to calcination gases (25-800°C) = 0.11 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (gas)}}$

Steam heating (100°C-800°C) = 0.178 $\frac{\text{kW}\cdot\text{hr}}{\text{lb (steam)}}$

TABLE 23

Power Inputs

Run No.	Main Electrodes, kW	Riser Electrodes, kW	Total Energy Below Melt, kW	Lid Heat, kW	Trough, kW	Spout, kW	Total Energy Above Melt, kW
5(131)	82.5	3	85.5	72	6	1	79
6(165)	60	3	63	76.5	6	1.5	84
7(165)	54	2.5	56.5	85.5	6	1.5	93
8(165)	52	3	55	74.7	6	1.5	82.2
8(air bubblers)	80	1	81	73.8	6	1.5	81.3

TABLE 24

Mass Flow Rates

Run No.	Air Inleakage, lb/hr	Slurry (25°C), lb/hr	Steam (800°C), lb/hr	Glass Flow, lb/hr	Calcination Gas Flow, lb/hr
5(131)	400	270	148	110(800°C)**	12
6(165)	850(400)*	215	118	87(1050°C)	10
7(165)	350	211	124	78(1050°C)	9
8(165)	350	193	106	78(1050°C)	9
8(air bubblers)	350	270	148	110(1050°C)	12

TABLE 25

Enthalpy Difference

Run No.	ΔH Air Inleakage, kW	ΔH Glass, kW	ΔH Steam, kW	ΔH Gases, kW	Total ΔH, kW
5(131)	44.1	13.5	77.6	1.3	136.5
6(165)	93.7(44.1)*	14.1	61.9	1.1	170.8(121.2)*
7(165)	38.6	12.6	65.0	1.0	117.2
8(165)	38.6	12.6	55.6	1.0	107.8
8(air bubblers)	38.6	17.8	77.6	1.4	135.4

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* Parentheses indicate values assuming 400 lb/hr air inleakage during Run 6.

** The original pour spout element poured glass at 800°C. It was replaced with a larger element after Run 5.

For all the runs considered, the melter plenum temperature was controlled at 800°C by varying the amount of lid heat. Temperature measurments made during Run 6 showed that the true off-gas temperature was equal to the measured plenum temperature. Thus, all gases leaving the melter plenum are at 800°C for each run. In Table 23, the total power going into the melter is divided into that below the melt line and that portion above the melt line. Only the main electrodes and riser electrodes produce heat below the melt line. Table 23 also shows that the power produced by the main electrodes is similar for Runs 5 and 8 (with air bubblers) while Runs 6, 7, and 8 are also similar, but at a much lower power setting. This was caused by the different glass compositions used (Table 26) and the dramatic effect produced by air sparging bubblers. Run 5 with Frit 131 glass used 82.5 kW by the main electrodes and achieved a melt rate of 9.2 lb/ft^2. With Frit 165, on Runs 6-8, the power needed by the main electrodes dropped by approximately 30%, along with the melt rate, until air sparging bubblers were used during the latter part of Run 8 to increase convection in the melter. The Frit 165 glass composition has a much higher viscosity (Table 26). In the LSFM, air sparging bubblers are needed to obtain melt rates equal to those obtained with the Frit 131 glass composition. The increased convection produced by air bubblers has a very dramatic effect on both electrode power and melt rate as it aids in heat transfer from the melt pool to the cold cap.

TABLE 26

Glass Composition

Component	Frit 131	Frit 165
SiO_2	57.9	68.0
B_2O_3	14.7	10.0
Li_2O	5.7	7.0
Na_2O	17.7	13.0
ZrO_2	0.5	1.0
MgO	2.0	1.0
TiO_2	1.0	-
La_2O_3	0.5	-
Viscosity at 1150°C	18 poise	55 poise

The amount of lid heat used during each run is also given in Table 23. The amount is very similar for all runs except Run 7. This is related back to the solids content of the incoming slurry (Table 21). All runs fed 45 wt % solid feed except Run 7 (41 wt %). Therefore, the amount of lid heat used during Run 7 was greater because more water vapor was heated in the melter plenum. However, to compare the amount of lid heat between different runs, the feed rate must also be considered. With a lower feed rate, the amount of lid heat used should be less unless more lid heat is being used to melt the cold cap. On Runs 6-8 the feed rate was lower than for Run 5, and so it appears that more lid heat is being transferred to the feedpile during these runs. This corresponds to a change in glass composition (to Frit 165), and so it appears that for Frit 165 feeds more lid heat is effectively used in the feedpile. This fact will be further examined later.

Table 24 gives air inleakage rates which were recorded by measurements in the off-gas line. For all runs except Run 6 the inleakage is 350 to 400 lb/hr. Because of this, the 850 lb/hr for Run 6 is somewhat suspect. As we will see later this value cannot be true, or at least it is not true for air inleakage into the melter plenum. Evidently, leakage was occurring somewhere in the off-gas line between the melter and the off-gas flow measurement device, which was a considerable distance downstream of the melter.

Energy Balance - Total Melter

Now that the power inputs, enthalpy changes of feed streams, and the conductive heat losses of the melter are known, an energy balance can be completed. To do this the total energy going into the melter should equal the amount of losses. By combining values for each run from Tables 23 and 25, and considering the conductive heat losses from the melter shell (31.6 kW, Table 27), an energy balance is achieved and given in Table 28.

TABLE 27

LSFM Conductive Energy Losses

	Heat Transfer Coefficient	Heat Loss, kW
Melter Bottom*	0.549 Btu/hr-ft^2-°F	3.9
Melter Sides (Below Glass)*	1.29 Btu/hr-ft^2-°F	18.9
Total Below Melt Line		22.8
Total Above Melt Line**		8.8
Total Conductive Losses		31.6 kW

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* Taken from the LSFM Design Basis. Assumes an 1150°C inside wall temperature and uses inside surface area. Heat losses through the electrode bus bars and the drain valve have been neglected.

** Includes losses in pour trough (1100°C), melter lid (800°C), and sides (800°C - above glass). The heat transfer coefficient varies.

TABLE 28

Energy Balance

Run No.	Total Heat Input, kW	Total Heat Losses, kW	% Difference
5	164.5	168.1	2.2
6	147	202.4(152.8*)	37.9(3.9)**
7	149.5	148.8	-0.5
8	137.2	139.4	1.6
8(air bubblers)	162.3	167.9*	3.4

---

* Assumes 400 lb/hr air inleakage.

** Included in the heat losses for Run 8 with air bubblers was a 0.9 kW loss to heat bubbler air.

Based on the percent difference of heat input to heat losses, the energy balance for each run considered is very accurate and within experimental error (~10%), except for Run 6. Clearly, a 37% difference indicates a large error somewhere. This has to be traced back to the air inleakage which was measured to be more than twice that of all other runs. Table 25 shows that the enthalpy change for 850 lb/hr air inleakage is 93.7 kilowatts. This value is greater than the total energy input above the melt line for that run (84.0 kW), and thus the air inleakage into the melter is incorrect. If the 850 lb/hr measured value is correct, then the leakage occurred in the off-gas line itself and not the melter plenum. If a more believable value of the actual melter air inleakage is used, such as 400 lb/hr, the energy balance comes out to only a 3.9% difference in energy input to energy losses. Thus, the 850 lb/hr air inleakage reported during Run 6 was not caused by extra inleakage into the melter plenum. Tables 24, 25, and 27 show in parentheses the energy balance for Run 6 assuming only 400 lb/hr air inleakage into the melter plenum.

In the LSFM, at least part of the air inleakage enters the melter in the pour spout/pour trough area and then passes on into the melter plenum where the air is further heated by the lid heaters to 800°C before exiting through the off-gas system. From Table 25 the amount of heat lost to air inleakage ranges from 38.6 kW to 44.1 kW. To calculate how much lid heat energy is absorbed by air inleakage, the lid heat is considered to be the total energy input above the melt in Table 23 (this includes the trough heaters and pour spout heater). Table 29 shows the percentage of the total lid heat which is lost to air inleakage. It is assumed that the main electrodes and riser electrodes contribute nothing to air inleakage energy losses.

TABLE 29

Percentage of Lid Heat Lost to Air Inleakage

Run No.	% Lost
5	56
6	52*
7	41
8	47
8 (air bubblers)	47

* Assumes 400 lb/hr air inleakage

On the average, approximately 50% of the lid heat supplied to the LSFM during run conditions is lost to air inleakage to the melter plenum. This indicates the severe energy loss the air inleakage has on this particular melter. It also shows that air inleakage should play a large part in designing lid heater power supplies for other melters, and that any melter design should include air inleakage minimization. Furthermore, the TDS value of 20 lb/hr seems very optimistic. Since air inleakage so closely influences heat requirements to the melter, a more realistic value for the DWPF melter should be used. Considering that the DWPF melter will operate at ~5 inches vacuum (compared to 1 inch for the LSFM), a minimum inleakage rate of 100 lb/hr should be used, and 400 lb/hr at the end of the melter life is certainly feasible.

Heat Transfer to the Cold Cap

Besides an energy balance around the entire melter, an energy balance around the portion of the melter below the melt line will show the amount of heat transferred from the bulk glass to the feedpile (cold cap). Again returning to Tables 23 and 25 and Figure 18, the heat transfer to the cold cap from the bulk glass was calculated and is shown in Table 30. The only losses from the bulk glass are conductive heat losses out the melter bottom and side. Note that the riser electrode energy is included in the calculations even though the riser electrodes are separated from the cold cap. This was done to simplify calculations. In addition, the majority of the riser energy is lost to conduction, and thus, this calculation essentially adds the riser energy and then subtracts it by subtracting the conductive heat losses. Furthermore, the riser electrode energy is small compared to the main electrode energy.

In a similar manner, a balance above the melt line will show the amount of lid heat transferred to the feedpile. The losses to the lid heat (above melt energy) include conductive losses, air inleakage losses, and also an energy loss to superheat the steam from its boiling temperature to the off-gas exiting temperature of 800°C. It is assumed that all of the superheating occurs above the feedpile in the melter vapor space. The results are also presented in Table 30. For Run 6 an air leakage rate of 400 lb/hr was used. Note that the pour trough energy and the pour spout energy are included as lid heat because all of their energy is lost to conduction or air inleakage.

TABLE 30

Feedpile Energy

Run No.	Wt %	Frit Type	Melt Rate, lb/hr	Joule-Heated to Feedpile, kW	Lid Heat to Feedpile, kW	% of Feedpile Energy from Lid Heat*
5	45	131	110	62.7	-0.5	0
6	45	165	87	40.2	9.9	19
7	41	165	78	33.7	23.3	40
8	45	165	78	32.2	15.7	34
8(air bubblers)	45	165	110	58.2	7.3	10

* This refers to the percentage of the total feedpile energy coming from the lid heat.

From Table 30 it is evident that much more heat is transferred from the melt pool to the feedpile with Frit 131 feeds. An average of Runs 6, 7, and 8 is 35.4 kW, which is 43% less than Run 5 with Frit 131.

By examining Table 30 more closely, the joule heat transferred to the feedpile for Run 6 with Frit 165 is significantly greater than Runs 7 and 8 with Frit 165. Mobay Frit 165 was used during Run 6 and possibly it has a lower viscosity than the Ramtec and APEC Frit 165 feeds used during Runs 7 and 8. Viscosity appears to have a large effect on heat transfer from the melt pool in the LSFM. Viscosity mesaurements of glass from Run 6 compared to Frit 165 glass for PNL (APEC vendor) showed that the PNL glass had an 18% higher viscosity. The same may be true for Run 6 versus Run 7 and Run 8 glass. This would account for the difference.

The amount of lid heat transferred to the feedpile is also shown and shows some very interesting results. With Frit 131 during Run 5 all of the lid heat was lost to air inleakage (44.1 kW), steam heating (26.6 kW), and conductive losses (8.8 kW) from the shell. Thus, all of the energy to melt the slurry solids and boil the slurry water was supplied from below the melt line by joule heating. With Frit 165 feeds, much more joule heat is effectively used in the feedpile. Whereas the lid heat for Run 5 supplied no energy to the feedpile, lid heat for Runs 6-8 supplied 10 to 40% of the total energy needed in the feedpile. Run 7 has the highest percentage (40) because the feed slurry has a lower solids content.

The solids content of the feed slurry affects energy input to the feedpile greatly because the boiling of the water in the slurry amounts to approximately 80% of the total energy needed in the feedpile. Even Run 8 with air bubblers (which increase convection and heat transfer from below the melt line) used more lid heat than Run 5 with Frit 131. Thus, it appears that Frit 165 feeds require more lid heat and less joule heat for melting. This implies that future melter designs should include an increase in the amount of lid heat available if more viscous glasses, such as Frit 165, are to be used.

The energy distribution of joule heat and lid heat to the total feedpile energy for all of the runs considered in this report is different than that which theory would predict. With an 800°C lid temperature, theory predicts that more than half the feedpile energy is supplied by lid heat. The results displayed in Table 30 contradict this and show that the bulk of the energy is supplied by joule heat. There are three factors which the theory does not include, but which seem to have an effect on LSFM performance - air inleakage, steam heating, and slurry solids to glass conversion (90%).

Early in this report it was shown that air inleakage absorbs approximately one-half of the lid heat energy. Although air does not absorb radiant energy, there is a loss by convection. Unlike air, steam evolving from the feedpile does absorb radiant energy as it passes through the melter plenum. Thus, the amount of radiant energy reaching the feedpile is reduced from that which theory predicts. In addition, the steam would also absorb energy by convection. The design of the LSFM lid heaters (12 sheathed glowbars extending 28 inches within the lid) provides a large surface which increases conductive/convective losses to both air inleakage and steam heating. Energy losses to either of these two sources is not included in the theory and would affect the lid heat the most.

Theory also assumes a 100% conversion of slurry solids to molten glass. With formated feeds the conversion is only 90%, with the remaining 10% being lost as gases. Because of this, an extra 10% of slurry solids (and the water which comes with it) must be fed to obtain the same mass of molten product. This would have a very significant effect on the theoretical results.

All three of the factors discussed would probably affect theoretical predictions, although it is not clear that they would account totally for the difference in theory and experimental results.

The results in Table 30 also suggest that melt rate problems on the LSFM may be lid heat related rather than joule heat related. On each run the lid heat to the feedpile should be 50% or more for an 800°C lid temperature. If the lid heat to feedpile value for each run was increased to equal the joule heat, then the melt rate for each run could be increased by 18 to 100%, depending on the particular run. However, with more viscous glasses, such as Frit 165, melt rate problems are a result of low joule-heat transfer (less convection) in addition to low lid heat transfer to the cold cap.

Another piece of information obtained from Table 30 is the total feedpile energy required per mass of glass produced (Table 31).

TABLE 31

Energy per Mass of Glass

Run No.	Wt %	Frit Type	Feedpile Energy per Mass of Glass, kW-hr/lb
5	45	131	0.57
6	45	165	0.58
7	41	165	0.73
8	45	165	0.61
8(air bubblers)	45	165	0.60

Two results are evident from Table 31. First, for 45 wt % solids feed the energy needed per mass of glass produced is similar for Frit 131 (0.57) and Frit 165 glass (0.58, 0.61, 0.60). Secondly, the solids content drastically affects the amount of energy needed in the feedpile. The value for Run 7 (0.73) is simply a result of the lower solids content of 41%. Of course, this could simply be calculated, but it is nice to confirm it with experimental results.

DWPF Flowmeters

Flow rate measurement will be required for both liquid and slurry feed streams in the DWPF. The slurry feed streams have been anticipated to be the most difficult feed streams to monitor for flow rate due to their abrasivity, variable rheology, and high solids content. Additional considerations for DWPF flowmeter applications are discussed in the subsequent paragraphs.

DWPF slurry feed streams will be highly radioactive. In the selection of candidate flowmeters, materials such as plastics and elastomers were avoided due to their degradation in radiation. High radiation is also destructive to electronic components such as semiconductors; therefore, electronic components must be either shielded or, preferably, remoted from radiation.

Because of the abrasivity of DWPF slurry feed streams containing glass frit, moving parts, orifices, and obstructions of any type were avoided in selecting candidate flowmeters.

Reliability is a strong concern for all DWPF process instrumentation and equipment. Equipment and instrument maintenance will generally be restricted to replacement. In the DWPF canyon, flowmeter replacement will require manipulation of both process jumpers and instrument jumpers.

Calibration of DWPF flowmeters will be required in cold non-radioactive service before installation in the "hot" canyon. Once installed, field calibration in most cases will not be possible; consequently, repeatable drift-free operation is essential.

The three flowmeter brands tested in the initial phase of the program were (1) Fischer and Porter Mag-X (magnetic), (2) Micro Motion (mass), and (3) Dynasonics (ultrasonic). Two additional types of flowmeters are currently undergoing evlauation at SRL-ETF. An ultrasonic flowmeter manufactured by Controlotron Corporation is being tested in conjunction with SRP for both DWPF and waste farm applications. Two ceramic-lined magnetic flowmeters manufactured by Krohne are currently installed. The Krohne flowmeters are being considered as alternatives to the Fischer and Porter glass-lined flowmeters because long-term supply of these flowmeters is questionable.

Instrument Description

Flowmeters selected for DWPF application featured obstructionless flow paths, remotable electronics, and radiation-tolerant transducer designs. All systems tested were powered by standard 110 VAC. A 4 to 20 mA output signal was standard with all systems.

Frequency output was provided with the Micro Motion and Mag-X systems. A more detailed description of each flowmeter system is contained in the subsequent paragraphs.

A 1/4-inch and a 2-inch Fischer and Porter Mag-X flowmeter were tested on the Erosion Test Loop. These flowmeters were manufactured in Germany and equipped with special glass-lined flow tubes. The Mag-X systems tested consisted of three components: a magnetic driver, a flow converter, and a flow transducer. The flow transducer may be remoted from the magnetic driver and flow converter up to 50 feet. In the system tested, the driver and converter were separate; however, the system may be purchased with the driver and converter integrally mounted. The Mag-X flow transducer consists of a glass-lined flow tube containing two embedded platinum electrodes and an electromagnetic coil. The Mag-X flowmeter is intended for in-line installation. Recommended interconnection between the flowmeter and the remote mounted driver and converter requires two 2-conductor-shielded signal cables. Two number 16 AWG insulated wires are required to supply line power.

A Micro Motion mass flowmeter with a 1-inch flow tube was tested. The flow transducer consists of a cantilevered U-shaped flow tube mounted in a heavy case. Magnetic position sensors are mounted on both legs of the U-shaped flow tube. During operation, the U-shaped flow tube is vibrated at a high frequency. As fluid flows through the flow tube, the legs of the U-shaped flow tube vibrate out of phase relative to each other. This phase relationship is determined by the tube geometry, tube compliance, and a Coriolis effect due to mass propagation through the flow tube. The phase information is transmitted to the processing electronics from the magnetic position sensors and is used to determine mass flow rate.

Interconnection between the flow transducer and the flow transmitter is accomplished by 6 single conductor wires in the flowmeter tested. The vendor claims the electronics can be remoted in excess of 100 ft from the flow transducer using three 2-conductor shielded signal cables. The remoted configuration was not tested in the program.

Two Dynasonic brand ultrasonic flowmeters were evaluated; a 1/4-inch flow tube transducer and a clamp-on transducer suitable for pipe sizes 1 inch or larger. Coupling gel is required between the clamp-on transducer and pipe mounting surface. The Dynasonic flowmeters tested were of the reflection or Doppler variety. Each ultrasonic transducer contains a transmitting and a receiving piezoelectric crystal. Flow rate determination is made by determining the frequency shift of acoustic energy reflected from bubbles or particles moving with the flow stream.

A Controlotron ultrasonic flowmeter system is currently being tested on the Erosion Test Loop. The flowmeter system consists of two clamp-on transducer units and a portable flow computer. Coupling gel is required between the transducers and pipe mounting surfaces.

The Controlotron flow measurement system consists of both a Doppler system and a time-difference system. Both flow measuring systems operate continuously. The system with the strongest signal is used to determine flow rate. The time-difference system determines flow rate by measuring the time difference required to send an ultrasonic signal from an upstream transducer to a downstream transducer and vice versa. This time difference is related to the bulk fluid velocity. The time-difference system is reputed to be more accurate than the Doppler system. Signal strength of the transmission system is reduced in streams bearing high solids requiring the Doppler system to take over.

Several Krohne ceramic-lined magnetic flowmeters have been purchased for evaluation. A 1/2-inch flowmeter is currently installed and operating. The Krohne magnetic flowmeter system operates similarly to the Fischer and Porter Mag-X system. The Krohne flow transducers are physically smaller in size than the Fischer and Porter flow transducers.

Test Equipment

Flowmeter testing was conducted on the Erosion Test Loop (ETL) Facility shown in Figure 22. The ETL is located at SRL-ETF. The ETL consists of a recirculation loop with a feed tank and rate tank. The loop is ~80 feet in length and consists of 2-inch and 1-1/2-inch S40 stainless steel pipe. The ETL was originally intended to provide pipe wear data but was modified to allow evaluation of slurry process instrumentation.

The ETL is equipped with a double diaphragm pump and a centrifugal pump arranged in parallel. Both pumps are capable of producing discharge rates in excess of 80 gpm. Because mechanical seals failed frequently in the centrifugal pump, the diaphragm pump was used for most test work. Continuous pen recorders were used to record flowmeter behavior during all phases of testing. Each flowmeter transmitter was equipped with an analog display.

Test Program and Procedures

Flowmeter testing and evaluation was conducted in three phases. The first phase of testing consisted of testing the flowmeters in slurry service. The second phase of testing consisted

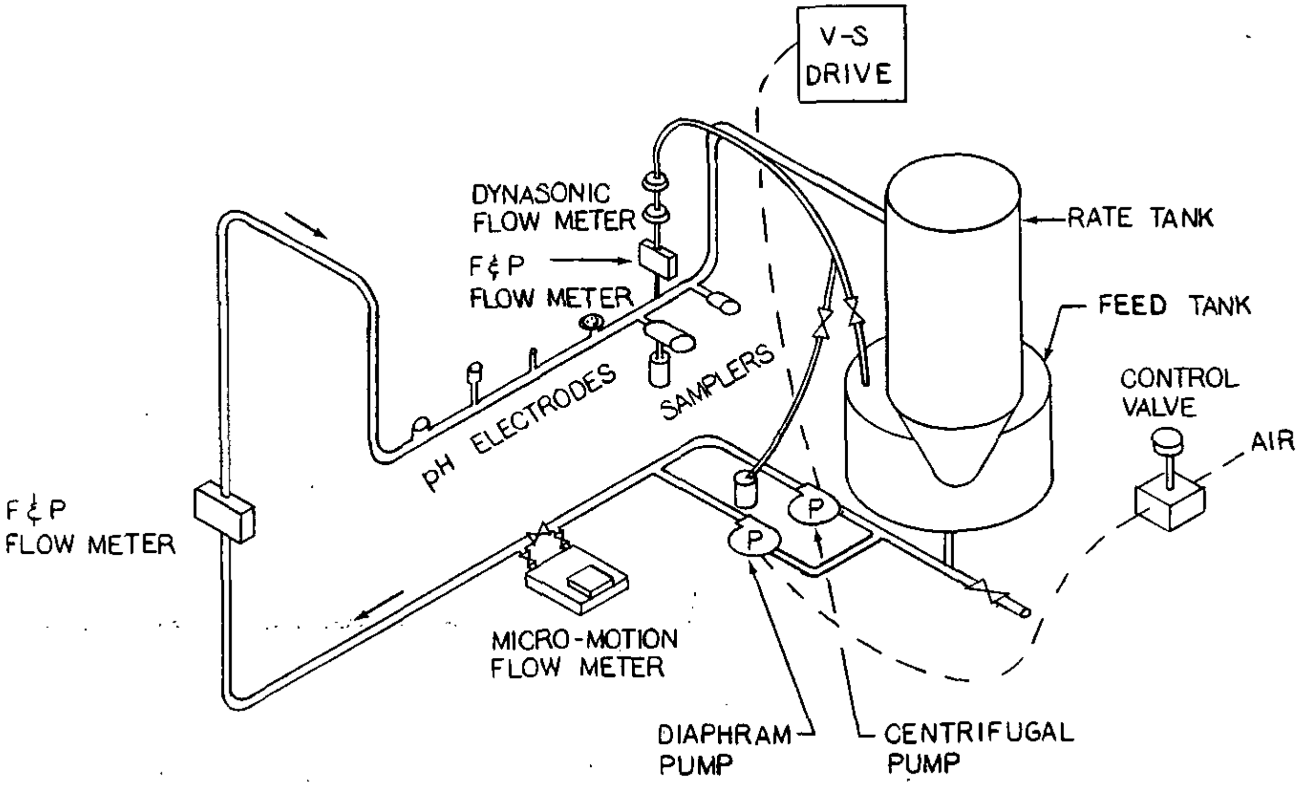

FIGURE 22. Erosion Test Loop

of the irradiation of flowmeter transducers. The third phase of testing consisted of electrical interconnection of flowmeter transducers and transmitters with canyon-type signal connectors.

Deployment of the candidate flowmeters on the Erosion Test Loop is shown in Figure 22. Sludge slurries and sludge/frit slurries ranging in solid concentration from 12 to 53 wt % were recirculated through the loop. Test slurries were analyzed for solids concentration and rheology by trained laboratory technicians. A Haake viscometer was used for rheological characterization. Flow rate measurement was determined with the ETL rate tank for the 2-inch Mag-X, the Micro Motion, and clamp-on Dynasonic flowmeters. The ETL rate tank is equipped with two sight glasses. Calculated volume between the centerlines of the two sight glasses is 34.7 gallons. During a typical flow rate measurement, loop flow was diverted into the rate tank. An operator then timed the interval required to fill the rate tank between sight glass centerlines. Flow rates of 10 to 90 gpm were possible with the ETL pumps. The corresponding fill rates of the rate tank ranged from 20 seconds to 3 minutes. Estimated accuracy of these rate measurements was ±5%.

For the 1/4-inch Dynasonic flowmeter and 1/4-inch Mag-X flowmeter, smaller calibrated vessels with volumes from 1 liter to 1 gallon were used for rate measurements. Estimated accuracy for these rate measurements was ±2%.

During rate measurements, flowmeter outputs were monitored on a process recorder. Flowmeter outputs were then compared to measured rates.

Initial calibration of all flowmeters except the ultrasonic flowmeters was done in 12 wt % synthetic sludge. This calibration was not changed throughout the remainder of the tests. The 1/4-inch ultrasonic flow tube transducer was initially calibrated in 12 wt % sludge and then recalibrated in 41 wt % slurry.

The clamp-on ultrasonic transducer was received midway through the test program. Initial calibration was in -80 mesh sludge/frit slurry containing 46 wt % solids.

Component radiation tolerance tests were carried out in the SRL gamma cell in Building 773-A. Irradiation rates in the gamma cell were 2 x 10^5 rads/hr. Total component dosage levels were near 10^8 rads. Anticipated irradiation rates of DWPF process instrumentation will reach 1 x 10^5 rads/hr when in contact with feed streams. Estimated total dosage for DWPF instruments is 10^8 rads for a 2-year life.

To simulate electrical hookup of candidate flowmeters in a canyon environment, prototypic signal connectors were obtained. Both multipin and coax signal connectors were used in the flowmeter-connector tests.

In the canyon, two signal connections will be required to pass electrical signals from a flowmeter transducer deployed in the "hot" side to the transmitter in the "cold" side. One signal connection will be required at the flowmeter and another signal connection will be required at the wall nozzle. The tests were arranged to simulate the two-connector canyon configuration.

Function of the flowmeters interconnected with the canyon connectors was established by observing flowmeter output at a known flow rate, observing flowmeter output at zero flow, and observing flowmeter output as flow was spanned from zero to full-scale and back again. In addition, each test was conducted for at least 1 hour at an established flow rate to detect output signal drift.

Discussion of Results

Figures 23-27 show the results of the calibration data acquired for the Fischer and Porter, Micro Motion, and Dynasonic flowmeters. Data are plotted with meter output in percent along the abscissa axis and measured flow rate, also in percent, along the ordinate axis. The solid line oriented at 45° and passing through the origin represents the ideal response of a flowmeter. Error is detemined by the magnitude of the horizontal offset of a data point from the ideal line. All flowmeters except the Micro Motion were calibrated to a full-scale reading of 10 ft/sec. The Micro Motion was calibrated to ~1100 lb/min full-scale (~30 ft/sec for slurry of density 1.4 g/cc).

Table 32 contains a summary of the slurry test history of the flowmeters. Approximately 1100 hours of testing were completed in slurry service for all flowmeters except the Micro Motion flowmeter and the Dynasonic clamp-on flowmeter. The Micro Motion flowmeter failed to operate after 700 hours of service. The Dynasonic clamp-on flowmeter was installed during the last 500 hours of the slurry test program.

Examination of Figure 23 shows calibration results in 12 wt % sludge. Accuracy of the Micro Motion and Mag-X flowmeters was within 5% of full-scale flow. Accuracy of the 1/4-inch Dynasonic flowmeter was considerably worse showing errors of up to 25% of full-scale flow. Linearity of 1/4-inch Dynasonic output was also poor.

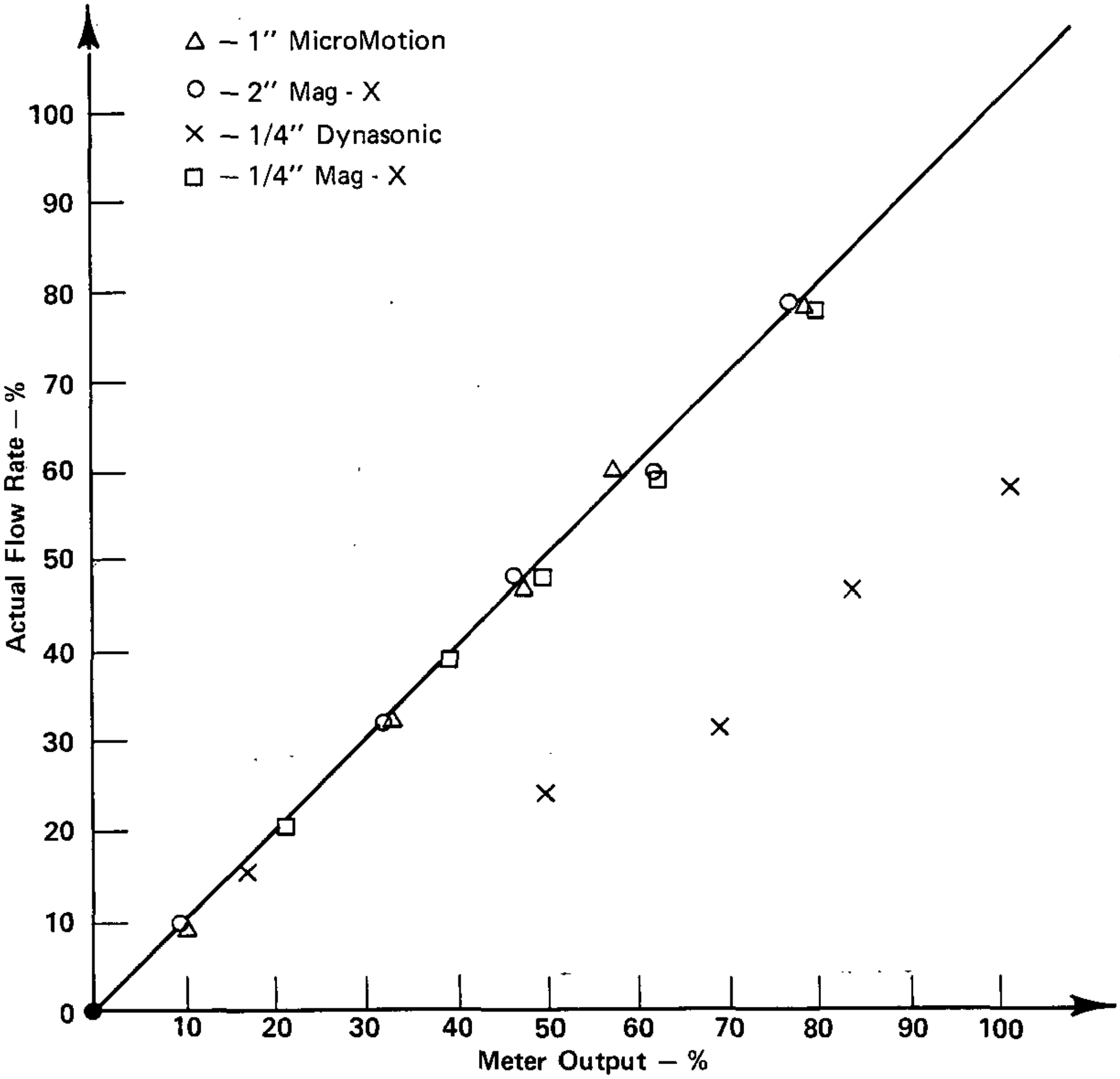

FIGURE 23. Flowmeter Calibration Data in 12.8 wt % Synthetic Sludge

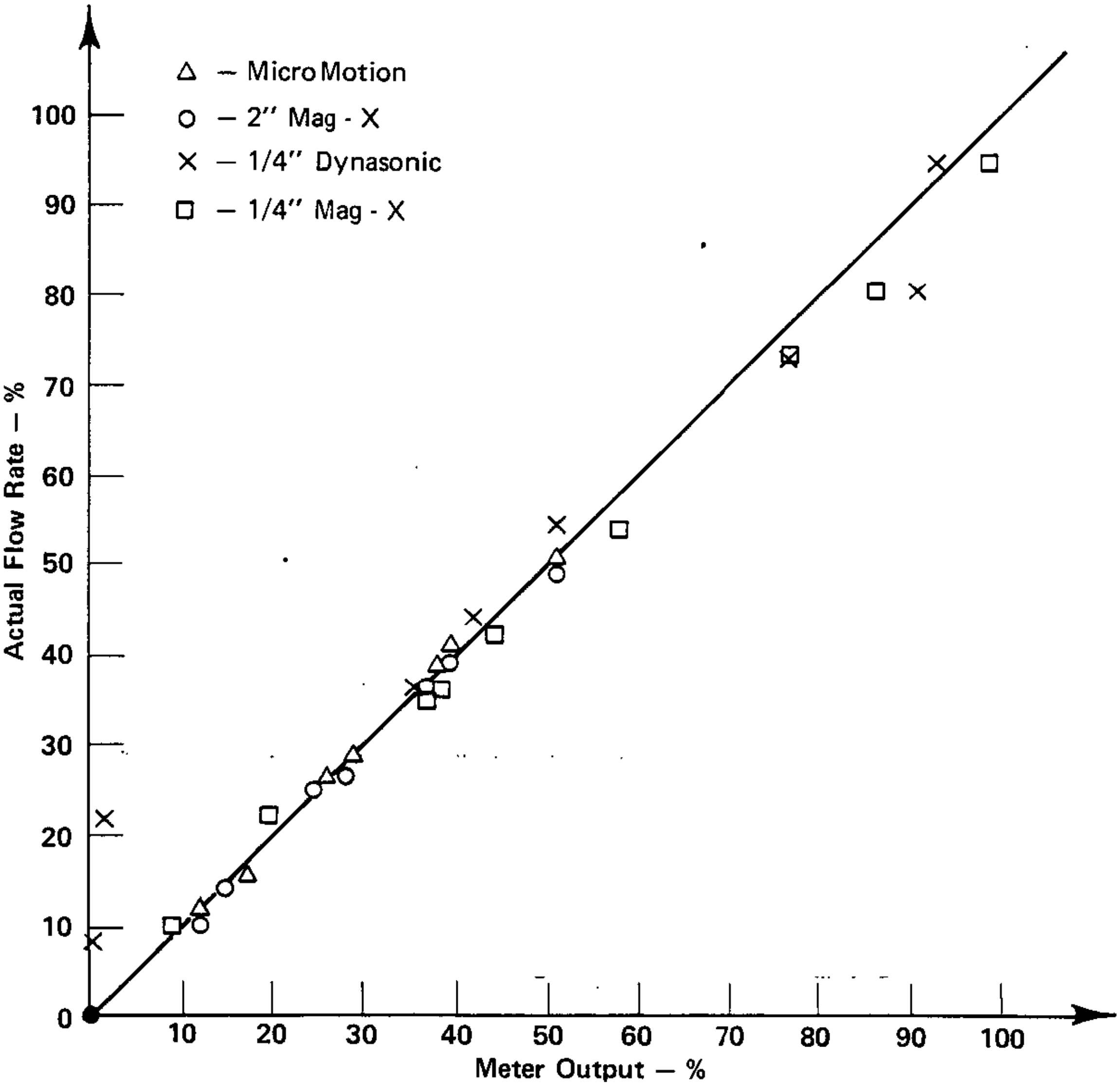

FIGURE 24. Flowmeter Calibration Data in 41 wt % -200 Mesh Frit/Sludge Slurry

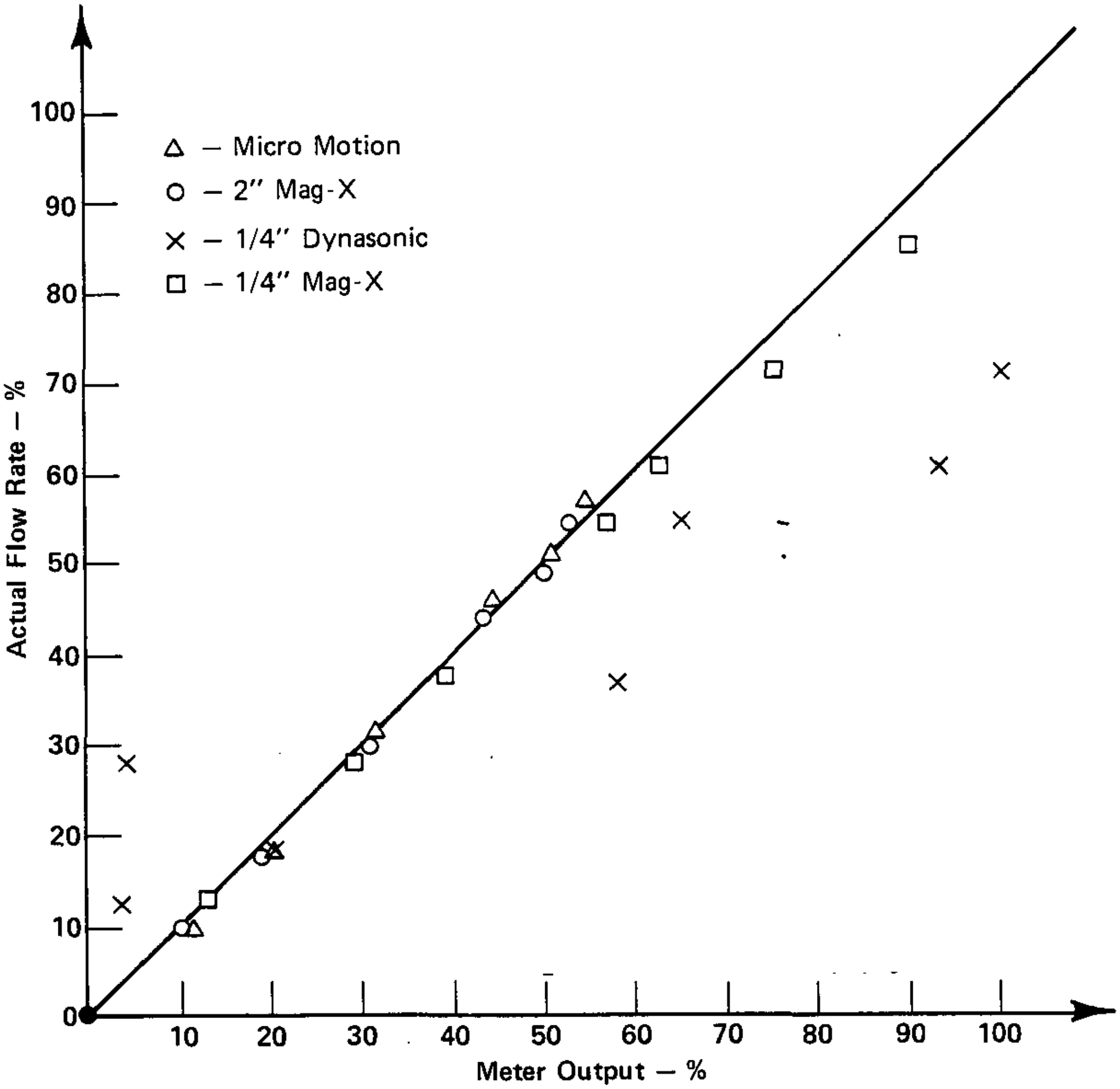

FIGURE 25. Flowmeter Calibration Data in 46 wt % -80 Mesh Frit/Sludge Slurry

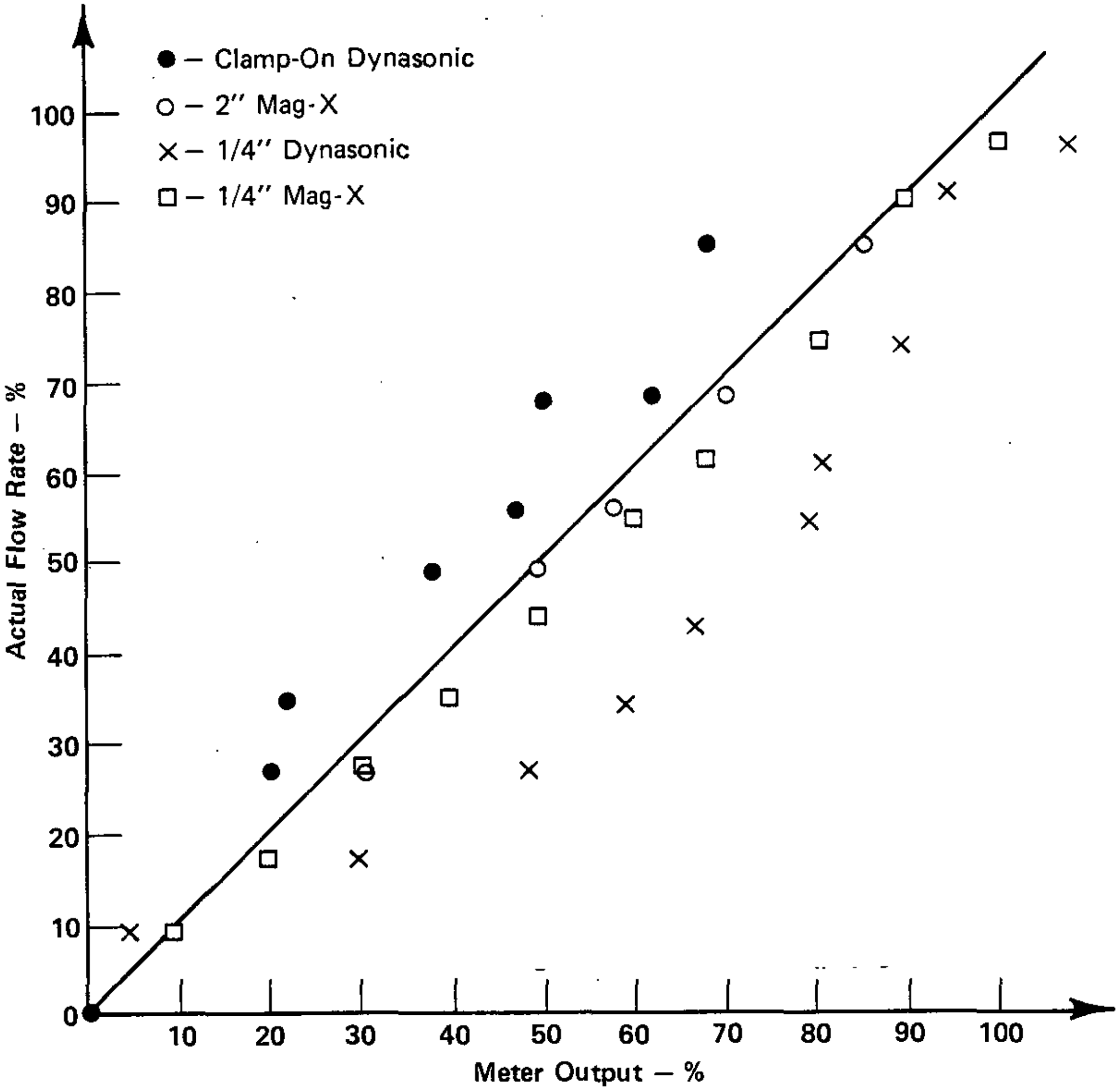

FIGURE 26. Flowmeter Calibration Data in 46 wt % -80 Mesh Frit/Sludge Slurry

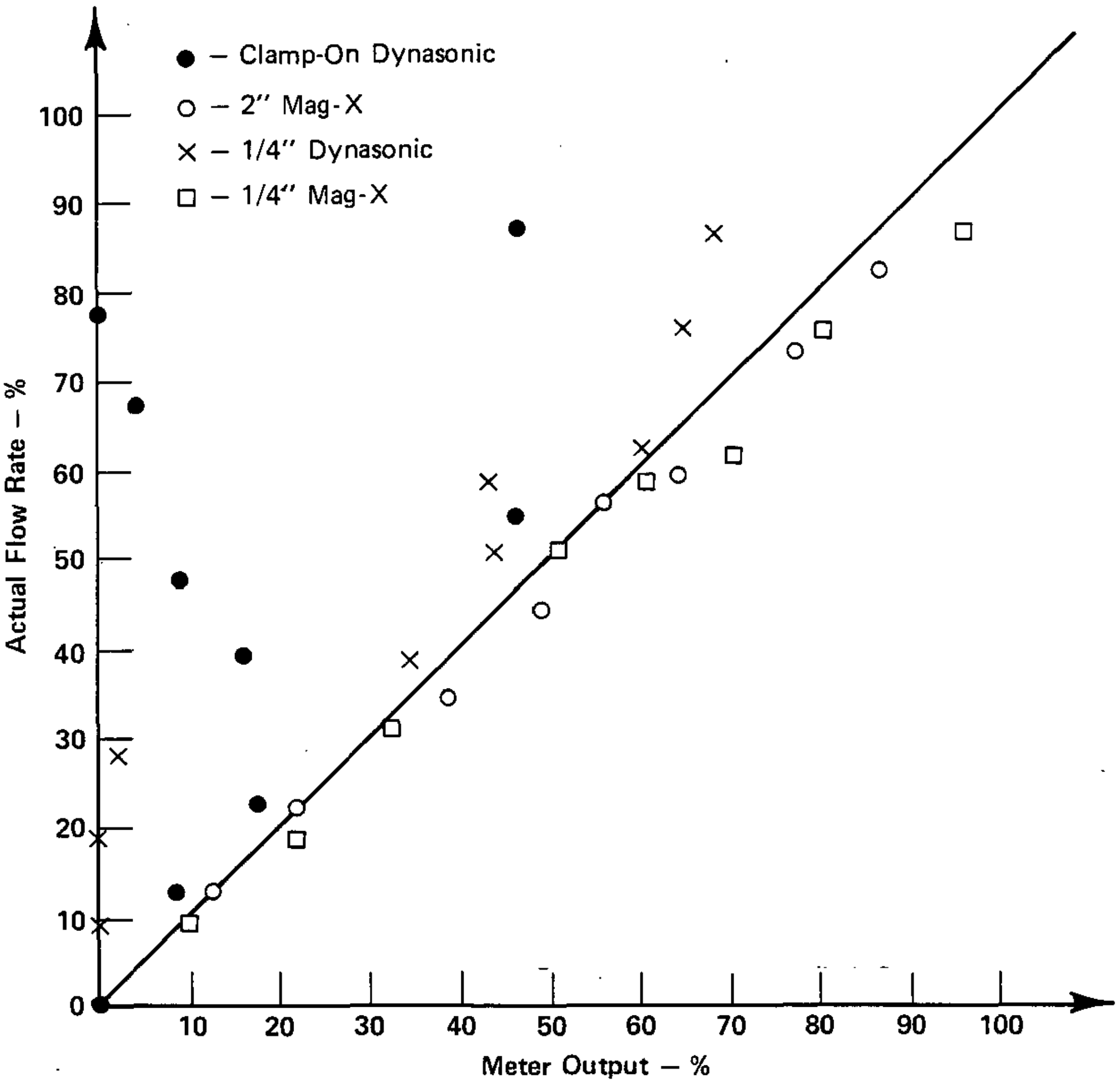

FIGURE 27. Flowmeter Calibration Data in 53 wt % -80 Mesh Frit/Sludge Slurry

TABLE 32

Flowmeter Test History

Test Material	Average Solids Concentration, wt %	Density, g/cc	Yield Stress, dynes/cm^2	Consistency, centipoise	Avg Flow Velocity, ft/sec	Test Duration, hr
Synthetic sludge	12	-	110	39	3-5	100
Formated sludge	23	1.33	90	18.5	3-5	10
-200 mesh frit/sludge slurry	41	1.38	105	32	3-5	400
50% -80, 50% -100 mesh frit/sludge slurry	46	1.40	80	30	3-5	250
-800 +200 mesh frit/sludge slurry	53	1.49	155	41	3-5	300

Figure 24 shows the calibration results for the flowmeters in 41 wt % sludge/frit slurry. Accuracy was within 5% of rate for the Micro Motion and 1/4-inch and 2-inch Mag-X flowmeters. Recalibration of the 1/4-inch Dynasonic flowmeter improved accuracy to within 10% of full scale.

Figure 25 shows the results of calibration tests in 46 wt % sludge/frit slurry. Accuracy of all flowmeters except the 1/4-inch Dynasonic remained within 5% of full-scale rate. Accuracy of the 1/4-inch Dynasonic degraded to ~30% of rate.

Figures 26 and 27 show calibration for the 1/4-inch and 2-inch Mag-X flowmeters and the 1/4-inch and clamp-on Dynasonic flowmeters. At this point in the test program, the Micro Motion flowmeter had stopped functioning. Figure 26 shows test data taken in 46 wt % sludge/frit slurry, as had Figure 25. Again, accuracy of the magnetic flowmeters was good remaining within 5% of full-scale rate. Both ultrasonic flowmeters showed lack of linearity and poor accuracy. Figure 27 shows calibration data acquired in sludge/frit slurry containing 53 wt % solids. Response of the magnetic flowmeters remained good; however, accuracy was reduced to 10% of full scale. Both ultrasonic flowmeters performed very poorly. A total lack of linearity and repeatability was shown with both ultrasonic flowmeters in this high solids bearing slurry.

In terms of precision and accuracy, both the 1/4-inch and 2-inch Mag-X flowmeters and the Micro Motion flowmeter performed well. Slurry rheology and solids concentration seemed to have minimal effects on flowmeter performance for these flowmeters. Long-term stability of calibration was also indicated.

Linearity and accuracy of the Dynasonic flowmeters were almost uniformly poor. Slurry rheology and solids concentration had a strong effect on meter output. It is suspected the inherent nonlinear nature of DWPF synthetic slurries induced the poor performance of the ultrasonic flowmeters tested.

The Doppler method employed by the Dynasonics flowmeters transmits acoustic signals through a pipe wall into the flow stream. The system relies on the reception of reflected acoustic energy. Flow rate determination is made by measurement of the frequency shift in the reflected signal. In high solids bearing streams, signal penetration depth would certainly be reduced; hence, signal reflections may only occur near the pipe wall or in the boundary layer preventing a good representation of the flow field. This effect may explain the poor performance of these meters in slurries.

