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WASTE MANAGEMENT PROGRAM TECHNICAL PROGRESS REPORT

JULY-DECEMBER, 1984

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

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Approved by

W. R. Stevens III, Section Director
Defense Waste Processing Division

Publication Date: October 1986

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ABSTRACT

This report provides information on operations and development programs for the management of radioactive wastes from operation of the Savannah River Plant and offplant participants. The studies on environmental and safety assessments, other support, in situ storage or disposal, waste form development and characterization, process and equipment development, and the Defense Waste Processing Facility are a part of the Long-Term Waste Management Technology Program. The following studies are reported for the SR Interim Waste Operations: tank farm operation, inspection program, burial ground operations, and waste transfer/tank replacement.

FOREWORD

This report provides information on the status of plant operations and research and development programs for the management of radioactive wastes at the Savannah River Plant and several offplant participating laboratories. These efforts are funded by the Office of Defense Waste and Byproducts Management (DWBM) of the U.S. Department of Energy.

This technical progress report consists of three general sections: Long-Term Waste Management Technology, Defense Waste Processing Facility, and SR Interim Waste Operations.

The section on long-term waste management technology summarizes research and development studies on the immobilization of defense high-level waste at all three U.S. sites (SRP, ICPP, and RHO). Immobilization of the waste consists of placing it in a high-integrity form with a very low potential for radionuclide release.

The basic plan for meeting the goal of immobilization of the DOE high-level waste is (1) to develop technology to support a realistic choice of waste form alternatives for each of the three (SRP, ICPP, and RHO) DOE sites, (2) to develop product and processing technology with sufficient scale-up to provide design data for full-scale facilities, and (3) to support R&D for construction and operation of immobilization facilities.

Current offplant participants in the long-term high-level waste management program are:

Idaho Chemical Processing Plant (ICPP)
Materials Characterization Center-PNL (MCC)
Materials Review Board-ANL (MRB)
Rockwell Hanford Operation (RHO)
Sandia National Laboratories (SNL)

In the reference design process at the Savannah River Plant, for high-level waste, the salt will be dissolved, and the resulting solution will be decontaminated. More than 99% of the ^{137}Cs and residual ^{90}Sr will be removed from the salt solution. The decontaminated liquid will be mixed with cement to form a grout that contains only a small fraction of the total hazardous radioactive material. The saltstone grout will be disposed of onsite in an engineered landfill. Sludge, which has been treated in the waste tanks to remove soluble aluminum compounds and soluble salts, will be combined with the recovered radionuclides from the salt solution, mixed with glass frit and fed to a glass melter. The combined radionuclides from the salt and sludge will be incorporated into borosilicate glass, sealed in canisters for shipment 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 - THIRD QUARTER

LONG-TERM WASTE MANAGEMENT TECHNOLOGY

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

A report on the cost trade-off study for ICPP HLW volume reduction was issued. (Page 17)

Modified Zirflex laboratory-scale studies and laboratory-scale glass melter studies continued. (Page 20)

Ceramic formulation development studies are reported. (Page 26)

Waste-form compliance test method and corrosion test method development continued. (Page 26)

Waste-form characterization work will be given emphasis in FY 85. (Page 31)

A condensed version of Data Package MCC-D1 was published in PNL-3990. (Page 33)

SR INTERIM WASTE OPERATIONS - PROCESS DEVELOPMENT

Several reports covering transuranic waste management have been issued. (Page 37)

DEFENSE WASTE PROCESSING FACILITY

Design is 65% complete and the design manpower is approximately 450. Construction of the vitrification building basemat has begun. Overall, construction is estimated at 3% complete. Site construction manpower is also 450. (Page 40)

WASTE MANAGEMENT

Tank farm operations, the inspection program, burial ground operations, and waste transfer/tank replacement are summarized for this time period. (Page 47)

CONTENTS — FOURTH QUARTER

CONTENTS, Contd

HIGHLIGHTS — FOURTH QUARTER

LONG-TERM WASTE MANAGEMENT TECHNOLOGY

Preliminary laboratory studies were completed for the modified Zirflex fuel dissolution process. (Page 55)

Neutralization of ICPP acid high-level liquid waste to separate radioactive components as precipitates from inert components may be a potential intermediate step in producing a reduced volume final waste form. (Page 58)

Low volume glass development activities discussed in this report include slurry feeding and frit development studies. (Page 61)