Some brief experience has been accumulated with the Controlotron ultrasonic flowmeter system mounted on a portion of 2-inch pipe in the ETL. Testing has shown that the *time-difference system* will not operate in DWPF slurries due to their high solids content. This means the flow measuring system defaults to the Doppler mode. The Controlotron system has exhibited problems with zero drift, and appeared sensitive to pipe vibration and transducer mounting. The system has been temporarily returned to Controlotron for a bench check. The unit is expected to be returned for further tests in June. No calibration data are yet available.

A 1/2-inch Krohne flowmeter has been installed recently at SRL-ETF. The flowmeter has been used in water and 53 wt % sludge/frit slurry. Figure 28 shows the limited data available for the 1/2-inch Krohne flowmeter. Repeatability between water and slurry calibrations are good. Linearity of response was also good. Average asccuracy was better than 5% of full scale.

Erosion wear measurements were made on the 1/4-inch and 2-inch Mag-X flowmeters and the 1/4-inch Dynasonic flowmeter. These wear measurements were based on weight loss by the transducers over the course of the test program. Table 33 contains the calculated yearly wear rates based on weight loss measurements. As evident from Table 33, predicted uniform wear rates for the meters tested are very low ranging from 0.5 to 1.5 mils/year on the diameter.

An ultrasonic thickness meter was used to survey points on the U-shaped flow tube of the Micro Motion flowmeter. Results were inconclusive. The thickness tester demonstrated a repeatability error of ±2 mils. This sensitivity was insufficient to detect wear in the Micro Motion flow tube.

The 1/4-inch Dynasonic transducer and an electromagnetic coil from a 2-inch Mag-X flowmeter were irradiated. The gamma cell located in 773-A was used for the radiation tests. Average dose rate was ~2 x 10^5 rads/hr. After receiving ~6 x 10^7 rads, the 1/4-inch Dynasonic flowmeter was checked for operation and performed normally, Table 34. The electromagnetic coil received a total dose of ~7 x 10^7 rads.

Coil insulation was checked for deterioration with a 9V resistance meter. (During normal operation, a Mag-X coil is excited at 3.5 Hz with a peak-to-peak voltage of 10 to 15 volts.) No breakdown of the insulation was observed. The electromagnetic coil is essentially the only portion of a magnetic flowmeter that could conceivably suffer in radiation. Size restrictions in the gamma cell prevented a complete meter to be irradiated. The only component identified as susceptible to radiation damage in the Micro Motion flowmeter was the drive coil used to vibrate the flow tube; however, it was not irradiated.

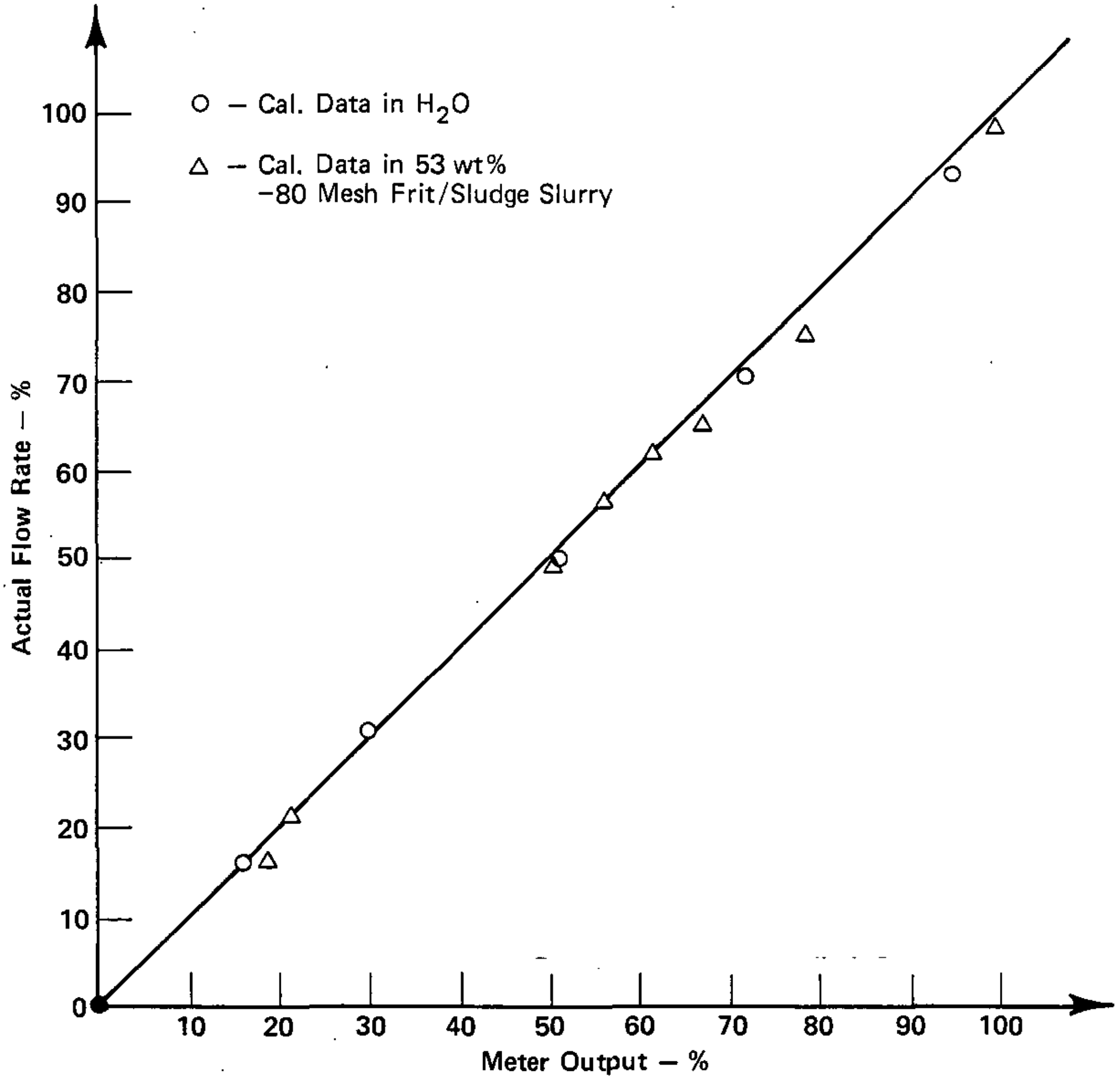

FIGURE 28. Krohne Flowmeter Calibration Data

TABLE 33

Erosion Wear Results

Flowmeter	Initial Weight, g	Final Weight, g	ΔW, g	Average Wear Rate, mpy
2-inch Mag-X	6132.4	6131.0	-1.4	0.5
1/4-inch Mag-X	2243.5	2243.0	-0.5	1.5
1/4-inch Dynasonic	776.9	776.1	-0.8	0.72

TABLE 34

Flowmeter Radiation Tests

Flowmeter	Average Irradiation Rate	Accumulated Dosage	Average Wear Rate, mpy
1/4-inch Dynasonic Transducer	2x10% rads/hr	$5.5\text{x}10^7$ rads	None
2-inch Mag-X Electromagnetic Coil	$2\text{x}10^5$ rads/hr	$7.35\text{x}10^7$ rads	None

Results of the flowmeter-canyon connector tests are tabulated in Table 35. The 2-inch Mag-X flowmeter and the 1/4-inch Dynasonic flowmeter were hooked up in various configurations. Premature failure of the Micro Motion flowmeter prevented its use in the connector tests. Testing indicated that both the magnetic and ultrasonic flowmeters would function normally with either the 40-pin signal connector or the coax connector if shielded signal cable was used.

TABLE 35

Flowmeter - Signal Connector Tests

Flowmeter	Canyon Connector Type	Interconnection Cables	Results
2-inch Mag-X	40-pin instrument	Six single conductor insulated	High noise levels
2-inch Mag-X	40-pin instrument	Two 2-conductor shielded	Normal operation
2-inch	Multiple coax	Two coax, 2 single conductor	Normal operation
1/4-inch Dynasonic	Coax	Two coax	Normal operation
1/4-inch Dynasonic	40-pin instrument	Two coax	Normal operation

Additional Observations

Calibration of the Dynasonic flowmeters was more difficult and time consuming than calibration of either the Micro Motion or Mag-X flowmeters. Overall, the Mag-X flowmeters were the easiest to calibrate.

An additional outstanding feature of the Mag-X flowmeters was their extremely safe drift-free zero in no-flow conditions. Both the Micro Motion and the Dynasonic clamp-on flowmeter exhibited unstable zeros that were affected by pipe vibration. For example, zero stability for these meters was affected by the operation of the ETL feed tank agitator which produced some pipe vibration. The 1/4-inch Dynasonic flowmeter did not appear sensitive to pipe vibration.

Installation requirements for the Micro Motion C-series flowmeters make them impractical for canyon applications. The Micro Motion C-series flowmeters require rigid mounting surfaces. With the flowmeter bolted directly to the mezzanine floor of the ETL facility, the meter exhibited an unstable zero and a tendency for the output to stick. To produce stable operation of the Micro Motion C100 tested, the flowmeter was bolted to the mezzanine floor through a special base consisting of two 75-lb steel plates atop two 1/4-inch-thick sheets of spongy neoprene. In a canyon environment, rigid mounting would be difficult. In-line and clamp-on flowmeters are much better suited to canyon deployment.

A large number of off-the-shelf Fischer and Porter magnetic flowmeters are currently installed at SRL-ETF in slurry service. Experience with these flowmeters has been uniformly good. No problems have yet been identified with magnetic-type flowmeters in slurry or water service at SRL-ETF.

Table 36 contains a final summary of the various considerations used to judge flowmeter applicability to the DWPF.

The following conclusions are supported by this study:

1) The Fischer and Porter Mag-X flowmeters demonstrated an average accuracy of better than 5% of full-scale rate for all slurries tested. Predicted service life of a Mag-X flowmeter is >2 years.

2) The Dynasonic ultrasonic flowmeters demonstrated poor linearity and an accuracy of 30% of full-scale rate. Predicted service life of a Dynasonic flowmeter is >2 years.

3) The Micro Motion model C-100 mass flowmeter demonstrated accuracy comparable to or exceeding the Mag-X systems. Reliability of this flowmeter is questionable. Mounting requirements for this flowmeter make it unsuitable for canyon application.

DWPF - Technical Information on Formic/Nitric Acid Reactions

Large quantities of both 90 wt % formic acid (for process feed adjustment) and 50 wt % nitric acid (for equipment decontamination) will be routinely handled in the DWPF. A basis was established early in the initial design phase to assure that the facility design precludes the uncontrolled mixing of these two acids. This criterion evolved from earlier discussions between SRL and SRP regarding the violent reactions that can occur. Provision for canyon vent-jumper changes during vessel decontamination has been included in the facility design to segregate the vapor phases of the two acids. This report presents technical data concerning formic/nitric acid chemistry and an assessment of the justification for the present design bases.

A vast amount of data is available in the literature on the chemistry of formic/nitric acid reactions, but none is more applicable than that published by SRL personnel. Based on their research, the following recommendations are set forth.

TABLE 36

Flowmeter Evaluation Summary

Flowmeter	Accuracy	Repeatability	Reliability	Wear Tolerance	Radiation Tolerance	Connector Performance	Installation Requirements	Predicted Service Life	Final Verdict
Fischer and Porter magnetic flowmeter	Good	Good	Good	Good	Good	Good	Good	>2 years	Recommended
Dynasonic ultrasonic flowmeter	Poor	Poor	Good	Good	Good	Good	Good	>2 years	Not Recommended
Micro Motion mass flowmeter	Good	Fair	Poor	-	-	-	Poor	?	Not Recommended
Krohne magnetic flowmeter	Good	Good	TBD	TBD	TBD	TBD	Good	TBD	Good Candidate
Controlotron ultrasonic flowmeter	TBD	TBD	TBD	Good	TBD	TBD	Good	TBD	Unlikely Candidate

1. The design of the cold feed transfer and handling facilities should be such to preclude any credible scenario where these two acids may be mixed in an uncontrolled manner.

2. Systems designed to contain spills of these two acids external to the process cell should guarantee that they cannot be combined until neutralized.

3. Provisions for canyon jumper changes during tank decontamination to segregate the vapor phases of the two acids are not warranted.

4. Serious consideration should be given to deleting the formic acid vent condenser (FAVC). As an alternative, if formic acid and mercury losses to the vent system are to be maintained as low as practical, utilize the FAVC only on the vent streams from the SRAT condenser and the mercury water wash tank (MWWT).

Discussion

The reaction between formic acid and nitric acid is autocatalytic and autothermal, and characterized by an induction period. During the induction period, the duration of which is a function of the acid concentrations and temperature, an autocatalytic agent is formed and accumulated. Once the critical concentration of the agent is reached, the reaction between the nitric acid and formic acid is initiated. At the concentrations of nitric/formic acid being handled in the DWPF, the reaction initially is extremely violent, accompanied by the rapid evolution of gas and heat.

The violent nature of the reaction may be illustrated by the following scenario. Assume a stoichiometric quantity of 90 wt % formic acid (at 25°C) is inadvertently combined suddenly with 200 gallons of 50 wt % nitric acid (10.4M) at 25°C. At the end of the induction period (approximately 5 minutes), the reaction will initiate, accompanied by the rapid elevation of the solution temperature to the boiling point and a rapid release of gas. The maximum rate of gas evolution in this scenario approaches 17,000 ft ^{3}/min.

The rate of reaction at 100°C for nitric acid in the range of 2 to 12M is a function of the cube of the nitric acid concentration. Assuming the denitration from 10.4M to 8M occurs in 2 minutes, the average rate of heat liberated exceeds 150,000 Btu/min. As the concentration of nitric acid falls, the rate of reaction slows markedly.

If the preceding scenario were to occur in a vessel, pressurization would result with the rupture of the vessel likely. Loss of the vessel contents via dip tubes and the overflow provision would be a certainty. Foam levels would reach nearly 7.0 times the initial liquid level. Where the mixing of the acids to occur outside a vessel, such as in a sump or diked area in an operating area, a serious hazard to operating personnel would occur from splattering acid.

During in-place decontamination of process vessels with nitric acid, the capability has been provided to route the nitric acid vapors directly to the process vessel vent header, thus bypassing the formic acid vent header, Figure 29. This avoids the mixing of nitric and formic acid vapors and the subsequent condensation of both acid vapors in the formic acid vent condenser. The justification for this design provision was assessed by evaluating the consequences of the following scenario.

- The melter feed tank is decontaminated with 12.5 wt % HNO_3 at 85°C. Resultant vapors are vented into the formic acid vent header.
- Mercury stripping and canister decontamination are assumed to be occurring simultaneously, resulting in the maximum credible flow of formic acid vapors into the same header.
- The melter feed tank vapor space is being purged with 171 lb/hr N_2 and 52 lb/hr O_2.
- The vapor is condensed at 15°C and the condensate subsequently warms to 50°C.

Based on these assumptions, the condensate discharged from the condenser would contain 0.009M HCOOH and 0.028M HNO_3. Assuming a batch reaction, the induction period is greater than 200 hours, far in excess of a credible period of accumulation in the slurry mix evaporator condensate tank before the contents are diluted and/or transferred to the recycle collection tank for neutralization. Even if the reaction were initiated, the rate of reaction at these concentrations would be nearly immeasurable.

A less credible scenario was assessed where the 50 wt % HNO_3 added to the vessel was not diluted. In this instance, the concentration of nitric and formic acid in the condensate would be 1.5M and 0.016M, respectively. Although the period of accumulation could conceivably exceed the calculated induction period of 22 hours, the amount of formic acid is sufficiently below the stoichiometric value to preclude any vigorous reaction and gas evolution. Extrapolation of the data for 2.0M HNO_3 in DP-1299 (Table 2) to a $HCOOH/HNO_3$ ratio of 0.108 indicates a peak gas evolution rate of 6 ft^3/min.

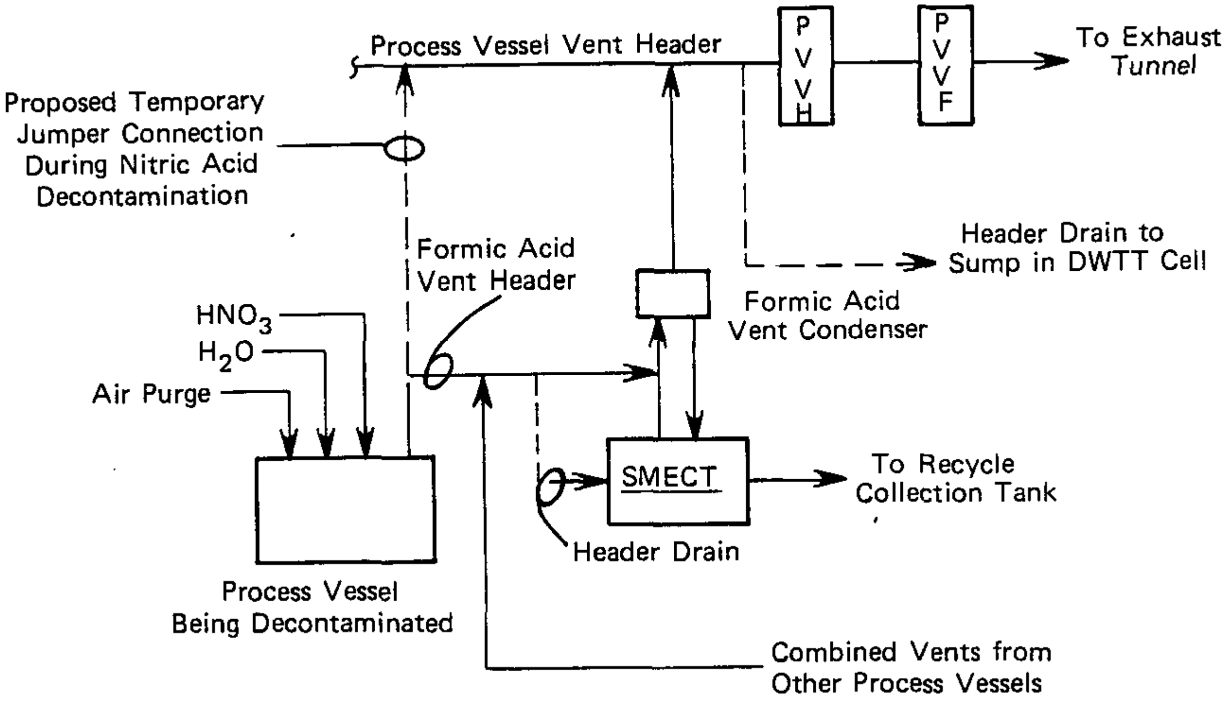

FIGURE 29. Tank Venting Schemes During Nitric Acid Decontamination of DWPF Process Vessels

The presence of both acid vapors together in the vent header does not appear to be a problem. Residence times are brief (less than 10 seconds), concentrations are low, and there is no opportunity for accumulation. These vapors were present in the vapor space above the reactants during all the denitration experiments and in the vapor line to the reflux condensers employed in many of the experiments. In none of the literature reviewed was any reference made to a problem in the vapor phase.

Results of recent research and devlopment activities suggest a reassessment of the actual need for the FAVC. Monitoring frit/water slurries following formic acid addition (at 0.01 lb HCOOH/lb frit) have indicated rapid consumption of the formic acid by the alkali fraction of the frit. This fact, coupled with lower formic acid requirement in the sludge receipt adjustment tank, has lowered the flow of acid into the vent header to about 0.016 lb/hr. This compares to 0.068 lb/hr HCOOH exiting the FAVC based on the 9/30/82 material balance. Mercury losses from the SRAT condenser during mercury stripping and from the MWWT during washing were calculated to be $<10^{-5}$ lb/hr (this assumed that only the air sparge to the MWWT equilibrates with the mercury).

Deletion of the FAVC will result in condensation occurring in the vent header. During normal operation, the blending of all vessel vents would result in about 7 lb/hr condensate being produced (t = 41°C). If the temperature of the combined vents were to equilibrate with the temperature of the process cell atmosphere (35°C), the rate of condensation would increase by about 28 lb/hr. This really shouldn't be a problem since the current facility design includes header drains. The concentration of formic acid in the condensate would be about 0.03M.

During acid decontamination of a tank, the rate of condensation in the vessel vent header would be greatly increased if the vessel being decontaminated does not have a condenser. For example, during nitric acid decontamination of the MFT, condensation rates in the PVVH could range from 130 to 200 lb/hr depending to what extent the temperature of the blended vessel vents equilibrates with the temperature of the process cell atmosphere. Resulting concentrations of formic (0.013M) and nitric (0.022M) acid in the condensate should present no problem as indicated in the earlier assessment in this report.

If condensate were to occur in the sand filter and exhaust tunnel, it is estimated that the condensate would be at a pH of about 4.0. Exposure of sand filter media and structural materials to this level of formic acid is apparently not a concern (ESD stated the higher formic acid level indicated in the 9/30/82 material balance was not a problem).

Nominal mercury and formic acid losses to the atmosphere do not appear to be a viable justification for retaining the FAVC which currently requires a refrigeration unit rated at about 300,000 pcu/hr. If it is desired to protect against inadvertent process releases of mercury and/or formic acid, it seems prudent to only route the vents from the SRAT condenser and the MWWT through the FAVC.

Graphite Slurry Restart of the Small Cylindrical Melter-2

The small cylindrical melter-2 (SCM-2) was successfully restarted using a graphite slurry. This startup method is being evaluated as a possible backup procedure in the event lid heaters fail. For initial startup or restart of a cold melter, some means must be available to heat the pure frit or glass to the joule heating temperature of 650 to 700°C. If lid heat is not available, a layer of graphite in the melt chamber can serve as the conducting medium between electrodes.

In this test, a layer of graphite (200 mesh powder) was sandwiched between two layers of frit in the melt chamber. Power was generated by passing current through the graphite layer between two temporary rod electrodes and later the existing upper electrode to throat electrode. Heat conducted from the graphite layer eventually melted the frit and reestablished joule heating in the glass. Although the test was successful, considerable difficulty was experienced in establishing and maintaining adequate contact between electrodes and graphite for power generation.

Prior to this test, graphite was successfully used to start up the small cylindrical melter (SCM) on three occasions. The first two tests were with a graphite powder, and the third test was with a graphite slurry. If graphite was used to restart a canyon melter, it would have to be pumped through the melter feed system in the form of a slurry. Consequently, the test described here for the SCM-2 was with a graphite slurry.

The graphite startup technique was first tested on the SCM in April of 1980. Five pounds of graphite powder were packed between two layers of Frit 211 in the melt chamber. The regular rod electrodes were then used to heat the graphite which in turn heated the frit by conduction. Joule effect in the glass was achieved within one hour, and the melter was slowly brought up to operating temperature over several days.

In the second test, joule heating of the glass was initiated in the same manner as before except that there was no frit layer on top of the graphite. This resulted in primarily radiant heat transfer from the graphite to the plenum walls and lid. Once again, startup was smooth and controllable.

The final test of the graphite startup technique conducted on the SCM involved the use of a graphite slurry. The SCM was shut down and allowed to cool while still full of glass. A buffer layer of Frit 131 was then pumped onto the frozen glass surface in slurry form and allowed to dry. After a pair of temporary rod electrodes were inserted into the frit, a 25 wt % graphite/water slurry was pumped into the melter. The electrodes were energized; however, adequate power generation could not be maintained until several more batches of graphite slurry were added to the melter and stainless steel base plates were welded to the electrodes. Joule heating of the glass was established within 24 hours after energizing the modified electrodes. The main electrodes were then energized, and normal heatup sequence was followed.

The graphite restart of the small cylindrical melter-2 (SCM-2) was very similar to the final test on the SCM. The melter was allowed to cool to ambient temperature with a tank full of glass as before. Rather than use temporary electrodes, though, an attempt was made to use the existing upper electrode to throat electrode firing path to heat the graphite.

Theory

Physical property data and equations establishing the parameters for graphite slurry startup in a cylindrical melter have been developed. These equations were adapted for the rectangular melt chamber of the SCM-2 as shown below.

For the undried slurry

$$W_s = \frac{W_g}{X_g} \qquad (1)$$

where

W_s = weight of slurry, g

W_g = weight of graphite, g

X_g = mass fraction of graphite

Also

$$h_s = \frac{W_s}{\rho_s l w} \qquad (2)$$

where

h_s = depth of slurry, cm

ρ_s = density of slurry, g/cm^3

l = length of melt chamber, cm

w = width of melt chamber, cm

Similarly for the dried graphite

$$h_g = \frac{W_s}{\rho_s\ lw} \tag{3}$$

where

h_g = depth of graphite, cm

ρ_g = density of dried graphite, g/cm^3

Resistance of a rectangular volume of conducting material is given by

$$R = \frac{l\rho_{el}}{w\ h} \tag{4}$$

where

R = electrical resistance, ohms

ρ_{el} = electrical resistivity, ohm-cm

h = depth of conducting material, cm

Substituting (2) and (3) into (4) gives

$$R_s = \frac{l^2\rho_{el}\rho_s}{W_s} \tag{5}$$

and

$$R_g = \frac{l^2\rho_{el}\rho_g}{W_g}$$

where

R_s, R_g = electrical resistances of slurry and dried graphite, respectively, ohms

For any given power supply

$$R_c = \frac{\Delta V_{max}}{I_{max}} \tag{7}$$

where

R_c = critical resistance, ohms

ΔV_{max} = maximum achievable potential, volts

V_{max} = maximum achievable current, amps

Thus, when $R < R_c$, current is limiting, and when $R > R_c$, voltage is limiting.

Achievable power is defined as

$$P = \Delta VI \qquad (8)$$

where

P = power, watts
ΔV = potential, volts
I = current, amps

Experimental

The graphite used in this test was a 200 mesh powder from Southwestern Graphite Company. Graphite/water and Frit 131/water slurries were prepared by mixing powder and water in a feed tank. Continuous agitation of the slurry was provided by a T-line laboratory stirrer.

The regular melter feed system was used to feed graphite and frit slurries into the SCM-2 (Figure 30). Using a variflow pump, the slurries were pumped through 4.3 meters of 3/8-inch-stainless steel tubing and 1 meter of 1/4-inch-PVC tubing before they entered the melter through the center feed device.

During restart of the SCM-2, temperatures were measured with Type K thermocouples in the melt chamber thermowell. Two thermocouples, one centered vertically in the glass and the other centered vertically in the graphite, were used as controls.

The two temporary electrodes were 1-inch-diameter 304L stainless steel rods, each 60 inches long. A 1/2-inch-diameter hole was drilled near one end of each rod to connect electrical leads. After inserting the electrodes in the east and west lid ports, the electrical leads for the lower electrode to throat were disconnected and then connected to the temporary electrodes. Relative placement of the temporary electrodes in the melter is shown in Figure 31.

Results and Discussion

All power to the SCM-2 was cut off on 12/22/82, and the melter was allowed to cool to ambient temperature with a tank full of Frit 131/Simulation-2 glass. At shutdown the glass depth was 8.0 inches. Actual testing began on 12/27/82 after the glass had cooled to about 33°C. Layering of frit and graphite in the melt chamber is shown in Figure 32. Test history is summarized in Figure 33 which shows the median graphite and glass temperatures versus time.

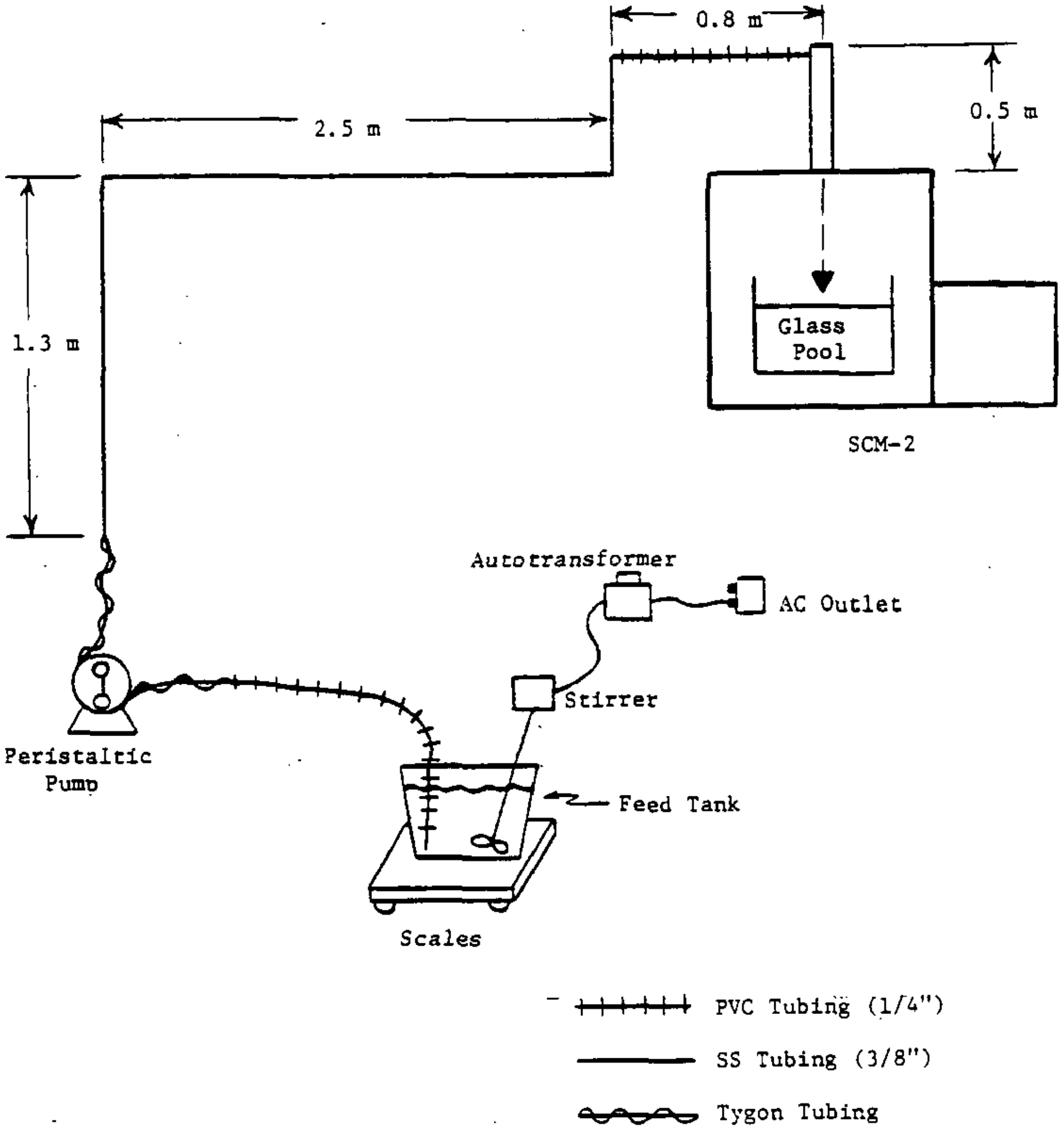

FIGURE 30. Experimental Apparatus for Graphite Slurry Restart

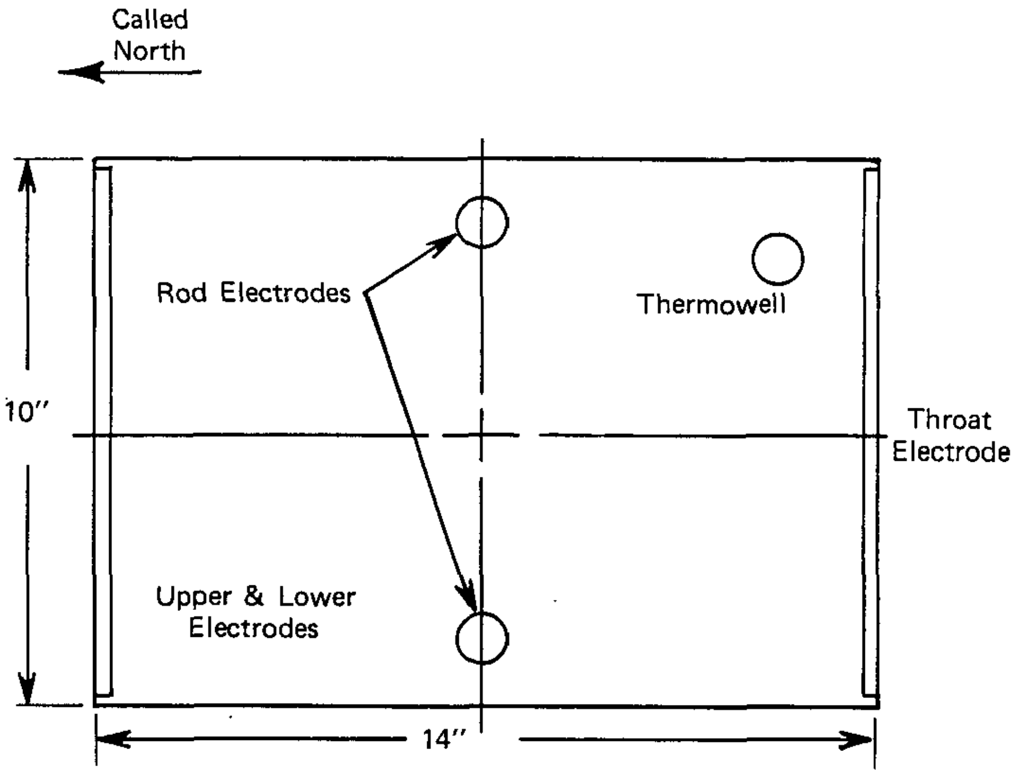

FIGURE 31. Top View of SCM-2 Melt Chamber Showing Location of Temporary Rod Electrodes

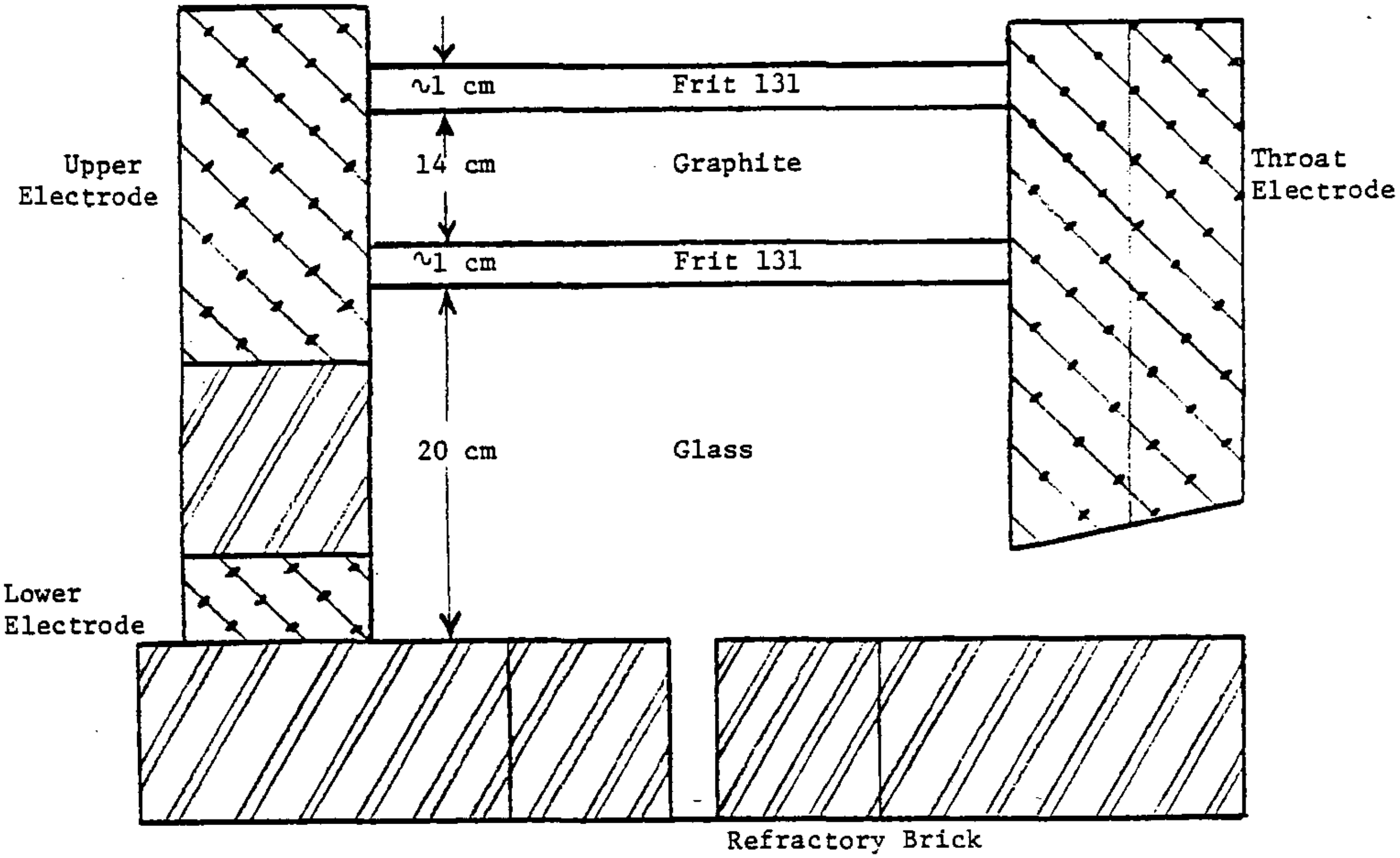

FIGURE 32. Vertical Section of Melt Chamber

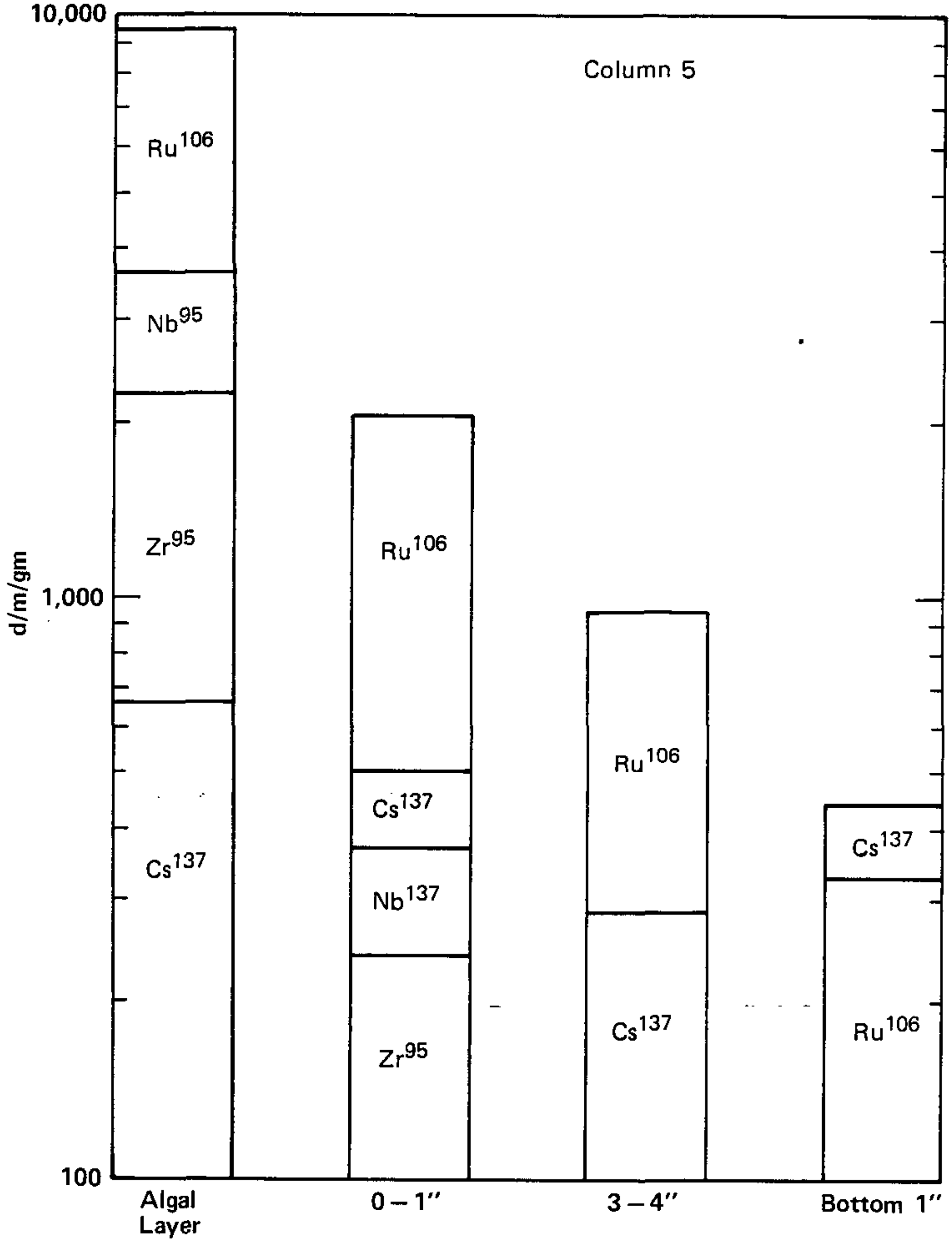

FIGURE 33. Median Temperatures of Graphite and Glass vs. Time

On 12/27, a 50 wt % Frit 131/water slurry (26 lb) was pumped through the melter feed system onto the frozen glass surface. The frit layer served as a buffer between the graphite and the waste in the glass. This minimized the possibility of metal oxides in the waste being reduced to metals by the graphite. After settling, depth of the frit layer was approximately 1 cm. Sixteen pounds of a 25 wt % graphite/water slurry were then pumped into the melter. This was the calculated amount of slurry needed to produce a resistance between electrodes of 0.4 ohm when dry (Equations 1 and 6). Both the frit and graphite slurries appeared to spread evenly over the melt surface.

After allowing the graphite to dry overnight, the upper electrode to the throat was energized. Graphite resistance, however, was too high (50 to 81 ohms) to generate sufficient power for heating. The power level did not exceed 0.6 kW. The high resistance was attributed to poor contact between the electrode surfaces and graphite. A later inspection of the melter after final shutdown revealed the presence of a glassy film covering all the electrode surfaces. Resistance of the graphite slurry without any evaporation or draining was calculated to be 51 ohms (Equation 5). This resistance drops rapidly as the graphite dries. When the upper electrode to throat was energized the graphite was still moist, but most of the water had drained away through cracks between the melter walls and glass, caused by contraction. This means the high resistance was primarily due to poor contact between graphite and electrodes and/or discontinuity in the graphite circuit.

A second batch of graphite equivalent to the first was added to the melter. The power level (1.1 kW) was slightly higher but still insufficient to heat the graphite. Over a 16-hour period, the power level dropped and temperatures changed very little. A third and final batch of graphite (16 lb) was pumped into the melter. A power level of 2 kW was attained, but after 3-1/2 hours the power had dropped to 1.2 kW. At that time a second batch of 50 wt % Frit 131/water slurry (26 lb) was added in an effort to pack down the graphite and consequently lower its resistance. The effects, however, were minimal.

Power to the upper electrode was cut off, and a pair of temporary rod electrodes were inserted in the graphite. Resistance between the two electrodes was almost 0 and power generation was more than adequate to begin heating up the graphite. For approximately 3 hours the graphite temperature remained at 99°C while all the water was driven off. Temperatures of graphite and glass then began to rise, but power to the electrodes was cut off for the weekend so as not to leave the melter on a ramp.

On 1/3/83, the temporary electrodes were reenergized and power generation was again more than adequate. Only 1 kW of energy was used in slowly heating the dry graphite layer from 23°C to 600°C. After reaching this temperature though, the power began fluctuating, and resistance increased. Streaks of radiation indicating the presence of molten glass were seen on the television monitor. Shortly thereafter the circuit between the graphite and electrodes was broken, and rapid cooling commenced. By the following morning, temperatures had fallen to less than 100°C. Efforts to reestablish graphite heating with the temporary electrodes were not successful.

The power to the temporary electrodes was cut off, and the upper electrode to throat was energized once again. For the first time, resistance was sufficiently low between the upper and throat electrodes to generate enough power to heat the graphite. Several reasons for this change are postulated. First, the overall resistance of the graphite was lower after it was dried out using the temporary electrodes. Second, the graphite may have shifted around during heating thus creating a more continuous and uniform circuit. Finally, rapid cooling after the temporary electrodes circuit broke may have caused some of the glass film to spall off the permanent electrode surfaces - increasing the effective contact area. A combination of the three conditions described above was most likely responsible for the change.

Graphite and glass were slowly heated (generally 10 to 20°C per hour) over several days using only the upper electrode to throat firing path. After 28 hours, the glass temperature had reached about 650°C and streaks of molten glass were observed. Then the glass temperature as measured in one thermowell dropped several hundred degrees in 1-1/2 hours (Figure 33). This occurred while the graphite temperature and power consumption continued to increase. This probably means that the temperature drop was very localized and was due to shifting current paths as the glass melted unevenly. The overall melter temperature continued to increase. After 3 hours, the glass temperature measured in the thermowell again began to increase. Within a short time the glass pool was definitely on the Joule effect.

On 1/7, a transition took place whereby the glass temperature continued to rise, but the graphite temperature began to drop. Temperatures then levelled off at 1000°C for the glass and 675°C for the graphite. At this point Joule heating of the glass was self-sustaining. The lower electrode to throat was energized to increase the glass temperature near the melter floor, and a day later the auxiliary heaters and riser electrode were energized to bring the melter to normal operating conditions. After several days most of the residual graphite had disappeared by oxidation. Slurry feeding resumed on 1/13/83.

Conclusions and Recommendations

- Graphite slurry restart of the SCM-2 was successful.
- Considerable difficulty was encountered in establishing and maintaining electrical contact between the electrodes and graphite.
- Although temporary electrodes were used for part of the test, the melter was eventually restarted using only the existing upper electrode to throat electrode firing path.
- The frit and graphite slurries were pumped through the melter feed system without difficulty and appeared to spread evenly in the melt chamber.
- Lid heaters remain the preferred method for startup or restart of a melter, but graphite slurry is a viable backup technique.

Further testing of the graphite startup technique is recommended to gain a better understanding of the problems that were encountered and to hopefully eliminate them. Of particular interest are the problems of establishing and maintaining both the continuity in the graphite circuit and the electrical contact between electrodes and graphite during heating. Also, other types of graphite should be tested. Some of this work can be performed in the laboratory using a plexiglas tank.

Bonding of Radioactive Contamination-1, Low Pressure Water Tests

The mechanisms by which radioactive contamination would be bonded to a DWPF canister surface are being investigated. When a clean, empty canister is introduced into the DWPF, its surface is likely to be contaminated by radioactive particles. When the canister is heated (during filling with molten glass) the contamination is bonded to the canister surface. The canister decontamination process for the DWPF, air-injected slurry blasting, was selected on the basis of its ability to remove contamination bonded to the canister by the most severe temperature conditions expected.

A better understanding of the mechanisms that bond contamination to a canister surface is currently being developed. This improved understanding could lead to the development of DWPF canister decontamination techniques which greatly extend the lifetime of process equipment. For example, much longer equipment lifetime would be expected if a water-only process was used in place of slurry blasting.

This following discussion describes the results of low pressure water tests to characterize the effect of several variables on the bonding of radioactive contamination.

Test Description

The effects of the following variables were investigated:

1. The original surface finish may affect decontamination (#1 and #2B surface finishes were evaluated).
2. Preoxidation is a possible pretreatment to reduce bonding of contamination (samples with and without such a treatment were tested).
3. The canister surface is postoxidized after it is contaminated (samples with and without such a treatment were tested).

A two-level factorial experiment was performed. Two specimens were run on each point of the test matrix shown in Figure 34. Contamination and oxidation conditions used in this test simulate those expected in the DWPF.

Experimental Procedure

The steps followed in carrying out these tests are shown in Figure 35 and are discussed below:

1. The appropriate specimens were preoxidized.
2. All specimens were contaminated by placing 0.05 cc of the contaminant in the center of one face.
3. All specimens were dried on a warm hot plate.
4. The specimens were then monitored.
5. The appropriate specimens were postoxidized.
6. Specimens were monitored again to determine the effect of postoxidation on the level of contamination.
7. All specimens were wiped with a piece of filter paper to remove transferable contamination.
8. They were monitored again to determine the amount of nontransferable contamination remaining on the surface.

Sludge Finish Number	Not Preoxidized		Preoxidized	
	Not Postoxidized	Postoxidized	Not Postoxidized	Postoxidized
1	$A_{1,2}$	$C_{1,2}$	$E_{1,2}$	$G_{1,2}$
2B	$B_{1,2}$	$D_{1,2}$	$F_{1,2}$	$H_{1,2}$

FIGURE 34. Test Matrix

1. Preoxidize
2. Contaminate
3. Dry
4. Monitor
5. Postoxidize
6. Monitor
7. Wipe
8. Monitor
9. Rinse
10. Smear

FIGURE 35. Experimental Procedure

9. Specimens were then rinsed with 50 mL of hot water from a polyethylene squeeze bottle.
10. They were smeared again to determine the total DF by the wiping and rinsing.

The results of monitoring the specimens are given in Table 37.

Effect of Variables

The average percent of contamination remaining on each specimen in the test matrix was determined, Table 38. A factorial analysis was performed to determine the statistical effect of each variable. The order of the effects of the variables is given in Figure 36.

Postoxidation

Postoxidation affected both the contamination level and the fraction of the contamination that is bonded to the surface (nontransferable contamination).

- Effect on Nontransferable Contamination

Heating contaminated specimens increased the fraction of contamination that is bonded to the surface so that it is not removed by a "smear." About 40% of the activity on the specimens simulating the unheated portion of the neck and flange area was nontransferable. On the specimens simulating the maximum degree of oxidation (600°C for 1 hour) 70% of the activity was nontransferable. Neither the original surface finish nor preoxidation affected the amount of nontransferable activity fixed on the surface.

- Effect on Contamination Level

The contamination level was reduced about 20% by postoxidation. This is attributed to volatilization of part of the contaminant.

Postoxidation was the variable that caused the greatest increase in nontransferable contamination. This is attributed to the particles of contamination either being mechanically entrapped in the oxide film, reacting with the oxide film, reacting with the surface, or a combination of all of the above plus any other unknown effect.

TABLE 37

Results of Specimen Monitoring

Spec No.	Smearable		Fixed		Total		After Baking On Contamination	
	Beta	Gamma	Beta	Gamma	Beta	Gamma	Beta	Gamma
A-1	400	80	800	46	1500	230		
A-2	600	80	600	46	1500	220		
B-1	800	80	180	40	1300	230		
B-2	310	70	800	46	1300	220		
C-1	310	80	800	45	1200	220	110	90
C-2	280	40	800	45	1200	230	1200	90
D-1	330	80	700	45	1400	230	1100	80
D-2	270	70	700	50	1400	210	1000	90
E-1	430	60	700	35	1200	200		
E-2	450	40	600	30	1300	190		
F-1	700	80	600	35	1500	210		
F-2	350	70	350	50	1000	210		
G-1	270	35	900	80	1500	180	1200	90
G-2	250	35	900	70	1500	180	1200	90
H-1	280	35	90	70	1200	200	1200	90
H-2	290	40	900	60	1200	200	1200	90

TABLE 38

Average Percent of Contamination Remaining

Surface Finish	Not Preoxidized		Preoxidized	
	Not Postoxidized	Postoxidized	Not Postoxidized	Postoxidized
No. 1	6.7	20	14.3	15.6
No. 2B	6.8	18.5	11.5	16.4

Preoxidation

Preoxidation increased the amount of nontransferable contamination on specimens not postoxidized. Mechanical entrapment of particles of contamination in surface imperfections of the oxide film is a possible cause. Preoxidation reduces the amount of nontransferable contamination on postoxidized specimens. Oxidation during postoxidation would be forming at the interface between the metal and the preoxidation oxide film. There would be less tendency to mechanically entrap contamination particles in this oxidation. Remember the preoxidation oxide film separates the contamination from the metal interface where additional oxidation would occur.

Variable	Degree of Effect
Postoxidation	Greatest Fixed Contamination
Preoxidation	Greatest Fixed Contamination
Preoxidation–Postoxidation Interaction	Greatest Fixed Contamination
Surface Finish	No Significant Effect

FIGURE 36. Effects of Variables

Preoxidation-Postoxidation Interactions

There is an interaction between the preoxidation and postoxidation variables, Table 39. Preoxidation increases the amount of nontransferable contamination on specimens that are not postoxidized from 6 to 13%. This is possibly due to particles of contamination becoming mechanically trapped in surface imperfections of the oxide film. On specimens that are postoxidized, however, preoxidation reduces the amount of nontransferable contamination from 20 to 18%.

TABLE 39

Interaction Between Preoxidation and Postoxidation

Postoxidized	Preoxidized	
	No	Yes
No	6.25%	12.5
Yes	20%	16.7

Surface Finish

There was no significant effect of surface finish in these studies. This may be due to the small difference between a #1 and a #2B surface finish.

Program

The tests described in this memorandum will be repeated with air-injected water blasting.

Investigation of the mechanism of contamination fixation will continue utilizing surface analysis capabilities. Nonradioactive materials simulating the type of contaminants expected in the DWPF will be baked on Type 304L stainless steel specimens. AUGER and electron spectroscopy for Chemical Analysis (ESCA) techniques will be used to determine if the materials are mechanically trapped in the oxide layer or if they are reacting with the oxide. The effect of processing variables will also be studied:

1. Effect of Atmosphere

Simulated contamination will be baked-on in air, He-H_2, and He.

2. Effect of Preoxidation

Since the present study found significant interaction between preoxidation and postoxidation, the effect of preoxidation on contamination bonding will be studied further. Surface analysis techniques will be used to determine if the particles of contamination react with the preoxidation oxide film during postoxidation and if that oxide film separates the contamination from the new oxide that forms.

Contaminated Water Processing Facility

Two contaminated water processing facilities (CWPF) are being proposed, one for F Area and one for H Area. The facilities are to treat both canyon cooling water and waste farm storm runoff in the event of an accidental radioactive release. Each CWPF is to be designed for intermittent operation and is to be capable of handling releases on the order of several curies to the maximum possible credible release, estimated to be 100,000 curies.

In the event of a release contaminated water is currently diverted to either seepage or lined retention basins, depending on its level of activity. Seepage basin limits are presently set at a maximum of 1000 d/m/mL beta-gamma and 100 d/m/mL alpha. The purpose of the CWPF's would be to decontaminate the diverted water so it can be sent directly to the creek or to existing seepage basins. This would eliminate the use of open-air retention basins for radioactive waste storage.

Diverted water flows can be as high as 1MM gal/day (750 gpm) and can remain at this rate for one or two weeks. The majority of the radioactivity in the water, however, can usually be contained in the first 1MM gallons. The treatment requirements of the water will also vary, depending on its level of activity.

This memorandum examines the use of a multistage water treatment process to arrive at the required water decontamination. Treatment steps include filtration, membrane separation, and ion exchange. The basic steps of the proposed process are reviewed here along with preliminary results obtained from ongoing laboratory investigations.

Process Description

The decontamination process will be designed to accommodate feeds as concentrated as 0.1 Ci/gallon. Processing steps include diversion, filtration, membrane separation, zeolite treatment, and ion exchange as follows (see Figure 37).

I. Cooling Water Diversion

- Diverted cooling water would go directly to a new 500,000 gallon hold tank. This would presumably contain at least 90% of the released activity.
- A second 1.5 million gallon hold tank would contain the rest of the water that might exceed seepage basin guidelines.

II. Filtration

- Solids will be removed from diverted cooling water in a two-stage filtration process.
- Filters will be back-washed to send entrained activity to liquid waste. (The degree of filter backwashing still needs to be determined.)

  A. The primary or coarse filtration medium will be a washable multimedia bed of sand, gravel, and activated charcoal for the purpose of removing large particulates as well as small amounts of organic material and chlorine.

  B. The secondary, or fine filtration system, will trap submicron particles (to 0.5 m). The filter will be regenerated by back-pulsing to a "hot" liquid waste stream. The filtration medium will be a durable sintered metal.

- The overall DF of the filtration system will exceed 10. This includes the entire spectrum of radionuclides in the theoretical yield calculations.

III. Membrane Decontamination System
(Either Reverse Osmosis or Electrodialysis)

- Effluent from the filtration system will be concentrated 30 times, with a decontamination factor (DF) of at least 10.
- Concentrate (waste) will be sent to the "hot" liquid waste stream.

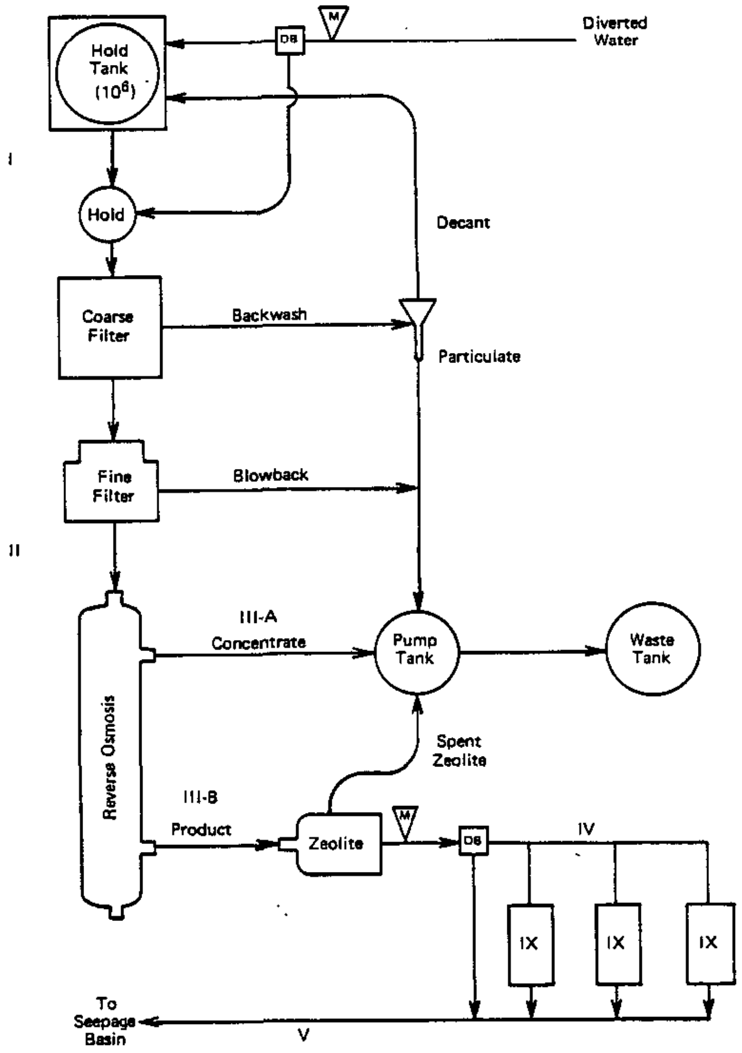

FIGURE 37. Contaminated Water Processing Facility

Key to the Contaminated Water Processing Facility Schematic

M = radiation monitor
DB = diversion box

Hold tank (10^6) = covered hold tank, 1 million gallon capacity (see Part I of Process Description)

Coarse filter = some type of multimedia filter (see Part II)

Fine filter = 0.5 m filter (see Part II)

Reverse Osmosis = (see Part III)

Zeolite = (see Part IV)

IX = mixed bed ion exchange resin, possibly in trailers (see Part V)

A. These conditions have been demonstrated in the laboratory for the treatment of process cooling water by reverse osmosis. [However, the treatment of storm water runoff from the tank farms may require a lower concentration factor or pH pretreatment to avoid the precipitation of silica.]

B. Electrodialysis (ED) may provide a poorer DF than reverse osmosis due to the presence of colloidal sized solid radioactive material. However, ED is compatible with a wide pH range, thus making it possible to maintain a high concentration factor from more concentrated liquids (i.e., pH adjustment of storm runoff pH adjustment to solubilize silica).

IV. Zeolite Treatment

- Effluent from Stage III will pass through a zeolite bed to remove the Sr-89, Sr-90, Cs-134, and Cs-137 from all diverted process water. DF will be about 10^2 for strontium and 10^3 for cesium, with about 200 ft^3 of zeolite required to treat one million gallons of cooling water.

- Inorganic zeolites will be used so that the exhausted material can be slurried to the waste tanks (through the "hot" liquid waste line).

  A. Either clinoptiloite or a mixture of IE-95® and A-51® (Union Carbide Corporation) will perform adequately.

- Zeolite treatment should provide sufficient decontamination "polishing" for most spills. In most cases, effluent from the zeolite column could go directly to the seepage basin, see Figure 37.

- Zeolite treatment would also extend the length of the ion exchange cycle by preventing early cesium breakthrough.

V. Ion Exchange

- The ion exchange portion of this process will be designed to "polish" effluents from the zeolite bed. It will be used only in the event that a large (>100 Ci) release cannot be adequately treated with reverse osmosis and zeolite.

- Resin beds will be stored in trailers, and will be regenerated, so that all high activity waste will be in liquid form. The regeneration facility already exists in H Area.

A. About 180 ft^3 of ion exchange resin can provide five-fold excess exchange capacity for the treatment of 1,000,000 gallons of contaminated process water (after 90% salt rejection in Stage III). This is equivalent to three ion exchange trailers of the type currently in use at SRP.

B. With a homogeneous feed, total loading of the 60 ft^3 bed in each of 3 trailers would be less than 200 Ci of gamma activity, even in the event of a 100,000 Ci release. However, in the event of such a major release, loading would be maintained at less than 20 Ci by sending the first 500,000 gallons of contaminated water to the tank farm for evaporation instead of through the CWPF.

C. Necessary DF's will be obtained by running two ion exchange beds in series, with regeneration/replacement in "leap-frog" fashion.

Conclusions

The process described here should provide the capacity to isolate and treat any radioactivity release up to 100,000 Ci of gamma activity to either the separations process cooling water or the storm water runoff from the tanks farms.

Reverse osmosis appears very promising in its ability to decontaminate spiked process water solutions, and it is especially valuable in removing activity that is associated with neutral submicron particles. However, filtration will have to be highly efficient to prevent excessive contamination of the reverse osmosis membranes. Ion exchange will also require thorough testing to assure that high DF can be obtained at the flow rates and salt concentrations demanded of this system. Experience with ion exchange decontamination at the reactor storage basins indicates that this portion of the system should be quite practical.

Summary of Full-Scale Filter Testing

The full-scale precipitation test facility (FPTF) was designed and built at the engineering test facility (ETF) in support of the salt decontamination demonstration taking place in Tank 48H. The facility uses a precipitation process to remove radionuclides from waste supernate. The objectives of the FPTF were to run-in the SRP filter assembly and to provide basic data on the operation of full-scale filters and on the effects of process variables on filtration. FPTF Run 1 and Run 2 were designed to meet these objectives.

FPTF Run 1 was the run-in of the SRP filter assembly. The assembly was tested with a simulated precipitate slurry of potassium tetraphenylborate before installation in Tank 48H to verify filter integrity and operability. Filter integrity was confirmed by filtrate analyses which showed potassium levels at the instrument detection limit. Filtrate rates as high as 40 to 50 gpm were obtained for over 16 hours during the run-in.

FPTF Run 2 was designed to examine the effects of process variables on filtration. A set of SRL filters identical in size to the SRP filters was used along with a low-shear diaphragm pump. This pump was the same make and model as the pump installed in Tank 48H for the salt decontamination demonstration. Filtrate rates from 0 to almost 70 gpm were measured at pressure drops up to 30 psi. An optimum feed rate range of 60 to 90 gpm was found, and feed rates higher than 90 to 100 gpm resulted in significantly less filtrate. Concentrating the precipitate slurry decreased the filtrate rate and lessened the effect of feed flow rate. No effects of backpulse interval were seen for dilute or concentrated solutions for intervals from 5 minutes up to 1 hour. Comparison of data from the FPTF and from Tank 48H obtained during the cold run-in shows good agreement for the effect of feed flow and pressure drop on filtrate rate.

The run-in of the SRP filter assembly successfully met its two objectives. Filter integrity was verified by analytical results which showed potassium levels at the instrument detection limits. Operation of the filters verified that adequate filtrate rates could be obtained and maintained. Water flushing the filter proved to be a good initial step to increase filtrate rate, to be followed by 0.1 to 0.4M oxalic acid cleaning if needed.

Run 2 established filter operating conditions and evaluated the effects of process variables in filtration. The data shows that the maximum filtrate rate is obtained at feed rates in the range of 60 to 90 gpm and the rate decreases rapidly above 100 gpm. Filtrate rate increases as pressure drop increases, but this increase is less significant as the pressure increases. In addition, the backpulse may become less effective due to the high main stream pressure. Increasing concentration decreases filtrate rate and less of an effect of feed flow rate is seen at higher concentrations. For full-scale filtration, the effect of backpulse interval is not as significant as it was at 1/4 scale. Even so, an interval of five minutes is recommended during Tank 48H operation to ensure good backpulsing of the filters. Other recommendations include keeping the feed flow rate in the optimum range of 60 to 90 gpm and using 40 psi pressure drop as the upper operating limit.

Sodium Titanate Filtration

Sodium tetraphenylborate and sodium titanate have been demonstrated as two reagents which can decontaminate high-level radioactive liquid waste containing cesium, strontium, and plutonium. By adding these reagents to a waste salt solution, cesium tetraphenylborate precipitates and sodium titanate particles adsorb strontium and plutonium. Via crossflow filtration, the solids are concentrated and a decontaminated filtrate is produced.

Summary

SRL has performed numerous studies on the filtering of cesium tetraphenylborate/sodium titanate slurry. Tests with simulated wastes have been performed at TNX and with actual wastes in the High Level Caves. This report discusses filtration with only sodium titanate particles in a simulated waste solution.

The filtration was done at TNX through a single 0.5-micron Mott Metallurgical sintered metal filter tube. This tube had the same diameter and half the length of the filters chosen for the in-tank salt processing demonstration. For 120 continuous hours, sodium titanate solution was passed through the filter with both the filtrate and concentrate returning to the feed tank. By adjusting the pressure drop across the filter, a constant filtrate rate was maintained. During the 120 hours, the pressure drop increased from 5 psi to 43 psi. The filtrate was maintained at a constant rate between 0.08 to 0.11 gpm per ft^2 of filter area. This dramatic increase in the pressure required to maintain a constant flow indicates severe pluggage of the filters by sodium titanate. This suggests that filtration of a sodium titanate only slurry is unfeasible.

Discussion

The TNX small-scale filter facility consists of a single vertical 5-foot, 5/8-inch ID, 0.5-micron Mott filter tube inside a 1-inch pipe. A Warren-Rupp SB-1A double diaphragm pump feeds the slurry through the filter from 2.25 inches off the bottom of a 45-gallon agitated tank. The filtrate and concentrate both are recycled to the feed tank (Figure 38).

The simulated waste solution consisted of 40 gallons of supernate with 1.02 liters of 75 grams/liter of methanol-based sodium titanate. Aromatic Flavors and Fragrances (AFF) of Atlanta prepared both solutions. The final sodium titanate concentration was 0.5 gram per liter of supernate.

During the test, a constant filtrate flow rate was maintained by adjusting the pressure drop across the filter. Pressure drop was adjusted by throttling the backpressure valve and/or increasing the pump discharge pressure (Figure 38). The feed rate to the filter of the slurry also was controlled at a constant value.

Test Results

Figure 39 is a graph of pressure drop across the filter during the 120 continuous hour test. The filtrate rate was held between 0.08 to 0.11 gpm/ft^2 of filter area. When the flow rate fell outside this range, the pressure was adjusted to bring it back to 0.10 to 0.11 gpm/ft^2. Initially, the filtrate rate was very sensitive to pressure drop. As the test progressed, additional pressure was required to adjust the filtrate rate. On the graph, flat data points actually represent a decrease in filtrate rate at constant pressure drop. Near the end of the 120-hour test, the pressure required to maintain the 0.08 to 0.11 gpm/ft^2 rate increased sharply. This implies that the filter pores were almost totally fouled.

Conclusions

Filtering a sodium titanate only slurry will cause filter pluggage in a relatively short period of time (approximately 120 hours). This contradicts the results of filtering sodium titanate with tetraphenylborate precipitates over extended periods of time. It is assumed that the precipitate acts as a filtering aid preventing pluggage of pores by the sodium titanate. (Sodium titanate has been identified as the main cause of filter plugging.) Maintenance of a constant flow rate of clear filtrate when filtering a sodium titanate only slurry, would require constant pressure adjustment. These points conclude that filtration of sodium titanate only slurries is impractical.

Reagents for the In-Tank Salt Processing Demonstration

A total of 36,012 pounds of sodium tetraphenylborate having an average purity of 99.1% and 2530 pounds of sodium titanate were used for the in-tank salt processing demonstration to remove cesium and strontium from High Level Waste. This report summarizes the procurement, preparation, and quality control of the reagents.

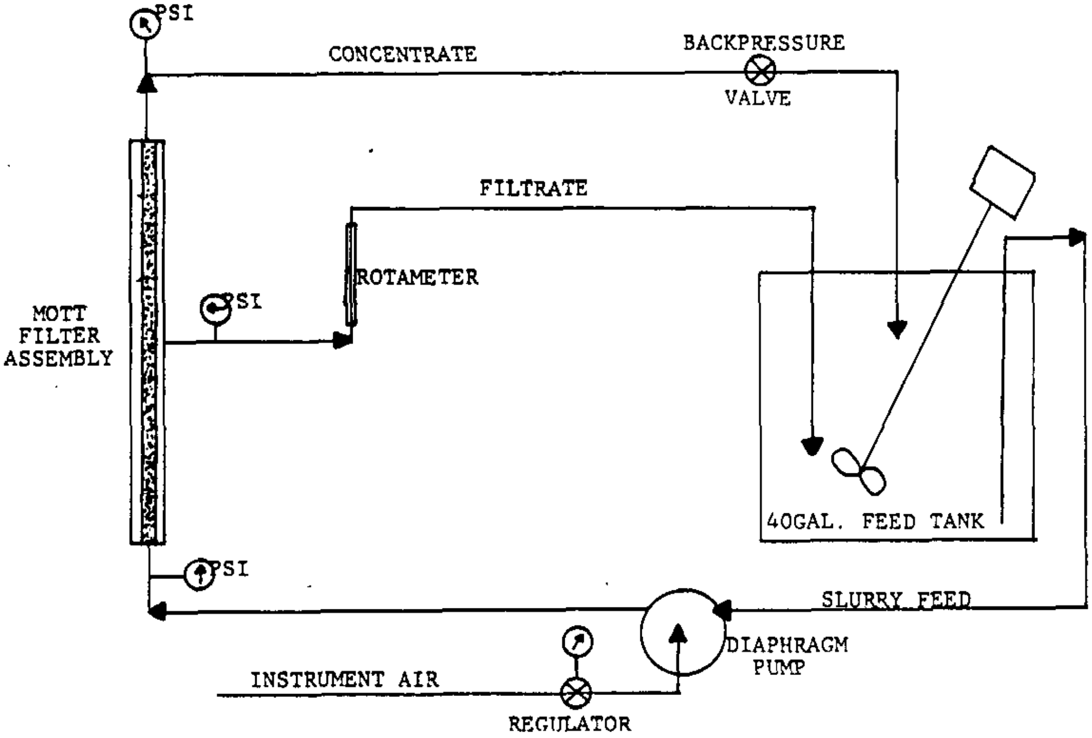

FIGURE 38. TNX Small-Scale Filter Faciity

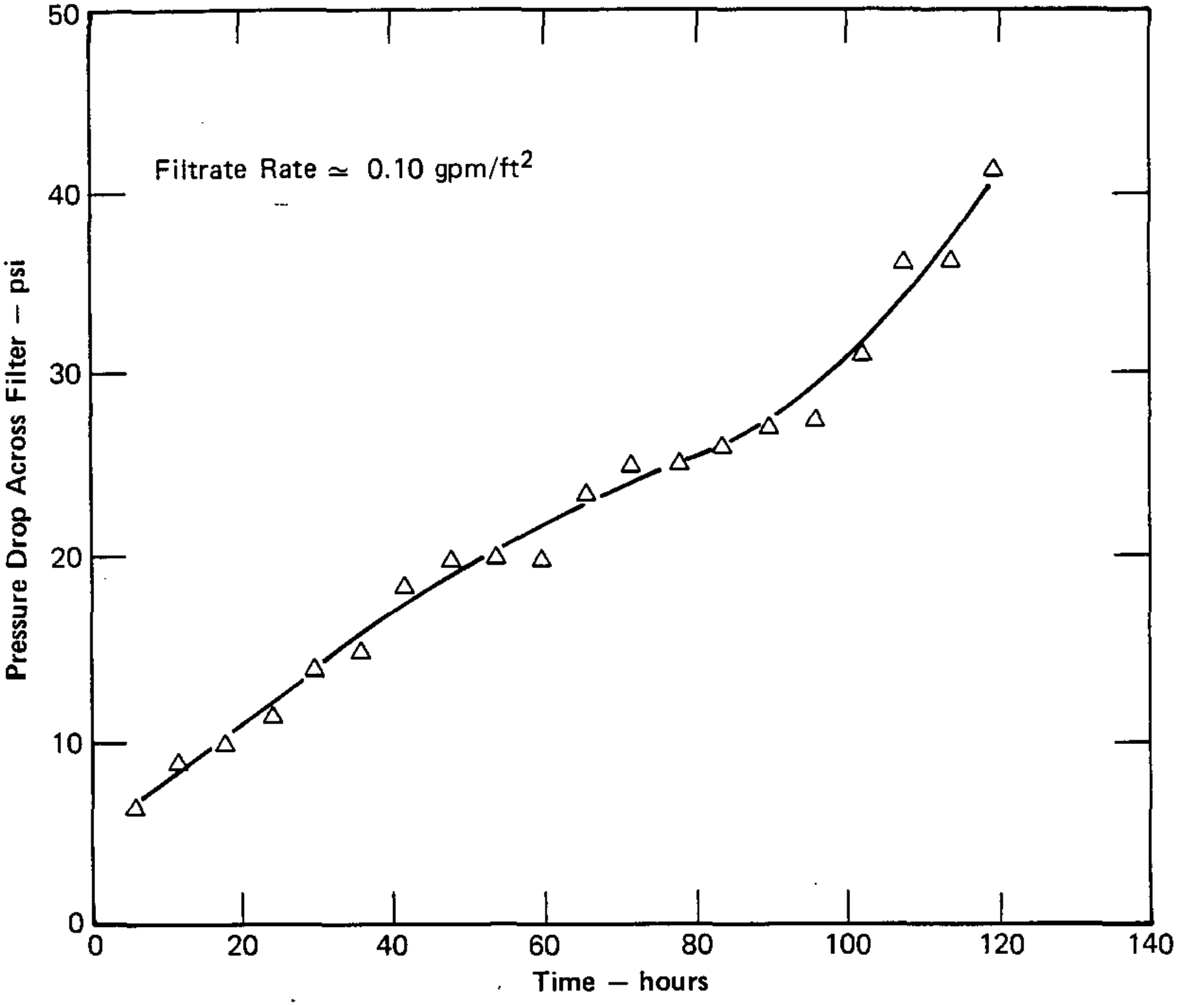

FIGURE 39. Small-Scale Filter Facility — Sodium Titanate Only

Background

A process has been developed to remove cesium and strontium from SRP High Level Waste. Two chemicals, sodium tetraphenylborate and sodium titanate can be added directly to a waste storage tank under a wide range of processing conditions. Sodium tetraphenylborate coprecipitates cesium and potassium as highly insoluble solids. Sodium titanate removes strontium by adsorption. To separate the solid materials containing the radionuclides from the decontaminated supernate a crossflow filtration system is utilized. The slurry flows through a sintered metal tube. Due to the pressure differential across the porous surface, material passes through the tubes producing decontaminated filtrate.

To determine the viability of this process, a 500,000-gallon demonstration was scheduled for Tank 48H at SRP. This document summarizes the purchase, preparation, handling, and quality control of the sodium tetraphenylborate (NaTPB) and sodium titanate (ST) used for the in-tank salt processing demonstration.

Sodium Tetraphenylborate Procurement and Quality Control

Four vendors supplied NaTPB for the Tank 48H in-tank demonstration. Boulder Scientific of Mead, Colorado, and Raylo Chemicals Ltd. of Edmonton, Alberta, supplied 35,000 pounds of NaTPB. AFF, Inc. of Marietta, Georgia, and Preiser Scientific of Charleston, West Virginia, supplied smaller quantities of material. 42,000 pounds of greater than 95% purity NaTPB was purchased for possible use in the demonstration and the cold chemical run-in.

To ensure a successful demonstration, a quality control program for NaTPB was developed. Samples were obtained from each drum and submitted to three tests.

- Loss of weight upon drying 1.5 g, 120°C, 24 hr, to determine residual solvent or water. Adapted from American Chemical Society (ACS) method.
- Gravimetric analysis for purity by precipitation of potassium. Adapted from ACS method.
- One composite sample from every 10 to 30 containers was prepared. The composite lot sample was tested with actual waste supernate for cesium decontamination factors.

Weight loss determinations were performed by the Engineering Lab at TNX. Percent purity was measured by Analytical Development. 14 composite samples were prepared and all demonstrated cesium DF's in excess of 1.5×10^4.

Sodium Tetraphenylborate Dissolution

36,012 pounds of NaTPB was used for the in-tank salt processing demonstration (3,200 lb for the cold run-in and 32,812 for the demonstration). To be used in processing, sodium tetraphenylborate must be dissolved as a 0.5M water solution with 0.1M NaOH added to stabilize the solution. To ensure complete dissolution of the NaTPB, the water was heated to about 35°C and the solution agitated for 4 hours.

Each batch (approximately 5000 gallons of 0.5M NaTPB) was analyzed for NaTPB by potassium precipitation.

Sodium Titanate Preparation

Sodium titanate is used to adsorb strontium. The monosodium titanate is prepared using the Sandia process as developed at SRL. Sodium (as sodium methylate) is reacted with tetraisopropyl titanate (titanium isopropoxide) and water in a methanol solution.

$$NaOCH_3 + 2Ti(OC_3H_7)_4 + 5H_2O \xrightarrow[CH_3OH]{} NaTi_2O_5H + 8C_3H_7OH + CH_3OH$$

The sodium titanate for the demonstration was prepared by AFF. AFF has a 300- and a 500-gallon still for use as reactors. 26,900 pounds of sodium titanate slurry was produced for the in-tank salt processing demonstration (2750 lb for the cold run-in and 24,150 for the demonstration). The material delivered by AFF settled more than similar laboratory-scale preparations at SRL. The amount of waste which settled was no problem for the demonstration.

The amount of solids in the AFF sodium titanate (approximately 94 g/L) is 10 to 12% higher than the solids loading seen in the lab. A possible explanation is that AFF actually distilled and concentrated the final product more than necessary. Insufficient information is available to complete the material balance, but considerable still leakage and evaporation would be possible. The material produced a strontium DF of greater than 400.

Total amount of sodium titanate in Tank 48H is 2530 lb which is 48% titanium.

The Concentration of Technetium-99 by Acid Distillation

Decontaminated waste salt supernate contains the equivalent of one metric ton of technetium. A process has been described for removing technetium by adsorption on the strong base ion exchange resin, Dowex® 1-X8, and if an efficient means for recovering the technetium from the resin was developed, technetium metal could be produced for commercial and research applications.

As reported here, Tc-99 can be eluted from Dowex® 1-X8 resin with nitric acid and concentrated by single-stage batch distillation. Operating the distillation to provide a net volumetric concentration factor exceeding 80, the resulting stream would contain roughly 0.25 gram of Tc-99 per liter. This stream could then be further concentrated, either by precipitation or by a second ion exchange cycle, to achieve quantitative Tc-99 recovery in a conveniently handled solution or solid form.

Discussion

Having first identified nitric acid as the best eluent for removing Tc-99 from Dowex® 1-X8, it was immediately recognized that this eluent was still not efficient enough to use in a once-through system. That is, without recycling, a volume of nitric acid equivalent to roughly 1/5th of the total supernate feed volume would be consumed. Also, the net concentration factor would be only 4-6, leaving the final recovery problem unsolved.

Experiments were performed with solutions of Tc-99 in nitric acid to determine if technetium would remain in solution while the nitric acid was distilled away. Such a distillation would simultaneously accomplish nitric acid regeneration and the concentration of technetium. Acid consumption would be reduced to the amount necessary for keeping technetium in solution in the still bottoms, thus providing a considerable savings in operations costs.

The final concentration step, converting technetium to an easily handled form, can probably be accomplished by precipitation of technetium from the neutralized still bottoms, as the heptasulfide. However, a second ion exchange step, to be followed by calcination of the resin, also appears to be quite promising as a means of producing technetium oxide from the still bottoms. A small, laboratory-scale process is now being designed to produce enough technetium to support experimental effort in this area.

Experimental

Adsorption of Tc-99 from Supernate Solutions Onto Dowex® 1-X8

Experiments were performed with 3 to 4 mL resin columns (A=0.636 cm^2) of Dowex® 1-X8 to estimate the capacity of the resin for removing TcO_4^- from decontaminated salt supernate. Using 200 to 400 mesh resin, 50% breakthrough was attained near 127 column volumes of 5.5M (sodium) supernate flowing at 24 column volumes per hour (Figure 40, Table 40). This amounts to 0.31% loading of the resin with pertechnetate. Supernate from Tank 24 contains 3 ppm of Tc-99, which would load the resin to 0.27% of capacity if the same k_d were applied (resin capacity is 1.4 meq/mL of resin bed).

The effects of tetraphenylborate (TPB) on adsorption efficiency were not addressed. However, recent work indicates that similar attainments can be achieved if more concentrated supernate solutions are used in the precipitation process (this change benefits technetium removal by decreasing TPB solubility while increasing TcO_4^- concentration).

Elution of Tc-99 from Dowex® 1-X8

Nitric acid was identified as the most convenient and efficient eluent. The elution of TcO_4^- from Dowex® 1-X8 was performed in conjunction with adsorption tests which defined the capacity of the resin for removing TcO_4^- from salt supernate. Thirty column volumes of 4M HNO_3 eluate removed virtually all of the loaded technetium (see Table 41, Figure 41). With 2M nitric acid, almost 80 bed volumes were required to achieve the same technetium recovery (99.7%). These results are consistent with data reported in the literature.

Several other eluents were tested for the ability to elute TcO_4^- from Dowex® 1-X8. These included both acidic and strongly basic solutions of soft (polarizable) anions and/or hydrophobic (organic) anions. Among the eluents tested were sulfate, thiosulfate, dithionate, permanganate, benzoate, and phthalate. None of these proved to be satisfactory.

The possibility of on-column reduction of TcO_4^- to TcO_2 as a means of regenerating column capacity was also tested. Thiosulfate and hydroxylamine solutions were used to perform this reduction. Unfortunately, any regenerated capacity for adsorbing TcO_4^- from supernate was consumed in the first few column volumes. This observation indicates either inefficient reduction, or dissolution of the reduced species, either by reoxidation or entrainment. In either case, the approach is unlikely to be successful.

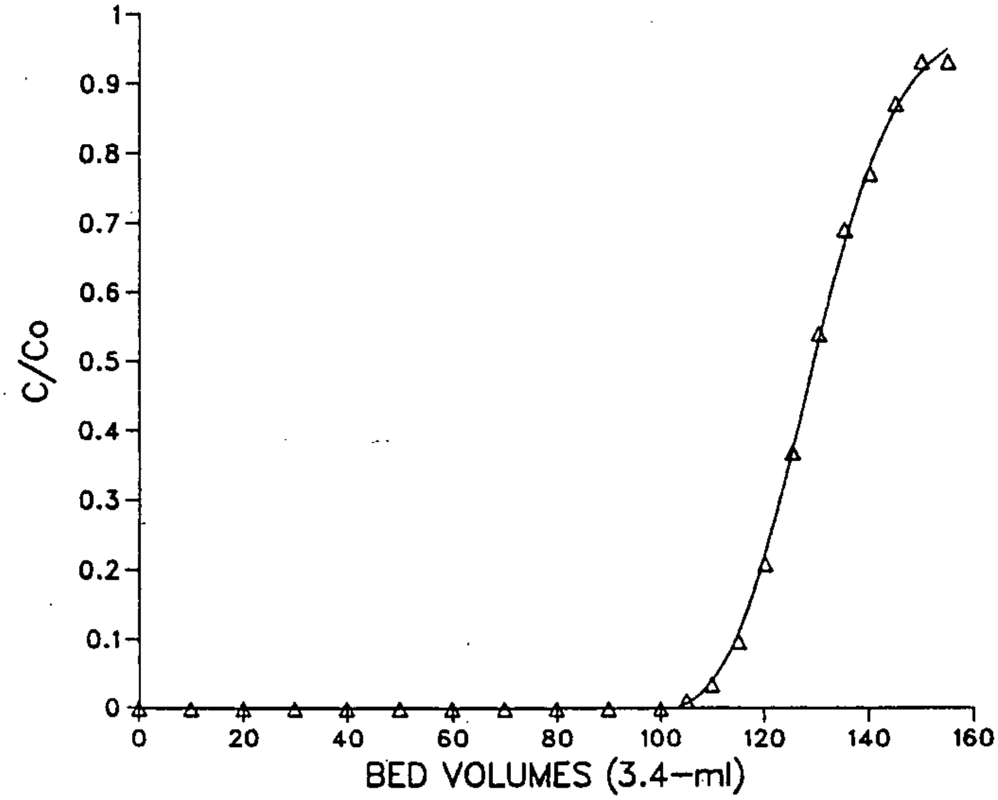

FIGURE 40. Breakthrough Curve: Tc-99 Adsorption from Simulated Supernate

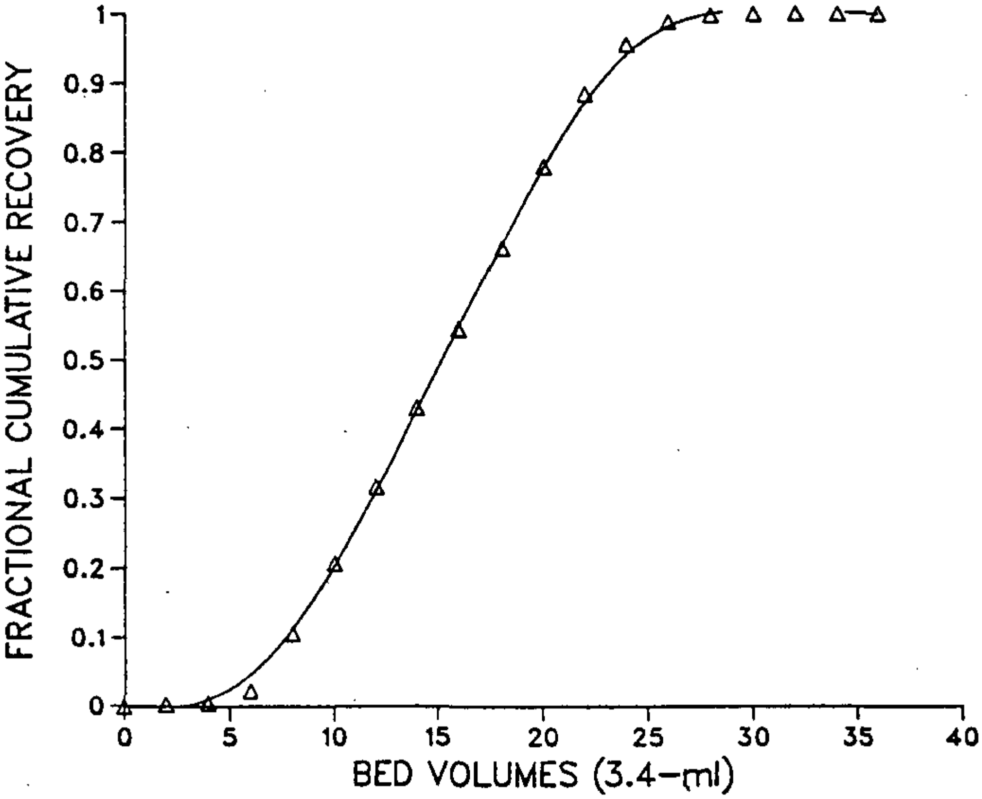

FIGURE 41. Tc-99 Elution from Dowex® 1-X8 with 4M HNO_3

TABLE 40

Tc-99 Adsorption Onto Dowex® 1-X8

Sample (Column Volume)	C/Co
10th	$<10^{-3}$
20	$<10^{-3}$
30	$<10^{-3}$
40	$<10^{-3}$
50	$<10^{-3}$
60	$<10^{-3}$
70	$<10^{-3}$
80	$<10^{-3}$
90	$<10^{-3}$
100	$<10^{-3}$
105	1.1×10^{-2}
110	3.5×10^{-2}
115	9.8×10^{-2}
120	2.1×10^{-1}
125	3.7×10^{-1}
130	5.4×10^{-1}
135	6.9×10^{-1}
140	7.7×10^{-1}
145	8.7×10^{-1}
150	9.3×10^{-1}
155	9.3×10^{-1}

Column Volume = 3.4 mL
Area = 0.636 cm^2
Flow = 1.42 mL/min
Resin Weight = 1.5 grams (dry weight)
Exchange Capacity = 1.4 meq/mL, 3.2 meq/g
Density = 0.44 gram dry weight/mL of bed volume

TABLE 41

Tc-99 Elution from Dowex® 1-X8 with 4M HNO_3

Column Volumes	Response*	Cumulative % Recovery
2	1.0 E4	0.30
4	6.7 E3	0.50
6	7.3 E4	2.3
8	2.7 E5	10.7
10	3.4 E5	20.8
12	3.7 E5	31.8
14	3.8 E5	43.2
16	3.8 E5	54.5
18	3.9 E5	66.1
20	3.9 E5	77.7
22	3.5 E5	88.1
24	2.4 E5	95.2
26	1.1 E5	98.5
28	3.3 E4	99.5
30	7.3 E3	99.7
32	2.1 E3	99.8
34	1.1 E3	99.8
36	9.3 E2	99.9
38	6.1 E2	
40	5.6 E2	
42	7.7 E2	
44	6.2 E2	
46	6.3 E2	
48	7.6 E2	
50	9.0 E2	
60	1.7 E2	
70	5 E0	
80	2.0 E2	
90	9.6 E1	
100	2.1 E1	

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* Response is in d/m per 200 μL sample as determined by beta scintillation counting. Column conditions as in Table 40.

Nitric Acid Distillation

Experimental

A simple one-stage distillation apparatus was used to recover nitric acid from 4M nitric acid eluent while concentrating the technetium in the still bottoms. The initial concentration in the still bottoms (Ci) was 5.4 x 10^5 d/m/mL, just under 15 ppm of Tc-99, the approximate (±10%) concentration expected in the actual process.

As shown in Table 42, such a still can be taken nearly to dryness without a major loss of technetium to the overheads, Figure 42. Cumulative losses in batch distillation were only about 2% at 20:1 volume reduction and approximately 90% acid recovery. Even after taking the still all the way to dryness, 85% of the technetium was recovered from the bottoms. Just over 3% went to the overheads and a balance of 12% of the original technetium activity was lost to the walls of the vessel and the condensation column. These results are consistent with observations of technetium behavior reported elsewhere.

The distillation of nitric acid has been well studied, but for the purposes of characterizing the behavior of this experimental system, nitric acid distillation data was also obtained. Table 43 lists some data obtained from the distillation of 4M nitric acid.

Data Treatment

Batch Distillation

Nitric acid distillation does not behave ideally. The well known nitric acid-water azeotrope forms at just over 68% nitric acid (38.3 mole % HNO_3). This was expected to complicate a technetium-nitric acid separation, but the data indicate that the $HTCO_4/HNO_3$ separation factor is reasonably constant over the course of a batch distillation.

Table 44 lists the mole fractions that were calculated for the batch distillation of nitric acid from technetium solutions. Vapor phase selectivity coefficients ($\alpha_{A/B}$) were calculated from the data and are recorded in Table 45. Although the selectivity coefficients for the distillation of water are strongly dependent on the composition of the still bottoms, the separation factor for nitric and pertechnic acids is reasonably constant. Therefore, the following relationship holds.

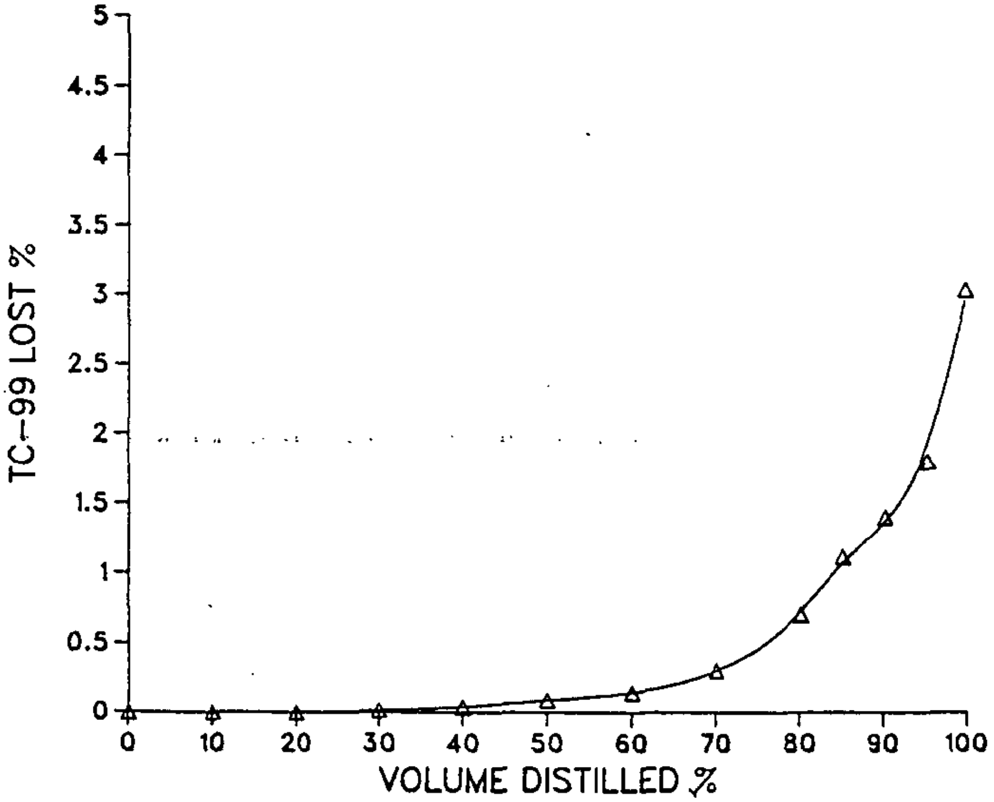


FIGURE 42. Batch Distillation: Cumulative Tc-99 Lost to Distillate

TABLE 42

Tc-99 Losses in Distillation of 4M HNO_3

Distillate Fraction, mL	Co,* d/m/200 µL	Fractional** Cumulative Loss	C_B,† d/m/200 µL	Co/C_B
0	<Background	-	1.08×10^5	-
9-10	<Background	-	1.20×10^5	$<4 \times 10^{-4}$
19-20	<Background	-	1.49×10^5	$<4 \times 10^{-4}$
29-30	1.82×10^2	1.7×10^{-4}	1.54×10^5	1.18×10^{-3}
39-40	2.83×10^2	4.2×10^{-4}	1.79×10^5	1.58×10^{-3}
49-50	5.13×10^2	9.3×10^{-4}	2.15×10^5	2.49×10^{-3}
59-60	6.12×10^2	1.49×10^{-3}	2.69×10^5	2.28×10^{-3}
69-70	1.72×10^3	3.09×10^{-3}	3.58×10^5	4.8×10^{-3}
79-80	5.09×10^3	7.08×10^{-3}	5.34×10^5	9.53×10^{-3}
84-85	7.45×10^3	1.12×10^{-2}	7.1×10^5	1.04×10^{-2}
89-90	6.31×10^3	1.41×10^{-2}	1.06×10^6	5.95×10^{-3}
94-95	8.45×10^3	1.81×10^{-2}	2.1×10^6	4.02×10^{-3}
99-99.5	2.66×10^4	3.04×10^{-2}	1.04×10^7	2.54×10^{-3}

---

* Co is the technetium concentration (activity) in the distillate over the 1-mL interval.

** Cumulative loss is calculated by taking the total technetium activity lost to the overheads and dividing by the total activity in the still initially.

† C_B is the concentration of technetium in the still bottoms after the 1-mL interval.

TABLE 43

Nitric Acid Recovery in Distillation of 4M HNO_3

Volume Fraction, mL	HNO_3		m-moles HNO_3 Distilled		HNO_3 Recovery, Cumulative
	Molarity	Temp, °C	Cumulative	Density, g/cm^3	
0-10	0.057	102	0.57	1.001	1.4×10^{-3}
10-20	0.086	102	1.43	1.002	3.5×10^{-3}
20-30	0.238	102	3.81	1.005	9.3×10^{-3}
30-40	0.397	103	7.78	1.007	1.9×10^{-2}
40-50	1.297	105	20.8	1.03	5.1×10^{-2}
50-60	2.50	108	45.8	1.08	0.11
60-70	5.44	111	100	1.18	0.24
70-80	6.33	114	163	1.20	0.40
80-90	11.32	117	277	1.33	0.68
90-100	13.20	119-123	409	1.37	1.0

TABLE 44

Molar Relationships for Tc/HNO_3 Distillation*

%D	S	X_{HNO_3}	X_{H_2O}	X_{Tc-99}	Y_{HNO_3}	Y_{H_2O}	Y_{Tc-99}
0	5.22	0.0785	0.92	2.77×10^{-6}	-	-	-
5	4.90	0.084	0.916	2.95×10^{-6}	0.0010	0.999	-
15	4.37	0.093	0.907	3.31×10^{-6}	0.0016	0.998	-
25	3.84	0.107	0.893	3.77×10^{-6}	0.0043	0.996	2.21×10^{-9}
35	3.29	0.125	0.875	4.40×10^{-6}	0.0073	0.973	5.67×10^{-9}
45	2.75	0.145	0.855	5.26×10^{-6}	0.024	0.976	1.02×10^{-8}
55	2.21	0.172	0.828	6.54×10^{-6}	0.046	0.954	1.43×10^{-8}
65	1.68	0.202	0.798	8.60×10^{-6}	0.104	0.896	3.01×10^{-8}
75	1.16	0.241	0.759	1.24×10^{-5}	0.124	0.876	8.95×10^{-8}
85	0.67	0.284	0.716	2.13×10^{-5}	0.244	0.756	1.70×10^{-7}
95	0.35	0.314	0.686	4.06×10^{-5}	0.295	0.705	5.01×10^{-7}

---

* %D is the volume percentage of 4M HNO_3 collected in overheads. S is the total number of moles left in the still bottoms at %D. X and Y are the mole fractions of components in the liquid and vapor phases, respectively.

TABLE 45

Vapor Phase Selectivity Coefficients*

%D	$\alpha\frac{H_2O}{HNO_3}$	$\alpha\frac{HNO_3}{Tc}$	$\alpha\frac{H_2O}{Tc}$
0	-	-	
5	92	0	
15	64	-	
25	28	69	1932
35	19	46	874
45	6.9	86	593
55	4.3	122	524
65	2.2	147	343
75	2.2	72	158
85	1.2	107	128
95	1.1	76	84
Average	-	91	-
S.D.	-	33	-

---

* See text for definitions.

$$-dS_A/-dS_B = Y_a/Y_B = \alpha_{AB}(X_A/X_B)$$

where S_A and S_B are the moles of components A and B in the still bottoms, respectively; and Y_i and X_i represent the mole fractions of each component (i) in the vapor and solution phases, respectively.

Integrating and substituting S_A/S_B for X_A/X_B yields the following equation

$$\ln \frac{S_{A(1)}}{S_{A(2)}} = \alpha \ln \frac{S_{B(1)}}{S_{B(2)}}$$

where the subscripts (1) and (2) denote the initial and final states of the system. By the convention used here, α is greater than one, meaning that component A is the more volatile of A and B.

Taking values from the data:

$\alpha HNO_3/HTcO_4 = 91 \pm 33$

$S_{A1} = 0.41$ mole

$S_{B1} = 1.46 \times 10^{-5}$ moles

Stipulating technetium recovery = 97% (R = 0.97)

$S_{B1}/S_{B2} = 1/R = 1.097$

Solving for S_{A2}:

$$\frac{S_{A1}}{S_{A2}} = 15.9 \qquad S_{A2} = \frac{0.41}{15.9} = 2.56 \times 10^{-2}$$

Acid recovery is:

$$\frac{S_{A1} - S_{A2}}{S_{A1}} = 0.937 \quad \text{or } 93.7\%$$

If α is reduced by one standard deviation to 58, R = 0.97, then:

$$\frac{S_{A1}}{S_{A2}} = 5.85 \qquad S_{A2} = 7.01 \times 10^{-2}$$

And then acid recovery is:

$$\frac{S_{A1} - S_{A2}}{S_{A1}} = 0.829 \quad \text{or } 82.9\%$$

In addition to being enhanced by rectification, acid recovery can also be increased significantly by reducing the technetium recovery requirements. At 95% technetium recovery (R = 0.95) and α = 58, nitric acid recovery is 94.9%.

Continuous "Steady State" Distillation

The nitric acid-technetium separation is also a promising candidate for continuous distillation with only slight rectification requirements. According to this data, a single plate system would ideally permit 73.8% conservation of nitric acid while recovering 97% of the technetium. The volumetric concentration factor for technetium would be roughly 20, equivalent to that of about 95% distillation of 4M HNO_3 (% by volume). Improved performance would be obtained by adding a rectification column to enhance the separation factor between HNO_3 and $HTcO_4$.

Final Concentration

As discussed in the previous two sections, the separation of nitric and pertechnic acid by distillation should be rather efficient. Nitric acid recoveries greater than 90% should be easily attained. The technetium concentrate would contain roughly 400 mg of Tc-99 in roughly 12 moles of nitrate as nitric acid.

Although the nitrate concentration could be reduced further by steam distillation, this may not be required. After neutralizing the residual nitric acid, technetium could be recovered either by precipitation or by adsorption on a weak base ion exchange bed.