Recent progress and current plans relating to the tetraphenylborate radiolysis subcontract were discussed with Professor R. J. Hanrahan at the University of Florida. A one year continuation of this work is recommended. (Page 63)

Slurry containing simulated acid hydrolysis products was fed to small cylindrical melter-2 (SCM-2) to determine its processability and to define off-gas chemistry. (Page 91)

The objective of the present acid hydrolysis study is to evaluate the durability of one glass containing simulated acid hydrolysis products, and to compare its durability to sludge-only glasses and to an ARM reference glass. The acid hydrolysis glasses were based on Frit 168. (Page 124)

The Experimental Canister Frit Blaster has been installed in the Equipment Test Facility and tested. Recommended modifications and additions are shown. Recommendations for nozzle locations are shown. (Page 137)

Experiments are being planned which will determine whether limiting crane speed or using other alloys will facilitate water-only blasting of the canister decontamination chamber cradle. (Page 142)

A chelating cation exchange resin has been demonstrated efficient and effective in removal of mercury from both simulated and actual diluted Tank 30H supernate, indicating that a properly designed column of this resin should be able to remove essentially all of the mercury from that stream. (Page 148)

Laboratory-scale batch tests and fluidized bed column tests show that ES-465 cation exchange resin removes >90% of the mercury formated simulated sludge and formated high-level radioactive sludge. (Page 156)

The most significant minor waste component observably affected by the in-tank aluminum dissolution process was mercury. The net amount of soluble mercury increased, which would increase the mercury load on the tank farm evaporators. (Page 162)

The in-tank sludge processing demonstration verified that processing SRP high-level radioactive sludge in a waste tank will remove 75% of the insoluble aluminum and wash the soluble salts from the sludge to produce DWPF feed material. (Page 195)

Design activities of the DWPF continued on schedule. The percent design completion advanced to approximately 72% by the end of the quarter and the physical construction to 4% complete. (Page 201)

SAVANNAH RIVER INTERIM WASTE OPERATIONS

In response to an EED recommendation for prevention of tube bundle pitting in evaporators on standby, inhibited water is being maintained in the 242-H and 242-F evaporator pots until their operation is resumed. (Page 213)

F-Area reel-type problems accounted for a significant reduction in waste volumes again in November. (Page 213)

The 242-F evaporator remained down. The 242-16F evaporator operated 700 hours with a space gain of 232,000 gallons. (Page 213)

Since its extensive cleaning in May 1984, the 2F cesium removal column has operated satisfactorily. (Page 214)

The level of the F-Area No. 3 seepage basin increased 17 inches to 85 inches in November. (Page 214)

In the Beta-Gamma Incinerator Demonstration, installation of the primary chamber firestep is complete. Over 600 boxes of simulated wastes were incinerated over a four-day period. Two difficulties were encountered during the test burn. (Page 215)

In the Experimental TRU Waste Assay Facility building design drawings were reviewed and approved. (Page 216)

The final revision of the Transuranic Waste Facility Data Report was transmitted to the Engineering Department at the end of November. (Page 216)

DOE is reviewing a $990,000 project to fund construction of the ADD material handling demonstration at TNX. (Page 217)

Construction of the PWI feed prep system at TNX is complete. (Page 217)

Work continues in preparation for restarting waste removal in Tank 17F. (Page 217)

Waste removal from Tank 22H to Tank 31H is expected to begin early 1986. (Page 218)

A periscopic inspection of Tank 48H showed no significant corrosion in the vapor space or in the precipitate-coated portions of the tank. (Page 219)

A pilot scale mercury removal column has been installed in the 2H receiver cell to test the mercury removal effectiveness of Duolite ES-466 polystyrene resin on evaporator overheads. (Page 220)

The collection of soil cores from beneath the H-Area seepage basins was started. (Page 220)

Installation of the site cap and the groundwater recharge system is 70% complete. (Page 222)

THIRD QUARTER

LONG-TERM WASTE MANAGEMENT

HIGH-LEVEL WASTE TECHNOLOGY

Environmental and Safety Assessments

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

Chapter 5, Facility Design, of the Preliminary Safety Analysis (PSA), DPST-82-675, is being revised by Bechtel Corp. personnel for the Engineering Department.

A supplement to the DWPF PSA covering saltstone preparation and burial in Z Area is being prepared. Process and project information needed for the supplement have recently been published in updated versions of the Technical Data Summary and Basic Data Report. Updated source terms for effluent releases are expected to become available in October. The current schedule calls for a draft of the supplement to be completed in the fourth quarter of CY 1984.