The best precipitation method identified so far removes Tc-99 as the heptasulfide using H_2S as the precipitating reagent. Other methods, including direct electrolytic reduction, are possible.

Alternatively, a weak base ion exchange resin could be used to adsorb technetium from the nitrate solution. The elimination of nitrate could be made as efficiently as desired by using additional column capacity to perform the NO_3^-/TcO_4^- separation as the adsorbed technetium was eluted from the column. Sodium might also be eliminated from the system, if desired, by using ammonium hydroxide as the final eluent. The technetium product would then be relatively clean, containing a small amount of nitrate and some ammonium hydroxide (which could be air-stripped).

As a second option, final concentration can be achieved by loading the resin with Tc-99 as heavily as possible. TcO_2 would then be produced by calcining the loaded resin.

Conclusions

Technetium-99 can be removed from defense waste supernate by adsorption on a strong base ion exchange resin and can be recovered from this resin by elution with nitric acid. The technetium in the nitric acid eluent can be concentrated by distillation, using either a batch or a continuous distillation process and recycling nitric acid from the overheads. Tc-99 would remain in the bottoms.

The recycle recovery of nitric acid would be determined by the efficiency of the distillation process, but roughly 94% can be recovered easily by batch distillation. The recovery of Tc-99 would approach 97% through the removal and preliminary concentration steps.

Technetium can be recovered as a final product by neutralizing the residual acid in the still bottoms and then treating this solution with a precipitation reagent. Alternatively, a weak base ion exchange resin can be used to adsorb technetium from the neutralized still bottoms. The technetium is either eluted as a relatively clean, concentrated aqueous solution, or converted to solid TcO_2 by calcining the resin.

The Analysis of Decontaminated Defense Waste Salt Supernate for Tc-99

This report describes a method that was recently developed to determine Tc-99 in DWPF decontaminated supernate solutions. The method, which is based on neutron activation, is directly compatible with a procedure that was recently described for I-129 analysis, and permits the specific detection of Tc-99 in the presence of tritium and numerous fission products. High-sodium concentrations and extreme alkalinity do not interfere with the analysis, which is sensitive to concentrations of less than 1 nCi/mL. Total analysis time, including standardization, activation, and counting, can be as little as 3 hours for one sample, with additional samples requiring less than 90 minutes. With the new computerized counting facilities that will be installed at SRL, overnight turnaround of routine samples could be arranged.

The method has been tested on both simulated and actual (Tank 24H) supernates. The results were in good agreement with those obtained by the previous method, which is based on solvent extraction and beta scintillation counting.

Discussion

Other Methods

The problem of technetium analysis arose recently when it was determined that technetium might be removed from the waste supernate prior to its disposal. Tc-99 is normally measured by beta scintillation counting, but this method has inherently poor energy discrimination, and is therefore subject to interferences by other beta emitters. Since it is necessary to measure Tc-99 accurately to monitor a technetium removal process, the ability to discriminate between Tc-99 and other beta emitters is very important.

This selectivity was achieved previously by extracting the technetium from a nitric acid solution with methyltricaprylammonium chloride (Aliquot-336) in xylene. However, special handling - including a precipitation and several extraction steps - is required. Sample processing is therefore quite slow (about 4 analyses/shift). Furthermore, experience with this method at SRL has shown that the quality of the extraction solvent is critically important and poor results have often been obtained.

Aside from selectivity, process monitoring also requires speed and sensitivity. The method that is currently being used at SRL to monitor Tc-99 in the environment is high-resolution mass spectrometry. It is perfectly specific and extremely sensitive, but it has two major disadvantages for this application. Extreme care is required in preparing samples so that no other radioactivity is present, and each analysis requires approximately ne week to perform. A separate "contained" system would be needed for supernate analysis.

There are several color-forming reagents that can be used to detect Tc-99, including furil-α-dioxime, thioglycolate, toluene-3,4 dithiol, and others. However, the use of these is subject to interferences from several matrix components, including molybdate, ruthenate, dichromate, and even nitrate. The procedures also require considerable time. Similar difficulties are encountered with gravimetric methods, and even plasma emission is difficult due to the viscosity of the matrix (DWPF supernate samples are routinely diluted 100:1 to reduce viscosity and optimize rebulization efficiency for ICP).

Neutron Activation Analysis of Tc-99 (NAA)

Basis

Neutron activation (NAA) has been used to analyze picogram quantities of Tc-99 in environmental samples. Compared to the methods discussed above, NAA has the advantages of specificity, sensitivity and, potentially, of quantitative accuracy. However, to achieve all of these for Tc-99 it is necessary to remove those sample components which may interfere with the analysis. For NASA, the major interference in defense waste supernate is sodium. Chlorine and bromine have interference potential, but are not concentrated enough to cause any problems with the analysis.

A simple and practical approach to the problem of separating Tc-99 from the overwhelming excess of sodium in salt supernate samples is to separate the two by ion exchange. Recent work has shown that Tc-99 is strongly adsorbed as TcO_4^- from defense waste salt supernate onto a quaternary ammonium anion exchange resin.

This is the same type of resin (Dowex® 1-X8) that was used for the analysis of I-129 in salt supernate, also by NAA. As described in the I-129 procedure, most of the sodium can be removed from the resin with distilled water. The resin can then be analyzed directly by NAA.

Batch Slurry Method

The distribution of pertechnetate between supernate and Dowex® 1-X8 was measured in batch experiments to confirm the strong adsorption behavior reported elsewhere. Conditions were typically 0.1 to 1.0 gram of resin in 10 mL of aqueous solution. The behavior of Tc-99 was monitored by beta scintillation analysis of the aqueous solution before and after equilibration. Distribution coefficients for technetium (g/gram resin)/(g/mL of solution) were typically greater than 100 (see Tables 46 and 47).

Analyses of Tc-99 in simulated supernate samples were attempted by a simple slurry technique. Resin and sample were mixed at 1:10 and 1:1 weight/volume ratios. The resin was separated from the liquid phase and then rinsed with distilled water. Tc-99 recovery was measured directly by neutron activation of the resin and checked by beta scintillation counting of the liquid phase. Removal efficiency for Tc-99 from the liquid phase was greater than 90% over three orders of magnitude in Tc-99 concentration for both resin/aqueous ratios. Neutron activation analysis was accurate to ±15% for samples containing more than 10 μg of Tc-99 (Table 48).

TABLE 46

Dowex® 1-X8 Batch Distribution Coefficients*

Tc-99 Concentration, final	K_d, mL/g
4.4×10^{-7}M	63
3.2×10^{-8}M	142
1.6×10^{-8}M	142
6.8×10^{-9}M	201

* Performed in aqueous solution of simulated supernate at 0.1 gram of resin (dry nitrate form) per 10.0 mL of solution.

TABLE 47

Synthetic Supernate Composition

Component	Prepared	June Analysis*	August Analysis**
OH^-	1.62	2.26	3.72
NO_3^-	2.2	2.14	1.73
NO_2^-	0.95	1.0	0.90
AlO_2^-	0.42	0.43	0.31
CO_3^{2-}	0.48	1.50	0.23
SO_4^{2-}	0.24	0.12	0.42
K^+	0.0095	0.0052	0.0023
Na^+	5.3	-	-

* Analytical Development Analysis No. 5655

** Analytical Development Analysis No. 10,093

TABLE 48

Resin Slurry Method*

Spike				Recovery		
				Measured by NAA		Measured by Scintillation Count, %**
d/m/mL	Total, µg	Resin Weight, g	Sample Volume, mL	µg	%	
1.36×10^3	3.6	10	100	7 ±2	194	93.5
	0.36	10	10	<2	555	91.0
6.80×10^3	18	10	100	20 ±2	111	93.5
	1.8	10	10	2 ±2	111	99.0
1.36×10^4	36	10	100	38 ±2	105	95.0
	3.6	10	10	7 ±2	194	97.8
1.36×10^5	360	10	100	290 ±15	81	97.0
	36	10	10	31 ±2	86	99.8

* Test with Tc-99 spiked simulated supernate.

** Percentage of initial activity recovered, calculated on the basis of activity left in solution (measured in duplicate).

Column Adsorption

Although the slurry concentration method can be used, the adsorption of TcO_4^- on a small resin column is preferred where accuracy and sensitivity are desired. The column method is more sensitive because it can concentrate a larger volume of sample. It is also more accurate because recoveries are consistently higher and more reproducible.

The mechanics of the column concentration method are actually very simple. A polyethylene insert is filled with resin to make a small column. The sample is passed through the column, followed by a second volume of distilled water. The resin column, insert and all, is then placed inside a polyethylene "rabbit" for neutron activation analysis. An intermediate drying step is also included if the sample is to be activated in a high-flux environment, but this is not required for activation at SRL's Cf-252 facility. All materials are pretested for their NAA "background".

The column concentration method was applied to the analysis of simulated supernate samples spiked with Tc-99, along with samples of decontaminated supernate from Tank 24H. The results are reported in Table 49.

The method was cross-checked against the Aliquot-226 beta scintillation counting procedure for one of the Tank 24H analyses. The sample and standard dilutions were received as a single blind experiment. Except for one of the standard dilutions, the results of the analyses were in excellent agreement. The odd sample was a 10-mL aliquot at 1:10 dilution of a Tank 24H sample. Representing the equivalent of a 1-mL sample, it contained less than 3 μg of Tc-99. Recovery was 192%, indicating that background from the resin was interfering and that the minimum detection level had been reached.

A second sample of Tank 24H supernate was analyzed with column concentration using the technique of standard additions to establish an approximate (3 point) calibration curve with larger samples. The results are plotted in Figure 43.

By linear regression, $X_0 = -120$ g, which is the amount of Tc-99 that was in each 50 mL of the original Tank 24H sample. Therefore, this sample contained 2.4 μg/mL of Tc-99. The correlation was 0.996. The estimated error from all sources was ±15%.

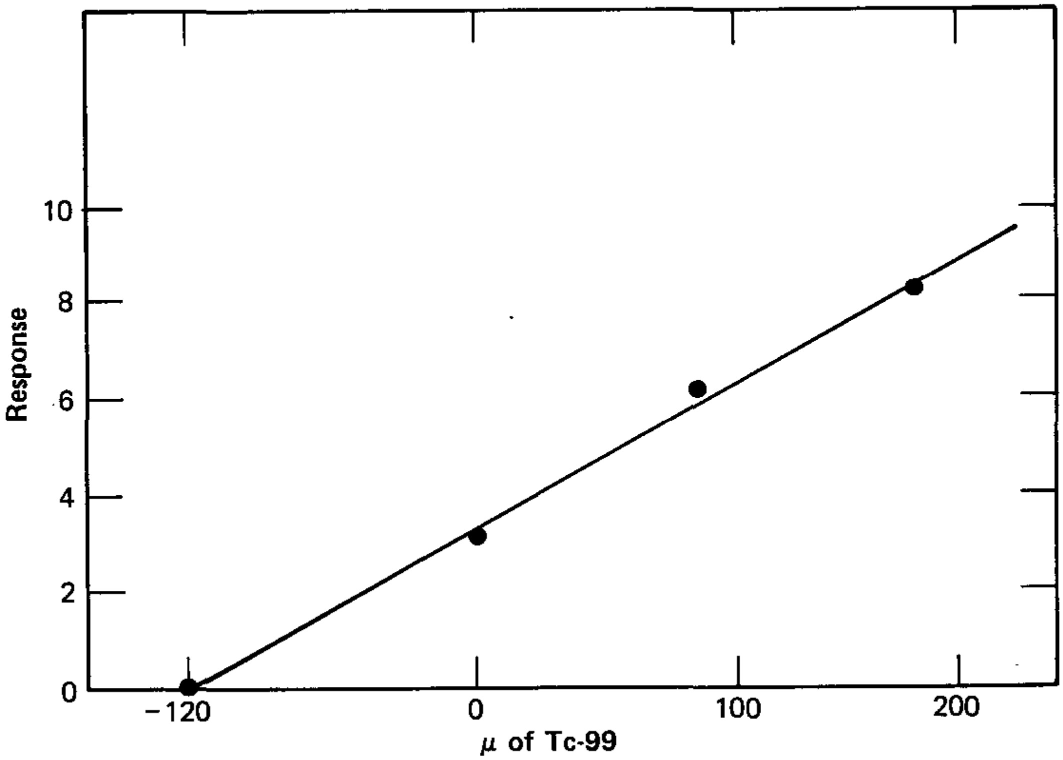


FIGURE 43. Response vs. Tc-99 Addition to Decontaminated Tank 24H Supernate

TABLE 49

Tc-99 Analysis*

	NAA		Extraction	
Sample	ppm	Calculated, d/m/mL	Procedure**	Direct Count
Tank 24-D	2.7	1.04×10^5	8.0×10^4 8.0×10^4	-
Tank 24-D	3.0	1.14×10^5	1.2×10^5 1.3×10^5	-
Tank 24-3D (45% of Tank 24-D)	1.3	4.83×10^4	-	-
Tank 24-4D (10% of Tank 24-D)	0.55	2.07×10^4	-	-
Spike - Supernate 7	3.9	1.35×10^5	-	1.37×10^5
Spike - Supernate 7	3.4	1.17×10^5	-	1.37×10^5

* Test with Tc-99 spiked simulated supernate.

** Two subsamples of the original sample were analyzed (in duplicate) at different times.

TBP Interference

Tetraphenylborate (TPB) has been shown to adversely affect the adsorption of TcO_4^- by Dowex® 1-X8. Therefore, a breakthrough curve was generated for TcO_4^- in simulated defense waste salt supernate (see Table 47) that was saturated with TPB. The breakthrough curve (Figure 44) was generated using a polyethylene insert column, just as it would be used in the analysis procedure. The volume of sample that could be concentrated for Tc-99 analysis is given by the column volumes at the acceptable breakthrough point multiplied by the volume of the resin column. Maximum sample volumes are therefore quite large.

Procedure for the Analysis of Tc-99 in Decontaminated Defense Waste Salt Supernate

Reagents, Materials, and Equipment

Dowex® 1-X8 (hydroxide form, 100-200 mesh*)
4M NaOH (chloride free)
Tc-99 standard solution
Ultrapure deionized water (NaCl free)
50 mL of sample (for duplicate 25-mL sample determination)
1M NaOH (for cleaning)
Drierite (or equivalent desiccant)
Neutron activation analysis rabbits
Polyethylene inserts for rabbits
Whatman #41 filter paper
Tygon tubing (for insert-to-pump connection)
Desiccator
Peristaltic pump
Engraver (to label rabbits)
Vacuum

Sample Preparation

1. Check that the sample is decontaminated defense waste salt supernate. Sample should be caustic and should contain $>0.01M\ NO_2^-$. Total nonvolatile beta-gamma activity should not exceed 10^5 d/m.**

---

* An equivalent resin AG1-X8® (Bio-Rad, Inc.), was also used with good results. The hydroxide conversion was made in our laboratory. Finer mesh resin (200-400 mesh) also works very well.

** For samples more radioactive than this, follow the decontamination procedure first.

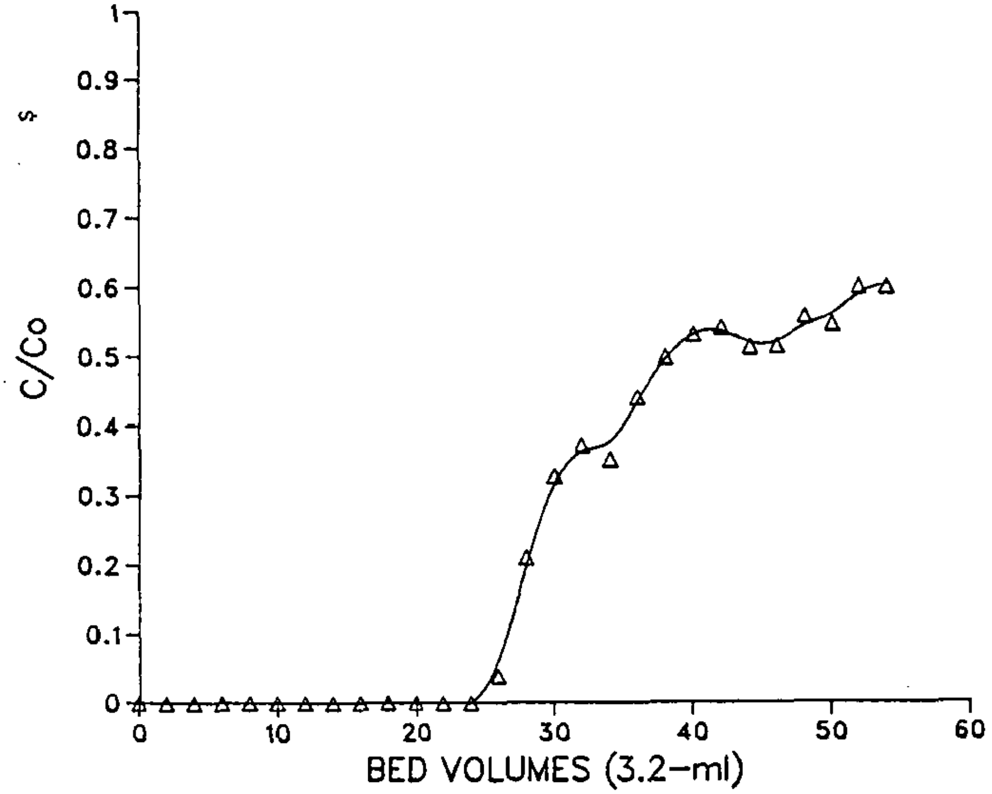


FIGURE 44. Tc-99 Adsorption from TPB-Saturated Simulated Supernate

2. The columns are prepared as follows:

   "Rabbit Columns" are made from polyethylene vials that fit exactly into the polyethylene "rabbits" used in pneumatically controlled sample changing for neutron activation analysis.

   Preparation of "Rabbit" Columns

   A. Drill a single 1-mm hole in the bottom of the vial.

   B. Cover the bottom (and hole with a piece of coarse filter paper (Whatman #41) cut to size).

   C. Fill the column with a slurry of Dowex® 1-X8 strong base anion exchange resin, or its equivalent (200-400 mesh, in the hydroxide form).

   D. Connect the column to a peristaltic pump with plastic tubing (Tygon connections were used here). Set pump to 0.5 mL/min, downflow.

3. Pass 5 to 50 mL of 4M NaOH through the entire system. (Approximately 50 mL of NaOH should be used if there is any chloride present on the resin.

4. Pass 25.0 mL of the salt supernate sample completely through the resin column.

5. Rinse column and tubing with 50 mL of deionized (ultrapure) water.

6. Pump or draw air through the column for 5 to 10 minutes, being careful not to allow enough pressure to tear the filter paper.

7. Remove the column and place in a desiccator to dry under vacuum (with $CaCl_2$).

8. Place the dry column in a "rabbit" for neutron activation. Place the columns upside down in the "rabbit."

9. "Rabbits" should be marked to indicate sample number and orientation prior to heat sealing (their lids).

Standardization

Analytical standards consist of aliquots of the salt supernate sample that have been spiked with a standardized Tc-99 solution (internal standard). At least three standards are normally required to demonstrate linear response and recovery by this technique of standard additions. However, once these are established, a single standard is sufficient to verify the recovery and response curves. Sample concentrations are then calculated by dividing the response by the slope of the calibration curve (counts/concentration).

With no anolyte present in the sample, the standard curve is linear, and should pass through the origin if response is normalized by subtracting the appropriate blank, see Figure 43.

Blanks

The analytical blank consists of a "rabbit column" that has been treated exactly the same as the samples with the exception of sample introduction itself. The major interferences arise from the resin matrix and residual sodium, both of which can be accounted for by this blank.

Additional blank tests were made with simulated salt supernate solutions that contained trace amounts of Cs-137, chromium, and other potential interferences. However, none of these appeared to be significant.

Discussion

The ion exchange concentration procedure is not designed for contaminated fission product waste. Samples of 15-year waste salt supernate which contain greater than 10^5 d/m/mL of nonvolatile beta-gamma activity should be decontaminated before being analyzed by this procedure.

Decontamination, specifically the removal of Cs-137, can be accomplished by the addition of an excess of sodium tetraphenylborate, or by passing the salt supernate sample through a cesium-specific ion exchange bed consisting of 200 to 325 mesh Cs-100® resin (Duolite Shamrock Corp.). For analytical purposes, a column of Cs-100 will decontaminate approximately 30 bed volumes of defense waste salt supernate.

For maximum accuracy, both decontamination methods require the employment of a yield monitor (Tc-99) to assure that Tc-99 is not being lost in the decontamination procedure. However, the loss of Tc-99 in decontamination and concentration is so slight that good accuracy can be obtained without one.

NEUTRON ACTIVATION PARAMETERS FOR I-129

(Cf-252)

Cycles: 30

Activation time: 30 sec

Decay time: 1 sec

Counting time: 1 sec

Energy monitored: 539.6 keV, 590.8 keV

Thermal neutron flux: 10^9 cm^{-2} sec^{-1}

Geometry: 2 cm (automated)

Detection limit (on Dowex® 1-X8 resin normal
sodium background): 3 μg

Conclusions

The Tc-99 concentration in defense waste salt supernate can be determined by neutron activation analysis of the concentrated material directly on an ion exchange substrate. This method is suitable for verifying the accuracy of other procedures that have been used to analyze Tc-99. With preparation, it could be competitive with the more established extraction procedure in terms of accuracy, reliability, and speed.

The detection limit of the method is determined by the counting background of the resin itself following activation. At present, the accurate measurement of Tc-99 is restricted to samples containing 3 μg or more of Tc-99. This could probably be reduced to less than 1 μg by careful modification of the procedure. For example, rinsing with $CsNO_3$ before washing out the sodium with distilled water could reduce interference from sodium exchanged on adsorbed TPB. Also, smaller amounts of resin should be used to reduce the detection limit for the analysis of small samples.

Preliminary Technical Data Summary Retrieved Waste Processing Facility

Introduction

This preliminary Technical Data Summary describes a reference process for solid transuranic (TRU) waste. The waste, amounting to 100,000 cubic feet and containing 500,000 Ci of TRU nuclides including 40 kilograms of ^{239}Pu, is currently stored on aboveground retrievable pads at the burial ground and was generated at the Savannah River Plant (SRP) and Laboratory (SRL) or sent here from other sites. Waste products from this new facility will either be shipped to Waste Isolation Pilot Plant (WIPP) in New Mexico, incinerated in the ^{238}Pu Waste Incineration (PWI), or processed at the Alpha Decontamination and Disassembly (ADD) facility. Ash from the PWI will be transferred to the SRP high-level waste system. Processed waste from the ADD will be buried at SRP as low-level waste or shipped to the WIPP. Spent decontamination solution from the ADD will also be transferred to the SRP high-level waste system.

Process Description

A retrieved waste processing (RWP) facility is needed to prepare stored TRU waste for either shipment to WIPP or for further processing at the SRP ADD and PWI facilities. The following process description assumes there will be three associated independent operating facilities at SRP:

- Alpha Decontamination and Disassembly Process (ADD)

Bulky noncombustible waste, wrapped in plastic and boxed in plywood containers, such as glove boxes which cannot be shipped to WIPP directly due to size or because of savings achieved by volume reduction will be processed in the ADD. This waste will be spray decontaminated with a series of aqueous solutions. Spent decontamination solutions will be transferred to the SRP high-level waste system. Equipment will then be disassembled remotely. A hot-pilot ADD cell is currently in operation at SRL to develop technical data for this process.

- ^{238}Pu Waste Incineration Process (PWI)

^{238}Pu combustible glove box line waste bagged into 55-gallon drums with sealed polyethylene liners that are not certifiable for shipment to WIPP (because of high-curie content and attendant hazardous radiolytic gas generation problems) will be processed in the PWI. This process will consist of a two shredder-air classified combustible waste feed preparation step, a two-stage electrically heated controlled-air incinerator, and an off-gas system consisting of air dilution cooling, sintered metal filtration, and HEPA filtration. Ash products will be transferred to the SRP high-level waste system.

- SRP WIPP Certification Facility

In this facility TRU waste will be certified for shipment to and receipt at WIPP. For example, waste must not contain pyrophorics, dispersible fines, etc. In this facility all necessary inspections (assay, x-ray, etc.) and documentation will be loaded onto specially designed trucks or rail car containers for transport to WIPP.

It is assumed that each of these processes are "stand alone" facilities with attendant assay systems.

In general, retrieved waste that can be directly sent to WIPP with minimal processing in the RWP will be optimized. Active neutron assay instrumentation will allow determination of whether these waste items are <100 nCi/g. Therefore, it is anticipated that some waste will be reclassified as low-level waste and either sent to the SRP Greater Confinement Disposal facility or be trench buried at SRP. ^{238}Pu combustible waste and materials not acceptable at WIPP (resins, solvents, etc.) will be repackaged at the RWP and then sent to the PWI. Bulky contaminated items will be overpacked at the RWP and sent to the ADD to be decontaminated and volume reduced. The new RWP facility will begin operation in 1988 and retrieved waste processing should be completed in 10 years. The individual tasks are described in the following sections. Flowsheets (Figures 45-53) are attached for each of the RWP steps.

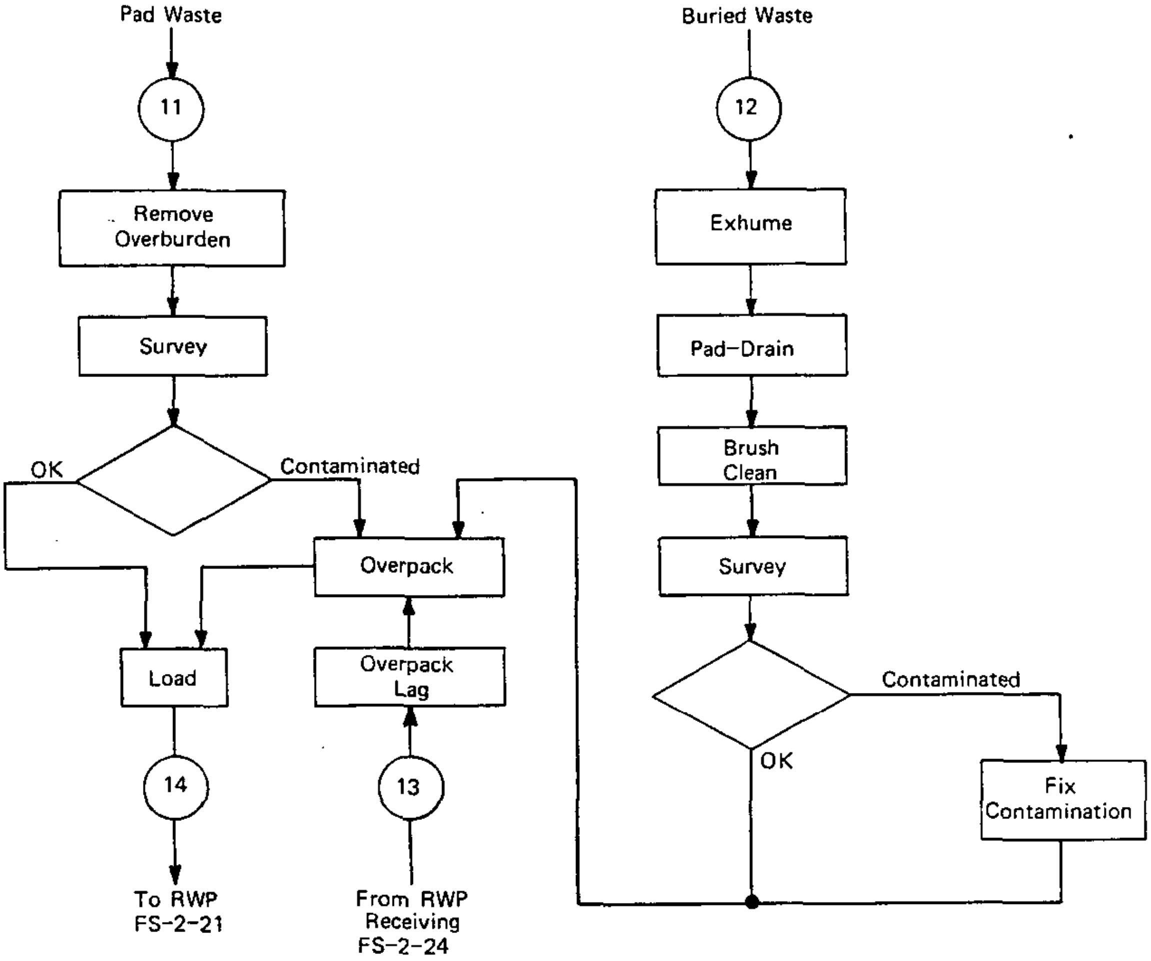


FIGURE 45. Waste Retrieval

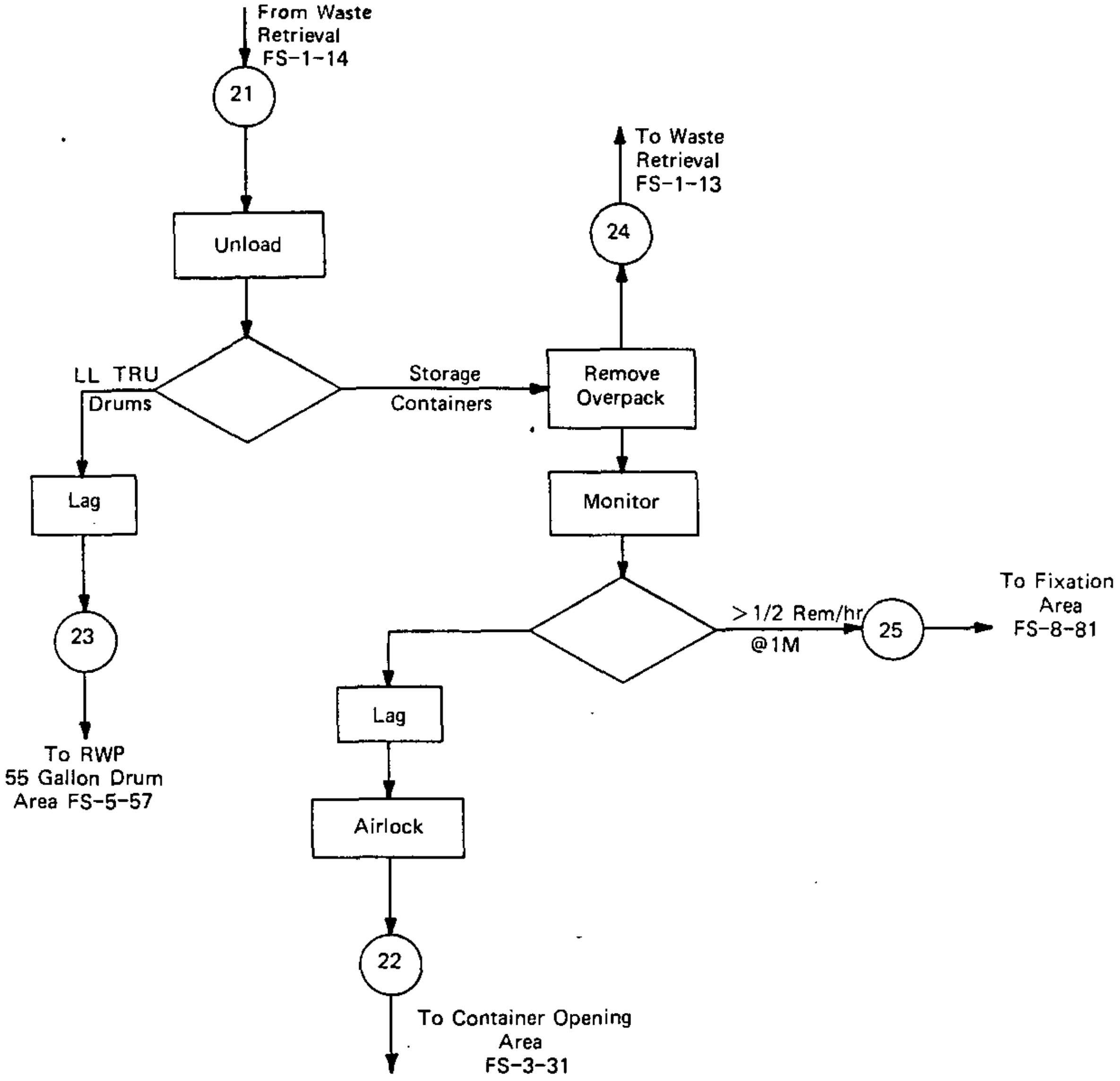


FIGURE 46. Receiving

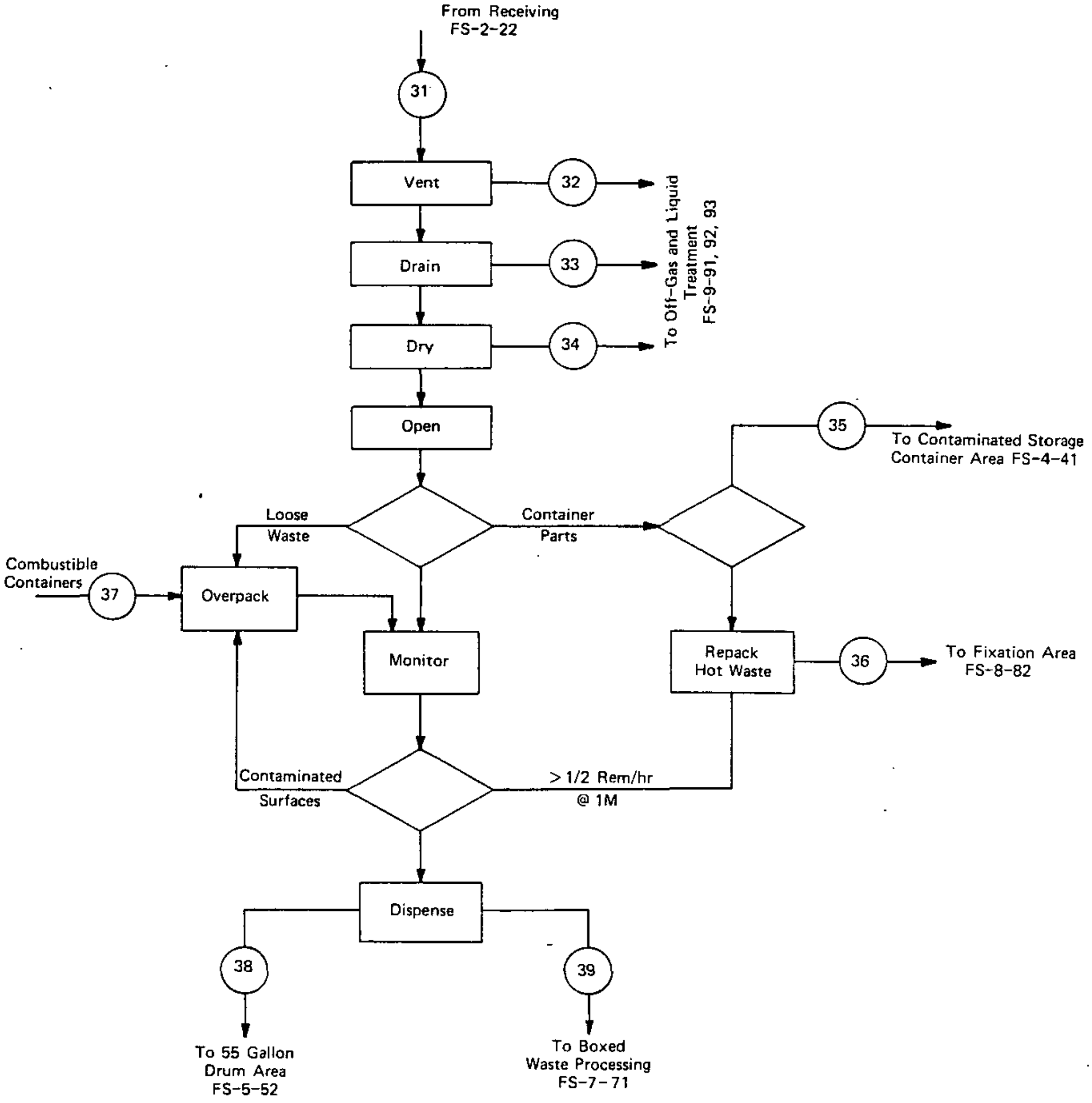
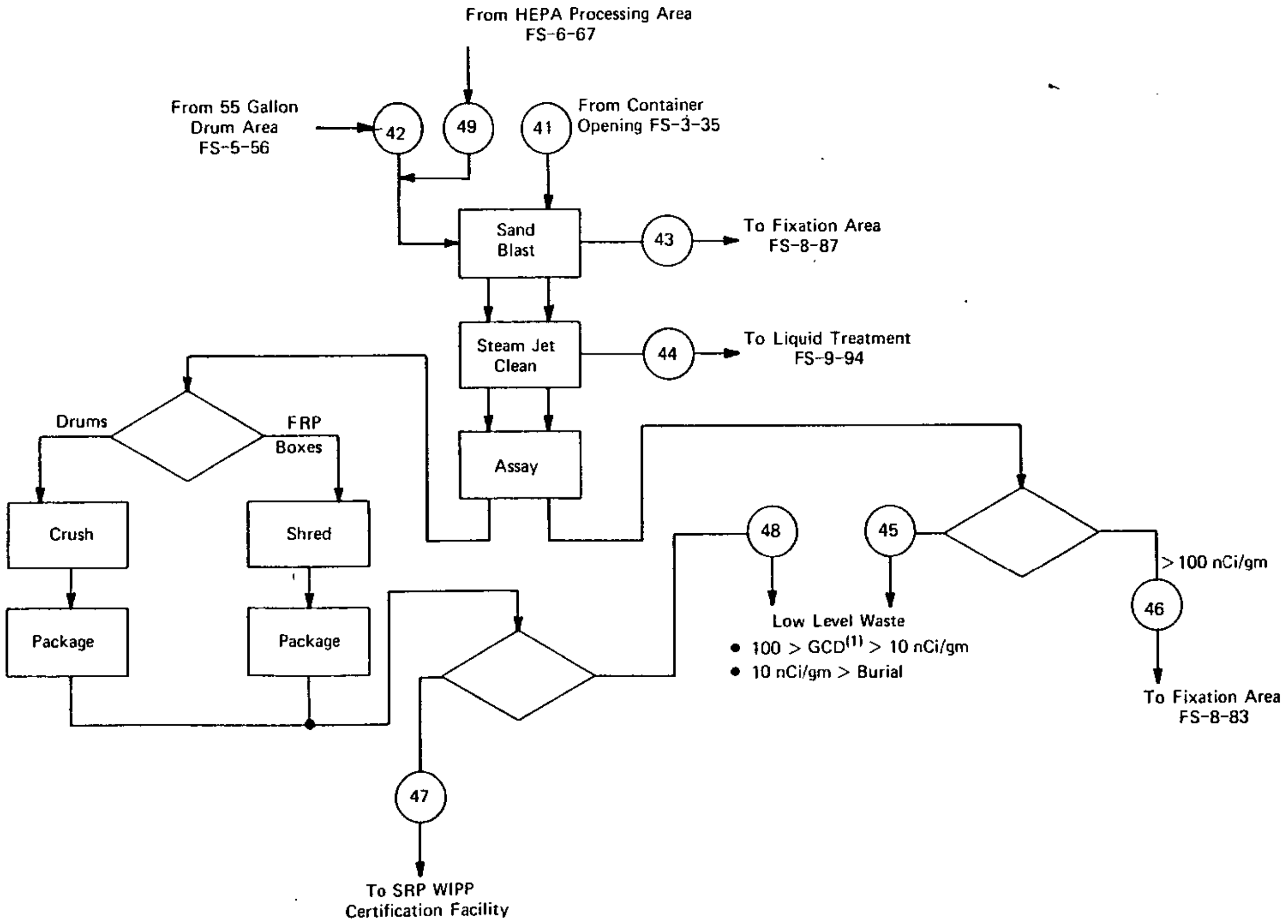
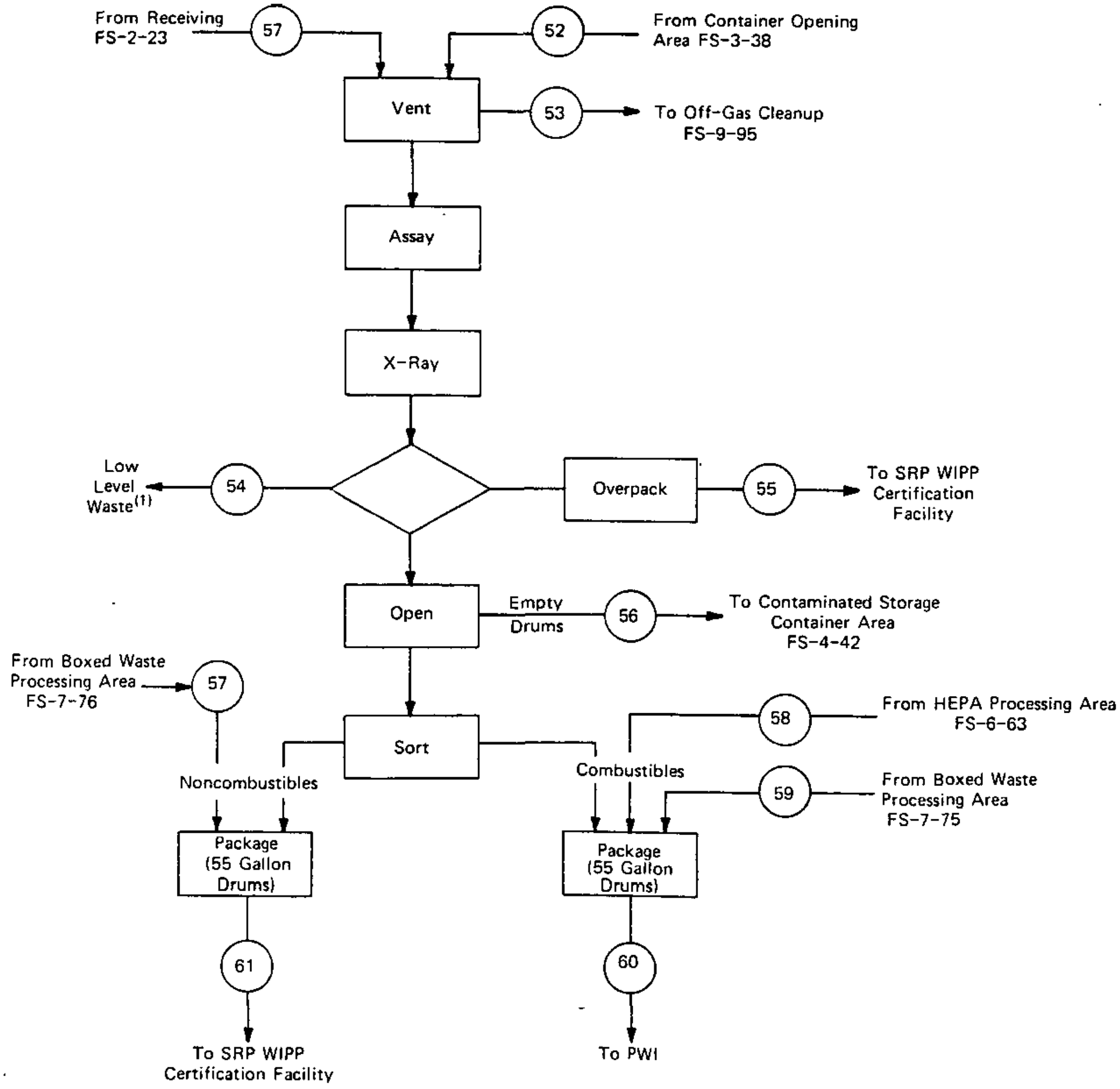


FIGURE 47. Container Opening



[1] Greater Confinement Disposal

FIGURE 48. Contaminated Storage Container Area



[1] See Comment on FS-4 for Low Level Waste Streams 48 and 45.

FIGURE 49. 55-Gallon Drum Area

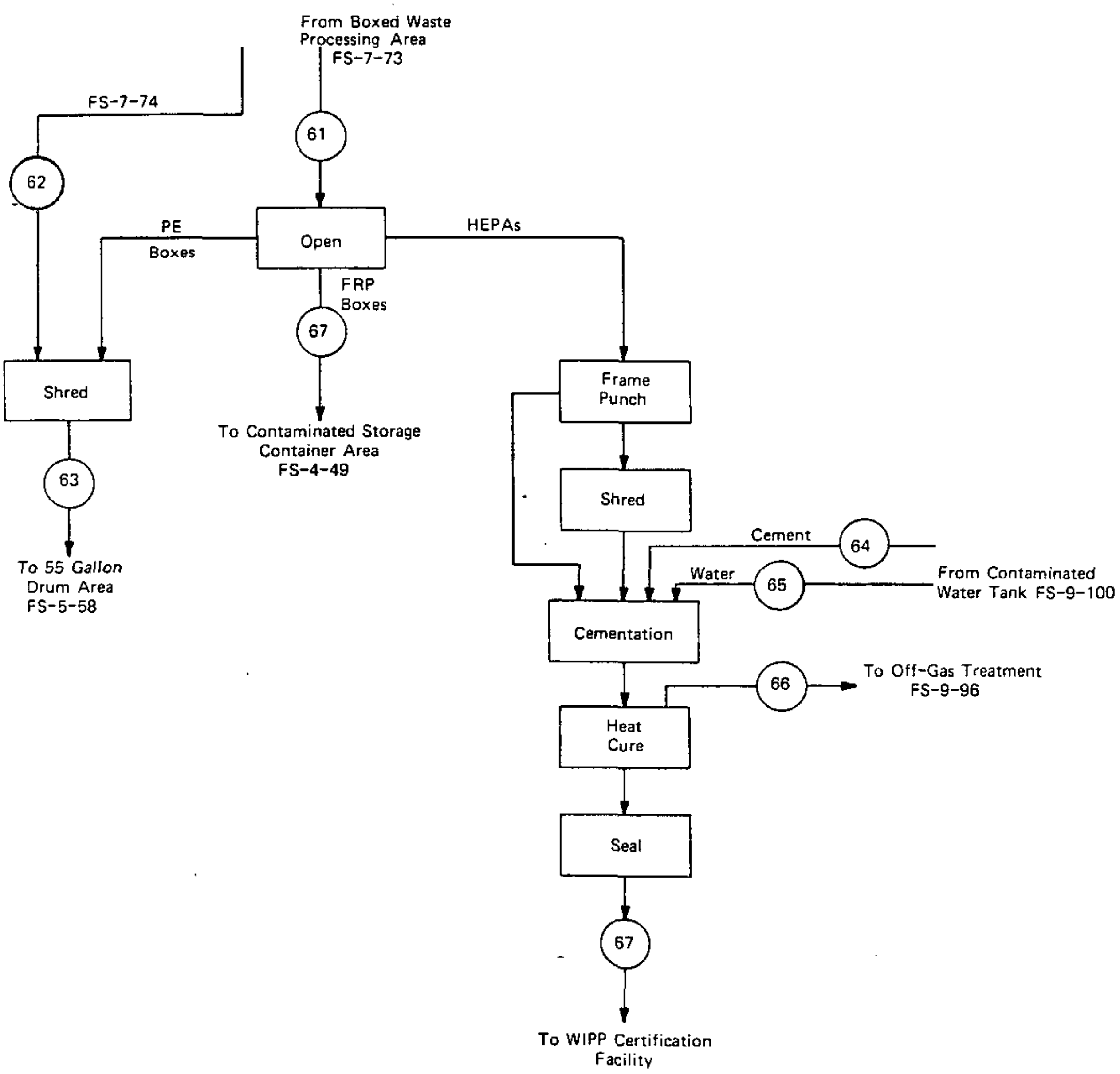


FIGURE 50. HEPA Processing Area

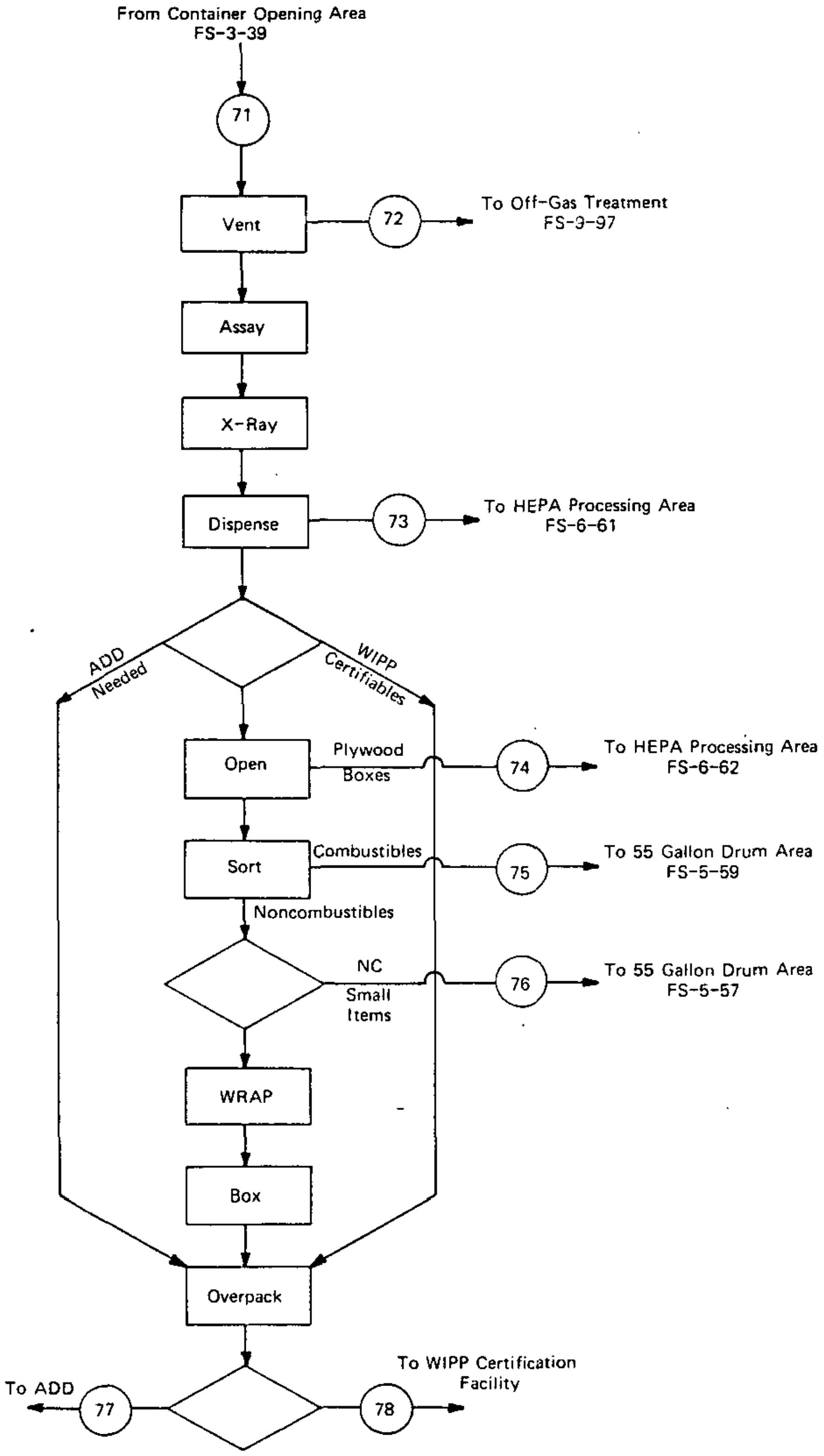
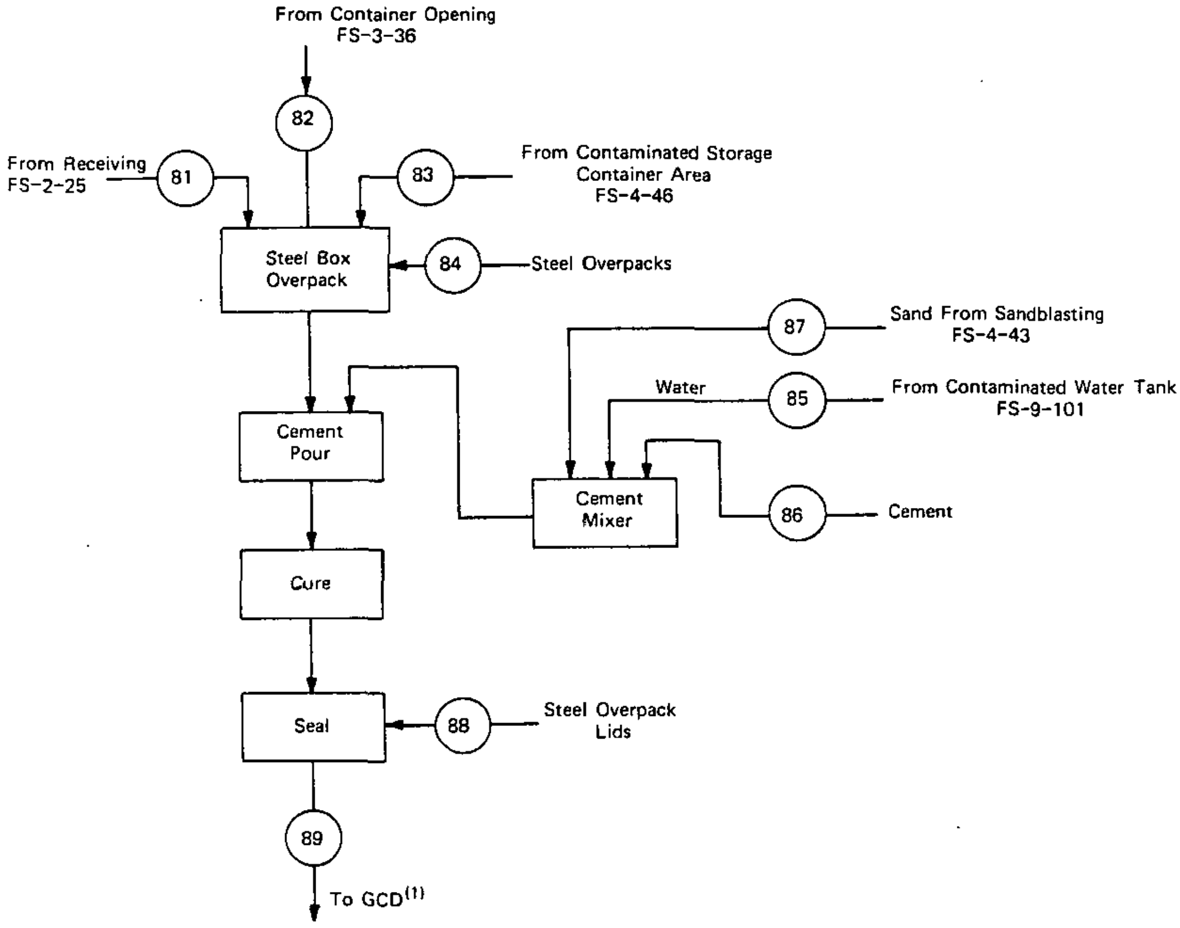


FIGURE 51. Boxed Waste Processing



(1)Greater Confinement Disposal

FIGURE 52. Fixation Area

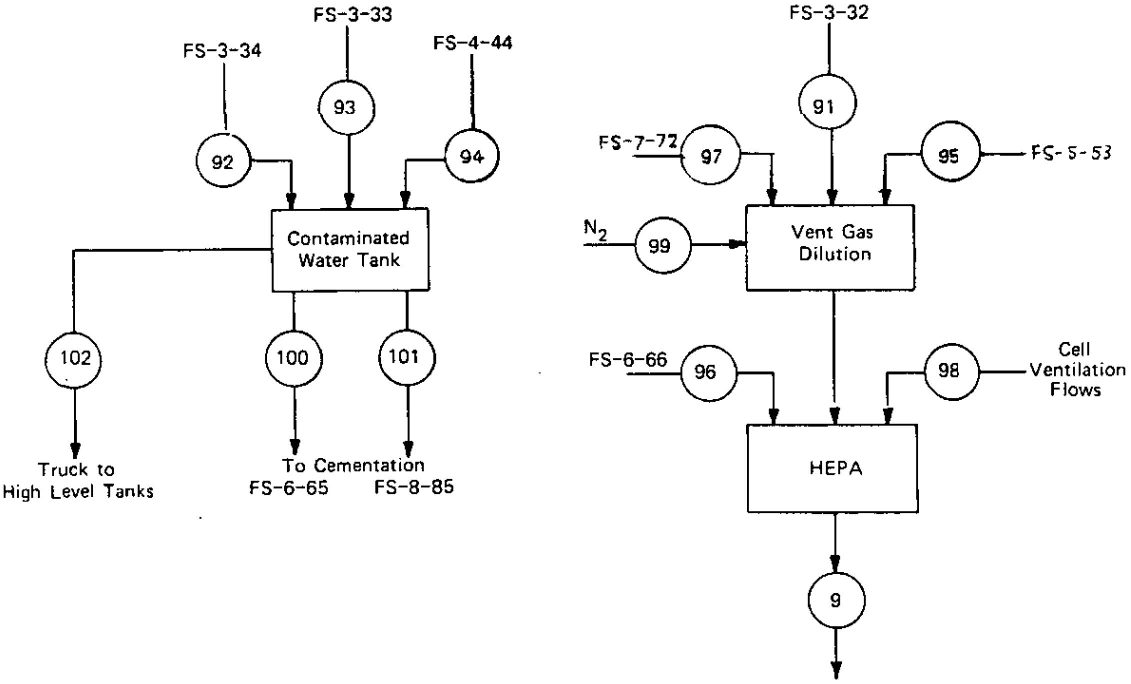


FIGURE 53. Miscellaneous Processing

• Waste Retrieval	Figure 45
• Receiving	Figure 46
• Container Opening	Figure 47
• Contaminated Storage Container Area	Figure 48
• 55-Gallon Drum Area	Figure 49
• HEPA Processing	Figure 50
• Boxed Waste Processing	Figure 51
• Fixation Area	Figure 52
• Miscellaneous Processing	Figure 53

Waste Retrieval (Figure 45)

Most solid waste in interim retrievable storage is in containers (Table 50) stored on concrete pads under a 4-foot mound of soil. The remainder is stored in concrete culverts in earthen trenches. Waste containers stored on the pad are retrieved by removal of the overburden of soil. Concrete containers buried in earthen trenches are exhumed with earth moving equipment and a crane. These containers are placed on a concrete pad to allow drainage of water, the pad is sloped, and drainage is collected in a sump.

TABLE 50

TRU Waste Containers

Outer Storage Container	Dimensions	Loaded Weight	Deliver Rate, per month
Concrete culverts*	7' diameter 7'6" high	10 tons	6
Concrete boxes	3'4" x 3'4" x 4'6"	4500 lb	4
55-gallon drums	2' diameter 3' high	120 lb	80
Miscellaneous containers	11.5' x 8.7' x 6.7' (max)**	10 tons (max)	4
Fiberglass boxes			
Metal transfer boxes	2' x 2' x 1'		
88-gallon drums			
Polyethylene boxes	2.8' x 2.8' x 1.5'		

---

* Each culvert will contain 14 drums.

** There is a total of 7 concrete vaults of this dimension.

The storage containers are designed to remain intact for a minimum of 20 years. Therefore, they should be contamination free (on outside surfaces) and have essentially their original structural strength at the time of retrieval. If a container is damaged during retrieval or if a galvanized steel storage drum is perforated by corrosion, the container will be overpacked in a larger container before transport to the processing facility. If a container has external contamination, it will be overpacked prior to transport.

All containers are checked for radiation level at each step of the process. Containers exceeding 0.5 rem/hr at one meter are transferred unopened by remote handling to the fixation area.

Retrieved Waste Process Facility Receiving (Figure 46)

Retrieved waste overpacks are removed and overpacks are returned to the burial ground for lag storage. Waste containers and drums are monitored. If any storage container dose rate exceeds 0.5 rem/hr at one meter, the storage container is sent directly to the fixation area. A two-week lag storage should be provided. Low-level, 55-gallon drums are monitored and lagged awaiting processing in the drum opening area. All other storage containers are eventually air-locked into the maximum resistant remotely operated container opening area.

Container Opening Area (Figure 47)

Storage containers are transferred via an air lock into this remotely operated, alpha-contained, maximum-resistance cell. Holes are drilled in the storage containers and potentially explosive gases, radiolytically formed during storage, are purged either by a vacuum or inert gas displacement. Holes are also drilled in the concrete containers to ensure drainage of all water that may have seeped in during underground storage. A drying system, as indicated should also be employed. The dried and vented storage containers are then remotely opened, and the contents are removed. In general, the contents of most containers will consist of:

- 55-gallon drums containing combustible and noncombustible glove box line waste
- Polyethylene boxes containing HEPA filters
- Metal boxes may contain miscellaneous equipment such as plastic wrap glove boxes in plywood cartons, or perhaps miscellaneous "trash" such as job control waste, HEPAs, and equipment pieces
- Contents in Mound burial boxes
- Buried culverts may contain loose waste such as cardboard cartons

SRL and SRP have ongoing stored waste characterization programs. When the primary containers are not intact, the waste is repacked in a combustible container for temporary handling. If external surfaces are contaminated, primary containers are either overpacked or contamination is fixed.

Waste components leaving the container opening area are primary containers (cardboard boxes, polyethylene boxes, plywood boxes, 55-gallon drums from culverts, 83-gallon drums, FRP boxes), storage containers and lids (concrete boxes, concrete culverts, and metal boxes), aqueous waste from drainage operations, storage container purge off-gases, and cell off-gases.

Primary waste containers are monitored to verify that: (1) the TRU content of the waste exceeds 100 nCi/g; (2) the contents do not exceed the criticality limit (if they do, boron is added and the contents diluted into less active wastes); and (3) the gamma and neutron radiation dose rates do not exceed the shielding capability of the facility. If the dose rate exceeds 0.5 rem/hr at one meter from the container, the container is repackaged in a contaminated concrete outer container. Then this waste is sent, without further processing, directly to the fixation step to be encased within the final storage container. Empty outer containers are also monitored.

Contaminated Storage Container Area (Figure 48)

Contaminated storage containers (culverts, drums, concrete, and fiberglass boxes) are decontaminated by sandblasting and steam jet cleaning. Waste containers that are decontaminated to less than 10 nCi/g are returned to the burial ground for burial, those between 10 to 100 nCi/g are sent to the Greater Confinement Disposal Facility, and those still contaminated greater than 100 nCi/g are further processed. Drums and fiberglass boxes that cannot be decontaminated below 100 nCi/g are reduced in volume by use of a drum crusher and shredder. These materials are then packaged in WIPP certifiable containers (55-gallon drums for example) and are sent to the SRP WIPP Certification Facility. Concrete boxes and culverts that cannot be decontaminated below 100 nCi/g are sent to the fixation step.

55-Gallon Processing Area (Figure 49)

Drums removed from culverts (>1/2 Ci TRU per drum) and low-level drums (>1/2 Ci TRU) which are pad stored outside of culverts, are processed identically. Drums are purged of potentially explosive radiolytic gases (and then are sealed with a plug to avoid contamination spread in subsequent steps). The Idaho National

Engineering Laboratory (INEL) has developed a drum-purging process which is recommended for estimating purposes. This step should be done in a maximum-resistance cell. All drums are then assayed by the neutron interrogation method developed by Los Alamos National Laboratory (LANL). Drums determined to be <100 nCi/g will be sent to either the Greater Confinement Disposal or trench burial if <10 nCi/g. Assay results will be used for criticality control in subsequent steps. Drums are then x-rayed in a system similar to the unit under development at the INEL. Assay and x-ray inspection will allow identification of ^{239}Pu drums that do not require further processing except for overpacking and transport to the SRP WIPP Certification Facility. That is, ^{239}Pu containing drums, which do not contain liquids, sludges, resin, dispersible fines, aerosols, pyrophorics (oily rags, solvents, etc.), and not more than a 1/2 Ci alpha will be overpacked and sent to the SRP WIPP Certification Facility.

Next, drums will be opened and their contents removed and sorted. Combustible waste will be repackaged in drums with plastic liners that are compatible with the PWI feed preparation process. Materials such as sludges, resins, and pyrophorics, as well as free liquids and solvents (to be absorbed on oil dry) will be sent to the PWI. Noncombustible waste will be packaged in 55-gallon drums and then sent to either the ADD facility or to the SRP WIPP certification facility depending on whether further processing at the ADD is cost-effective.

HEPA, Glove Box, and Miscellaneous Equipment Processing Area (Figures 50 and 51)

Boxes of waste must also be vented and then resealed in the same way as 55-gallon drums. In the next step, these waste materials are assayed and x-rayed with similar equipment specified for 55-gallon drums in the 55-gallon processing area. Polyethylene boxes containing HEPAs will be opened and the HEPAs will be removed. HEPAs will be punched from their frames, and HEPA materials will be shredded. Shredded HEPAs and frames will be encapsulated in cement. To eliminate any subsequent pressurization problems, the cement-waste form centerline temperature must be heated to 200°C after curing to drive off all free water. The container is then sealed. Contaminated water and sand from sandblasting will be used for cement makeup.

Combustible primary containers will be shredded and eventually transferred to the PWI in 55-gallon drums consistent with the PWI feed system. If sorting is required, containers will be opened and combustible and noncombustible waste items will be sorted and processed in the 55-gallon sorting operation. Noncombustible equipment pieces are either overpacked and sent to the SRP WIPP

Certification Facility or to the ADD process depending upon the cost effectiveness of D&D.

Fixation Step (Figure 52)

In this area, storage containers that cannot be decontaminated below 100 nCi/g and "high-level" waste (>0.5 rem/hr at one meter) will be encapsulated in leach-resistant concrete. Containers will also be overpacked with steel boxes. Encapsulated materials are then sent to the Greater Confinement Disposal Facility.

Miscellaneous Processes (Figure 53)

Off-gas and water streams are consolidated on this flowsheet.

General Design Considerations

The design basis for the RWP is a 10-year operating period. The maximum instantaneous inventory of plutonium in the process building area will be limited to 340 g of ^{239}Pu and 2 kg of ^{238}Pu. Consideration should be given to the need that these facilities should meet the minimum design criteria for new plutonium facilities.

Major design considerations are the containment of transuranium nuclides, criticality control, and the processing of heterogeneous wastes varying in form from paper to glove boxes. Wherever practical, waste should be handled remotely to protect operating personnel from contaminated broken glass, sharp pieces of metal, corrosive chemicals, etc. The design of the processing facility must provide for isolation of unit operations to prevent the spread of contamination and should allow for routine decontamination. Provisions must be made to remotely move waste and contaminated storage containers through the process including bulky equipment and heavy culverts. Extra machinery equipment and any other critical items that are susceptible to failure should be provided as part of this project. Simple equipment change-out and remote repair of equipment are also design considerations.

General Safety

Special design consideration should be given to minimizing the explosion and fire potential. The potential for explosion of accumulated flammable vapor is greatest during periods of storage container and primary container venting, therefore, automatic control and emergency power should be provided.

Nuclear and Radiation Safety

Nuclear safety is maintained throughout the processing facility by critically safe geometry designs for all liquid vessels, specific decontamination vessels, and by comprehensive material and radiometric balances in solid waste flow paths. Shielding will be required for both neutron and gamma radiation. The ^{238}Pu waste from Mound Laboratory will be approximately 25 years old and contain gamma-emitting daughter nuclides from the decay of ^{236}Pu. The curium wastes will also contain gamma activity. These wastes form a small fraction of the solid waste. The major volume of waste is contaminated with ^{239}Pu and negligible gamma emitters. Unless the gamma or neutron emission rates exceed 0.5 rem/hr at one meter from the primary waste container, these wastes will be diluted into the ^{239}Pu wastes prior to transfer to either the PWI, ADD, or WIPP Certification Facility to minimize the required shielding of the volume reduction steps. High-level gamma wastes are repackaged in contaminated concrete storage containers and transferred directly to the fixation process without volume reduction processing in this facility. Neutron shielding will be required because of transuranic (α,n) reactions and ^{252}Cf wastes. For constant occupancy area design for $<1/2$ mrem/hr and for areas occupied less than 10% of the time 5 mrem/hr.

Location and Co-Use of Facilities

The RWP plant should be located near the PWI, ADD, and WIPP Certification Facilities.

An Incineration Demonstration at Savannah River

A full-scale incineration process for Savannah River Plant (SRP) low-level beta-gamma combustible waste was demonstrated at the Savannah River Laboratory (SRL) using nonradioactive wastes. From October 1981 through September 1982, 15,700 kilograms of solid waste and 5.7 m^3 of solvent were incinerated. Emissions of off-gas components (NO_x, SO_2, CO, and particulates) were well below South Carolina state standards. Volume reductions of 20:1 for solid waste and 7:1 for Purex solvent/lime slurry were achieved. Presently, the process is being upgraded by SRP to accept radioactive wastes. During a two-year SRP demonstration, the facility will be used to incinerate slightly radioactive (<900 $\mu Ci/m^3$) solvent and suspect level (<1 mR/hr at 0.0254 m) solid wastes.

BACKGROUND

An incineration development program is in progress at the Savannah River Laboratory in support of waste management objectives of the Savannah River Plant and the Department of Energy. Currently, solid waste contaminated with low levels of beta-gamma emitters is buried in shallow trenches in an onsite burial ground. Incineration has been proposed as the primary method for volume reduction since 60% of the solid waste generated is combustible. The reduced volume of the waste would extend the life of the burial ground. Also, ash residue solidified in cement and packaged in steel drums would improve burial ground practices.

Spent solvent used in the Purex process for the radiochemical separation of plutonium and uranium is also stored at the SRP burial ground in underground tanks. Currently, there are 568 m^3 in storage with an annual generation rate of 7.6 m^3/yr. The liquid is composed of n-paraffin, a kerosene-like diluent, and tributylphosphate (TBP). The solvent is only slightly radioactive with the principal beta-gamma nuclides being ruthenium, cesium, and strontium. Burning a Purex solvent/lime slurry by spray injection is the reference method for final disposal.

After a survey of the incineration processes being tested and demonstrated at nuclear installations in the United States and Europe, a full-scale facility based on a two-stage, controlled-air incinerator and a dry off-gas system was designed. The demonstration facility, called the Solid/Solvent Waste Incineration Facility for Testing (SWIFT), has been installed and operated at SRL.

INTRODUCTION

The incinerator has successfully completed five test runs with simulated, boxed solid waste and four test runs with uncontaminated Purex solvent. 15,700 kilograms of solid waste containing paper, cotton fiber, red rubber, polyethylene, and polyvinyl chloride was burned. Tests were conducted in week-long campaigns. During the five solids campaigns, waste was burned as individual components and as a standard waste mix (Tables 51 and 52).

TABLE 51

Summary of Solid/Solvent Waste Burning Campaigns

		Amount of Waste Burned		
Run Number	Duration of Incineration, hr	Weight, kg	Volume, m^3	Type of Waste Burned
Solid 1	4	972	10	Computer Paper
Solid 2	20	3,028	28	Computer Paper/ Cotton
Solid 3	38	4,776	43	Waste Mix w/o PVC
Solid 4	21	2,724	30	Red Rubber/Waste Mix/PE
Solvent 1	7	-	0.76	n-Paraffin
Solvent 2	6	-	1.0	n-Paraffin
Solvent 3	8	-	1.1	Purex Slurry
Solid 5	32	4,169	41	Waste Mix w/PVC
Solvent 4	19	-	2.8	Purex Slurry w/TCE
Totals	155	15,668	154 5.7	Solid Solvent

TABLE 52

Solid/Solvent Waste Compositions

Component	Solid Waste Mix w/o PVC, wt %	Solid Waste Mix w/PVC, wt %
Polyethylene (PE)	23	23
Red Rubber (SBR)	19	19
Cotton Fiber	29	25
Computer Paper	29	-
Polyvinyl Chloride (PVC)	-	8
Brown Reinforced Paper	-	25

Component	Purex Slurry, %	Purex Slurry w/TCE, %
n-Paraffin ($C_{12}H_{26}$)	75 volume	72.2 volume
Tributylphosphate (TBP)	25 volume	25 volume
Calcium Hydroxide [$Ca(OH)_2$]	18 weight	36 weight
1,1,1-Trichloroethane (TCE)	-	2.8 volume

5.7 m^3 of uncontaminated Purex solvent was incinerated (Table 51). The solvent was sprayed into the incinerator primary chamber as a slurry with calcium hydroxide (Table 52). The calcium acts as a fixative for the phosphorus that is released during TBP incineration. Without the fixative, phosphoric acid fumes would be formed that would accelerate long-term corrosion rates and cause filter blinding.

These tests demonstrated the incinerator's flexibility in burning the wide range of SRP waste, proved the operability of a dry off-gas system, debugged the process controls, and identified and corrected several design oversights.

PROCESS DESCRIPTION

General

Processing steps in the Solid/Solvent Waste Incineration Facility for Testing (SWIFT) include waste preparation and feeding, incineration, semicontinuous ash removal, ash residue packaging, and off-gas cleanup.

The incinerator is a two-stage controlled-air unit manufactured by Environmental Control Products of Charlotte, North Carolina. The term "controlled air" denotes the incinerator design feature that permits control of the quantity and location of combustion air. In two-stage combustion, waste is semipyrolyzed in the fuel-rich primary chamber. The low air flow into the chamber is introduced through several underfire air ports on the side of the hearth. This air flow is low enough to avoid excessive ash entrainment. Combustion air flow (100 to 200% excess) is supplied at the entrance to the secondary chamber to oxidize the partial combustion products to H_2O and CO_2. The oxygen concentration in each chamber is continuously measured with online analyzers.

Normal operating temperatures are 800 to 900°C in the primary chamber and 1000°C in the secondary chamber. The control system maintains these temperatures by modulating two diesel-oil-fired burners and the combustion air flows. The burners are used mainly to heat the incinerator to minimum burning temperatures. When waste feeding begins, the heat of combustion released from the burning material serves as the primary heat source. The amount of air entering the chambers is then used to control the temperatures.

This incinerator has two hydraulic rams for removing ash from the primary chamber. Off-gases from the secondary chamber pass through a refractory-lined duct before entering the spray quench. In the spray quench, the incinerator off-gases are cooled from 1000 to 180°C using two air-atomized water sprays. During incineration of polyvinyl chloride (PVC) and the degreaser 1,1,1-trichloroethane (TCE), an aqueous sodium carbonate solution was tested in the spray quench. The purpose of this test was to establish the feasibility of neutralizing gaseous HCl to reduce chloride emissions and corrosion problems. The gases leaving the spray quench are maintained above the dewpoint so no secondary liquid waste streams are generated. The cooled gases are then filtered using a baghouse that contains envelope-type Nomex® (Du Pont) fabric bags. The filter efficiency is rated at 98% for particles one micron in diameter.

Two 60-hp induced-draft blowers maintain a negative pressure in the process and exhaust the off-gases to the atmosphere through a 35-ft stack.

Solids Preparation and Feeding

Solid waste was fed to the incinerator in 0.38 and 0.61-m^3 boxes. These boxes were prepared before each run so that the waste compositions, packing densities, and box weights were known. The boxes were then fed to the primary chamber of the incinerator with a hydraulic feed ram. Feed rates up to 180 kg per hour were demonstrated.

Solvent Feeding

The primary components of the solvent feed system were an agitated feed tank and two pumps. After uncontaminated Purex solvent and calcium hydroxide fixative were slurried in the feed tank, a centrifugal pump drew solvent from the bottom of the tank and recirculated it back. This recirculating pump aided in suspending the solids in the slurry and supplied solvent to the inlet of the feed pump.

A piston-type metering pump was used to feed solvent to the incinerator. The solvent flow rate was varied by manually controlling the speed of the feed pump. The solvent slurry was sprayed into the primary incinerator chamber at the reference feed rate of 0.14 m^3 per hour.

SUMMARY OF RESULTS

The following key process elements were demonstrated during the one-year research program:

1. The system proved flexible enough to burn a wide variety of materials with a wide range of heat release values and instantaneous air demands at the reference feed rates.

2. Parameters for operating the dry off-gas system were optimized. With the dry system, off-gases are cooled, filtered, and maintained above the dewpoint until they are exhausted to the atmosphere. Thus, there are no secondary liquid waste streams that require treatment.

3. Process temperatures and vacuum were controlled automatically.

4. The phosphorus released by burning tributylphosphate was fixed by using calcium hydroxide as a fixative. This minimizes the formation of phosphoric acids and reduces long-term corrosion rates and filter blinding.

5. Ash was removed from the incinerator on a semicontinuous basis. The incinerator has two rams for displacing ash. The first ram moves the ash the length of the hearth and tumbles it into an ashdrop. The second ram pushes the ash the length of the removal duct and into a 0.2-m^3 drum.

6. Volume reduction ratios were determined for both solid and solvent incineration. The volume reduction for solids was 20:1 for a 95% reduction in volume; solvents were reduced by a ratio of 7:1 for an 86% reduction in volume.

DISCUSSION

The system proved flexible enough to burn a wide variety of materials with a wide range of heat release values and instantaneous air demands at the reference feed rates. Pure polyethylene was burned at 180 kg/hr to determine operating characteristics of the SWIFT under the highest anticipated heat release conditions. Pure red rubber was burned at the reference rate to check if the incinerator air capacity was sufficient to maintain the exit oxygen level greater than 5%. Red rubber (SBR), which was used to simulate latex incineration, has a high instantaneous air demand. Other unique materials that were incinerated include PVC and TCE, which release hydrochloric acid, and a slurry of Purex solvent and calcium hydroxide. In all cases, the SWIFT pressure and temperature process controls functioned as designed.

The dry off-gas system eliminates secondary liquid waste streams that would require treatment. The dry off-gas system also simplifies operation. The main component of the dry off-gas system is the spray quench. The test program demonstrated that the spray quench could control the baghouse inlet temperature within design specifications. Aqueous sodium carbonate spray drying to neutralize gaseous HCl was also demonstrated. However, the ash produced during solids incineration was found to neutralize greater than 90% of the HCl released without sodium carbonate addition. The baghouse utilized pulse blowback for removing flyash from the bags. The semicontinuous blowback was capable of maintaining the baghouse pressure drop below 500 newton/meter^2. In general, the material balance for ash yielded a total system DF of 1400 and a baghouse DF of 210. Particulate and gaseous (NO_x, SO_2, CO, and HCl) emissions as determined by an EPA Method 5 sampling train were well below South Carolina state standards and all anticipated Federal emission regulations (Table 53).

TABLE 53

Typical Off-Gas Air Quality

Component	Solid Waste Burning* Air Quality, μg/m^3	Solvent Waste Burning* Air Quality, μg/m^3	South Carolina State Air Quality Standard, μg/m^3
NO_x	0.4	1.1	100
SO_2	4.4	2.5	1300
HCl	2.4	2.9	Not specified
CO	<160	<160	40,000
Particulates	0.02	0.04	60

* Values were calculated for a point one kilometer from a 10-m stack using a dilution factor of 1×10^{-4} s/m^3.

A key feature of the SWIFT design that was demonstrated is the automatic vacuum control system. This system maintains a vacuum of 249 newton/meter^2 in the secondary incinerator chamber by means of induced draft blowers and an automatic vacuum control valve. This is necessary since the incinerator will be put into radioactive service during the second phase of the incinerator program. One area of difficulty caused by vacuum operation was that air inleakage adversely affected incinerator temperature control. After air inleakage points were closed, temperature control via underfire air modulation was achieved.

In the burning of tributylphosphate, phosphorus is released to form phosphoric acid. Phosphoric acid would cause long-term equipment corrosion and blinding of the baghouse filters. To minimize acid formation, calcium hydroxide was slurried with the tributylphosphate/n-paraffin solvent prior to spraying the solvent into the incinerator. During incineration the phosphorus reacts with calcium and oxygen to form various calcium-phosphorus oxides. All of these products are refractory solids that primarily deentrain in the incinerator primary chamber or are filtered from the off-gases by the baghouse.

The incinerator at Savannah River is unique in that it utilizes two hydraulic rams for ash removal. The first, an internal ram, pushes ash the length of a 3-m hearth until it falls into a rectangular ash drop in the bottom of the primary chamber. The second ram, an ash pusher, removes the ash from the ash drop, pushes it through a horizontal cooling duct, and deposits it in a 0.2-m^3 drum. These rams are cycled by automatic timers.

Initial tests proved that the ash pusher was inadequate for removing ash from the ash drop. The original ash pusher was a short ram of hollow metal construction. The concept for this design was to displace cooled ash from the cooling duct and into a drum by pushing newly formed ash behind it. This method of ash displacement was not successful because ash compacted and plugged in the ceramic-lined cooling duct. A new ash pusher ram was designed and installed. This ram was designed to stroke all but the last 0.30 m of the removal duct and provide positive displacement for the ash. The ram was also ceramic-filled for improved dimensional stability. The new ash pusher succesfully removed ash on a semicontinuous basis during operation.

Volume reduction ratios were determined for both solid and solvent incineration. In general, the volume reduction for solids was 20:1, and solvents were reduced by a ratio of 7:1. The volume reduction data for each run can be found in Table 54. Volume reduction for solvent was less than for solid due to calcium hydroxide addition. It should be noted that the primary objective of solvent incineration is to provide a permanent means of disposal to eliminate underground tank storage. There was a wide range of volume reduction factors due to various inert contents in the simulated solid waste materials.

TABLE 54

Summary of Ash Collected from Incinerator Runs

Run Number	Ash Fraction Reaching Baghouse	Reduction Ratio Weight	Reduction Ratio Volume
Solid 1	-	22	45
Solid 2	0.07	12	22
Solid 3	0.11	9	17
Solid 4	0.10	3	15
Solid 5	0.21	8	22
Solvent 3	0.17	8	7
Solvent 4	0.17	5	8

Solvent Incineration in the SWIFT

INTRODUCTION

The Solvent Waste Incineration Facility for Testing (SWIFT) burned 1520 gallons of nonradioactive solvents in four campaign runs. A feed system, the solvent injection system, sprayed solvents into the primary chamber of the incinerator.

The main objective of these tests was to develop and demonstrate an effective method for permanently disposing of the 150,000 gallons of spent Purex solvent that is being stored in underground tanks in the burial ground and the 2000 gallons that are generated annually. Previously, no adequate method of disposing of slightly radioactive solvents has been employed at Savannah River.

Secondly, it is desirable to eventually burn other radioactive and nonradioactive solvents in the incineration facility. These solvents include 1,1,1-trichloroethane, turbine oils, and scintillation fluids.

The four solvent-burning campaigns of the SWIFT demonstrated the capability to burn pure n-paraffin, a slurry of calcium hydroxide and 30% by volume tributylphosphate (TBP) in n-paraffin (Purex solvent), and a slurry of calcium hydroxide and Purex solvent with 3% by volume 1,1,1-trichloroethane. When simulated Purex solvent was incinerated, calcium hydroxide was added. The calcium hydroxide chemically reacted the phosphorus released during TBP burning to form a refractory solid. This was done to prevent filter blinding and minimize long-term corrosion from phosphoric acid.

This report describes all of the solvent incineration that was conducted in the SWIFT.

SUMMARY

The incineration of n-paraffin, tributylphosphate (TBP), and calcium hydroxide slurries was demonstrated using the Solvent Waste Incineration Facility for Testing and the Solvent Injection System. The injection system proved capable of pumping slurries, keeping them agitated to prevent settling, and spraying them into the primary incinerator chamber for burning. These demonstrate that the 150,000 gallons of spent Purex solvent (70% n-paraffin and 30% TBP) that has been stored in the burial ground can now be disposed of through incineration.

In the second phase of the incineration demonstration, SRP will modify the facility for radioactive service and incinerate suspect level solid wastes and spent Purex solvents. Phase II testing is scheduled to begin in mid-1983 and continue for two years.

This incineration facility is also being evaluated for the incineration of site-generated nonradioactive hazardous solvents.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were derived from carefully analyzing the operating conditions and analytical results from Solvent Runs 1 through 4. Recommendations for improving the process and its operation are also included.

1. Air inleakage around the solids feed charging door was excessive. This air inleakage made primary chamber temperature control impossible. Temperature control via modulating primary chamber underfire air was obtained only after sealing around the charging door with Refrasil® (Armco Co.), a cloth insulating material. To maintain proper incinerator control, it is essential that air inleakage to the primary chamber be minimized.

2. A feed stream with a calcium-to-phosphorus mole ratio of 3 is recommended to provide the best conversion of phosphorus to refractory Ca-P oxides. Higher fixation conversion of phosphorus in the primary chamber will greatly reduce downstream deposits of phosphorus-rich Ca-O oxides. A conversion of 60% using a 1.38 feed stream Ca/P mole ratio was demonstrated at SRL. Lab-scale spray burning work indicates the highest conversion at a Ca/P ratio of 3. In addition, crucible tests show increasing fixation of phosphorus with increasing Ca/P ratios. Pumping and spraying problems are not anticipated based on slurry viscosity data. Dilution with a nonphosphorus bearing organic liquid is recommended if spraying and pumping problems are encountered in Phase II testing.

3. Fine atomization of the solvent slurry is necessary to react the phosphorus in the primary chamber. Solvent Run 3 gave good atomization but resulted in plugging problems at the nozzle. In Solvent Run 4 the atomization was not as good, but the plugging problems were eliminated. To obtain the optimum requirements for good atomization and no plugging, it is recommended that a Bete Fog Nozzle TF6N made of Hastelloy® C (Cabot Corp.) be used with air atomization. The nozzle has a tapered inside diameter with no internal components and was used in Solvent Run 4. This nozzle combined with air atomization of 0.08 pound of air per pound of solvent will give the proper size droplets for combustion. This should be tested during the cold run-in of Phase II.

4. The orientation of the spray nozzle is important to obtain the maximum residence time for incineration and to obtain maximum deentrainment of solids in the primary chamber. The present location and orientation of the solvent spray nozzle is unacceptable because of the potential for buildup on the firestep. To prevent this buildup the spray nozzle should be pointed approximately 25 to 30° downward from the horizontal and pointed downstream in the primary chamber. To obtain maximum residence times, the nozzle should be placed as close to the anterior of the primary chamber as possible.

5. Sodium carbonate addition should be eliminated from the spray quench. The neutralization of HCl with sodium carbonate solution was ineffective during solvent tests. Results from solids burning tests showed that ash and fly ash react with HCl releases by PVC incineration, and stack releases are environmentally acceptable with or without Na_2CO_3 spray drying.

6. Rust from carbon steel lines was a source of nozzle plugging in Solvent Run 1. It is recommended that stainless steel lines be used for the solvent system piping of Phase II.

DISCUSSION

Facility Description

Processing steps in the SWIFT included liquid waste feeding, incineration, ash collection, and off-gas cooling and filtering. Figure 54 shows the conceptual flowsheet for solvent incineration.

Liquid waste was fed to the SWIFT incinerator by the solvent injection system, Figure 55. The primary components of the system were an agitated feed tank and three pumps.

The fill pump was used exclusively to add solvents to the feed tank from 55-gallon drums. The pump is a self-priming model with a 16-gallon per minute capacity. A safety interlock from a high-level switch in the feed tank was used to stop the fill pump and prevent the feed tank from overfilling.

A 50-gallon per minute centrifugal pump drew solvent from the bottom of the 500-gallon feed tank and circulated it back to the tank. To aid in suspending calcium hydroxide particles in the solvent, the recirculating line returned the slurry countercurrent to the flow of the agitator in the feed tank. The recirculating pump supplied solvent to the inlet of the feed pump.

A positive displacement metering pump was used as the feed pump for feeding solvents to the incinerator. The solvent flow rate was varied by manually controlling this feed pump.

The incinerator is a two-stage, controlled-air unit produced by Environmental Control Products, Charlotte, North Carolina. This incinerator has two hydraulic rams for removing ash from the primary chamber. Off-gases pass through a refractory-lined duct to the spray quench.

In the spray quench, the incinerator off-gases are cooled from 1000 to 180°C using two air-atomized water sprays. During 1,1,1-trichloroethane incineration, a sodium carbonate solution was used in the spray quench to neutralize the HCl that was generated.

The cooled gases were then filtered using a baghouse that contained Nomex® (Du Pont) fabric bags. The efficiency of the filters was rated at 98% for particles one micron in diameter.

Two 60-hp induced-draft blowers were used to maintain a negative pressure in the process and exhaust the off-gases to the atmosphere through a 35-ft stack.

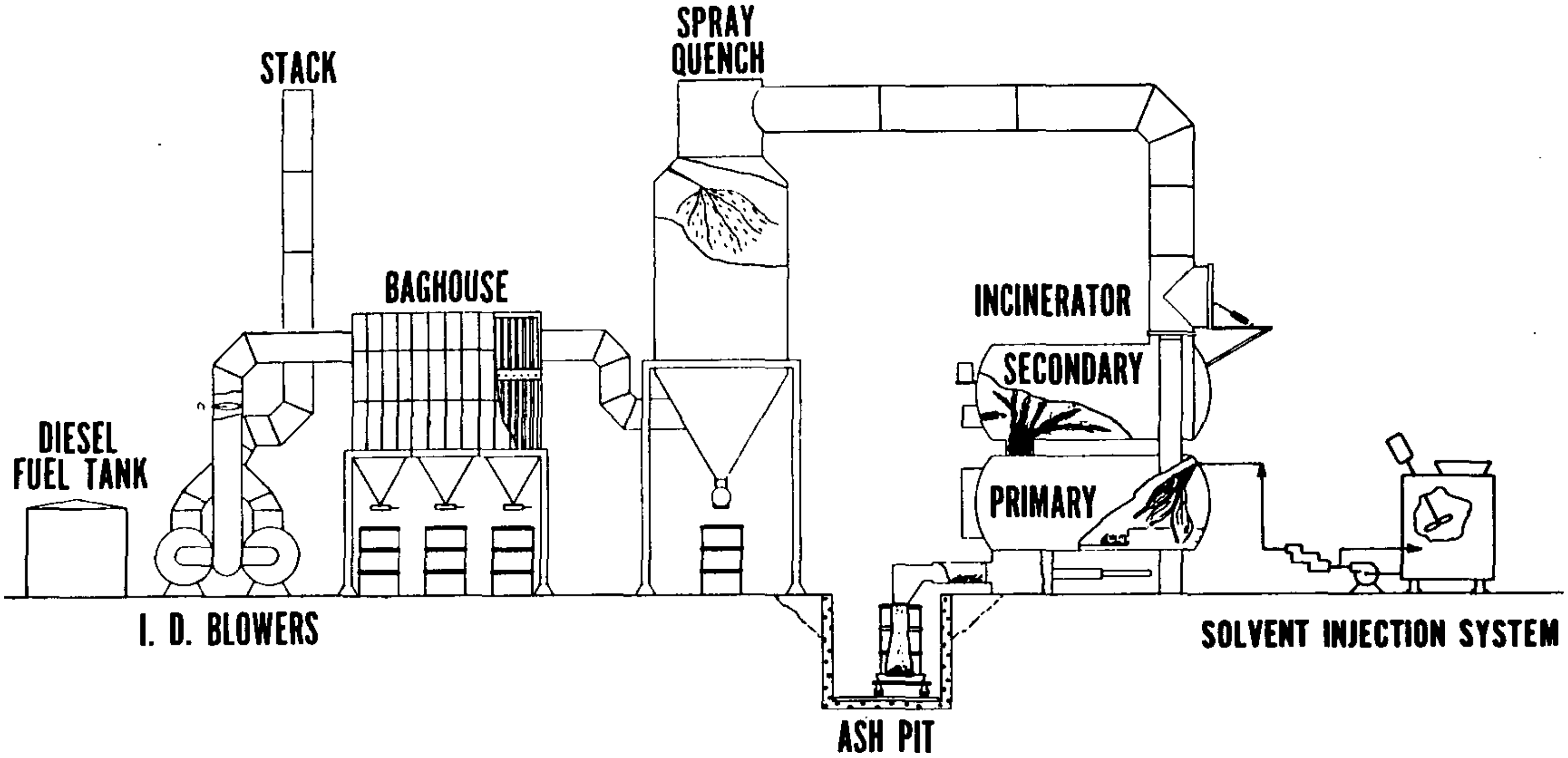


FIGURE 54. Solvent Incineration Flowsheet

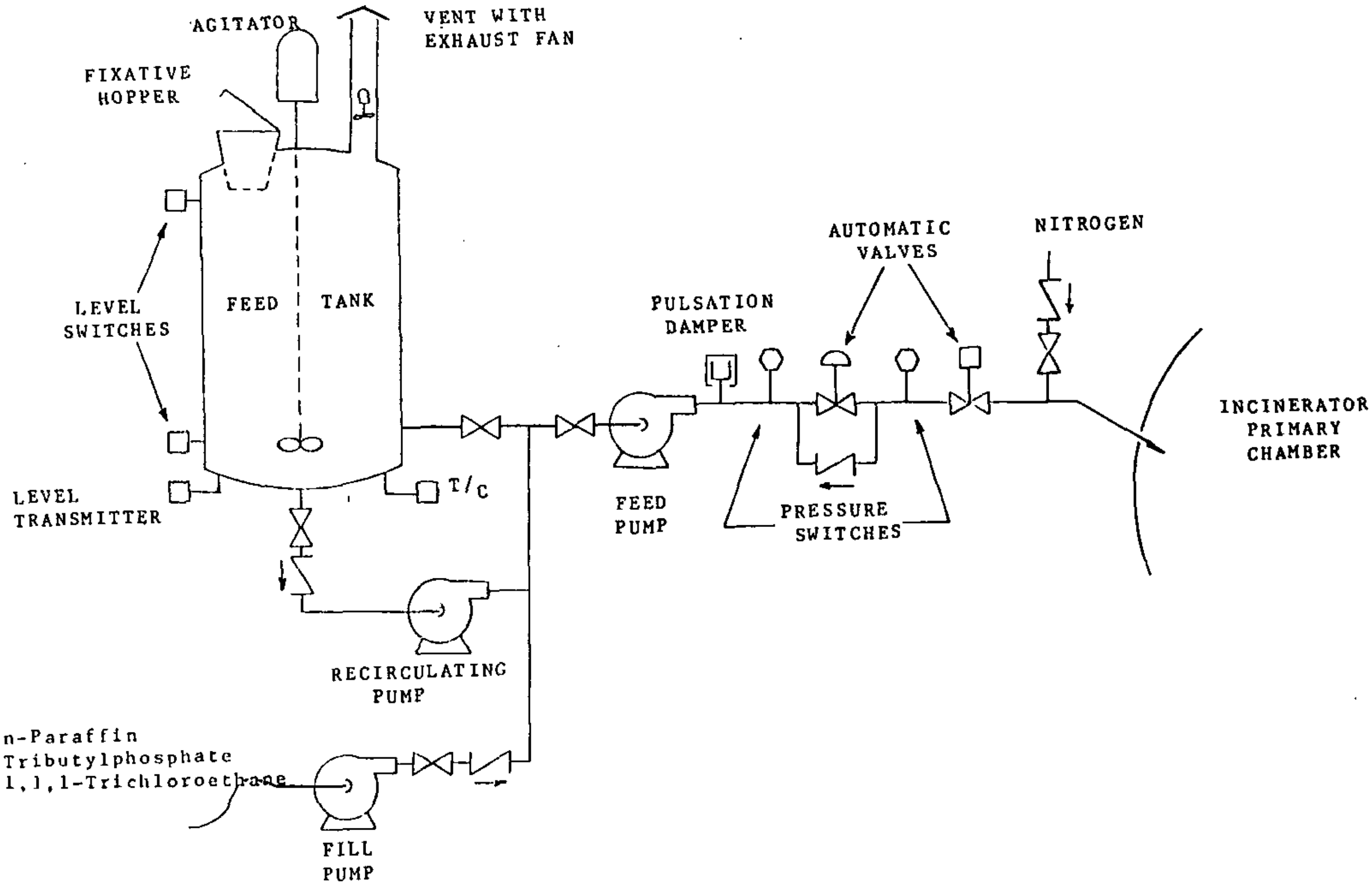


FIGURE 55. SWIFT Solvent Injection System Flowsheet

Controlled Air Incineration Theory

The SWIFT utilizes a controlled-air incinerator. Temperatures and burning rates in the primary and secondary incinerator chambers are maintained by controlling the quantity of air introduced to each chamber. Operating temperatures must be maintained in a range that is above the temperature required for complete thermal destruction and below temperatures that would damage the incinerator refractory lining. The limits of this range have been set at 650 and 1200°C, respectively.

The SWIFT unit has a total of four air blowers. Diesel fuel is used to preheat the incinerator, and two blowers supply air to atomize this fuel. The primary and secondary burners consume fuel and air in stoichiometric proportions. This provides the hottest and most efficient flames for preheating the incinerator prior to waste burning.

Two blowers feed air for the combustion of waste. The first, the underfire blower, adds air in the hearth area of the primary chamber. The primary is designed to operate with substoichiometric levels of air. This means that the oxygen required for burning is limited so that the solid or liquid waste is destroyed, but pyrolysis gases that are generated burn in the secondary chamber. Because only part of the waste releases its thermal energy in the primary, the temperature is lower than if all of the waste was completely incinerated in the primary. Therefore, the primary chamber temperature can be controlled by controlling the air fed to the chamber. The primary temperature increases when more air (oxygen) is added to more completely burn the waste, and it decreases when less air is added. Excessive air inleakage into the primary chamber destroys the effective temperature control of the underfire air blower.

The final blower supplies excess or overfire air to the secondary chamber. Complete combustion is obtained by maintaining an excess level of air (oxygen) in the secondary chamber. A minimum level of 5% excess oxygen has been established. The secondary temperature control operates in an opposite manner from the primary. Because the waste burns to completion in the secondary, additional air serves to cool the chamber. By decreasing the air supplied to the secondary, the temperature in the chamber will increase. Air inleakage to the secondary chamber normally is not a problem.

Figure 56 shows a typical operating curve with temperature as a function of the oxygen quantity. The dashed line indicates the stoichiometric quantity of oxygen required for incineration. The

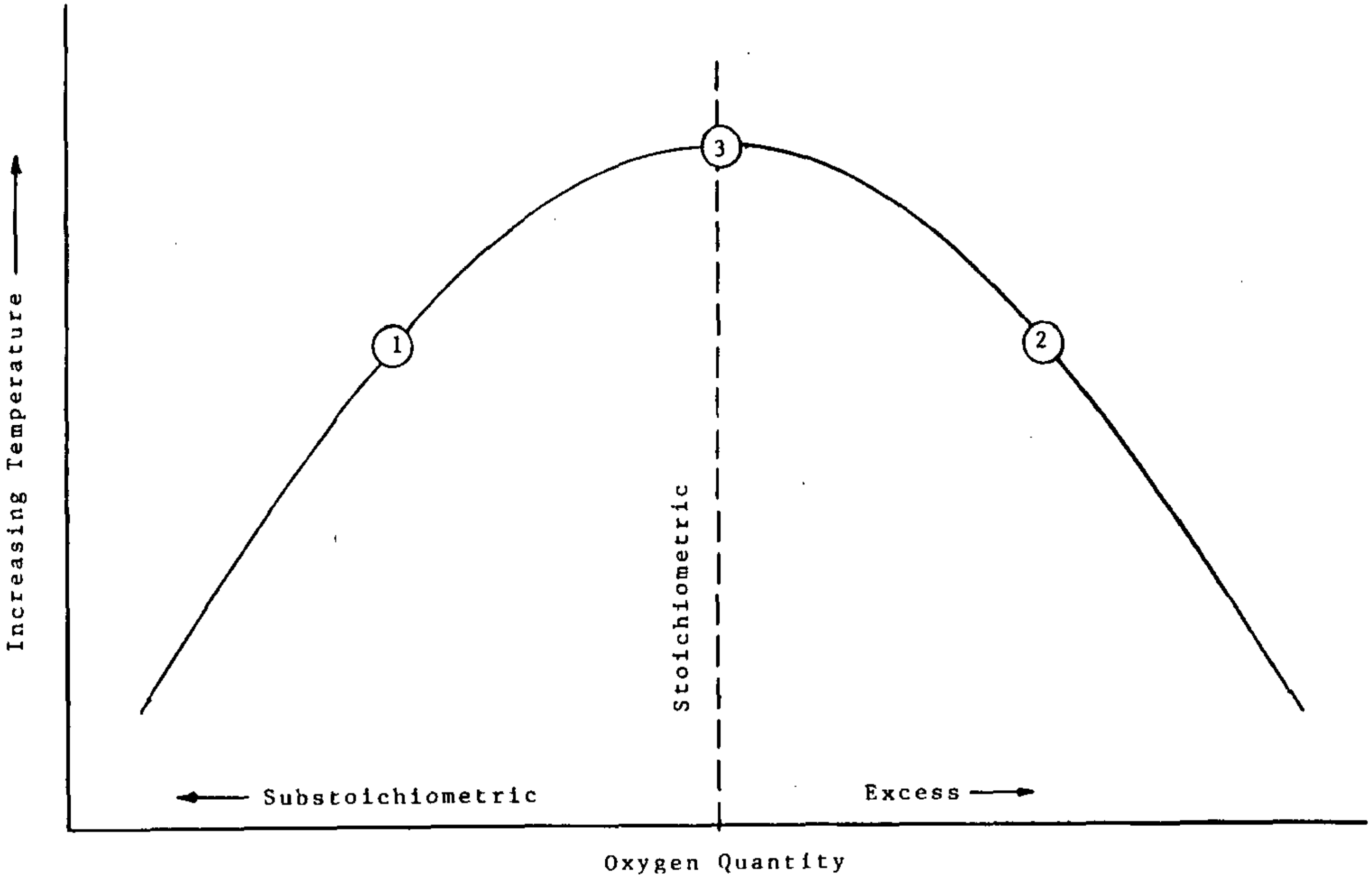


FIGURE 56. Typical Operating Curve for Controlled Air Incineration

highest operating temperatures can be obtained by burning stoichiometrically (Point 3). This is the case for both the primary and secondary burners. The primary chamber is normally operated at Point 1 on the graph, and the secondary is operated at Point 2.

FACILITY OPERATION

Incinerator Temperatures and Oxygen Levels

The steady-state operating temperatures and oxygen levels in the primary and secondary incinerator chambers were functions of controlled-air addition, air inleakage, and the solvent composition and feed rate.