OTHER SUPPORT

Cost Trade-Off Study for ICPP HLW Volume Reduction

The report, Cost Trade-Off Study of Potential Processes to Reduce ICPP HLW Volume, WIN-131, was issued. It evaluates cost effectiveness of potential head-end and immobilization processes for long-term waste management options for repository disposal of ICPP high-level wastes. The potential high-level waste volume reduction processes considered in WIN-131 include:

- The glass melter waste immobilization process to give a low-fluoride low-volume glass waste form,
- The hot isostatic press (HIP) waste immobilization process to give a ceramic or glass-ceramic waste form,
- The modified Zirflex fuel dissolution process,
- The process to remove the inert material, ZrF_4, from the HLLW after fuel dissolution and uranium extraction,
- The modified Fluorinel fuel dissolution process, using enriched boron B-10 as a neutron poison.

These processes are combined into ten ICPP processing options for cost evaluation. Major assumptions used in the evaluation are shown in Table 1.

The waste volumes which result from the ten different ICPP processing options vary from approximately 21,000 canisters of ceramic to 72,750 canisters of glass. The completion dates vary from FY 2033 to FY 2072. The alternative processing options reduce the HLW volumes over the base-case option from 1.1 to 4 times.

Total costs and cost breakdown in FY 1986 dollars were developed for each option. The options can cost from $11.3 to $18.6 billion. Five options using ceramic or glass-ceramic waste forms are the least expensive and range from $11.3 to $13.0 billion; five options using a glass waste form are the most expensive, ranging from $16.9 to $18.6 billion. Since some of the options use technologies such as Modified Zirflex and ZrF_4 removal, which have not been developed for ICPP HLW, the cost estimates are less accurate for these options.

The dissolution, extraction, and interim waste management costs are similar for all options, ranging from $5.2 to $5.8 billion, and cover the time period from FY 1983 to FY 2032 for dissolution and extraction processes and FY 1985 to FY 2007 for interim waste management. The long-term waste processing costs vary from $3.0 to $5.5 billion and cover the time period from FY 2007 to completion of processing, which can vary from FY 2032 to FY 2072. Disposal costs show the greatest variation from $2.5 to $9.8 billion, because of the variation in HLW volume.

The largest impact on total costs can be traced to the volume of HLW produced. A lower waste volume will result in lower transportation and disposal costs and in less time required to immobilize the waste. Since annual operating costs are significant, reduced operating time periods result in lower overall waste immobilization costs. Over the operating period for all options, the facility costs have a relatively low impact on total costs.

Conclusions and Recommendations

Based on this economic study and the underlying assumptions used, the major conclusions and recommendations include:

- Development of low-volume waste forms such as ceramic and glass-ceramic materials should be continued to immobilize ICPP HLW because the use of these products alone may be the most practical method to reduce total waste management system costs.

TABLE 1

ICPP Fuel Processing and Waste Immobilization Assumptions

ICPP Fuel Processing	
Time Period	FY 1985 through FY 2032. No fuel processing after FY 2032.
Rate	Long-term plant processing rate projections.
Base-Case Process	Fluorinel fuel dissolution and extraction.
Alternative Processes	Modified Zirflex fuel dissolution after FY 2007.
	Modified Fluorinel fuel dissolution after FY 1992-1997.
ICPP HLW Immobilization	
Time Period	From FY 2008 until as late as required to process calcined waste backlog plus decontamination waste after fuel processing is shut down in FY 2032.
HLW Immobilization Rate	Interim HLW operations from FY 1985 through FY 2007. No interim HLW operations after FY 2007.
	1700 canisters per year for base-case glass and modified Fluorinel glass options.
	1000 canisters per year for low-volume glass, HIP-ceramic, HIP-glass-ceramic, Modified Zirflex-ceramic, Modified Zirflex-glass, ZrF_4 removal-ceramic, ZrF_4 removal-glass, modified Fluorinel-ceramic options.
Base-Case HLW Immobilization	NWCF calcination through FY 2007.
	Glass melter after FY 2007 for HLLW and stored calcine.

- The feasibility and practicality of Modified Zirflex and ZrF_4 removal processes for reducing ICPP HLW volume should be evaluated further. Waste forms for the resulting HLW should be evaluated to determine practical waste loadings.

- R&D on Modified Zirflex and ZrF_4 removal processes should be continued in case there are additional constraints to reduce ICPP HLW volume to as low as possible.