Controlled air was fed to the incinerator based on signals from controllers that monitored the primary and secondary temperatures. When more controlled air was supplied to either incinerator chamber, oxygen levels increased. When additional controlled air was added to the primary chamber during substoichiometric operation, only a temperature rise was recorded. This was an indication that the primary was operating closer to stoichiometric conditions.

Air inleakage played an important role during solvent testing. The major source of air inleakage was around the solids feed charging door. This air inleakage was minimized prior to Solvent Runs 3 and 4 by sealing around the charging door with Refrasil®, as cloth-insulating material. The effect of reducing this air inleakage can be seen by comparing the steady-state operating temperatures from Solvent Runs 1 and 4 in Table 55. N-paraffin was incinerated at 37 gallons per hour during Solvent Run 1, and the primary operating temperature was 1150°C. During this time, the damper for the underfire air blower was completely closed and excess air inleakage alone was supplying the oxygen required for incineration. In Solvent Run 4, n-paraffin was burned at 40 gallons per hour, and the primary operating temperature was only 810°C. With reduced air inleakage, the underfire air blower was able to supply the proper amount of oxygen to control the temperature. This comparison demonstrated the importance of minimizing air inleakage to the primary incinerator chamber.

Steady-state operating conditions were obtained quickly after beginning to burn solvents. Oxygen levels stabilized within ten minutes from the time solvents began burning, and steady-state temperatures were normally attained in one to two hours. Steady-state temperatures were maintained without the primary burner and only occasional operation of the secondary burner. This was accounted for by the relatively high (19,000 Btu/hr) heat value for n-paraffin, the major constituent in the solvent.

TABLE 55

Steady-State Incineration Date

Solvent Run	Waste Feed	Calibrated* Feed Rate, gal/hr	Measured** Feed Rate, gal/hr	Steady State Primary Temp, °C	Steady State Secondary Temp, °C	Primary O_2 Level, %	Secondary O_2 Level, %
1	n-Paraffin	18	29.0	1120	720	2.5	12.5
1	n-Paraffin	37	36.0	>1150†	>800†	Subst††	10.5
2	n-Paraffin	45	44.6	>1170†	980	Subst††	7.5
3	TBP/n-Paraffin	45	29	870	910	Subst††	N/A¶
3	TBP/n-Paraffin	32	18	800	850	Subst††	N/A¶
4	n-Paraffin	40	39	>810†	>920†	Subst††	N/A¶
4	TBP/TCE/ n-Paraffin	40	37	1060	930	Subst††	N/A¶

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* Feed pump calibrated during water tests.

** Using data from feed tank level readings.

† Steady state had not been attained by this reading.

†† Substoichiometric oxygen level.

¶ Not available.

Levels of substoichiometric oxygen in the primary chamber and excess oxygen in the secondary chamber were recorded while burning solvents. The primary chamber appeared black and smoky. The secondary burned the remaining solvent and black smoke to completion. Under good spray atomizing conditions as in Solvent Run 3, solvent burning could be ceased, and the chambers would clear up within one or two minutes. Under poor atomizing conditions, solvent would continue to burn in the primary hearth area for as long as ten minutes after the feed pump was stopped.

The solvent compositions and feed rates for each run are tabulated in Table 55.

Spray Quench Operability

The spray quench operated well throughout solvent testing. It automatically cooled the incinerator off-gases from near 1000°C to 180°C. Several difficulties did hamper perfect spray quench performance.

Alignment of the spray quench nozzles is very important. To achieve maximum cooling capabilities, these nozzles should be pointed straight down. In this manner, the sprays would not impinge on the tank wall and cause water to drip from the bottom of the quench tank.

Proper alignment of the spray quench nozzles would also minimize the buildup of sodium carbonate on the spray quench walls. An estimated 171 pounds of solids accumulated on the spray quench walls during Solvent Run 4. A chemical analysis of the solids showed that it was 34% by weight sodium. By comparison, pure sodium carbonate is 43% by weight sodium. This is a positive indication that the buildup was caused by sodium carbonate addition. Also, the sodium carbonate was not as effective in neutralizing HCl as originally anticipated. This is illustrated in Table 56 by comparing HCl release rates for Solvent Run 4. Because of the process problems it could cause and the poor neutralization efficiencies, it is recommended that sodium carbonate addition be removed from the reference flowsheet.

Toward the end of Solvent Run 4, the spray quench high-pressure drop alarm sounded. It was discovered that material had collected on the spray quench distributor plates. This material was about 30% phosphorus and 22% calcium. This buildup on the top distributor plate is the result of burning only 1050 gallons of solvent slurry. It was estimated that 21 pounds accumulated on the top distributor plate and 16 pounds accumulated on the lower distributor plate.

TABLE 56

Off-Gas Release Rates, g/hr

Run No.	HCl	SO_2	NO_x	H_3PO_4	Particulate	Total Stack Flow, lb/hr
Solvent-3*	Data Not Obtained			20	-	20,800
Solvent-4*	1050	179	628	26	22	20,600
Solvent-4**	1140	39	113	82	75	17,070
Solvent-4**	1070	44	137	10	35	15,600
Solvent-4**	Special Particulate Test				13	

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* No neutralization in use in the spray quench.

** Na_2CO_3 neutralization used in the spray quench.

Baghouse Operation

Ash was collected from the baghouse by reverse air pulsing the bags with 90 psi air. This shook the ash loose and allowed it to drop into one of three hoppers at the bottom of the baghouse. Ash was removed from the baghouse at the end of each run.

The ash was very fine and black. Baghouse ash from Solvent Run 4 had a mean particle diameter of 10 microns and contained 25% carbon. The analysis for baghouse ash from Solvent Runs 3 and 4 is shown in Table 57.

Ash from Solvent Run 4 was sent to Hazards Research Corporation of Rockaway, New Jersety, for explosion testing. Their results show that the solvent incinerator ash that was collected in the baghouse has no explosion potential.

Solvent Injection System Operation

The solvent injection system was designed by the Savannah River Laboratory (SRL) and was installed by Du Pont Construction. Construction turned the facility over for Waste Disposal Technology to take custodianship in July of 1982.

Electrical checkout procedures were conducted in August. These procedures confirmed proper operation of the fill pump, recirculating pump, agitator, feed pump, and vent fan.

Testing of the solvent system with water was conducted next. The feed tank was filled with water to check the level transmitter calibration. This calibration is a function of the specific gravity of the contents in the tank as is shown in Figure 57.

The recirculating pump, agitator, and feed pump were tested with water. The feed pump was calibrated and used to test the high and low feed line pressure interlocks. The feed pump calibration is shown in Figure 58.

Two spray nozzles were tested with water. Both nozzles were produced by Spraying Systems Co. The first nozzle produced a 50° full-cone spray pattern, and the second produced a 120° full-cone spray pattern. The feed pump calibrations for the two spray nozzles were nearly identical.

TABLE 57

Summation of Solvent Runs 3 and 4 — Material Balances

		Phosphorus		Calcium		Mole Ratio	Chlorine*	
Location	Weight, lb	Avg wt %	Net, lb	Avg wt %	Net, lb	P/Ca	Avg wt %	Net, lb
Feed								
n-Paraffin	3540	0	0	0	0		0	0
TBP	2130	11.6	248	0	0		0	0
$Ca(OH)_2$	977	0	0	54.2	30		0	0
1,1,1-TCE	246	0	0	0	0		80.9	199
Incinerator								
Primary	1047	8.04	84.2	39.6	415	0.26	0.41	3.6
Secondary	49	16.4	8.05	35.7	17.5	0.59	0.19	0.03
Incl. Ductwork	100**	17.1	17.1	17.9	17.9	0.95	0.44	0.44
Spray Quench								
Dist Plate 1	20.6**	30.1	6.2	21.5	3.43	1.8	0	0
Dist Plate 2	15.8**	18.0	2.84	5.9	0.94	3.9	0.81	0.13
Walls	171**	1.72	2.94	0.68	1.16	3.3	20.6	35.2
Ductwork	30**	6.84	2.05	1.21	0.36	5.7	15.0	4.5
Baghouse								
Ash	219	10.9	23.8	4.04	8.84	3.5	18.3	33.0
On Bags	60**	10.9	6.5	4.04	2.4	3.5	18.3	11.0
Off-Gas	1.06×10^6	0.00049	5.2	ND†	ND†		0.013	69.9
		64%	(159)	88%	(469)		79%	(158)

---

* Solvent Run 4 only.

** Estimated.

† Not Detected.

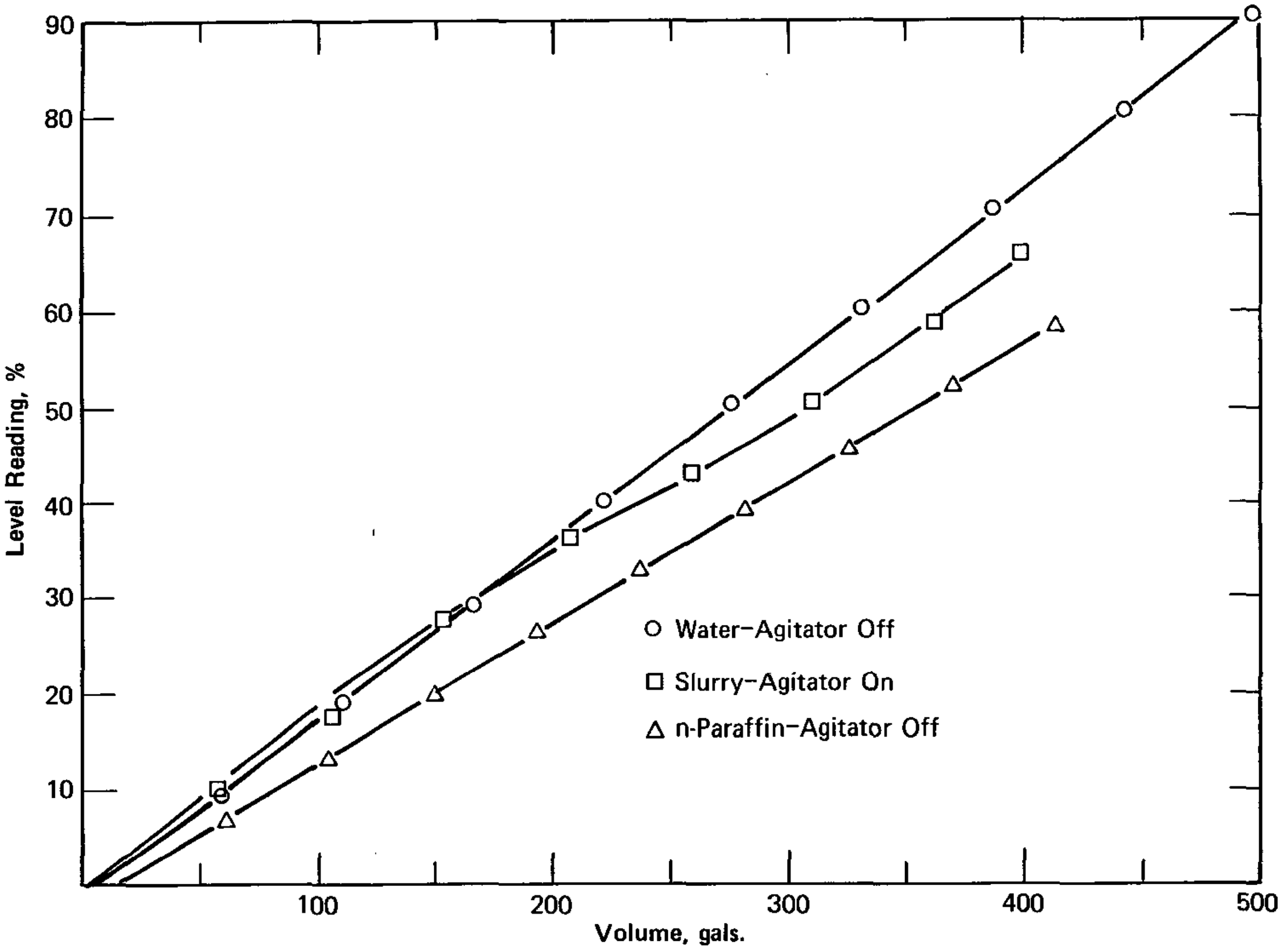

FIGURE 57. Feed Tank Level Calibration

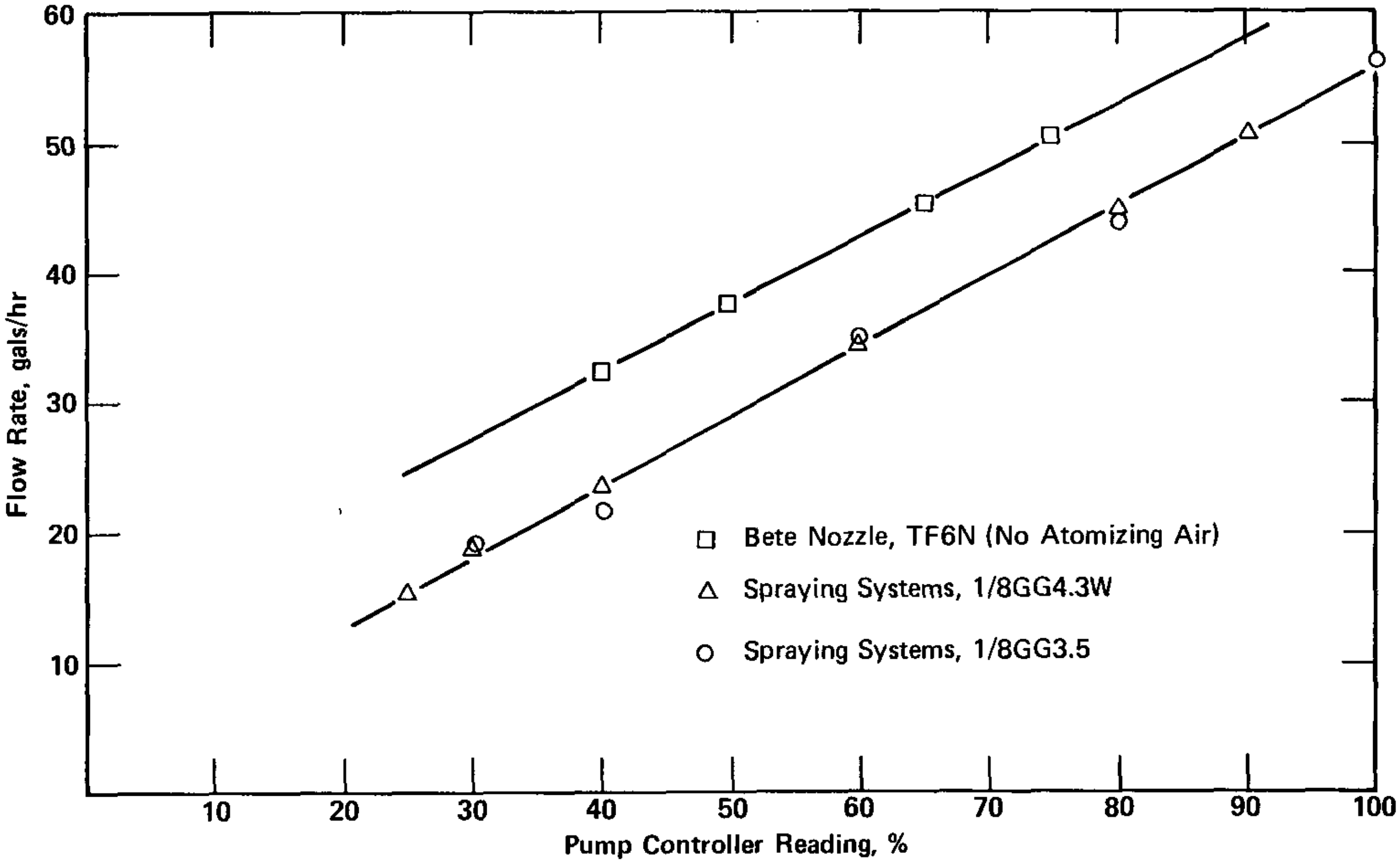

FIGURE 58. Feed Pump Calibration with Water

Four runs were conducted in which solvents were burned in the incinerator. In the initial two solvent runs, only n-paraffin was burned. These runs were conducted to further test the solvent injection system and obtain steady-state operating data. Two hundred gallons of n-paraffin were burned during Solvent Run 1. Incineration was conducted at feed rates of 29 and 37 gallons per hour before the ultraviolet (UV) amplifier for the secondary burner failed. The secondary burner could not maintain a flame, and the primary burner alone could not maintain sufficient operating temperatures to continue the run.

Two hundred seventy gallons of n-paraffin were burned during Solvent Run 2. n-Paraffin was fed to the incinerator at 45 gallons per hour during this run. Incinerator temperatures and oxygen levels were recorded for near steady-state operation before the 440V transformer tripped. The transformer tripped eleven more times before the run was terminated.

During Solvent Run 3, a slurry of TBP, n-paraffin, and calcium hydroxide was burned at feed rates of 29 and 18 gallons per hour. This slurry contained 0.92 times the amount of calcium hydroxide required to stoichiometrically react all of the phosphorus to $Ca_3(PO_4)_2$. The chemical analysis showed that the solvent was 25% by volume TBP, and the slurry averaged 18% by weight solids.

Plugging problems hampered Solvent Run 3. The run was terminated when the spray nozzle and the strainer before the recirculating pump plugged and the seals in the positive closure valve ruptured. After the run had ended, the solvent lines were disassembled and flushed with water. The strainer just before the recirculating pump was completely plugged with calcium hydroxide. The fine mesh screen in this strainer was replaced with a screen with 1/4-inch openings to allow the passage of the slurry. The eventual plugging of this strainer explains why the measured flow rates are so low compared to the calibrated flow rates that were set on the feed pump (Table 55).

Good atomization was noted during Solvent Run 3. This led to a 60% phosphorus fixation efficiency in the primary chamber and very white sandy product. During incineration the feed pump could be stopped, and burnout would cease within 10 seconds.

Seven hundred fifty gallons of slurry were incinerated during Solvent Run 4. This mixture contained 1.2 times the amount of calcium required to react all of the phosphorus to $Ca_3(PO_4)_2$. The slurry contained 36% by weight calcium hydroxide, and the liquid averaged 25% TBP and 2.8% 1,1,1-trichloroethane. Incineration was maintained at 40 gallons per hour and was interrupted only to add solvent and calcium hydroxide to the feed tank.

The nozzle arrangement for Run 4 was modified to eliminate the plugging problems encountered in Run 3. An air line was added to the nozzle arrangement to atomize the solvent. Because of mechanical problems, this air was not used during the run. A nozzle made by Bete Fog Nozzle was used. This nozzle has a tapered inner diameter and no internal components. Also, a plunger with a drill bit was added to the arrangement in the event that the nozzle should plug.

Plugging problems were eliminated with the new nozzle arrangement. The feed line maintained a pressure of 40 psi for nearly 20 hours of operation. But, because the atomization was not effective, other disadvantages were noted. A large mound of solids formed just below the nozzle on the firestep. After about 12 hours of operation, this mound of solids was removed from the firestep by poking a metal rod in where the spray nozzle had been withdrawn. The ash product was lumpy and was not moved by the internal ram very well. Also, solvent required ten minutes to burn off when the feed pump was stopped. Most of the burning was taking place from a puddle in the hearth of the primary. This type of burning reduced the phosphorus fixation efficiency to 42%.

Good atomization and the proper spray nozzle arrangement are important to solvent incineration. Before beginning Phase II, the solvent nozzle should be relocated within the incinerator. It is recommended that the nozzle be inserted in the end of the primary chamber near the ram feeder and pointed axially. This will minimize impingement of the solvent in the incinerator and allow the solid product to be sprayed into the hearth area. The spray nozzle manufactured by Bete Fog Nozzle should be used with atomizing air. This will minimize any potential for plugging and permit the solvent to burn without forming a pool in the primary chamber.

Relief Analysis of the Solid/Solvent Waste Incinerator Facility for Testing (SWIFT)

Introduction

The two safety evaluations of the SWIFT completed at SRL both identified a H_2-air explosion in the primary chamber of the incinerator as the worst credible accident. This situation could result from a loss of power. Without power, oxygen could not be supplied to the incinerator and H_2 would be generated by pyrolysis of the incinerator contents. During a restart with the introduction of air, any spark could initiate an explosion. In both memoranda, the conclusion was reached that such an explosion would be contained by the incinerator shell. Since these reports were issued, an investigation into the structural strength of the incinerator and spray quench has revealed that both the incinerator and spray quench would not contain such an explosion. This fact is supported by calculations and analyses done by the vendors of the incinerator, Environmental Control Products (ECP), and the spray quench, Bayliss Industries, Inc. Also, the Engineering Services Division (ESD) states from experience that any incinerator explosions are of low energy and therefore are not H_2-air explosions. ECP reports no knowledge of any internal explosions in any of its incinerators in the field. Thus, the H_2-air explosion thought possible in the incinerator is highly unlikely.

ESD was contacted to perform a relief analysis of the SWIFT and to recommend a method of explosion protection. This report summarizes the investigation for each component of the SWIFT and suggests alternatives for explosion protection for the system.

DISCUSSION

Incinerator

The original calculations presented in the safety evaluation done at SRL indicated that the incinerator shell could withstand a maximum pressure rise of 66.7 psi. The maximum pressure rise calculated for a H_2-air explosion is 43.1 psig. Therefore, the incinerator shell would contain such an explosion. After further calculations by SRL indicated that several incinerator components (charging door and both cleanout doors) would not withstand the 43.1 psig pressure rise, ECP was contacted and asked to provide an analysis of their incinerator design. The analysis included the maximum explosion pressure expected during operation, 45.5 psig from a methane-stoichiometric O_2 explosion, and the structural strength of their incinerator design. The analysis had been done earlier for an incinerator purchased by Du Pont and operated at the May Plant. Their analysis indicated that the cleanout doors and charging door would not withstand the anticipated explosion pressure. However, they also state that from their field experience, no internal explosions have been reported.

ESD was then contacted to advise SRL on the preferred method of explosion protection. The methods normally considered by ESD for explosion protection and/or prevention are inerting, suppression, barricading, venting, and containment. For the SWIFT, ESD recommends containment at a design pressure of 50 psig. However, discussions with Waste Management Technology (WMT) indicate that this is an impractical solution. The design pressure of 50 psig would have to be verified including radiographs of the incinerator welds. This process would be much too expensive and time consuming. Therefore, the use of inerting or purging is recommended. These methods are much more practical and will impact on the project schedule less than any of the other common methods of explosion protection/prevention. A N_2 purge was installed and tested at SRL with limited success. However, a design change such as multiple injection points would improve this system. Other alternatives to be considered are an air purge activated by the emergency power system or the emergency power system allowing an orderly shutdown and/or restart. Since there is no clear choice or advantage between these alternatives, a study group consisting of representatives from Waste Disposal Technology (WDT), WMT, and Waste Management Operations (WMO) should be formed to evaluate these alternatives. The basis for a final recommendation should be safety, practicality, and impact on the project schedule.

ESD provided vent areas for a H_2-air explosion as part of their investigation. However, from their experience, explosions in incinerators are of low energy, probably because CO is the major fuel, and does not exhibit the high-energy release of a H_2-air explosion.

Refractory-Lined Ductwork

No structural analysis of the refractory-lined ductwork was undertaken at SRL, but the ductwork would also have to contain a 50-psig explosion as projected by ESD. With inerting/purging, this ductwork would be protected and therefore would not need any modifications. If this ductwork is replaced during Phase III, it should meet the 50-psig design pressure.

Spray Quench

In the original safety analyses, an explosion or explosion propagation in the spray quench was not addressed. An investigation into this area revealed two major points: (1) an explosion or explosion propagation in the spray quench is possible and (2) the top of the spray quench would fail during an explosion.

Talks with ESD indicated that an explosion or explosion propagation in the spray quench could and probably would result from an explosion in the incinerator. A pressure wave and flame front would travel downstram from the incinerator into the spray quench transmitting explosion pressures to the spray quench. A rupture of the spray quench could result.

Knowing that large pressure rises (approximately 40 psig) could be transmitted to the spray quench, calculations were performed for the weakest member, the flat circular top, of the spray quench to determine its damage pressure. Also the vendor, Bayliss Industries, Inc., was asked to provide an analysis of the top of the spray quench. In both cases the top failed at approximately 2.5 psig. Thus, some sort of explosion protection is required. ESD recommends, as with the incinerator, that the top portion of the spray quench, including the top plate and cylinder extending down to the main chamber, be strengthened to withstand a 30-psig pressure rise. As with the incinerator, strengthening the spray quench to 50 psig is impractical. With an inerting/purge system the spray quench would be protected if the proper volume of gas is flushed or diluted. Therefore, no modifications will be needed for the spray quench. However, if the spray quench is used during Phase III, modifications to strengthen it to 50 psig should be scheduled. ESD also provided vent areas for a H_2-air explosion as part of their investigation.

Baghouse

As a part of the ESD analysis, the dirty air volume and the provided vent area of the Phase II baghouse was used to obtain peak pressure for typical baghouse explosions. However, baghouse explosions are highly unlikely due to two reasons: (1) the spray quench will serve as an effective propagation arrestor, and (2) results of explosion potential testing for both solvent and solid baghouse ash were negative. Therefore, the present baghouse design will not have to be modified before startup of Phase II.

CONCLUSIONS

It is recommended that three alternatives be investigated by a study group consisting of representatives from WDTD, WMT, and WMO. The three alternatives are a N_2 purge, an air addition, and extension of the emergency power system. The alternatives should be evaluated based on safety, practicality, and the impact on the project schedule. However, if a new incinerator is specified for Phase III, it should have a design pressure of 50 psig as proposed by ESD.

SWIFT Off-Gas Composition Calculations

INTRODUCTION

Gas samples were taken during incinerator operation to determine the composition of the exhaust and ensure that emissions met state standards. Stack sampling data were also used to measure the efficiency of the neutralization and fixation process of chlorine and phosphorus.

Table 58 shows the stack samples taken and the waste incinerated at the time of the sample. Sampling was usually initiated one hour after waste feeding was started or changed, so that each sample would be representative of the indicated incinerator operation.

EQUIPMENT DESCRIPTION

A Method 5 Stack Sampler purchased from Research Appliance Company, Cambridge, MD, was used during these tests. The sampler conforms with Government guidelines discussed in the Federal Register (August 8, 1977). Procedures written by the EPA were used as guidelines for operation. The EPA instructions are directed toward coal or oil-fired power plants with large stack exhausts that must comply with standards on particulate and chemical (SO_2, NO_x, HCl, CO) emissions. SRL used the sampler predominantly as a research tool, with a short turaround time to enable taking more than one sample during each run.

Stack flow is first measured by a reverse type Pitot tube. The assembly is moved across the stack diameter to the seven sampling points which best represent the flow. At each point, the differential between the static and impact pressure is measured by an inclined manometer. Stack velocity is determined for each point by the following equation:

$$v = K_p C_p (\Delta P)^{1/2} \quad \frac{T_s}{M_s P_s}$$

where

$$K_p = 85.49 \, \frac{\text{ft}}{\text{sec}} \quad \frac{(\text{lb/lb mole})(\text{in. Hg})}{(^\circ\text{F})(\text{in. } H_2O)}^{\;1/2}$$

(Units Conversion Factor)

C_p = 0.84, Pitot tube coefficient

T_s = 672°R, stack temperature

M_s = 29 lb/lb mole, stack molecular weight

P_s = 29.93 in. Hg stack pressure

v = ft/sec, stack velocity

TABLE 58

Stack Sampling Schedule

Run No.	Date	Waste Burned	Pollutant Sampled for
Solid 4	4/5/82	Red Rubber	HCl, SO_2, NO_x
Solid 4	4/6/82	Waste Mix with PVC*	HCl, SO_2, NO_x
Solid 4	4/6/82	Waste Mix with PVC**	HCl, SO_2, NO_x
Solid 4	4/7/82	Polyethylene and Waste Burndown*	HCl, SO_2, NO_x
Solid 6	5/18/82	Diesel Fuel	Particulate
Solvent 3	8/31/82	n-Paraffin and TBP with Lime*	PO_4, SO_2, NO_x
Solvent 3	8/31/82	n-Paraffin and TBP with Lime*	PO_4, SO_2, NO_x
Solid 7	9/15/82	Waste Mix with PVC*	HCl, SO_2, NO_x
Solid 7	9/16/82	Waste Mix with PVC**	HCl, SO_2, NO_x
Solid 7	9/16/82	Waste Mix with PVC**	HCl, SO_2, NO_x
Solvent 4	9/29/82	n-Paraffin, TBP, 1,1,1-TCE with Lime*	HCl, SO_2, NO_x
Solvent 4	9/29/82	n-Paraffin, TBP, 1,1,1-TCE with Lime**	HCl, SO_2, NO_x
Solvent 4	9/29/82	n-Paraffin, TBP, with Lime, Higher Concentration of TCE**	HCl, SO_2, NO_x

---

* No neutralization in use.

** Na_2CO_3 neutralization used in the spray quench.

The velocity is then arithmetically averaged over the stack diameter as follows:

$$\bar{V} = \frac{\sum_{i-1}^{N}}{N} V_i$$

where

$\bar{V}$ = Average stack velocity, ft/sec

N = Number of stack sampling points, normally seven (7)

And, the average stack velocity is converted to volumetric and mass flows by:

$$\dot{V} = \bar{v} * A * 60 \frac{\text{sec}}{\text{min}}$$

and

$$\dot{Q} = \dot{V} * \rho_{gas}$$

$\dot{V}$ = Average volumetric flow rate, ft^3/min

$\bar{V}$ = Average stack velocity, ft/sec

A = 3.141 ft^2, stack cross-sectional area

$\dot{Q}$ = Average mass flow rate (lb/min)

ρ gas = 0.055 lb/ft^3, gas density

After the velocity traverse is complete, a sample is pulled into a probe located next to the Pitot tube. The probe is moved to each traverse point and a sample is pulled for 2 to 3 minutes. The gas flows through a particulate filter and a series of bubblers immersed in an ice bath. The first bubbler contains distilled water, the next two contain one molar NaOH, and the final bubbler contains silica gel. The impinger train is designed to scrub HCl, SO_2, CO_2, and NO_x from the stack gas sample. Exhaust at 100°C is cooled to 21°C at the exit of the impinger train, so water in the stack gas also condenses into the bubblers. The noncondensible gas leaving the impinger (N_2, O_2, CO_2) is pulled through a dry meter to accurately determine the volume of the sample and exhausted to the atmosphere. During the last sampling period, a grab sample of this gas is collected in a plastic bag.

SAMPLE ANALYSIS

As mentioned earlier, a filter is the first part of the sampling train. A glass fiber filter rated for 99% removal at 0.3 micron captured particulate from the off-gas. The amount of solids in the gas was very small and only trace amounts were collected during a normal sample period (24 minutes). Two special tests were performed to determine particulate concentration by pulling a sample for several hours. These tests, taken during Solid Run 6 and Solvent Run 4, indicate particulate release rates of 13 g/hr. The solids that pass through the baghouse are very fine (<2 microns in diameter).

Various analytical techniques were used to determine the composition of the bubbler solutions. The content in the bubblers were first weighed to determine the amount of water condensed at each stage. Samples of the solution in Stages 1, 2, and 3 were then analyzed by ion chromatograph, neutron activation, and carbon coulometrics. Ion chromatograph measures the quantity (ppm) of SO^{-2}, Cl^{-}, NO_2^{-}, and NO_3^{-} in the solution. Neutron activation was used as a backup method for determining chlorine since water shift peaks in the ion chromatograph occasionally masked the chlorine peak. Results from total carbon analysis were converted to the amount of CO_2 scrubbed from the gas by the NaOH. CO_2 also was present in the gas collection bag at the end of the run indicating that the removal efficiency was not complete. The quantity of CO_2 reported for Solid Run 4 was adjusted to include CO_2 not removed by the bubblers.

RELEASE RATE CALCULATIONS

The release rate of each pollutant can be calculated in three steps as follows:

1. Determine the total quantity of the component collected

$$Q_{comp} = X * Y * C$$

where

Q_{comp} = total quantity of the component collected, grams

X = concentration of component in the bubbler, ppm

Y = final weight of bubbler solution, grams

C = 1×10^{-6} (g/g soln)/ppm [Conversion Factor]

2. Determine the total quantity of gas pulled through the stack sampler:

$$V_{gas} = DGM_{Final} \quad DGM_{INIT} + V_{WAT}$$

where

V_{gas} = total volume of gas, ft^3

DGM_{Final} = final dry gas meter reading, ft^3

DGM_{INIT} = initial dry gas meter reading, ft^3

V_{WAT} = volume of water vapor, ft^3

Note: Water condensed must be converted to an equivalent volume of vapor according to the stack temperature.

3. Determine the release rate, g/hr, by the following equation:

$$R_{comp} = \frac{Q_{comp}}{V_{gas}} * \dot{V}$$

where

R_{comp} = release rate for one component, g/hr

Q_{comp} = total quantity of the component collected, grams

V_{gas} = total volume of gas, ft^3

$\dot{V}$ = average volumetric flow rate, ft^3/min

Release rates for each component were used to determine a corresponding air quality at a point one kilometer from the stack. Dilution factors developed at SRL which convert a source release rate to an air concentration a given distance away were used. To compare the air quality with state standards by statistical averaging constants as prescribed by SCDHEC, the concentrations were multiplied by statistical averaging constants for various intervals. Stack sample data were based on a 3-minute sample at each point in the stack, and were related to the standard sampling interval, see Table 59, by the following equation:

$$K = \frac{\text{Time of Sample Interval}}{\text{Time of Standard Interval}}^{0.17}$$

TABLE 59

State Standards for Pollutants, μg/m^3

Pollutant	State Standard	Measuring Interval	K
SO_2	1,300	3 hours	0.5
NO_x	100	Annual	0.064
HCl	N.S.*	30 days	0.098
Particulate	60	Annual	0.064
CO	40,000	1 hour	0.602

---

* There is no state standard for HCl. The sampling interval for HF is used.

STACK GAS RESULTS

Table 60 gives the calculated release rates and air quality for incinerator exhaust during the following runs:

- Solvent Run 3 - n-Paraffin and TBP with lime
- Solid Run 7 - Long-Term Campaign
- Solvent Run 4 - n-Paraffin, TBP, and TCE with lime

Concentrations of HCl and H_3PO_4 in the stack gas were used to determine the effectiveness of neutralization and fixation during PVC, TBP, and TCE incineration.

TABLE 60

Pollutant Release Rates, g/hr

Run No.	HCl	SO_2	NO_x	H_3PO_4	Particulate	Total Stack Flow, lb/hr
Solvent 3	Data not obtained			20	-	20,800
Solvent 4*	1050	179	628	26	22	20,600
Solvent 4**	1140	39	113	82	75	17,070
Solvent 4**	1070	44	137	10	35	15,600
Solvent 4**	Special particulate test				13	
Solid 7*	1430	695	84	-	1.2	24,020
Solid 7**	14	15	33	-	1.2	18,320
Solid 7**	707	9	23	-	1.2	22,920

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* No neutralization in use in the spray quench.
** Na_2CO_3 neutralization used in the spray quench.

LIMITATIONS OF STACK SAMPLING

The stack gas calculations have certain limitations and should not be treated as absolute values. The following items must be considered when evaluating stack gas composition:

1. Efforts were made to draw a representative sample.

2. Calculations were based on the assumption that HCl, SO_2, and NO_x were totally scrubbed from the off-gas in the three liquid bubblers.

3. Ion chromatography and neutron activation results were often in the low range of the analytical device. Results of "less than" a given quantity were used as if the concentration were at that specified limit. This causes the calculated concentration to be higher than the actual composition (conservative method).

4. CO was not detected in any gas sample, but gas chromatography detection limits are only 0.5%. Even if CO had been present at that level, the composition would still be below state standards.

5. During a normal sampling interval, only trace amounts of particulate (<0.0010 g) were captured on the filter. Only two accurate measurements of particulate levels were made (during Solid 6 and Solvent 4).

6. Isokinetic sampling was not obtained at all times. Since particulate levels were very low and the chemical concentrations were of greater concern, isokinetic sampling rates were not important. Nonisokinetic sampling only affects results of particulate results because particulate collection is subject to inertial effects.

Ashcrete Demonstration Scope

A process to solidify beta-gamma incinerator ash in concrete, called ashcrete, is envisioned to be included in the Phase II and Phase III demonstration of the beta-gamma incinerator (BGI). At the present time, the ashcrete program has completed formulation studies at Stock Equipment Co. and has installed a drum tumbler at the Savannah River Laboratory.

The overall scope of the ashcrete program is to: (1) specify process equipment, (2) install and test the process equipment at TNX, and (3) to relocate the process equipment to the BGI site in H Area. The TNX tumbler has been used to determine the best drum lid closure ring and gasket to prevent spillage of the ashcrete product from the drum during tumble mixing and will be used for additional formulation and solidification studies prior to the delivery of the automatic tumble-mixer equipment to TNX. Although additional work remains to be completed, the basic scope of the ashcrete process has been determined.

Background

The primary purpose of the ashcrete process is to mix BGI ash product into a cement waste form which will immobilize the ash during burial and provide an additional barrier to soil and groundwater contamination and reduce burial ground subsidence. A major goal of the program is to provide a simple, off-the-shelf vendor available process which can be easily integrated into the existing BGI process with a minimum of additional steps.

The operating procedures of the incinerator are for the lid of an empty 55-gallon drum to be removed and the drum placed in the incinerator ashout port. The drum is filled with ash, and the drum lid is replaced. The drum is then placed in a storage area for further processing. The ashcrete solidification process must interface the incinerator operations at this point. The process must achieve solidification of the drum contents without any steps prior to ashout which will interfere with incinerator operations. The requirements of the process are:

Process Requirements

1. Commercially available nuclear radwaste system with other installations in place, an experienced field engineering service, and a strong industry reputation.

2. Equipment must be able to process an ash of large particle size which contains tramp metallic objects and large solid agglomerates.

3. Enclosed process area with fully automatic equipment and handling features which will minimize operator exposure to radiation (both surface contamination and airborne) hazards and dust-related respiratory hazards.

4. Minimal process equipment radiation contamination due to direct contact with adioactive ash.

5. No storage or handling of ash following incinerator ash drum loading.

6. Ability to decontaminate the process equipment.

The vendors of radwaste equipment which can be considered for the ashcrete program are Stock Equipment Co., UNC Nuclear Industries, Atcor Engineered Systems, and Delaware Custom Materials.

The Delaware Custom Materials system was rejected because it failed to meet a number of requirements. The UNC and Atcor systems were also rejected because a number of the process steps required in these systems violated the above requirements. Both the UNC and Atcor systems use basically the same steps.

The Stock system is the only commercially available process which meets the above requirements. The Stock system is a completely enclosed apparatus which has automatic features for drum handling and processing. A 55-gallon drum filled with BGI ash is loaded into the enclosure. The 4-inch cap in the center of the drum lid is automatically removed, and the required amount of water, cement, and sand are added automatically. The 4-inch cap is then automatically replaced, and the drum is tumbled end-over-end for 20 minutes to mix the ash into concrete. At the end of the 45-minute process period, the drum is automatically removed from the enclosure, and the contents are solidified and ready for storage and burial.

The Stock system was chosen because of all the available commercial systems studied, this system requires the least additional steps, is mechanically uncomplicated, and is most compatible with the existing incinerator equipment.

Cement was chosen for the solidification material because of its low cost, ease of handling, and history of use onplant.

Two design questions which arose once the Stock system was chosen was the leak potential of full-bore drum lids during tumbling, and the best material to use to backfill the drums after mixing.

The standard Stock system uses 55-gallon drums with a welded top, which has a 4-inch bung assembly in the center of the top. Because the BGI ash may have large, solid agglomerates, a 4-inch opening is unsuitable for ash loading at the BGI and a full-bore open top drum is required. Full-bore drum lids with a 4-inch center bung assembly are available through Stock. The use of a full-bore lid in the drum tumbler introduces the potential for leakage of ashcrete product around the edges of the lid during tumbling operation. A number of tests were conducted at SRL and Stock to determine the best method of closure of drums to prevent leakage. The SRL tests used sand and water in new galvanized drums. These drums have lids, closure rings, and gaskets specially designed to provide a tight seal. The drums were filled with sand

and water and tumbled 30 minutes. No leakage was observed. On February 3 and 4, 1983, Stock conducted a full-scale, 55-gallon drum solidification test of BGI solid waste ash and Purex solvent ash. These tests were conducted in galvanized drums with a Stock-provided full-bore lid with the 4-inch center bung assembly. No leakage was observed in these tests. Both the SRL and Stock tests indicate that leakage will not be a problem.

The other design concern with using the Stock system was the determination of the best material to use to backfill the drums after mixing. The density of BGI ash averaged 0.51 g/mL, and the average density of the ashcrete product is 1.7 g/mL. Because of the density difference, a drum 90% full of ash will be 76% full of ashcrete product. The drum should be 80% full of the final product to limit the potential of burial ground subsidence and to meet the goals of the Greater Confinement Disposal concept. Sand was chosen as the backfill material because it is relatively easy to handle, is relatively clean (dustless), requires the fewest additional steps, is relatively inexpensive, and mixes easily with the ashcrete product.

Program Objective

The primary objectives of the ashcrete program are:

- To encapsulate BGI ash in concrete using 55-gallon drums.
- To specify process equipment and complete fabrication by 9/30/83.
- To initially install the process equipment at SRL. At SRL the equipment will be run in and solidification studies performed. After evaluation and optimization, the process equipment will be relocated to the BGI site and turned over to SRP.

Figure 59 illustrates the ashcrete program milestones.

During the SRL phase of the program cold ash will be obtained from the early stages of the Phase II demonstration of the BGI and solidified by the ashcrete process equipment installed at SRL. During this stage, only a fraction of the BGI ash product will be solidified into ashcrete. Once the process is evaluated and demonstrated, the ashcrete process equipment will be moved to the BGI site. Following run-in and testing at the BGI site, full-time operation will begin.

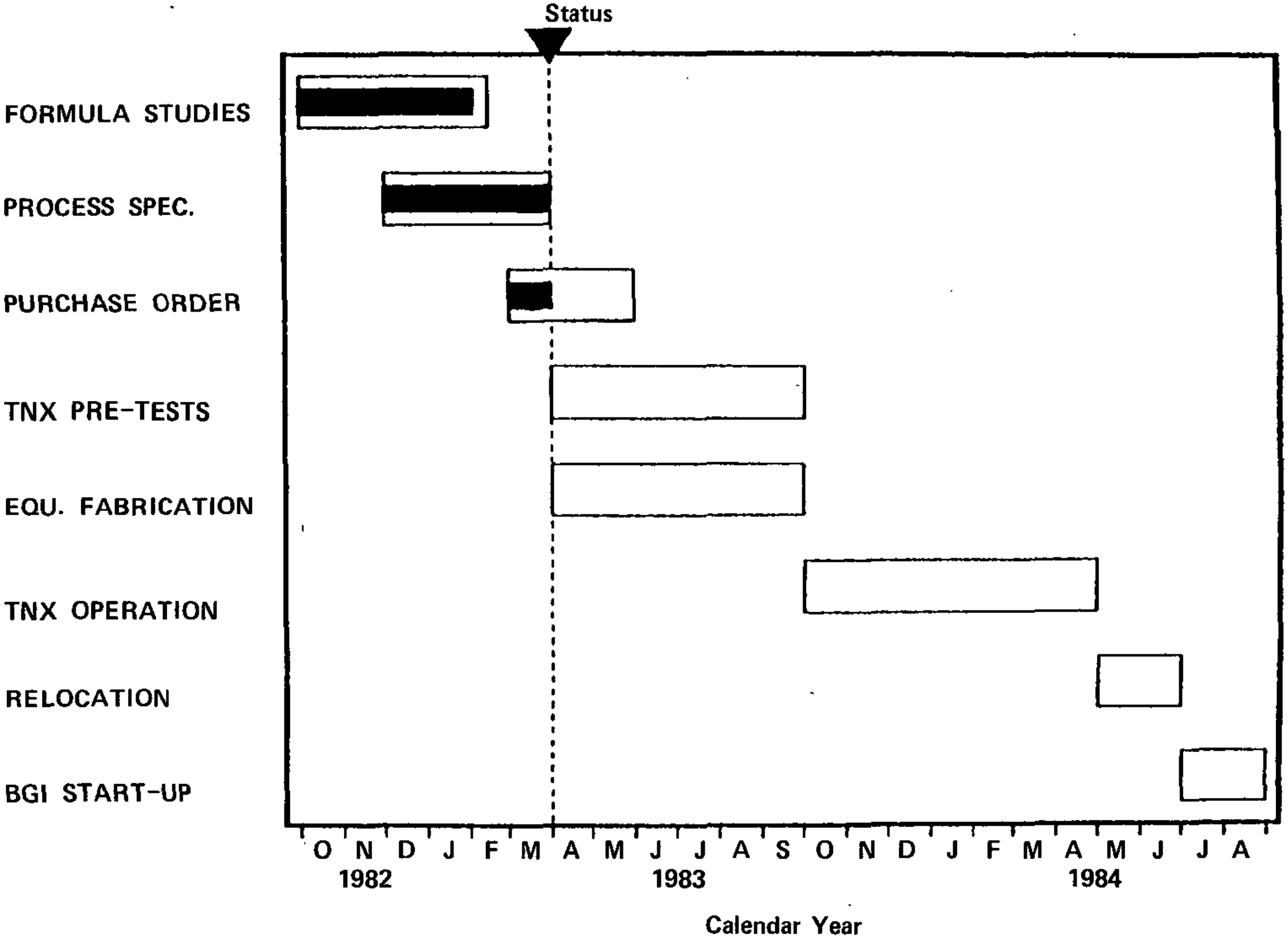

FIGURE 59. Ashcrete Timetable

Process Description

The basic steps of the ash solidification are listed below. Incinerator ash is loaded into an empty 55-gallon drum until the drum is 90% full. The drum is then filled with water and mixed by end-over-end tumbling to reduce the ash void volume. Following the initial tumble step, the required amounts of cement and additional water are added. The drum is closed and end-over-end tumbled to mix the ashcrete product. Following mixing, the drum contents will be compacted due to the density difference between the dry material and ashcrete product. The resulting void space will be filled by sand. After mixing, the drum contents level is determined, and the drum is filled with sand until the drum is 80% full. The drum is tumbled again to mix the sand into the ashcrete product. The drum is then placed in a preburial storage area to allow the contents to set. At the end of the storage period, the drum is buried.

Analysis of Burial Ground Grid Wells for Mercury

Results from analyses of 88 groundwater wells in or near the 643-G and 643-7G low-level, radioactive waste burial grounds show a general decrease in the concentration of mercury from last year. Results were obtained using the full standard procedure recommended by the EPA.[15] The maximum observed concentration was 0.79 part per billion (ppb) compared to a drinking water standard of 2.0 ppb. 83% of the wells had less than 0.1 ppb of mercury, which has been estimated as the natural background concentration in the eastern U.S.[16] All of the wells showing significant mercury levels were located in 643-G.

No mercury was observed outside of the burial ground. Wells both upflow from the burial grounds, and in the center of the flow path of water out of the burial ground, showed no mercury. The evidence shows that migration of mercury does occur, but it is slow enough that dilution or removal by soil reduces it to levels below the detection limit well before it could possibly outcrop.

Background

The concentration of mercury in the groundwater under the low-level, radioactive-waste burial ground (643-G and 643-7G) has been a concern since the mid 1970s, when it was estimated that up to 10 tons of mercury metal contaminated with tritium had been buried. Since 1978, an annual sampling of groundwater from the burial ground has been analyzed for mercury. The concentrations are shown in Table 61 for comparison to this year's results.

In March of 1982, it was decided to submit samples to an offsite laboratory to allow the complete procedure of the EPA method for mercury analysis to be performed. Environmental Chemical and Sciences Laboratory (New Ellenton, SC) was chosen because of its proximity and capabilities. They have carried out the analyses for this year's sampling as well as the March 1982 sampling. Standards and blanks were submitted along with the samples for QA purposes.

Results

In November of 1982, samples were collected from 86 groundwater monitoring wells located within the 643-G and 643-7G burial grounds and 2 wells located outside these facilities. The same sampling procedures (including acid preservation and prewashed bottles) were used as in previous years. Well BG-109 is located approximately 500 yd to the east of the 643-7G burial ground, along the water table divide, and is upflow from any buried waste. It serves as a control well. PDQ5 is located 200 yd south of 643-G and is sampled at depth in the middle of the plume of tritium which outlines the groundwater flow path from the buried waste.

The results from the November 1982 sampling are included in Table 61. Of the 86 burial ground wells, only 15 show mercury concentrations above 0.1 ppb, which is the estimated natural background. Eight of these are above 0.2 ppb. No mercury was seen in PDQ5 or BG-109. All 8 of the wells with statistically significant mercury concentrations were located in the 643-G burial ground, and all but C-17 had shown elevated mercury levels at some time in the past. As a comparison, in November 1981, the maximum concentration was 1.40 ppb (70% of the drinking water standard) with 21 wells above the 0.1 ppb level. In March of 1982, the maximum concentration was 1.56 ppb.

TABLE 61

Hg Concentrations in Groundwater, ppb

Well No.	Nov 1977	Nov 1978	Nov 1979	Nov 1981	March 1982	Nov 1982
A-1	<0.1	<0.02	0.6	<0.1	<0.05	<0.05
3	<0.1	<0.02	0.7	<0.1	0.05	0.05
5	1.2	<0.02	0.4	<0.1	0.32	0.35
7	<0.1	<0.02	0.6	<0.1	<0.05	<0.05
9	0.1	<0.02	0.4	<0.1	0.06	0.08
11	<0.1	<0.02	0.4	<0.1	0.15	<0.05
19	0.1	<0.02	0.6	<0.1	0.26	<0.05
21	<0.1	<0.02	0.2	<0.1	<0.05	0.07
23	-	<0.02	<0.2	<0.1	0.13	<0.05
32	1.0	0.74	0.9	0.7	0.42	0.32
34	<0.1	<0.02	0.4	<0.1	<0.05	0.05
36	0.11	<0.02	0.6	<0.1	0.07	<0.05
C-1	<0.1	<0.02	<0.2	<0.1	0.05	<0.05
3	<0.1	0.06	0.4	<0.1	0.10	<0.05
5	<0.1	<0.02	0.6	-	<0.05	<0.05
7	0.1	<0.02	0.7	0.3	0.43	0.19
9	<0.1	<0.02	<0.2	<0.1	<0.05	<0.05
11	0.15	<0.02	-	-	-	<0.05
13	<0.1	<0.02	<0.2	<0.1	0.05	<0.05
15	<0.1	<0.02	0.4	<0.1	<0.05	0.08
17	-	-	-	<0.1	0.06	0.22
19	-	<0.02	0.4	<0.1	<0.05	<0.05
21	0.7	0.36	1.3	1.3	1.56	0.69
23	0.1	<0.02	0.3	0.4	0.76	0.79
30	0.1	<0.02	0.4	<0.1	0.22	0.11
32	0.1	<0.02	<0.2	<0.1	<0.05	0.13
34	1.0	<0.02	0.3	-	0.43	<0.05
36	<0.1	<0.02	0.3	<0.1	<0.05	0.15
E-1	<0.1	<0.02	<0.2	<0.1	<0.05	<0.05
3	<0.1	<0.02	<0.2	<0.1	0.05	0.19
5	<0.1	<0.02	0.4	<0.1	0.06	0.05
7	<0.1	<0.02	0.3	<0.1	0.05	<0.05
9	<0.1	<0.02	0.5	<0.1	0.05	<0.05
13	<0.1	<0.02	<0.2	<0.1	<0.05	<0.05
15	-	<0.02	0.8	-	-	-

- Indicates well was not analyzed.

Number following < sign indicates the detection limit for the measurement.

TABLE 61, Contd

Well No.	Nov 1977	Nov 1978	Nov 1979	Nov 1981	March 1982	Nov 1982
E-17	-	<0.02	0.3	0	<0.05	<0.05
19	0.13	<0.02	<0.2	0.2	0.06	<0.05
21	<0.1	<0.02	<0.2	<0.1	0.15	<0.05
23	<0.1	<0.02	0.4	0.2	<0.05	<0.05
30	<0.1	<0.02	<0.2	<0.1	<0.05	<0.05
32	<0.1	<0.02	0.6	<0.1	<0.05	0.09
34	<0.1	<0.02	0.5	<0.1	<0.05	<0.05
36	<0.1	<0.02	0.4	<0.1	<0.05	<0.05
G-1	<0.1	<0.02	0.4	<0.1	<0.05	<0.05
3	<0.1	<0.02	0.3	<0.1	<0.05	<0.05
5	<0.1	<0.02	0.4	<0.1	0.07	0.09
7	<0.1	<0.02	0.3	<0.1	<0.05	0.06
9	<0.1	<0.02	0.4	<0.1	<0.05	0.08
13	<0.1	<0.02	0.5	<0.1	<0.05	<0.05
15	<0.1	<0.02	0.5	<0.1	<0.05	<0.05
17	0.1	<0.02	0.3	<0.1	0.78	0.20
19	<0.1	<0.02	0.3	<0.1	<0.05	<0.05
21	1.4	0.63	0.3	<0.1	<0.05	0.05
23	2.4	0.57	0.5	0.1	0.33	<0.05
28	-	<0.02	0.6	<0.1	0.07	0.49
30	-	<0.02	0.5	<0.1	<0.05	<0.05
32	<0.1	<0.02	0.5	<0.1	<0.05	0.09
34	<0.1	<0.02	<0.2	<0.1	0.05	0.06
36	<0.1	<0.02	0.5	<0.1	<0.05	<0.05
I-1	-	<0.02	0.5	1.4	0.20	0.08
3	-	<0.02	-	-	-	-
5	-	<0.02	0.4	<0.1	0.05	0.06
7	-	<0.02	0.3	<0.1	<0.05	0.05
9	-	<0.02	0.5	<0.1	0.06	0.06
13	-	<0.02	0.6	0.4	0.51	0.26
15	-	<0.02	0.6	<0.1	<0.05	<0.05
17	-	<0.02	0.2	<0.1	<0.05	<0.05

TABLE 61, Contd

Well No.	Nov 1977	Nov 1978	Nov 1979	Nov 1981	March 1982	Nov 1982
22-04	-	-	-	0.3	0.06	0.12
06	-	-	-	0.2	<0.05	<0.05
08	-	-	-	0.3	<0.05	0.07
10	-	-	-	0.3	<0.05	<0.05
12	-	-	-	0.1	<0.05	0.08
16	-	-	-	0.2	<0.05	<0.05
18	-	-	-	0.5	<0.05	<0.05
20	-	-	-	<0.1	<0.05	<0.05
22	-	-	-	0.5	<0.05	<0.05
24-02	-	-	-	<0.1	<0.05	<0.05
04	-	-	-	0.2	0.10	0.13
06	-	-	-	<0.1	<0.05	<0.05
08	-	-	-	<0.1	<0.05	<0.05
10	-	-	-	<0.1	<0.05	0.08
20	-	-	-	0.2	0.05	0.11
22	-	-	-	<0.1	<0.05	<0.05
26-20	-	-	-	0.2	<0.05	0.06
22	-	-	-	-	0.07	<0.05
28-18	-	-	-	<0.1	0.05	<0.05
20	-	-	-	0.2	<0.05	<0.05
22	-	-	-	<0.1	<0.05	0.06
PDQ5	-	-	-	<0.2	-	<0.1
BG-109a	-	-	-	<0.1	<0.05	<0.05
109b	-	-	-	<0.1	<0.05	<0.05
1.0 ppb standard	-	-	-	1.2	1.02	1.09
0.1 ppb standard	-	-	-	0.4	0.12	0.17
2.0 ppb standard	-	-	-	2.3	2.28	2.06
Distilled water	-	-	-	0.2	<0.05	<0.05

Conclusions and Recommendations

Several general conclusions can be drawn from the data. First, the decreasing concentrations in most of the contaminated wells show that the mercury does migrate through the soil. As it migrates, it is either removed by the soil or diluted with uncontaminated groundwater. No mercury is detected in Well PDQ5 which is downflow of the source and confirmed to be in the flow path. This means that measurable quantities of Hg from the burial ground should not reach the outcrop into Four Mile Creek in the foreseeable future. The outcrop point is considerably further downflow than is PDQ5. Second, the fact that little or no contamination is observed in 643-G shows that metallic mercury is the source of the contamination. This is because the shipments of mercury metal from H Area were stopped before 643-7G began to receive waste, and no other changes in burial practices which would affect mercury contamination occurred at that time.

Solid Radioactive Waste Generation and Disposal — Naval Reactor Fuel Materials Facility

This memorandum describes the low-level solid radioactive waste expected to be generated by the new Naval Reactor Fuel Materials Facility (FMF) and assesses the compatibility of this waste with the proposed greater confinement disposal facility (GCD).

The FMF will start up in 1986-1987 and will produce about 25,000 cubic feet (700 m^3) of solid waste annually, containing five kilograms of very highly enriched uranium (VHE) which is inseparable from the waste and is regarded as scrap. Of this waste, 5000 cubic feet (140 m^3) will contain four kilograms of VHE in a sludge that also has a high nitrate content. This sludge will be either solidified in cement, placed in drums and disposed of in the GCD, or it will be disposed of as saltcrete in a landfill operation similar to or the same as the operation for the saltcrete from the DWPF process. The remaining 20,000 cubic feet (560 m^3), containing one kilogram of VHE, will be disposed of by a combination of incineration and shallow land burial. Ash from the incineration of combustible material will be solidified in cement, drummed and placed in the GCD. The noncombustible fraction will be placed in shallow land burial. All stabilized waste from the FMF will be compatible with emplacement in the GCD.

The GCD will be a near-zero release facility. Waste containers will be stabilized to prevent future trench subsidence; burial will be deep enough to prevent root and animal intrusion. A compacted clay cap will be used to reduce water percolation to the waste forms. A GCD demonstration will be operated in the present burial ground in 1983. When the present burial ground is filled in the early 1990's, the next burial area will also contain a GCD facility that would suitably dispose of the FMF stabilized waste.

Description of FMF Solid Waste

The annual generation rate of radioactive solid waste from the FMF will be 25,000 cubic feet. The radioactivity in the waste results from unrecoverable highly enriched uranium (1.8 wt % ^{234}U, 97.3 wt % ^{235}U, and 0.9 wt % ^{238}U, at 1.153×10^{-4} Ci/g), amounting to 5 kg of VHE uranium, or 0.57 Ci disposed of per year, Table 62. The waste will be in three forms: sludge, combustible waste, and noncombustible waste.

Sludge

About 80% of the VHE uranium, or 4 kg, will be in the sludge that will result from the evaporative treatment of the process water waste from the FMF. The specific activity of the sludge is 2.2 nCi/g, Table 63. About 3000 gallons of process water waste will be produced per day, which will contain significant quantities of nitrate, aluminum, and sodium ions. A study by the wastewater can be evaporated at a pH of 8 to a residue that makes good saltcrete. The composition of the waste water prior to evaporation is expected to be:

Ion	Mols/Day
F^-	640
Cl^-	610
NO_3^-	4925 (310 kg/day)
Al^{+++}	1270 (34 kg/day)
NH_4^+	950
Na^+	2200 (53 kg/day)
H^+	1170
Organics	360
OH^-	1780

TABLE 62

Specific Activity of FMF Uranium

Isotope	Wt %	Half Life, y	Curies in one gram of Mixture	Activity, %	Grams Disposed Per Year	Curies Per Year
^{234}U	1.8	2.4×10^{5}	1.11×10^{-4}	98.2	90	0.56
^{235}U	97.3	7.0×10^{8}	2.1×10^{-6}	1.8	4865	0.01
^{238}U	0.9	4.5×10^{9}	3.0×10^{-9}	0.003	45	1.5×10^{-5}

TABLE 63

Specific Activities in the FMF Waste

Sludge

5000 cubic feet of sludge containing 4 kg VHE uranium, density 1.5

Specific activity = 2.2×10^{-9} Ci/g
= 2.2 nCi/g

In cement, sludge is 30% by weight; density = 1.8

Specific activity = 0.5 nCi/g

Combustible Waste

12,000 cubic feet containing 0.6 kg VHE uranium, density 1.0

Specific activity = 0.2 nCi/g

When incinerated, volume reduction 1/20, and when stabilised in cement, volume ratio ash/cement = 0.2:1

Specific activity in cement = 4 nCi/g

Noncombustible Waste

8000 cubic feet containing 0.4 kg VHE uranium, density 1.5

Specific activity = 0.14 nCi/g

A volume reduction of a factor of 20 is achieved by evaporation. The residue sludge, which is to be mixed with cement, will contain:

Ion	Percent in Sludge
F^-	20
Cl^-	60
NO_3^-	100
Al^{+++}	100
NH_4^+	100
Na^+	100
Organics	0

When cement is added to the residue, all the ammonia will be released. The crush strength of the concrete after a setup time of 28 days was measured as 2000 psi. The appearance and setup times of the concrete are equivalent to those of good saltcrete made previously at SRL.

The pH of the residue used to make good saltcrete can range from two to 13, and the salt content can be as high as 56% by weight of the cement. A 30% by weight mixture of sludge in concrete is used to determine the volume of waste to be emplaced.

Combustible Waste

The bulk of the waste, 12,000 cubic feet, will be combustible waste containing about 0.6 kg of VHE uranium each year. This waste, because of its very low specific activity, should be readily incinerated. By 1986 to 1987, the beta-gamma incinerator will be operating on contaminated plant waste. The specific activity will be about 0.2 nCi/g in the bulk waste, and 4 nCi/g in the ash.

Noncombustible Waste

The annual production of noncombustible waste will be 8000 cubic feet, containing 0.4 kg of VHE uranium, with a specific activity of 0.1 nCi/g. At this very low level of activity, it will not be economically justifiable to decontaminate the waste to a lower level.

It is probable that a fraction of the process-generated waste described above will not be separable into combustible and noncombustible fractions. Criticality considerations mandate that the

FMF process be conducted in many small hoods, with small lines and small tanks and valves. It will be difficult, during cleanup operations, to separate the small pieces of combustible waste from the noncombustible. However, by 1986 to 1987, waste generators will be required to expend considerable effort on partitioning their waste into combustible and noncombustible fractions. For the purpose of this document, it is assumed that the partitioning of the process waste into the two fractions will be accomplished.

Method of Disposal

The present inventory of enriched uranium in the SRP burial ground, in trenches, is 320,000 cubic feet as of December 31, 1982. It contains 0.27 Ci of enriched uranium. The total inventory of depleted, natural, and enriched uranium that has been disposed of in trenches is over one million cubic feet, Table 64. If the FMF waste were not treated by volume reduction or stabilization, the present volume of enriched uranium waste in the burial ground would increase by 8% per year, and the curie content by 200% (because of the high specific activity of ^{234}U in the VHE uranium). However, the FMF waste will be treated because:

- The sludge contains a large amount of nitrate. It will have to be stabilized and placed in a GCD or a saltcrete landfill.
- Volume reduction processes will be operable by the time the FMF starts up. Incineration will be standard operating procedure.
- Improved methods of waste disposal, such as the GCD, will also be standard operating procedure.

The expected treatment and disposal of the FMF waste is described below. A summary is given in Table 65.

Sludge

The sludge created by evaporation of the FMF process water waste stream will produce good saltcrete. The sludge will be mixed 30% by weight with cement and water, and either (1) placed in steel drums in a GCD facility, or (2) in a saltcrete landfill similar to the landfill planned for the DWPF saltcrete.

The generation rate of drums will be about 3000 per year. After emplacement in the GCD facility, the drums themselves will be encased in concrete, covered with at least 16 feet of clay, 2 feet of which will be compacted to reduce water percolation to the waste.

TABLE 64

Inventory of Uranium Waste in SRP Burial Ground in Trenches, as of December 31, 1982

Uranium Waste	Volume, ft^3	Curies
Depleted	308,000	46 *
Enriched	320,000	0.27
Natural	935,000	3.0
Totals	1,560,000	49

---

* Contains some fission products

TABLE 65

Disposal of Annual Production of FMC Solid Waste

Type of Waste	Volume, ft^3	VHE, U kg	Container	Drums/yr*	Waste Treatment	Drums/yr After Treatment	Final Deposition
Process Waste							
Combustible - paper, clothes, gloves, shoe covers, etc.	12,000	0.6	Steel drums or boxes	1800**	Incineration, stabilized in cement	100	GCD
Noncombustible - valves, glass, metal pipe, tools	8,000	0.4	Steel drums or boxes	1200**	None	1200	Shallow land burial
Sludge							
From treatment of process water	3,000† gal	4††	Steel drums or concrete monoliths in saltcrete trench	-	Stabilize in cement	3000¶	GCD, or saltcrete trench

---

* Drums per year if no waste treatment

** Seven cubic feet per drum

† 5000 cubic feet per day

†† Assume 80% of VHE uranium is in sludge

¶ 2200 drums/year if 50% sludge mixture in cement; 3300 drums/year if 30% sludge in cement

If placed in the reference design saltcrete landfill, the FMF saltcrete would fill about 30 linear feet of trench a year, taking 4.6 years to fill up the standard length trench of 135 feet.

This amount of nitrate to be disposed of per year in the FMF sludge is large — 1.1×10^5 kg. This value is one-tenth of the amount of nitrate plus nitrite that will be disposed of each year in the DWPF saltcrete process. A comparison of the two saltcretes is given below:

Source	Input, gpm	Nitrate/ Nitrite, ppm	Radionuclides, nCi/g	Nitrates Emplaced, kg/yr
DWPF saltcrete	10	8,600 NO_3 2,600 NO_2	55	11.5×10^5
FMF saltcrete	2.1	27,000 NO_3	0.6	1.1×10^5

Both saltcretes are classified as low-level waste. The DWPF saltcrete contains 26 different radionuclides at 55 nCi/g, while the FMF saltcrete contains three radionuclides at 0.6 nCi/g. The DWPF saltcrete will be formed with cement, clayey soil, and Possolith. It will have a permeability of 5×10^{-7} cm/sec, and will be placed in a landfill with 16 feet of clay cover that includes a compacted clay cap. The low permeability of the saltcrete ensures that the drinking water standards for nitrates and nitrites in the groundwater beneath the landfill will be met.

Present plans for the FMF saltcrete are that it will be formed with cement with a permeability of about 10^{-7} cm/sec. If placed in a saltcrete landfill, the formulation of the FMF saltcrete will be changed to be the same as the DWPF saltcrete, with a permeability of approximately 10^{-10} cm/sec.

Combustible Process Waste

The 12,000 cubic feet of combustible waste will be incinerated with a volume reduction of 20. The ash will be stabilized in cement with a volume increase of about 20% and placed in galvanized steel drums. The annual production of filled drums will be about 100. This waste form will be placed in the GCD facility to ensure confinement of the ash.

Noncombustible Process Waste

The noncombustible waste, 8000 cubic feet containing 0.4 kg of VHE uranium, will have a low specific activity of 0.14 nCi/g. Decontamination will not be required. The waste will be placed in steel drums or boxes in a shallow land burial area of the burial ground. If the waste is drummed, there will be 1200 drums per year emplaced. If a trench efficiency (volume of trench space/volume of waste) of four is used (currently the volume is about seven), about 100 linear feet of standard trench will be used per year. The drummed waste will be covered with at least four feet of soil.

COMPATIBILITY OF FMF WASTE WITH THE GCD FACILITY

The solid waste from the FMF that is in the form of stabilized ash in drums, and sludge stabilized in cement in drums, will be compatibile with placement in the GCD facility.

A Capillary Barrier for a Dry Burial Environment

INTRODUCTION AND SUMMARY

This report describes a capillary barrier to reduce rainwater infiltration into the proposed saltcrete landfill. The barrier, a subsurface gravel layer installed over each saltcrete trench (Figure 60), interrupts the natural capillaries in the unsaturated soil which transmit infiltrating water from the surface to the water table. Under unsaturated conditions, which normally exist from just below the soil surface down to the water table, a subsurface gravel layer will divert most infiltrating water around the buried saltcrete.

The most environmentally significant components of DWPF saltcrete are soluble, nonradioactive salts which will not decay during long-term confinement, as will radionuclides. Efforts to achieve total containment would, therefore, perpetuate the possibility of a massive salt release in the event of containment failure. The saltcrete landfill is, accordingly, designed to allow slow, controlled release at an acceptable rate. To maintain groundwater quality the landfill will have no function for many hundreds of years.

The low water permeability of the saltcrete matrix will restrict salt release to acceptable rates.[17] By reducing the amount of moisture that contacts the buried saltcrete, the capillary barrier will provide additional assurance of slow salt release. Principal advantages of the gravel layer capillary barriers are:

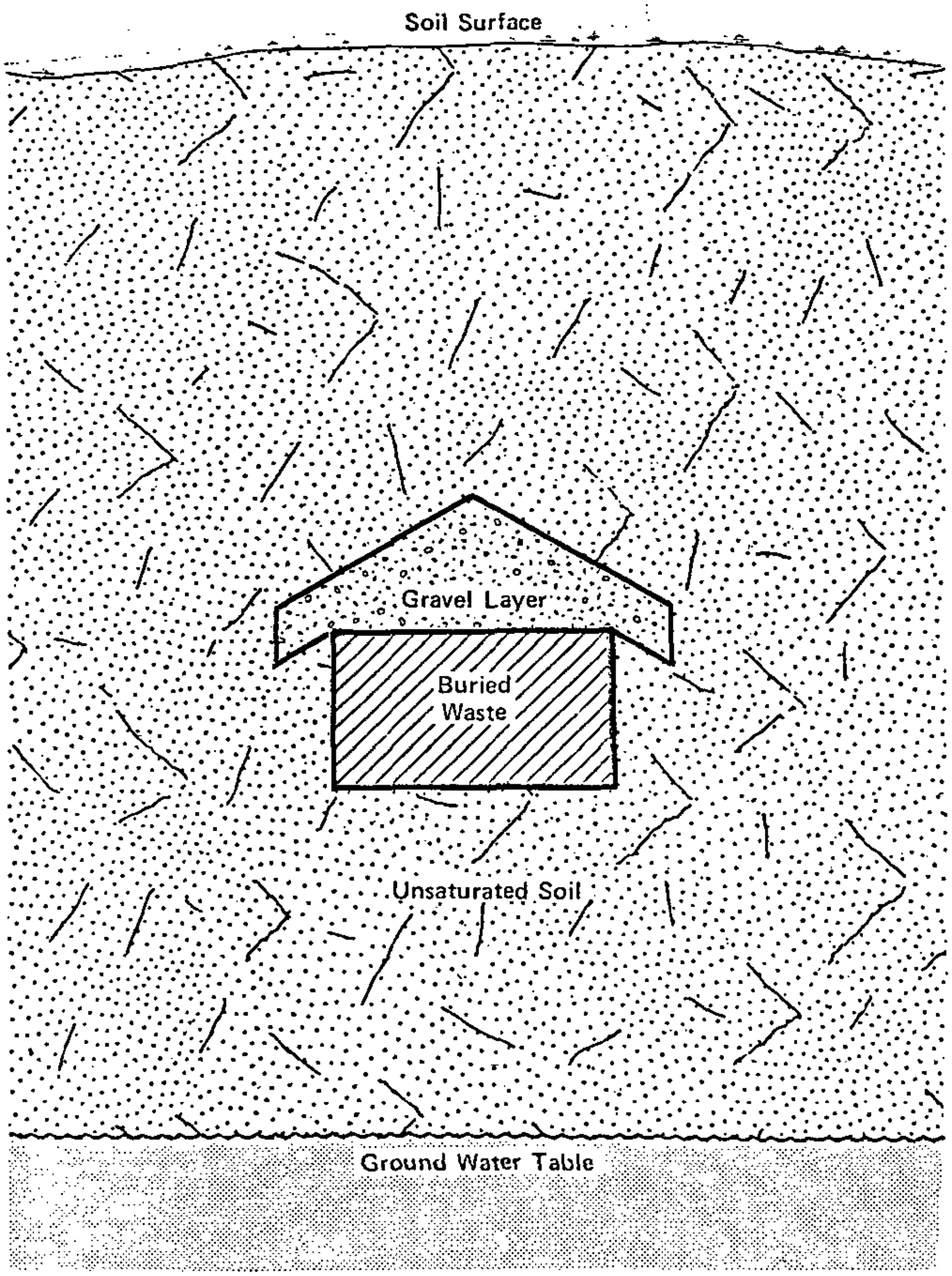

FIGURE 60. Gravel Layer Capillary Barrier

1. Durable material; the gravel itself will not degrade during long-term burial as will man-made barrier materials.

2. Durable structure; displacements due to backfill settling that could crack a clay barrier will not disrupt the gravel layer.

3. Long effective life; soil fines may in time illuviate downward and decrease the gravel layer's effectiveness. However, this is preferred to the more disruptive cracking failure of a clay layer or of man-made materials.

4. Familiar installation techniques; the gravel layer requires only simple, familiar techniques and equipment for installation.

Principal disadvantages are that capillary barriers are unfamiliar to most persons outside the soil physics community and that field experience in their design and construction is lacking.

UNSATURATED FLOW PRINCIPALS

To better visualize how a capillary barrier works to provide the desired environment for saltcrete burial, consider how infiltrating rainwater moves downward through unsaturated soil. The unsaturated zone normally extends from the soil surface to the groundwater table. Its depth or thickness varies from zero in wet, swampy areas where groundwater is at the surface, to many feet in high uplands. It averages about 40 feet at the SRP burial ground and more than 60 feet at sites being considered for saltcrete burial. The identifying characteristic of the unsaturated zone is the presence of both air and water in the soil pores. This contrasts with all water and no air in saturated soil, as exists below the groundwater table.

Most solids throughout the United States are composed predominantly of mineral particles that include sand, salt, and clay-size particles. The pores between the particles also range from very small to relatively large, depending on the size distribution and arrangement of the particles. An important feature of soil pores is that they are interconnected in all directions. Thus, the soil pore space is a three-dimensional network of large, intermediate, and small pores. It is through this network of pores that infiltrating rainwater travels to the groundwater table.

During heavy rainfall, water often accumulates temporarily on level areas and a thin layer of soil at the surface may become saturated. However, this condition seldom extends more than a few centimeters below the surface. From that depth to the water table the soil remains unsaturated, with both air and water occupying the soil pores.

At the saturated surface, water fills all of the soil pores. Under this condition the water pressure equals atmospheric pressure. With increasing depth, the soil water pressure rapidly becomes less than atmospheric, or negative, as the available water (limited by the soil's permeability) is insufficient to satisfy the capillary attraction or suction forces of the small pores. Thus, at a shallow depth, saturation gives way to unsaturation, and the larger, noncapillary soil pores become air-filled as water occupies only the capillary pores. The slow, downward movement of the water continues due to gravity, but it is confined to the capillary size pores due to their water-attracting forces, or more properly to the soil's matric potential. So, unsaturation prevails from a shallow depth below the surface all the way down to the water table.

With continued infiltration the temporary surface ponding disappears and even the surface soil becomes unsaturated as air enters the larger pores there. With time, drainage throughout the soil's depth empties progressively smaller capillary pores and the pressure of the water remaining in the soil becomes increasingly negative. Within four or five days following rainfall, a condition force of gravity on the remaining soil water is balanced by the capillary forces holding it in only the smaller pores. All pores larger than those capable of holding water by capillarity against the force of gravity will have drained and become air-filled, and all smaller pores will remain water filled. Essentially no further downward flow then occurs until more infiltration is received.

HOW A CAPILLARY BARRIER WORKS

It is important to bear in mind that water in the unsaturated zone exists under negative pressure. This means that it cannot flow from unsaturated soil into uncapillary voids. It is confined entirely to the soil's capillary size pores. Only if the soil becomes saturated can the soil water flow into noncapillary voids.

Thus, a layer of coarse-pore gravel in unsaturated soil can form a barrier to water flow through the soil's capillary pores. The gravel layer's noncapillary pores interrupt the vertical continuity of the water-conducting capillaries in the soil, and unsaturated flow cannot proceed across the barrier. The water then must follow one of the two courses. It may divert laterally in the soil above the gravel layer to maintain unsaturated flow bypassing the barrier and the zone immediately under it. A sloping top surface on the gravel layer facilitates this. Or the water may accumulate in the soil above the barrier until saturation is reached (soil water pressure equals atmospheric), after which it can leak from the soil into the large gravel pores by saturated flow.

Both of these soil water phenomena are observed above naturally-occurring clay lenses. Unsaturation is maintained in the soil where the clay lens is small or where its top surface slopes to facilitate lateral flow around the lens. But where the clay lens is extensive and flat-topped, an intermittent perched water table may develop.

In its field application, a capillary barrier of optimum design can be expected to divert water by unsaturated flow around it most of the time. Prolonged, very heavy rainfall, as occurs infrequently, may result in saturation and leakage across the barrier. An important feature, however, is that following leakage, as infiltration declines, unsaturated conditions return in both the soil and the gravel layer, and the capillary barrier resumes functioning as effectively as before.

The capillary barrier principle, while not familiar to many outside the field of Soil Physics, has been understood for many years. It was described in 1917 by Alway and McDole[18] who observed that the soil above a noncapillary sand layer had a higher water content than did a similar soil without the sand layer. Subsequent investigators[19 20 21] explained the effect of a gravel layer's size, its top surface slope, and the above-gravel "wick" soil's hydraulic conductivity on maintaining unsaturation. They also suggested applications for capillary barriers which included reducing infiltration into buried waste.

Recent investigators have included capillary barriers in field studies aimed at improved burial for radioactive waste. Rancon[22] reported no appreciable moisture transport across the soil-gravel interface during five years of rainfall and irrigation on a capillary barrier field test at Cadarache, France. DePoorter, et al[23] have in progress a field test of capillary barriers to control the transport of radionuclides both upward and downward from buried waste under arid conditions. No results have yet been reported. Another field study was recently initiated by Johnson et al[24] to compare the performance of capillary barriers with other waste trench caps under humid conditions. No data are yet available.

In 1976, Frind, Gillham, and Pickens[25] made a computer-modeled study of capillary barriers for excluding infiltration from buried waste. They simulated the performance of gravel layer barriers in soil under transient soil water conditions with variables of seven gravel layer geometries, two soil textures, two water fluxes, and two soil-water volumes, for a total of 56 different combinations. They maintained the width of the protected waste at 6 meters, and they sloped the upper soil-gravel interface, as shown in Figure 60, to enhance lateral flow around the barrier.

These investigators reported that when heavy infiltration caused leakage, the gravel layer and the soil above it dried out during the subsequent period of reduced infiltration and the system resumed unsaturated functioning without loss of effectiveness.

Their conclusions were that a capillary barrier would act as an umbrella over buried waste to exclude all infiltration except that caused by prolonged, heavy rainfall, normally of infrequent occurrence.

A computer-modeled gravel layer capillary barrier 14 meters wide was recently evaluated under steady-state soil water conditions by INTERA. A barrier this large is adequate to protect large-scale saltcrete burials in the field. INTERA's results showed no significant infiltration penetrating the barrier under SRP rainfall conditions. Nitrate leached from the saltcrete under the gravel layer to the groundwater leached less than 1% of the allowable concentration in drinking water.

LABORATORY TEST

To gain hands-on experience with a gravel layer capillary barrier, a laboratory test was operated using two 55-gallon drums of SRP burial ground soil, as shown in Figure 61. The test drum contained a subsurface layer of medium gravel (0.5 to 1.0 inch diameter), and the control drum contained no gravel. Each drum contained 0.5 pound of NaCl to provide chloride for water tracing. A water sprinkler above each drum was timer-controlled to supply 0.13 inches of simulated rain daily. This was more than three times the average rate of infiltration at SRP. No runoff occurred and evaporation was prevented by plastic covers over the drums. Percolate water effluent from each drum was collected daily and analyzed for chloride.

The test operated for 37 days, and results are shown in Figure 62. During that period no chloride was detected in effluent from the test drum. Approximately half of the NaCl leached from the control and was accounted for as chloride measured in the effluent. These results show show that soil water did not leak into the gravel layer in spite of sustained high infiltration. The drum test effectively demonstrated the capillary barrier's operation under low stress conditions.

To observe the performance of a capillary barrier under field conditions, a larger scale test was recently put in operation. The test utilizes two 6 feet in diameter by 10 feet deep field lysimeters of clayey sand at the SRP burial ground. The test lysimeter contains a subsurface gravel layer 3 feet in diameter and 2 feet

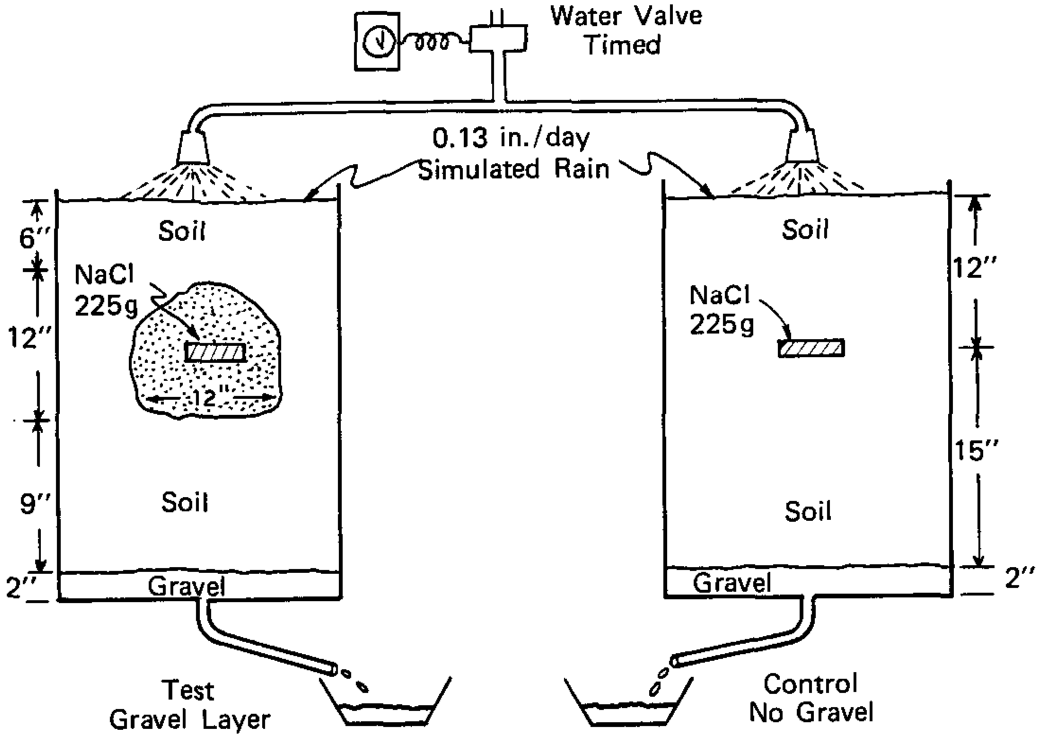

FIGURE 61. Laboratory Test of Capillary Barrier

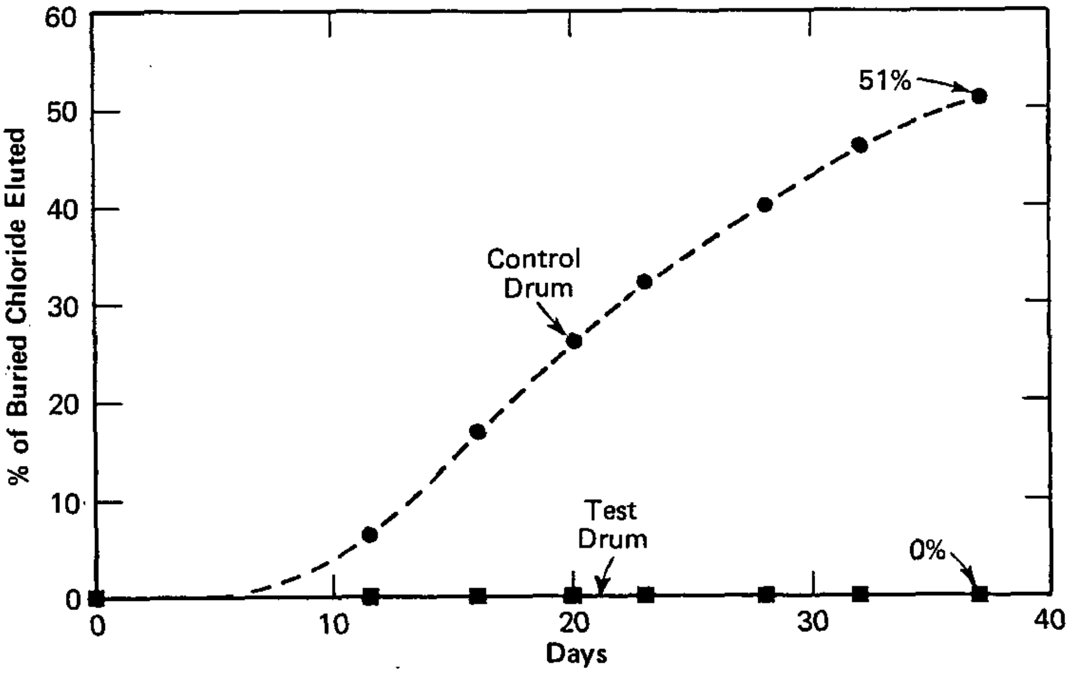

FIGURE 62. Results of Laboratory Test of a Capillary Barrier

thick, 2 feet below the soil surface. The control lysimeter contains no gravel. Each lysimeter contains one pound of solid NaCl implanted 4 feet below the soil surface as a source of chloride for water tracing. Except for their larger dimensions the lysimeters are similar to the drums shown in Figure 61. More importantly, the lysimeters receive only natural rainfall, and ambient evaporation is unrestricted. At the time of this writing, the field test has operated for two months and rainfall has produced only a small volume of effluent from each lysimeter. No chloride has yet been detected in either effluent, and the test is continuing.

In addition to the continuing lysimeter field test, a larger pilot-scale field test is being installed. This test will utilize real saltcrete mixed from SRP waste Tank 24H supernate to form three 5 x 10 x 15 foot blocks which will be buried for comparative leach testing. A gravel layer capillary barrier with sloping top, covered with 5 feet of soil, will be installed above one of the buried blocks. The second block will have a protective clay cap. The third block will have no protective cap and only soil cover. Individual, Hypalon-lined troughs will be installed 5 feet below each buried saltcrete block to collect all infiltrating rainwaters from the vicinity of the block. The test will receive water only from rainfall. Performance of the two caps and the unprotected block will be evaluated on the basis of leached salt concentrations in the water collected. The test will begin operation in March 1983.

Contaminant Release from Saltcrete

INTRODUCTION AND SUMMARY

Saltcrete buried in a landfill in the unsaturated zone will be leached by two mechanisms. One is a mechanism controlled by the diffusion of salts out of saltcrete. The second mechanism is dissolution and removal of salts from the saltcrete by permeating water. The second mechanism has been the object of much study during the past two years because of its potential to dominate salt releases from saltcrete.

Recently a new saltcrete formulation has been developed which has a very low permeability (2 to 5 x 10^{-10} cm/sec). Computer modeling of landfill designs containing this low permeability saltcrete shows that the permeation mechanism has been reduced so that NO_3^-/NO_2^- released by this mechanism will be well below the EPA drinking water limit. Other waste constituents are also released at acceptable rates by this mechanism, Table 66.

Leach testing by immersing saltcrete specimens in water has given leach rates of 10^{-5} g/cm^2/day. For the realistic case of leaching in the unsaturated zone (e.g., for waste above the water table) there is good documentation to show that diffusion release is one to two orders of magnitude slower than for immersion in water. Therefore, 2 x 10^{-7} g/cm^2/day is a more reasonable leach rate to use for estimating diffusion controlled salt releases.

Release of waste constituents by the combined mechanisms will be at an acceptable rate, Table 66.

The values shown in Table 66 should be used as best current estimates of the performance of saltcrete in the reference disposal case. They will be updated periodically as further experimental work is completed.

RESULTS AND DISCUSSION

Permeation Mechanism

The permeation mechanism for leaching saltcrete has been the mechanism of greatest concern because water moving through saltcrete in laboratory tests come out nearly saturated with salts. These solutions contain up to 31 wt % $NaNO_3/NaNO_2$. To meet the drinking water standard for N (3.2 ppm for the DWPF mixture of $NaNO_3$ and $NaNO_2$), such a solution would require a 17,000 fold dilution. This means that only one part in 17,000 of the rainwater infiltrating the disposal site (6 x 10^{-5} fraction) could flow through the saltcrete and that the remainder must flow around the saltcrete and be available to dilute the saturated solution.

TABLE 66

Release Rates of Waste Constituents

Element (Unit)	Concentration in Saltcrete	Permeation Controlled Release	Diffusion Controlled Release	Total Groundwater Content	Drinking Water Standards*	Concentration in McQueen's Branch**	Concentration in Upper Three Runs Creek at F Road†	Concentration in Upper Three Runs Creek at the Savannah River (Plant Boundary)††
N (ppm)	11,200	0.03	0.02	0.05	3.2	4×10^{-3}	6×10^{-5}	3×10^{-5}
F (ppm)	90	2×10^{-4}	2×10^{-4}	4×10^{-4}	1.4	3×10^{-5}	4×10^{-7}	2×10^{-7}
Cr (ppm)	50	1×10^{-4}	1×10^{-4}	2×10^{-4}	0.05	2×10^{-5}	2×10^{-7}	1×10^{-7}
Hg (ppm)	0.004	1×10^{-8}	1×10^{-8}	2×10^{-8}	0.002	2×10^{-9}	2×10^{-11}	1×10^{-11}
Ag (ppm)	0.0003	8×10^{-10}	6×10^{-10}	1.4×10^{-9}	0.05	1.2×10^{-10}	1.5×10^{-12}	9×10^{-13}
C_6H_6 (ppm)	180**	5×10^{-4}	4×10^{-4}	9×10^{-4}	0.35†	8×10^{-5}	1×10^{-6}	6×10^{-7}
^{90}Sr (pCi/L)	3×10^{5}	0.9	0.7	1.6	8	0.14	1.8×10^{-3}	1.1×10^{-3}
^{99}Tc (pCi/L)	2×10^{-7}††	50	40	90	900	8	0.1	0.06
^{129}I (pCi/L)	1×10^{5}	0.3	0.3	0.6	1	0.05	7×10^{-4}	4×10^{-4}
^{137}Cs (pCi/L)	1×10^{7}	35	29	64	200	5	7×10^{-2}	4×10^{-2}

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* EPA 570/9-76-003, National Interim Primary Drinking Water Regulations

** Based on measured flow rate of 2 cfs

† Based on measured flow rate of 150 cfs

†† Based on measured flow rate of 270 cfs

Intera Environmental Consultants, Inc., of Houston, TX, has modeled various saltcrete landfill designs for SRL to assess the fractions of flow through and around saltcrete. Intera calculations have shown that drinking water standards can be met by surrounding the former reference saltcrete composition (10^{-7} cm/sec) with low permeability clay (10^{-9} cm/sec). Intera has recently completed calculations using the low permeability measured for a new saltcrete formulations using the low permeability measured for a new saltcrete formulation in which SRP soil is substituted for a portion of the cement (5×10^{-10} cm/sec). These calculations show that for a saltcrete block alone, the flow through the block is only 9×10^{-6} of the infiltrating rainwater (giving 0.5 ppm N due to this mechanism). Protection of the block by a 10^{-8} cm/sec clay reduces the flow through the saltcrete further to 5×10^{-7} of the water infiltrating the landfill surface above clay cap (giving 0.03 ppm N). The values are well below drinking water standards. The new saltcrete formulation (5×10^{-10} cm/sec) covered by a clay cap (10^{-8} cm/sec) is the new reference disposal method. Estimated releases of some important contaminants are shown in Table 66.

Diffusion Mechanism

With the greatly reduced contribution from the permeation mechanism, diffusion controlled leaching becomes a potentially important contributor to the total release. Bulk leach rates of 10^{-5} g/cm^2/day have been measured for saltcrete in laboratory testing where saltcrete samples were immersed in distilled water. Calculation of $NaNO_3/NaNO_2$ releases from saltcrete in a landfill based on a 10^{-5} g/cm^2/day leach rate gives a groundwater concentration of 1 to 2 ppm N, which is below drinking water standards. This number is, however, unrealistically high for saltcrete in a landfill burial situation.

The 10^{-5} g/cm^2/day leach rate was measured in the laboratory by dipping saltcrete in water. In a landfill, saltcrete will contact much less water since it will be in an unsaturated zone. Also, the transportation of leached salts away from the saltcrete surface will be slowed because of the slow flow of water through the soil. This will cause a reduced concentration differential which will slow diffusion of salts from within the saltcrete. More importantly, since the saltcrete will be unsaturated the diffusivity of the salts through the saltcrete will be greatly reduced.

Particle phase diffusivities (unsaturated leaching) are commonly 10^{-1} to 10^{-4} times those of fluid phase diffusivities (saturated leaching test). Diffusivity of soluble salts and radionuclides through unsaturated clay layers have been measured and found to be a factor of 50 times less than fluid phase diffusivities. Thus, a bulk leach rate of 2×10^{-7} g/cm^2/day is more realistic for estimating salt releases from saltcrete in a landfill. Estimated releases from saltcrete by this mechanism are shown in Table 66. Unsaturated soil column leach tests which will allow only release of salts from saltcrete by the diffusion mechanism are being set up to verify this leach rate.

Quality Assurance

Intera Environmental Consultants were selected to do the landfill modeling from a number of well qualified companies based on written bids and proposals. Meetings were held with all interested SRL personnel and Intera personnel to input into the models. Leaching mechanisms were thoroughly discussed in these meetings. The material properties supplied to Intera by SRL were from well documented studies. The computer code used for the modeling was compared to other codes available and the results were similar.

Conclusion

The low permeability of the new saltcrete formulation makes leaching by the permeation mechanism so small that the diffusion mechanism becomes of possible importance. Therefore, estimates of salt and radionuclide releases from saltcrete have been made assuming both mechanisms, Table 66.

Calculation of releases of salts and radionuclides from the new saltcrete formulation in the unsaturated zone shows that the groundwater at the saltcrete landfill boundary will be well below drinking water standards for all chemicals and radionuclides.

AIRBORNE NUCLEAR WASTE DISPERSION DATA

The Atlantic Coast Unique Regional Atmospheric Tracer Experiment (ACURATE) interim report for the period March 1982 through September 1982 has been issued as DP-1651.

The calculated values for the F- and H-Area ^{85}Kr emissions for the period October 1982 through January 1983 have been received from the Environmental Analysis and Planning Division. Measured ^{85}Kr hourly emission data from H Area have been compared to the calculated hourly emission data for the period October 21 through November 11, 1982. The calculated values averaged 46% more than the measured values with a range between 38% to 68% for the five runs. All the fuel processed for these five runs came from SRP. The H-Area stack monitor has been recalibrated. Futher comparisons will be made when the H-Area data become available.

An ACURATE program review was held at the Savannah River Laboratory, Aiken, SC, on June 29, 1983. Plans were formulated for an orderly closing down of the five ACURATE ^{85}Kr cryogenic air sampling stations. Air Resources Laboratory (ARL) presented plots of the measured ^{85}Kr for each of the sampling stations for the period March 9, 1982, through April 15, 1983. AIRCO presented a summary of the recent cryogenic sampler malfunction at the Tarboro, NC, station. The sampler had a mechanical malfunction and failed to collect the ^{85}Kr for the period from June 3 through June 29, 1983. The equipment has been repaired, and the station is now back on line.

DEFENSE WASTE PROCESSING FACILITY

Summary

Design progress for the DWPF is proceeding satisfactorily. At the end of the quarter, the design is estimated to about 30% complete. Bechtel currently has about 370 employees assigned to the design effort.

Actual construction of the DWPF is expected to begin in early FY-1984 with some early site work planned for late FY-1983.

Revisions to the melter off-gas system resulted in an estimated eight-week delay in the project with mechanical completion currently anticipated for January 1988.

Vitrification Building

Seismic and structural design of the vitrification building remains on schedule. Detailed equipment location drawings were issued.

Several equipment rearrangements and minor building modifications were requested as a result of the review and studies. These include the following:

- Process steam condensate tanks are being relocated from outside the vitrification building to the south end of the first level west corridor to improve confinement and minimize potential exposure of personnel to radiation in the event of a process vessel coil leak.
- The process frit slurry tank is being relocated from the south end of the first level west corridor to an equivalent location on the third level as a result of changes in the concept of the frit handling system.
- The regulated chilled water system refrigeration machines are being relocated from the third level to the roof because of an increase in the size of the machines.

- An airlock is being provided from the roof to the maintenance and storage areas for the crane maintenance area vertical lift shielding door. This will provide a safer and more practical path for removing and supplying parts for the door and its mechanism.

- Other minor equipment rearrangements are being made as necessary to accommodate the above changes.

SRP Health Protection completed a study of the shielding requirements of the major walls for the tunnel and first level of the 221-S building. In general, the independent calculations confirm Bechtel calculations.

Rack Piping Studies

The current reference rack piping design is a vertical five lane array of pipe jumpers with in-line connectors with the operating nut above the pipe. Individual rack pipe jumpers cannot be removed unless all upper jumpers are removed first. Studies of methods of simplifying the design have been completed.

The revised scheme provides for in-line connectors in the top three positions and right-angle connectors in the bottom two positions. All connectors will be individually removable.

Process Vessel Ventilation Systems

The current design basis requires that vapors from formic acid containing tanks be segregated from nitric acid containing tanks. As a result the design provides for two 10-inch headers (formic and process vessel vent) with provisions for jumper connections at each vessel space. A formic acid vent condenser is provided to reduce the formic acid concentration in the exhaust air.

As a result of an SRL assessment of nitric and formic acid segregation requirements, the following recommendations will be incorporated into continuing DWPF design:

- Segregation of formic and nitric acid vapors in the remotely operated chemical process cell will not be required. The large formic acid vent header which runs the entire length of the chemical process cell will be depleted if economically justified.

- To maintain mercury and formic acid emissions as low as practical, the sludge receipt and adjustment tank, slurry mix evaporator, slurry mix evaporator condensate tank, and mercury water wash tank will continue to vent to the formic acid vent condenser (FAVC). Due to the close proximity of these tanks, this will result in a shorter, smaller header. Other formic acid containing tanks (spent frit hold, canister decontamination chambers, etc.) will vent directly to the process vessel vent header. Reduction of the air handling requirements for the FAVC may also result in reducing the chilled water requirements.

- The mercury vent condenser in the mercury purification vessel vent was deleted and the vent system connected to the mercury water wash tank to simplify equipment and reduce mercury releases to the atmosphere.

- Combine sample and mercury purification cell drains into a single header which drains to the recycle collection tank rather than using separate formic and nitric acid drains for each cell.

- For personel protection, the liquid and vapor streams for nitric and formic acids in cold feed areas will remain isolated as in present design.

Melter Off-Gas System

A study model of the melter off-gas system was completed by Bechtel and reviewed by Du Pont during April.

As a result of the model review, several changes to simplify the system were proposed. These changes reflect concerns about the complexity of some jumpers and the vulnerability of the 3-way valves in the present design.

To allow system simplification and elimination of three 3-way valves and eight 2-way valves, the design criterion for ^{137}Cs releases was relaxed from 0.3 mCi to 3 mCi/yr as permitted by the Environmental Impact Statement. This eliminates the need for two gas atomized scrubbers in series and allows the system to be divided into two parallel trains - one primary and one backup. Subsequently, to optimize the arrangement, Bechtel studied eight alternative equipment layouts. The layout selected for continuing design utilizes the area south of the melt cell which was occupied by the process vessel vent system. The vent system was relocated to the southern part of the chemical process cell.

This layout provides:

- Succeeding equipment located close together to minimize jumper complexity.

- Reduction in the length of the large 12-inch quencher discharge lines.
- More effective utilization of the space located south of the melt cell.

These changes also incorporated horizontal steam scrubbers (Hydro-Sonic®) which recent tests at ETF have shown to be three to four times more effective than the vertical gas atomized scrubbers previously specified.

This equipment rearrangement resulted in an estimated eight-week delay in project completion.

Canister Decontamination

Conceptual design of the DWPF canister decontamination unit is complete and detailed design has begun.

AES has transmitted to Bechtel the primary requirements for canister decontamination equipment arrangements, wall penetrations, and services. Bechtel has begun cell design and process flow drawings.

SRP has recommended canister decontamination conditions which have been transmitted to AES. The canister spot decontamination process, high pressure slurry blasting, has been changed to air-injected slurry blasting. This eliminates the need for a high pressure water system.

Inner Canister Closure

Equipment Engineering Department (EED) completed preliminary tests of inner canister closure (ICC) design and selected to design for process qualification. The selected design uses a 304L tapered plug and a Nitronic® 60 sleeve.

The tapered plug allows easy seating in a remote environment. However, both the plug and the sleeve can be pushed into the canister for the final weld closure.

Equipment Engineering Department (EED) has completed 40 of the 50 closures necessary for demonstration of the inner canister closure (ICC) process. Using a helium leak check test, all closures were water tight. However, the force required to press the sleeve and plug into the canister (making room for the final weld plug) varied from 37,000 to 106,000 pounds. The force appears to be a function of the design of the plug and sleeve, and the temperature difference between the plug and the sleeve at insertion. Although the design basis force for the DWPF push-in station is 150,000 pounds, EED is attempting to determine the specific factors which influence the push-in force and specify an ICC process which will result in less variation in the push-in force.

During normal pouring, some canister nozzles may not be hot enough to seal. Canisters filled on the drain turntable will be cool before the canisters can be sealed. Induction heating is being tested at ETF as a method of reheating the nozzles. It may be necessary to remove the plug and sleeve and use an alternative method for canister closure.

A method of verifying that the inner canister closure is water tight prior to decontaminating the exterior of the canister is required (water entering the canister might result in stress corrosive cracking). Helium leak checking has been demonstrated in an acceptable method. However, helium leak checking in a remotely operated canyon facility will be difficult. To perform that task, EED is assembling a rate of pressure rise (decay of vacuum) leak tester. Southwest Research Institute is testing loss of pressure methods (pressure is applied above the seal and inleakage is measured).

Currently Bechtel is designing the ICC reheat/seal verification station using induction heating and decay of vacuum as the reference process. Drawings issued for review are scheduled for December 1983.

Computer and Distributed Control System

General distributed control system (DCS) specifications were prepared to standardize equipment for DWPF, two JB-Line improvement projects, and the Naval Fuels Program. A general DCS specification and an addendum for each project will be sent to the vendors; Fisher Controls, Foxboro, Honeywell, EMC, and Beckman Instruments. The bid packages will also contain a general specification for a separate programmable logic controller (PLC) with an addendum for each project because some of these vendors must bid separate PLC with their equipment. The general DCS and PLC specifications have been reviewed at SRP by the Process Digital Equipment Committee. The schedule for 1983 is as follows:

- Early May — issue bids for DWPF
- June — issue bids for JB-Line projects
- September — select a common vendor

Bids for the Naval Fuels Program are not scheduled to be issued until late November 1983, but the same vendor will probably be selected since the general specifications will contain the capabilities needed for all four programs.

The DWPF bid package will contain documentation for the sludge receipt and adjustment tank as an example since documentation for the entire process will not be available.

Bid packages for the distributed control system (DCS) were issued to five prospective vendors on May 6. The vendors were Beckman, EMC Controls, Fisher Controls, Foxboro, and Honeywell. Beckman subsequently declined to bid. Prebid clarification meetings with the four remaining vendors were held in San Francisco during the week of May 23. Bechtel has extended the bid due date from June 15 to July 5. The bids will be evaluated based on the requirements of the five SRP projects.

Weld Test Cell Instrumentation

The weld test cell operation is unusual in that actual operation of the major equipment occurs only for one and one-half seconds during canister welding. During this welding period, most of the data necessary for diagnostic and historical purposes must be gathered. It is planned to use a high-speed data acquisition system (DAS) that will record almost all parameters, derive certain parameters (e.g., ram velocity and acceleration), plot desired graphs, print hard copy report, and transmit data for quality assurance and historical purposes directly to the computer for storage. In addition, an oscillograph (high speed, oscilloscope-based plotter) will be used for particularly fast moving parameters such as voltage and current wave forms. Most of the parameters will be directly recorded in the data acquisition system (DAS) memory. That is, analog signals from the sensors will be digitized by a data conditioner and entered directly into memory. Manual entry will be necessary for only a few parameters.

Glass Frit Handling

Bechtel has completed preliminary equipment selection and layout for the receipt and handling of frit in tote bins. A warehouse area for bin storage and an area for slurry makeup are required. The warehouse is 50 feet x 60 feet and houses 160 bins, a floor scale, and a bin cleaning area. It provides rain protection and is not provided with heating or air conditioning. The slurry preparation area is 24 feet x 50 feet x 60 feet high. This area houses a bin inverter, delumper, bucket or belt elevator, screener, magnetic separator, weigh bin, and slurry makeup tank. This area is heated for freeze protection only. Both areas are to be located just outside the east side of 221-S and south of 210-S to minimize pumping distances to feed tanks inside 221-S. In early May, Bechtel is to complete an estimate of cost and schedule impact for this change.

Exhaust Air Stack

During May, Bechtel, AES, SRL, and DWPF liaison established criteria for calculating the Zone 1 (chemical process cell) exhaust air stack dimensions. These criteria were:

- An eructation of the sludge receipt and adjustment tank will be the design basis accident.
- Accident spill volume is based on the suspension of 100 mg material per cubic meter of cell atmosphere.
- Accident duration is 15 minutes.
- Maximum allowable ^{238}Pu concentration at air intakes on 221-S roof is 2×10^{-12} μCi/cm^3.
- Dispersion calculations will be based on meteorological data from the H-Area weather tower.
- Coning stack top is acceptable to increase air exit velocity and plume rise.
- NRC Regulation Guide 1.145 is basis for design.
- Reduction of activity from fallout or plating in transient through tunnels is not assumed.
- Sand filter efficiency is assumed to be 99.97%.
- Air flow through the stack is 100,000 cfm.

Subsequently, it was determined that the exhaust stack would be 151 feet in height.

Cooling Towers

Current design provides for two cooling towers. One tower is dedicated to process usage (86°F water), the second to H&V (95°F water).

Due to recent changes in the process cooling water requirements, the process tower water flow increased from approximately 1200 gpm to 2700 gpm. At the same time the H&V tower flow decreased from approximately 6000 gpm to 5000 gpm. The process cooling tower and the H&V cooling tower were combined to reduce costs.

Water Wells

The current design provides for use of raw, untreated well water as cooling water in the event of loss of the cooling tower. The increased cooling water demand discussed above also resulted in significant increase in the emergency cooling water requirements. Based on the emergency water requirements the capacity of the two 1000 gpm wells was increased to 1500 gpm. No changes in well casing diameter or depth will be necessary; larger pumps will be required.

Saltstone

A draft Basic Data Report for the saltstone project was issued for comment.

During May a decision was made to change from a "fixed" to a "transportable" mixing plant for saltstone. The primary reason for the change is due to the high shear stress (600 dynes/cm^2) and pumping difficulties experienced recently with the new saltstone which includes soil in the formulation. Initially, the new saltstone exhibited a shear stress of about 1100 dynes/cm^2, but this was reduced to 600 dynes/cm^2 by increasing the salt solution-to-solids ratio by about 15%. These values were confirmed in tests by both SRL and the Engineering Test Center. Also, use of various commercial additives produced no significant additional improvement in saltstone properties above what had already been achieved with the Pozzolith 122-R in the formulation.

Pumping saltstone grout with a shear stress of 600 dynes/cm^2 through very long (2000 to 3000 feet) pipe lines would require high pressures, cause excessive pump wear and the pipe line would be difficult to clean (following production outages) before grout set-up occurs. With a transportable mix plant, the saltstone mixer would be postitioned near the trench being filled, thus alleviating problems by reducing pumping distances to less than 500 feet.

During tests simulating continuous mixing with a 5 to 6 minute residence time in a high-dispersion type mixer at the Engineering Test Center, the shear stress of saltstone grout rose gradually to an excessive 2000 dynes/cm^2. The action of the mixer in breaking up clay particles in the soil and the subsequent action of the NaOH in simulated waste solution on the clay is suspected as the cause of the thickening of the grout. Further investigation is planned, including the effect of residence time as well as changing the type of mixer.

Operations and Patrol Guardhouse Buildings

AES was requested to separate the operations and patrol guardhouse facilities into two separate buildings. The decision to separate the facilities was made because of recent decisions to subcontract plant security forces and to provide additional hardening of existing guardhouses.

The additional hardening of the guardhouse to a UL Class IV structure is consistent with increased plant security. The Operations Building (704-S) will be expanded to include additional offices, training rooms, and a room to display the models used by Construction. Revised basic data were submitted to AES during July for the Operations Building.

DWPF Mockup Facilities

A decision was made to provide DWPF equipment mockup facilities in Building 717-F. Placement of the mockup in the high bay of 717-F building will require moving Separations shop equipment, including jumper fabrication facilities, to revised or new facilities. In addition, DWPF jumper fabrication and pump and agitator run-in facilities will be included.

Basic data for developing a cost estimate were transmitted to AES during July.

Quality Assurance

Quality Assurance assessment of the DWPF continued during the quarter.

A Defense Waste Processing Facility Project Quality Assurance Plan was approved during May. The plan was transmitted to DOE in June for acknowledgement.

Three Quality Assurance training sessions were held for personnel in the SRP and San Francisco DWPF liaison groups. Training was provided for 27 members of the liaison groups. The training emphasized the new site and project QA Plans and the application of QA to normal work activities.

SAVANNAH RIVER INTERIM WASTE OPERATIONS

LIQUID WASTE STORAGE OPERATIONS AND RELATED ACTIVITIES

Surveillance and Maintenance

F-Area Pump Tank 3

Pump Tank 3, which receives high-heat waste from the canyon, was down from April 10 to April 22 due to an open circuit in the pump electrical contacts. The Shielded Crane Manipulator was used to investigate the problem and to install a new electrical jumper in FPP-3.

Waste Tank Purge Condenser Shell Pitting

Ultrasonic thickness measurements by EED (in lieu of hydrostatic testing) have detected pitting in some of the waste tank purge condenser shells. The condensers with the most severe pitting serve Tanks 9H and 11H in H Area. These condensers have a design pressure of 75 psi and a current operating pressure of 45 to 50 psi. A stress analysis was recently completed for Tank 9H condenser by EED which indicated there is no fracture potential unless an array of pits develops (especially if the array is along a longitudinal axis). An array of pits has not been detected on any condenser, and so no immediate safety concern exists. Semi-annual inspections have been established in the Waste Management Operations (WMO) tickler system for Tank 9H through 16H condensers to monitor for any increase in pit depth or the development of an array of pits. A reassessment of the condition of the condensers will be made in August.

Tank 9H Cooling Coil Leak

A failed cooling coil (No. 10) was discovered on May 2 in Tank 9H. A steady decrease in the east surge tank level at a rate of 6 gph was first noticed in early March, and approximately 9000 gallons leaked into Tank 9H before the failed cooling coil was located. This is the ninth vertical cooling coil failure in Tank 9H leaving 25 unstable cooling coils. The radiolytic heat generation in the tank is low, and no problems in cooling the waste are expected.

Tank 41H Supernate Samples

On April 22, a 100 mL dip sample taken from Tank 41H, a concentrate receiver, indicated that the 1.1 million gallons of supernate was above the Technical Standard limit of 5.5M HNO_3^-. However, variability within the analyses and a recheck one month later suggest that the real problem is in sample handling and/or the analytical technique. Three analyses of the original sample varied between 5.5M and 7.0M NO_3^-. Such variability has been experienced before. The recheck was made after 443,000 gallons had been removed and 57,000 gallons of new concentrate added. The nitrate was well within the limit of 2.5M. Such a change in content is very unlikely. Therefore, Waste Management Technology will review sample handling and analytical techniques to determine if changes are appropriate. Even if the original samples were correct, risk of stress corrosion cracking of the tank would be extremely low based upon recent tests at SRL.

Tank 39H Heat Study

Radiolytic decay heat removal from Tank 39H was calculated based upon May 10 conditions and was in good agreement with the heat generation rate calculated from TAFI (computer program). The heat removals and losses to the various cooling systems were calculated and are summarized below:

Source	Btu/hr
Chromate CW	1,123,000
Annulus air	329,000
Purge exhaust	10,000
Losses to ground	150,000
Total	1,612,000

Tank 39H heat generation as of April 20, calculated using the TAFI computer program, was 1,759,000 Btu/hr.

Tank 39H bottom steel temperatures which are being monitored closely have remained low during the first fill cycle of fresh high heat waste. The maximum bottom steel temperature observed was 63°C. A sludge sounding made on April 13 indicated a sludge level of 1.2 inches.

Waste Concentration

Cesium Removal Columns

As a result of pluggage problems experienced in the past with cesium removal columns, SRL examined dry zeolite particles from three different resin lots. SRL used both a scanning electron microscope (SEM) and energy dispersive x-rays to identify any relative physical and/or chemical differences. No chemical differences between the three zeolite lots were found. However, particles from one lot did appear smaller, smoother, and more circular than particles from the other two lots. The other two lots seemed to have an open, porous surface containing more channels.

The zeolite samples were also soaked in a 0.01M sodium hydroxide solution (pH-12) for two weeks. After both one week and two weeks the zeolite samples were examined. Again, the dispersive energy x-rays showed no gross chemical difference among the resin lots. Examination with the SEM showed some differences in the physical appearance of the zeolite samples. Further investigation is required to determine the significance of these physical differences.

(HCTS) Loop Line Update

Continuous leaking at the spoolpiece in Tank 36H prevented successful 60 psig standard hydrostatic pressure testing of the HCTS loop line to Tanks 35H to 37H. A new hydrostatic pressure test procedure to pressurize to over 100 psig and check the repaired area for any indication of leaks was written and successfully performed during May. The jacket at Cleanout Port 3 is being replaced, and the loop line will be returned to service after the jacket replacement is completed and the area is backfilled.

Low-Level Effluent Waste

F-Area Seepage Basins

The F-Area seepage basins continue to exhibit low seepage rates. Because of reduced influx and little rainfall, the level of Basin No. 3 dropped 13 inches during May and June. This is the lowest level recorded since December 1982.

The short-term SRL study has been completed. Laboratory percolation tests were performed on 12 soil columns taken from the F-Area No. 3 seepage basin. The feed to the 12 columns included basin water, basin water adjusted to a pH of 7, potassium permanganate ($KMnO_4$), sodium sulfide (Na_2S), oxalic acid, hydrogen peroxide

(H_2O_2), nitric acid (HNO_3), and sulfuric acid (H_2SO_4). Approximately 10,000 data points were collected during the study. The isotopic profiles of the sediment cores were established both before and after chemical solutions were fed to the column. Also, effluent samples were collected from the column discharge. The analysis will enable the movement of radionuclides and hazardous ions to be determined as a result of chemical additions to the soil columns.

Formal recommendations have not yet been issued by SRL for a means of increasing seepage from the basins. However, laboratory results indicate that oxalic acid could provide an immediate surge in seepage rate, but would only be a temporary improvement.

The addition of three feet of earth around the three F-Area seepage basins was completed. This increased the basin storage capacity by approximately 40 percent.

SRL Seepage Basin Closure

Coordination of SRP and SRL groups in activities related to the permanent closure of the SRL earthen seepage basins continued during the second quarter of CY-1983. A program for gathering information to better define the chemical and radioactive inventory in the basins, and to define the spatial extent of any chemical contamination of the groundwater in the basin vicinity has been prepared. The data obtained in this investigation will supplement currently available data and provide the technical basis for the final closure to the seepage basins.

Groundwater evaluation will require completion of high-confidence statical comparisons between upgradient background consistuent concentrations (pH, conductance, metals, organics, pesticides) and downgradient constituent concentrations. A suitable background well in the northwestern sector of SRP has been drilled; sampling is anticipated to begin during the third quarter of CY-1983.

Additional closure documentation will be required in the forthcoming quarters. Once the spatial extent of any potential radioactive and chemical contamination has been determined, a closure plan will be written. Other closure documentation will include a cost/benefit analysis of closure options, a memorandum outlining the integration with site strategy for mixed waste disposal, and a likely reclassification document of the basin as a South Carolina hazardous waste facility.

The preparation of a draft closure plan summarizing all available chemical information on the SRL seepage basins is under way.

Old TNX Basin Closure Investigation

An extensive investigation program is under way to study the current disposition of the old TNX basin (Building 904-76G). This basin was in active operation from 1958 through 1980, and was used to receive hazardous waste discharges from TNX.

Constituents and compounds historically discharged to this basin include low-level radioactive materials, corrosive wastes, oxidizers, and flammable liquids. The total quantity of the waste discharged to the basin is not known. However, an estimated 74 pounds of mercury in the form of mercuric nitrate was discharged to the basin over its lifetime.

In 1980, four groundwater wells were drilled around the basin. One of the wells is inoperative. Eight of twelve analysis results from the operative wells over four quarters indicate mercury is in the groundwater in excess of the 0.002 mg/L drinking water standard. The maximum determined concentration was 0.521 mg/L.

Additional information is required to determine whether constituent concentrations are statistically significant between background upgradient and downgradient wells. DOE has also committed that drinking water standards will be met at the SRP boundary, which includes the Savannah River. Future investigation will provide the basis for determining whether additional closure action is required.

Groundwater Protection Report

Contributions addressing the (700 Area) SRL and 100-Area seepage basins were prepared for the draft Groundwater Protection Report (DP-1653), which is being revised in expanded form. The contributions describe current usage, previous discharges, groundwater monitoring results, and the status of groundwater quality protection activities.

Radioactive Releases to the F-Area Seepage Basins

All radioactive releases to the F-Area seepage basins during the months of February, March, and April were below the monthly and prorated year-to-date release guides.

Releases to the H-Area Seepage Basins

All radioactive releases to the H-Area seepage basins in February and March were below the monthly and prorated year-to-date release guides. However, during April the monthly release guide for ^{124}Sb and ^{125}Sb was slightly exceeded.

The yearly release guide for ^{124}Sb and ^{125}Sb is 0.20 Ci with the prorated monthly guide being 0.0167 Ci. Actual releases of ^{124}Sb and ^{125}Sb totaled 0.020 Ci. The year-to-date total is still well below the prorated year-to-date guide (0.035 Ci vs. 0.0667 Ci).

Based on the sum of the May weekly releases, the prorated monthly release guide will also be exceeded. The monthly total has not been reported yet.

The source of the ^{124}Sb and ^{125}Sb is suspected to be RBOF/RRF waste stored in Tank 23H. The level of waste in Tank 23H was rapidly depleted in April and May by direct processing through the Tank 24H cesium removal column (CRC). Tank 23H direct feed to the CRC has been temporarily discontinued awaiting analysis of a sample taken on June 9. The results will be used to determine a new feed schedule for Tank 23H to ensure monthly release guides are not exceeded in the future.

Mercury Releases to the H-Area Seepage Basins

Mercury released to the H-Area seepage basins decreased from six pounds in February to two pounds in March and April, respectively. In April all releases of mercury through the H-Area trebler were below the concentration which would classify a stream as hazardous. This concentration is 200 ppb (one hundred times the drinking water standard) and was established by SCDHEC. Investigation continues to determine the cause of the relatively high amounts of mercury released between October 1982 and February 1983. Weekly composite samples from the 242-H and 242-16H evaporator overheads are being analyzed to determine the concentration of mercury in the overheads.

Contaminated Water Control

SRL's Waste Processing Technology Division began process development work for the contaminated water control facilities in March. Preliminary waste characterization work on diluted canyon first-cycle feed and neutralized high-activity waste indicate that from 80 to 90 percent of the radionuclides will be removed by a 0.8 μm filter.

A small-scale, reverse-osmosis unit was installed in the High Level Caves in April. Preliminary runs with diluted first-cycle feed were made at operating pressures from 200 to 400 psig. Ninety to 94 percent rejection rates (determined by measuring effluent conductivity) were obtained using a Permasep® (Du Pont) Model B-9 membrane. Volume reductions of 30:1 were achieved.

Based on this preliminary work, it appears feasible to design a processing facility which uses filtration, followed by reverse osmosis, then ion exchange for decontaminating radioactive water from a release to the canyon cooling water system.

A purchase order was written in April for a small-scale electrodialysis unit for testing in the High Level Caves. The unit should be operable in August.

A tenth-scale processing facility is being planned for TNX. The facility will include a submicron filtration system, both a spiral-wound and hollow-fiber reverse-osmosis system and an ion exchange column. The facility should be operating with cold feeds by March 1984.

Test results from SRL's Waste Processing Technology Division will be incorporated in basic design data to be issued to the Du Pont Engineering Department by June 30. The scope of work provides two million gallons of covered storage for contaminated canyon cooling water, and 500,000 gallons of covered storage for contaminated tank farm runoff water. A smaller 75 gpm processing facility will replace the previously scoped 750 gpm processing facility which was designed to process at the canyon's minimum flow. This concept limits the total volume of any one canyon release to two million gallons. The total volume of contaminated storm water released during any one incident is not expected to exceed the provided 500,000 gallons of storage capacity. However, since tank farm storm water cannot actually be controlled, provisions will be made to allow the storm water hold basin to overflow into the canyon cooling water hold basin. The existing retention basin would only be used for procedural storm water diversions (i.e., inoperable storm water monitor), when the risk of contamination is low.

The 75 gpm processing facility will consist of:

- Mixed media filters which contain a layer of activated carbon for the removal of organics and chlorine.
- Submicron filters for the removal of insoluble radionuclides (50% of the total radionuclides).
- A one permeate pass reverse-osmosis sytem; concentrate staged to achieve a 30:1 volume reduction.
- Mixed-bed ion exchange columns for polishing.

The processing facility should achieve an overall decontamination factor (DF) of approximately 30,000. This will be more than adequate for processing the majority of releases down to creek discharge limits. However, for releases with a large radioactive content (>280 curies) which require a higher DF, the contaminated water could either be recycled through the processing facility or sent to a tank farm waste storage tank without processing. Figure 63 is the flowsheet for this scope of work.

Nonradioactive Hazardous Waste

NRHW Interim Storage Facilities

Construction of the new NRHW Storage Facility, Building 709-G, was completed in April. Waste Management Operations accepted the new storage facility from Construction on May 9, 1983. The majority of the waste in Building 710-U will be moved to Building 709-G. However, Building 710-U will continue to be used for storage of nonignitable, solid hazardous waste.

NRHW Landfill NEPA Evaluation

A National Environmental Protection Act (NEPA) checklist was completed for the nonradioactive hazardous waste landfill in April. Items requiring further action include an environmental evaluation of the burial of solid waste and site clearance/excavation and a safety analysis of handling toxic wastes placed in the landfill. In addition, a Resource Conservation and Recovery Act (RCRA) permit will be required for the landfill. The Environmental Analysis and Planning section of SRL will coordinate further study of the safety and environmental impact of the NRHW landfill, and Energy Conservation and Environmental Control will coordinate RCRA-permitting activities.

The CMP Pits/Silverton Road Site

A statement of work was written during April detailing the specifications to be followed during the hazardous waste and contaminated soil removal operations at the CMP pits. It was also reviewed by both DOE and SCDHEC during April. The statement of work was issued along with a purchase requisition to Purchasing. It was incorporated into a bid package which was sent to qualified hazardous waste management contractors in June. Contract proposals are due for evaluation by mid-July.

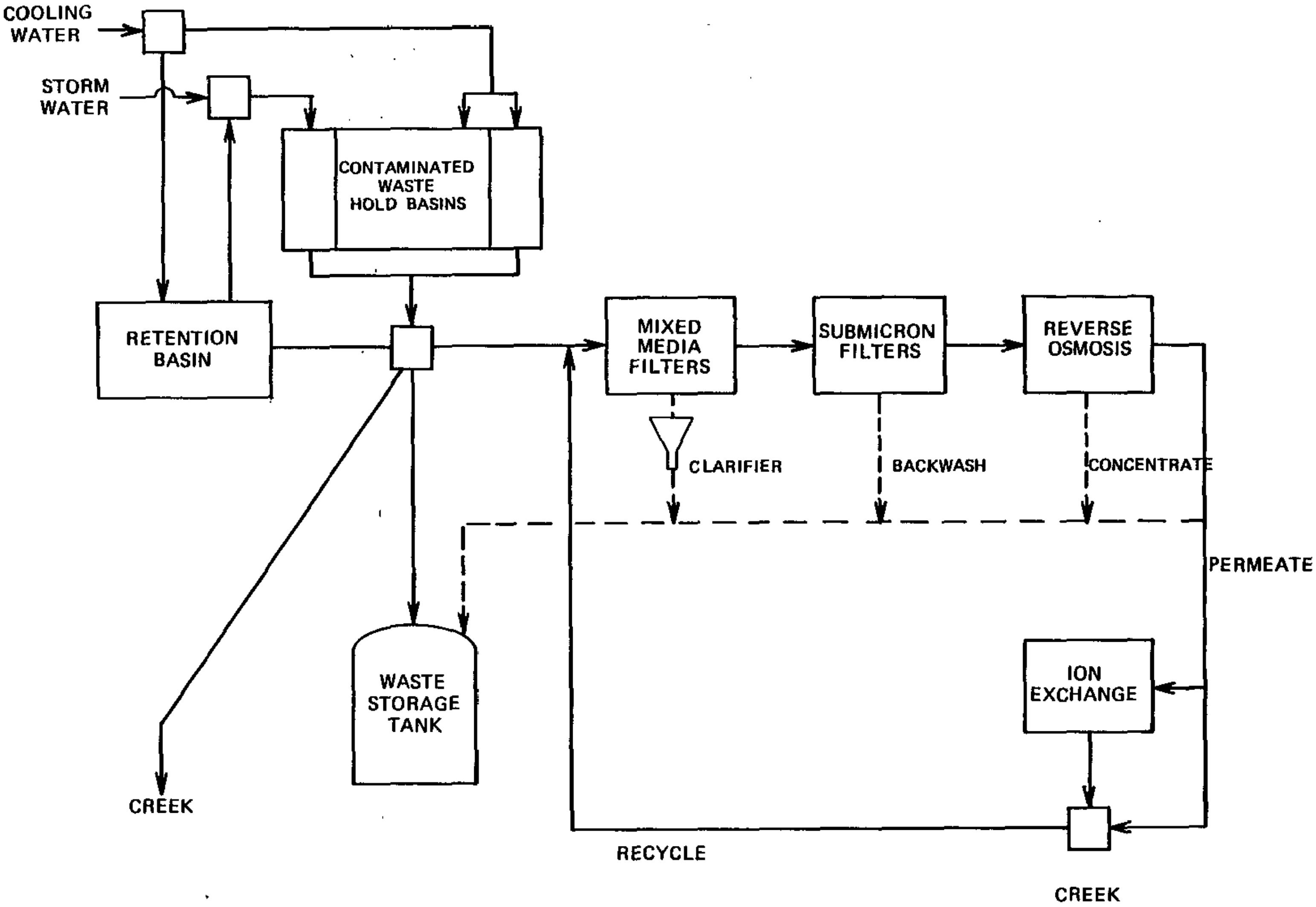

FIGURE 63. Process Flowsheet

The NEPA documentation was prepared in June and the process was initiated for obtaining approval for waste removal from the CMP pits. SRL recommended that a memo-to-file be written for this work. Final determination of required NEPA documentation will be made by DOE.

Waste removal is scheduled to begin at the CMP pits in September baring any delays in obtaining State approval of the waste removal plan and in providing the appropriate level of NEPA documentation.

Groundwater Contamination Studies

Groundwater studies were initiated in April at the Silverton Road waste site and the CMP pits to determine the extent of chlorinated organic contamination. Perclene and triclene were detected in the groundwater near each site. Groundwater programs were developed by an ESD consultant for both locations. Installation of additional monitoring wells is scheduled to begin in early July. Installation of sampling pumps in existing monitoring wells was completed at the Silverton Road waste site during June. Sample pump installation is in progress at the CMP pits.

Tank Replacement/Waste Transfer

Mechanical Agitation Salt Removal

An estimated 437,000 gallons of salt (77% of the original) have been transferred from Tank 24H to date in about 1,250,000 gal of solution. Plans for completing salt removal in Tank 24H are being developed.

Density-Driven Salt Removal

Authorization was routed for approval in April to permit storing high-nitrate solution (>5.5M) in Tank 20F, based on SRL test results which show low risk for stress-corrosion cracking.

An April sample analysis (Table 67) of the interstitial salt solution in Tank 10H indicates both nitrate and corrosion inhibitor concentrations were outside technical standard limits. The solution drained from the salt after supernate was transferred from Tank 10H.

Two 100-mL dip samples were taken from Tank 10H (Riser 1) on May 21 and sent to 772-F for analysis. These samples were taken for comparison with the supernate samples taken in April, which indicated the interstitial salt solution in Tank 10H was above the technical standard (TS) nitrate concentration limit. Based on SRL tests to extend the TS nitrate concentration limit to 8.5M, there is low risk for nitrate induced stress corrosion cracking at Tank 10H chemical composition. A test authorization is being written to permit extended storage of the solution in Tank 10H.

TABLE 67

Analysis of Interstitial Salt Solution (Tank 10H)

Tank No.	1983 Date	Sp. Gr.	Conc., mols/liter NO_3^-	NO_2^-	OH^-	pH	Tank Service	Lab
10H*	3/26	1.41	6.63	0.25	0.68	13.5	Salt Tank	772-F

* Outside Technical Standard Limits

Technical Standard Revision to Salt Removal

Revision of the TS limits on waste tank contents is planned to permit safe storage of high nitrate solutions generated by salt removal. The Technical Standards limits concentrations of nitrate, nitrite, and hydroxide to prevent nitrate-induced stress corrosion cracking. The current standards limit nitrate concentrations to 5.5M or less because data were not available at higher nitrate concentrations. The planned revision will allow up to 8.5M nitrate concentrations. The revision will be based on SRL tests of solutions of 5.5 to 8.5M nitrate and steel of the same type as that used in waste tank construction.

Salt Decontamination Demonstration

The salt decontamination demonstration was completed on April 14 with the end of the third precipitate wash. The final sodium ion concentration in the Tank 48H precipitate was 0.15M versus a goal of less than 0.225M. A total of 191,000 gallons of wash water in 3 batch washes was required. Filtered wash water was transferred to Tank 49H.

After filtering the decontaminated supernate, filters were cleaned with 2 wt % oxalic acid. The first precipitate water wash was completed on March 31. A total of 78,000 gallons of filtered wash water was transferred to Tank 49H at an average ^{137}Cs activity of 5300 d/m/mL. During filtration, the filtrate flow was 25 to 45 gpm with a pressure drop across the filters of 4 to 6 psi. The average process flow rate was 120 gpm.

During water addition for the first wash, hydrocarbon concentrations in the purge exhaust increased substantially. Analyses of Tank 48H interior air purge gas samples showed benzene concentrations as high as 115 ppm. Qualitative monitor readings indicated that peak hydrocarbon concentrations may have exceeded measured values. Benzene concentrations in the tank vapor space returned to about 10 ppm in less than two days (based on HP readings). Readings taken in the work areas around the tank purge exhaust showed no detectable benzene. Personal monitors worn temporarily by operating personnel indicated no benzene exposure.

Benzene levels peaked again during the second water wash at about 70 ppm. Benzene concentration in the tank purge decreased to <20 ppm, within two days after wash water addition, and continued to decline during the third wash. Concentration of benzene in Tank 48H purge and personnel areas will continue to be checked periodically. The second precipitate wash was completed on April 12. Sixty-six thousand gallons of water were added for the second water wash. The filtration was performed in two steps. The first filtration step reduced the tank liquid level to 11 inches. During a second filtration step, precipitate was concentrated further by reducing the tank level to 6.2 inches. During the first filtration step, filtrate flow was 30 to 45 gpm with a 6 to 7 psi pressure drop across the filters. The process flow averaged 110 gpm. During the final concentration, filtrate flow rates began to drop at a Tank 48H liquid level of 9 inches (4 to 5 wt % solids), and decayed at 10 gpm at a level of 6 inches. The process flow rate dropped to 35 gpm. A constant filter pressure drop of 7 psig was maintained during the concentration test. The average ^{137}Cs activity in the filtrate was 13,600 d/m/mL. Cesium activity as high as 10^5 d/m/mL had been expected during the second wash.

The third precipitate wash was completed on April 14. The precipitate was continuously washed by operating the two Tank 48H agitation pumps and metering well water into the tank during filtration. During the test, the filtrate flow was 34 gpm with a filter pressure drop of 5 psi. The process flow was 125 gpm. Agitation caused filtrate flow rates to decay about 1 to 2 gpm between filter backpulses. Prior to agitation, filtrate flow decay was about 1/2 gpm between backpulses. No other changes in process conditions were observed. About 7,000 gallons of filtered wash water was transferred to Tank 49H during the continuous wash. The ^{137}Cs activity in the filtrate averaged about 76,500 d/m/mL.

After the final wash, the filters in Tank 48H were cleaned with 1500 gallons of 2 wt % oxalic acid. Fifteen hundred gallons of 30 wt % sodium nitrite was added to Tank 48H on April 19 to increase the nitrate concentration above 0.1M. A final 10-gallon sample was taken from the tank on April 21.

Analysis of the 10-gallon sample showed a nitrite concentration of 0.23M in the precipitate solution. The Test Authorization minimum requirement for long term storage is 0.1M NO_2^-. Another 10-gallon sample was taken from the tank on May 20 with the agitation pumps running to obtain a more representative sample of the tank contents. (An insufficient amount of precipitate solids were collected in the first sample.) Lab results indicated that the sample contained a significant amount of precipitate solids.

Analysis of dip and peristaltic samples taken from different levels in Tank 49H showed a nitrite concentration of 0.27M. Dip and peristaltic samples were pulled from different levels in Tank 50H on May 20 and 22, respectively, to check for salt solution layering.

Essentially all Cs-137 activity was concentrated in a small amount of solids present in each sample. Three more peristaltic samples pulled from Tank 50H on June 14 also contained cesium-bearing solids. Sample analyses are presented in Table 68. Filtration of these samples through a 0.45 micron disk filter reduced the cesium activity to below detection limits. The solids are thought to be cesium tetraphenylborate which precipitated after filtrate transfer to Tank 50H. Bulk cesium activity was close to the calculated average of 7500 d/m/mL. Samples indicated that the solids may be more contaminated near the tank bottom but are below the suction of the pump to be used for loading HM trailers during the saltcrete demonstration.

Gas samples, taken from the purge exhausts of Tanks 48H, 49H, and 50H on May 16, were analyzed for organics at the Experimental Station to provide information on hydrocarbon levels in the tank purge air for design of upgraded salt processing facilities.

Benzene was detected only in the Tank 48H sample at 3 ppm. Methanol was detected in all three samples; the highest level was 164 ppm in the Tank 50H sample.

Two additional gas samples taken from the Tank 50H purge on June 7 showed methanol levels of 161 and 169 ppm. These concentrations are to be expected since methanol was a major component (12 vol %) of the sodium titanate chemical slurry. Methanol concentrations are well below the LEL of 6% (60,000 ppm) in air and the technical standard limit for organic vapor in waste tanks of 0.5 vol %. A sample taken in the general area of the Tank 50H purge exhaust showed a methanol level of 8.8 ppm. No personnel hazards exist since this is well below the TLV of 200 ppm for methanol.

TABLE 68

Tank 50H Filtrate Activity

Sample Elevation*	Radionuclide, d/m/mL Bulk Cs-137	Cs-137 After Filtering	Ru-106	Sb-125
Surface	5500	<700**	15,300	9300
78 inches	6400	<200**	14,200	9500
37 inches	5500	<200	14,900	9100
25 inches	6200	<200	15,300	9100
Bottom	26,600	<700	15,500	9300

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* Above tank bottom

** Monitor sensitivity changes with background radiation

Saltstone Demonstration

Construction began work in April on the Tank 50H loading station. The station will be used for filling a HM trailer with decontaminated salt solution for transport to the saltcrete demonstration site in the burial ground.

Long-Term Salt Decontamination

Waste Management and Engineering Department representatives met in April to revise the scope of work for long-term salt processing.

Revisions include the following:

- The number of filter bundles was reduced from eight to two. The filter area remained the same. Reducing the number of bundles reduces the size of the filter box.
- Improved benzene monitoring equipment was requested. Based on the benzene releases experienced during the demonstration, an accurate benzene monitor is required to measure benzene concentration in the purge air stream. Engineering was also requested to include cost allowance for a benzene scrubber system on the tank purge exhaust.
- An in-line inhibitor system for the filter cleaning solution was requested. Two weight percent oxide used in the filter cleaning operation must be neutralized before being returned to Tank 48H.

The in-line neutralization system used for the demonstration added ~18 times the volume of caustic required for neutralization. Long-term facilities should minimize excess caustic addition.

- Evaluation of valve selection and ease of maintenance of the backpulse filter cleaning system was recommended. During the demonstration, backpulse valve-leakage (internal and external) created maintenance problems.

The VGA estimate for the Tank 48H upgrade was $21.6 million. The VGA was prepared based on the Draft Basic Data Report issued November 15, 1982. Since then several design changes have been made which are expected to reduce the cost significantly. These changes will be incorporated in the Basic Data and will be reflected in the CAC estimate, due in February 1984.

The final basic data report is being written. This report will be used for the CAC, Current Appraisal of Cost.

The Tank 50H loading station was completed during June. The estimate startup date for the loading station and saltstone demonstration facilities is in the fall. One of two nonradioactive tests was constructed at the Saltstone Demonstration Site in June. This test confirmed mixer acceptability. The second test, conducted during the week of June 20, will transfer saltstone mixture through 40 feet of pipe to a test trench.

Tank 17F Salt/Sludge Removal

Tank 17F salt and sludge removal is scheduled to begin September 1, 1983, and will require about nine months to complete. About one million gallons of layered salt and sludge will be removed from Tank 17F in approximately six batches. Between 1.5 and 2.3 million gallons of inhibited water will be added to Tank 17F. The salt and sludge will be slurried with long-shaft slurry pumps. An adjustable length transfer pump will transfer the slurry solution to Tank 18F where the sludge will settle. The clear supernate remaining in Tank 18F will be decanted to an evaporator feed tank.

Tank 15H Sludge Removal and Processing

Disassembly and removal of obsolete equipment from Tank 15A was approximately 75% complete by June. Since the last report, Construction has removed the Riser 1 thermowell, the Riser 2 HAW sampler, and the berm over the transfer line from Tank 16H annulus to Tank 15H. By June the Du Pont Engineering Department design effort for Tank 15H facilities was approximately 80% complete.

Tank 16H Annulus Cleaning Demonstration

Construction of the annulus cleaning demonstration facility was completed in April. Waste Management Operations is preparing to remove the plugged annulus transfer jet in IP65 and install a replacement 25 gpm transfer jet. This work must be completed prior to the start of the annulus cleaning demonstration which was rescheduled in July to start up in 1985 after sludge removal in Tank 15H is complete. About 335,000 gallons of solution (containing <1 Ci/gal) from Tank 16H annulus washes and Tank 15H slurry pump seal water leakage will be added to Tank 15H during Tank 16H annulus cleaning. Tank 15H has 13 known inactive leaksites and currently containing about 270,000 gallons of aged high-heat waste (HHW) sludge and 150,000 gallons of supernate. Delaying annulus cleaning in Tank 16H until sludge removal is complete in Tank 15H substantially reduces the consequences of reactivating leaksites as a result of adding oxalic acid from Tank 16H annulus cleaning.

In-Tank Sludge Processing Demonstration

About 48,000 gallons of accumulated slurry pump seal water leakage in Tank 42H was transferred to Tank 43H on March 29.

Seals on the chemical metering pumps for Tanks 42H inhibited water system were repaired; the seal water system was returned to normal operation in April.

Waste Transfer Program Status

Electrical equipment installation continues on Tank 17F and in the 241-74F control building. Other waste removal construction remains suspended until funding is approved.

Initial TNX run-in of the three slurry pumps for Tank 17F was conducted in April. However, two of the three slurry pumps were run in with ungrooved top and bottom bearings. The correct top and bottom grooved bearings were installed in May and the pumps were run in again. The telescoping transfer pump was also run in during May.

Construction installed the three slurry pumps and the telescoping transfer pump in Tank 17F during June. Variable speed drives are now being run in for both F- and H-Area sludge removal slurry pumps.

Concrete foundations are being prepared to the Tanks 19F and 20F support steel. The Tank 19F foundation and one of the Tank 20F foundations were poured during the month of June. Excavation continues for the remaining Tank 20F foundations.

Also during June, operations accepted the 241-74H sludge removal control building H&V system with minor exceptions.

Extended Sludge Processing

A design review for extended sludge processing was held in May with representatives of Waste Management and the Engineering Department. Sludge processing facility prints and Tank 15H D&R and equipment requirements were discussed. Changes were as follows:

- The telescoping transfer pump (TTJ) in Tank 42H will be installed to allow operation at variable depths.
- The Tank 42H valve box will be changed to allow the TTJ to transfer to either Tank 43H or DB-7 without jet modification.
- The Plant is responsible for developing an in-line solids detector to monitor sludge solids in the transfer line.
- The oxalic acid makeup facility in F Area was deleted. Oxalic acid will be trucked from H Area to F Area.
- The nitrite and caustic storage tanks for inhibited water makeup will be combined for both F and H Areas.
- Inhibited water makeup facilities will use automatic metering pumps with pH control.
- Tank 51H slurry pump locations were revised.

Tank 15H sludge will be the next sludge processed in Tank 42H. Construction has started disassembly and removal of obsolete equipment on Tank 15H. To date, Construction has removed the high liquid level conductivity probe, thermocouples from Risers 1, 3, and 8, the berm around the transfer jet, and about 15 feet of the transfer line to Tank 13H.

Mechanical Seal Development

SRL/TNX is testing a mechanical seal for the Bingham-Willamette slurry pumps. The seal was designed and built by the Durometallic Corp. The design basis for the seal was to provide a maximum seal leakage rate of 20 cc/min. After about 800 hours of operation in

SRL's single discharge pump, the seal was removed for inspection in June. The seal faces were in excellent condition with no grooves or scratches. The seal leakage rate was less than 20 cc/min.

The 0.4 gph seal was reinstalled in the quad volute pump in June. Also, a second mechanical seal was installed in a Tank 16H type slurry pump. Testing of both seals in water will resume in early July. After receipt and installation of a third seal in a Tank 16H type pump testing will begin using kaolin clay slurries.

The first radioactive service for the new mechanical seals is planned for the two new slurry pumps on Tank 15H (October 1984).

Solid Waste Storage and Related Activities

Low-Level Waste Management

The review draft of the assessment for burial of classified naval waste in the SRP burial ground has been upgraded for receipts through calendar year 1982. The projection of future receipts also has been updated. In addition, corrections to COBRA entries have been included in a final report.

WIPP Certification Program

Advanced authorization for $300,000 was received in April to begin procurement of the TRU waste assay system. This money will be used to complete system design, for the purchase of equipment and materials with a long delivery time, and to begin instrument checkout. A purchase requisition for these items is presently being routed for approval.

Section II of the Inventory Workoff Plan Draft document was completed in April and submitted to DOE/ALO and TWSO on schedule. The Inventory Workoff Plan is being prepared this year in support of the WIPP Certification Program. Section II consisted of 17 tables characterizing all trench, contaminated soil, and retrievably stored TRU waste at the Savannah River site. Included were waste generation rate projections through 2015 and projected waste shipping scheduled to the WIPP. The remaining sections of the document are to be submitted in August 1983.

Comments were received in April from the TRU waste generating areas and other departments involved in certification activities for the Savannah River Certification Plan for Newly Generated, Contact-Handled, TRU Waste.

A meeting was held in May with representatives from the Savannah River TRU waste generating areas. No significant difficulties in meeting requirements of the present Certification Plan draft were identified. Comments were received from the WIPP Review Committee in May for the draft Savannah River Certification Plan. These comments were then incorporated into the final documents which were formally submitted to DOE and the WIPP Review Committee for approval.

The WIPP Review Committee met with Waste Management Technology personnel in June to review comments on the Savannah River Certification Plan for Newly-Generated, Contact Handled TRU Waste. Comments indicated the need to provide additional descriptions of QA controls which will ensure that packaged waste meet the WIPP criteria. The committee has recommended that the Certification Plan be revised and formally submitted for WIPP approval after the comments have been resolved. A tour of TRU waste generating and storage facilities by members of the WIPP Review Committee has been scheduled for July.

The conceptual design and scope of work were completed in June for the building which will house the TRU Waste Assay System. This 1700 ft^2 building is to be located adjacent to the new office building in the burial ground. Several design changes were made on the assay system. A vertical door was chosen because of its safer operating mode and reduced floor space requirements. Borated rubber and borated polyethylene will be added to the assay chamber exterior walls. This should improve system sensitivity by reducing the effects of background radiation.

A program is under way to procure nondestructive examination equipment in support of the WIPP Certification Program.

These systems, which are similar to airport baggage inspection systems, can examine the contents inside a standard 55-gallon drum containing a variety of waste matrices. The purpose will be to identify liquids, sludges, and other items in WIPP-intended waste package which may not meet the WIPP waste acceptance criteria. Several types of commercially available x-ray and gamma ray inspection systems are currently being tested at vendor sites to determine suitability for use at SRP.

Plutonium-238 Waste Incinerator (PWI)

SRL and Waste Management continue to develop the process design to install the PWI at TNX by October 1983. The design developed for a new primary combustion chamber to incinerate ^{238}Pu contaminated waste is an electrically heated Shirco incinerator which uses a rotating wire mesh belt to convey shredded waste slowly through the primary chamber. The Shirco unit appears to overcome many of the problems associated with the old ceramic tube/ram design tested at TNX in the Incinerator Components Test Facility (ICTF). Due to the metal/insulation construction, the unit can be heated up or cooled down in approximately 30 minutes, versus 18 hours for the old ceramic tube design. Primary chamber heater replacement is simpler because the heating elements are bayonet silicon-carbide tubes which can be inserted and removed externally from the primary chamber. The ceramic tube design required disassembly as the heaters wrapped around the outside of the primary chamber.

In January, a four-hour test was conducted on the Shirco incinerator in Dallas, TX, to evaluate the design for potential application to the PWI. Enough information was obtained to conduct a two-week test in March. Based on the successful test, SRL plans to purchase a Shirco unit for cold testing, scheduled to begin in the fourth quarter of FY-1983. Waste Management will help develop specifications for the purchase to ensure the unit will duplicate one which can be used in a radioactive environment. A bid on the unit from Shirco is expected soon. Development of the design of the PWI process continued in May so that the feed system, the incinerator, and the off-gas treatment equipment could be purchased by September 30, 1983, from the SRL operating budget.

The incinerator feed system will consist of two shredders in series interconnected by Pax pumps which convey the shredded material from one shredder to the other, and then on to the precombustion chamber of the incinerator. Shred Pax Corp. (Chicago, IL) will provide an estimate for the equipment by mid-June. A local engineering firm will be used to design the interface between the feed preparation system and the incinerator.

The off-gas equipment consists of a sintered metal filter unit (particulate removal) HEPA filters, and a blower used to maintain the entire incineration system under vacuum as well as to vent the off-gases to the atmosphere. Purchase of these items through SRL will also be expedited in order to meet the September 30 deadline. SRL and Waste Management are concurrently preparing the purchase requisitions to ensure that all deadlines are met. The cooperative effort will allow this PWI system (to be tested at TNX) to exactly duplicate the equipment that would be required for a plant facility.

Specifications for the feed preparation system of the Shirco incinerator (primary and secondary chambers) the sintered metal filters, the HEPA filters, and blower were submitted to Purchasing in June to obtain bids from qualified vendors. To ensure quality fabrication, a Du Pont Engineering Department and Quality Assurance Field Representative (QAFR) will be issued to the project. Additional mechanical and E&I reviews will be provided by ESD and SRP personnel. This cooperative effort will allow the PWI to be designed for eventual radioactive service once the cold demonstration at TNX is completed. A cost funded project by the plant (Waste Management) would then only have to provide the building and service utilities for the process.

Project Beta Gamma Incinerator

Construction of the Beta-Gamma Incinerator (BGI) Facility is 80 to 85% complete. The installation of the interior lighting was completed in April, and installation of service piping continues. Also during April, the baghouse and spray quench tower ash-out enclosures were installed and the 5000-gallon storage tank was received and installed.

The operating permit from SCDHEC has been delayed to allow the Hazardous Waste Group in DHEC to review the application.

Solvent from Tank S-32 in the burial ground was sampled and analyzed in April for ^{235}U; none was found. Monitor sensitivity is 0.03 g/gal. The sample was taken from a trial analysis to ensure no criticality potential exists in the incinerator if solvent is burned. Samples from both the solvent and aqueous phase of each tank in the burial ground will be taken and analyzed in the same manner.

The emergency generator was delivered and installed during May. The wiring, ductwork assemblies, and feed ram enclosure are nearing completion. Also during May, WMT prepared a list of setpoints for the controllers in the BGI process. A timeline for Phase II, III, and NRHW (Nonradioactive Hazardous Waste) operations was prepared and distributed. Phase II "hot" operation is scheduled for CY-1984 and CY-1985. NRHW operating permit tests are planned for CY-1986. Phase III and NRHW operation will begin in CY-1988.

SRL tests showed that under poor operating conditions, solids can build up on the distributor plates of the spray quench tank. Several measures are being taken to eliminate this potential problem. Construction has been contracted to clean the spray quench tank for an estimated $9,300. The old distributor plates will be replaced by vanes to channel the off-gas flow. These vanes are a standard vendor design. A purchase order for $13,340 has been routed through SRL to buy these vanes.

The Canberra assay system will be delivered in June and installed by Maintenance in August. Members of SRL and WMT visited Canberra in May for a demonstration of the assay equipment.

The cages and bags for the baghouse arrived in May. The vendor was brought onsite to assist with the bag and cage installation. Ten percent of the bags were found damaged onsite and required replacement; 32 of the cages require repair or replacement, and the tubesheet was not cut to the proper dimensions.

The baghouse vendor visited SRP on June 11-13 and modified the tubesheet to meet the design specifications. Over 100 bags and cages were installed. The baghouse assembly will be completed when the replacement bags and cages arrive.

A list of spare parts was generated in June, and EP numbers were assigned to equipment so that parts can be ordered.

During June, the H-Area Criticality Committee reviewed the Nuclear Safety Program for the BGI and found it to be adequate with no Nuclear Incident Monitor (NIM) system.

An incinerator consultant for Du Pont visited SRP in June and recommended either meeting Engineering Standard K6R or strengthening parts of the incinerator to withstand a sudden short pressure rise of 50 psi. The first recommendation is being followed.

The continuous air monitors were delivered in June and installation is in progress. The domestic water header cleanout is in progress, and the critical points checklist nears completion. As of June, procedures for the facility are approximately 25% complete.

Also during June, an RTA was written to SRL concerning the high temperature effect from the process stack on the stack continuous air monitor. SRL will make a recommendation soon.

SRL is also developing the ashcrete process to solidify ash from the BGI, and the design for this process is 90% complete. DOE has awarded a $100,000 subcontract for Stock Equipment Company to begin fabrication. The equipment delivery is expected by the end of FY-1983.

Consideration was given to installation of the ashcrete process directly in H Area and performing the cold run-in at the BGI site. But, because it would require greater than nine months to obtain the approvals, design, and site preparations for the project, it was decided to continue with SRL's plan for a run-in at TNX and an eventual move to the BGI site.

SRL and WMT personnel visited Stock Equipment Co. in May to review the ashcrete design. Stock has completed their formulation studies for ashcrete, and their report is expected in June. Stock is scheduled to deliver the ashcrete equipment by October.

Ashcrete Process Development

Members of WMT and SRL reviewed Stock Equipment Company design for the ashcrete process during June. Stock has developed and transmitted an acceptable general design. Details for the design are still being developed. The primary components of the design include a stainless steel chamber, solids hoppers with live-bottom bins, a drum tumbler, self-propelled transfer cart, and unbagging system.

An RTA for $875,000 was written and approved in June for WDT/SRL to develop, procure, and test the ashcrete process. The RTA calls for SRL to fully document their test work with a final report, vendor information, a spare parts list, operating procedures, and recommendations for installation at Building 230-H (BGI).

A basic data report is being prepared for draft approvals.

Leaking Storage Box in the Burial Ground

A Separations storage box containing a canyon batch evaporator was discovered leaking liquid in the 643-7G burial ground on June 9. This box (SRP No. 78) was being moved to a new location when liquid was observed seeping from one corner of the box. The box was then fitted with a plastic diaper and placed in the intermediate-level burial trench under special procedure. Five hundred pounds of absorbent material were added to the box to immobilize the liquid remaining within the box.

Surface contamination was confined to a 1.5 acre site with the highest level of contamination being directly under the box (4500 mrad beta-gamma). 20,170 ft^3 of contaminated soil from the storage pad area, and the storm drainage ditch were removed and buried. Downstream soil and water analysis confirmed that no activity was released from the burial gound. The source of liquid in the box is thought to be rainwater entering the box over the past 1-1/2 years.

Equipment Retirement and Reclamation (ERR) Facility

Basic Design Waste Package for the ERR Facility, was written and submitted for comments. The final package incorporating comments will be issued by June 30.

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