- Development of glass waste forms and processees should be continued to provide a backup technology if some unforeseen problems arise in the ceramic or glass-ceramic processes. The low-volume glass process does provide a cost advantage over the base-case glass process and should be further evaluated.

- Practical modification to the Fluorinel dissolution process, including those not evaluated in this report, should be evaluated further to determine waste volume reductions and potential long-term cost savings. The substitution of enriched B-10 for boron as a neutron poison appears promising based on projected long-term costs, but will cost more in the short term. The processing modifications should be made as soon as practical after their impacts are identified and resolved to reduce stored waste volume.

- System costs for the other ICPP waste management alternative strategies, which use near-surface disposal at the ICPP of stabilized calcine, should also be evaluated and compared to the system costs of this study, which only considered repository disposal of ICPP immobilized HLW.

Modified Zirflex Laboratory-Scale Studies

The Modified Zirflex process was selected for laboratory experimentation. The laboratory studies involved dissolution of Zircaloy-2 coupons in a mixture of 5.5M ammonium fluoride and 0.5M ammonium nitrate at several temperatures. The effects of a soluble neutron poison (boric acid) on the dissolution rate at several temperatures were also studied. Several Zircaloy-2 coupons were oxidized to produce an oxide coating of about 0.001 inch. These coupons were dissolved at various temperatures in the unpoisoned dissolvent. The dissolution rate was greatly reduced by the oxide coating. The initial rate constants for the dissolution appears to be first order with respect to uncomplexed flow rate, however, the overall reaction appears to be second order.

The following table summarizes the data collected:

T°C	Conc. NH_4F M	Conc. H_3BO_3	Conc. NH_4NO_3	Initial Rate Constant, $mg/min\text{-}cm^2$
97	5.5	0.00	0.5	14.8
97	9.3	0.93	0.5	7.8
97	5.5	0.00	0.5	5.1 (oxidized coupon)

The initial rate constants at 80°C are 7 to 10 times lower than at 97°C and at 70°C are about 20 times lower than at 97°C.

Laboratory-scale precipitation of the dissolver product has been conducted using NH_3 gas and NH_4OH. Each method was able to precipitate more than 99% of the zirconium at a pH of 9.1 to 9.8. Dissolver product from the dissolution of the oxide-coated coupons and from the poisoned dissolvent discussed above precipitated in a similar manner. Preliminary size analysis of the precipitate indicates that it is relatively coarse with about 50% of the mass being greater than 90 microns and 70% being greater than 38 microns.

The settling characteristics of the precipitate differ depending upon the method used (NH_3 gas or NH_4OH liquid) and the rate of addition. In general both methods produce a dense precipitate which settles to about 30 to 35% of its original volume in about 2 to 3 hours. The settled solids consist of 16 to 26% dry solids and were filtered to produce a cake of about 30% solids. The cake formed rapidly with no blinding of the coarse, Whatman #41 paper. The settled solids were also dewatered by centrifugation to produce a slurry with a solids constant of about 25%. Both methods produced a clear supernate.

Laboratory-Scale Glass Melter Studies

Slurry feeding of a laboratory-scale melter has been successfully performed. Feed, in the initial tests, was composed of liquid simulated zirconia waste - Frit 127 (>140 mesh) and combined in proportions to result in a glass product of 33% waste loading. Fluoride present in the waste was immobilized by the addition of excess calcium nitrate.

Results of initial feeding studies indicated that the melter could be fed at a minimum practical rate of 15 mL/min. To reduce this feed rate, slurry was prepared using Frit 127 ground to finer size (<200 mesh). Grinding frit to this size resulted in a decrease in minimum practical feed rate to 6 mL/min. The temperatures obtained during melter feeding, idling and cold cap dissolution operations are given in Table 2. Electrode current density during these operations, performed under Joule heating conditions, varied between 2.02 and 2.47 amps/in^2. During slurry feeding operations a porous, voluminous residue formed on top of the melt. Residue buildup on top of the melt was accompanied by the emission of water vapor and oxides of nitrogen which caused the cold cap to bubble, but not to froth significantly.

Frit and waste glasses produced from slurry feeding of the laboratory-scale melter were translucent green in color and very uniform in appearance. Their appearance was equal to, or better, than those produced by vitrifying solid feed on a crucible scale, or in the laboratory or pilot-scale melters. A summary of the properties determined to date of the slurry fed glasses and the calcine fed glasses is given in Table 3.

Frit Development Studies for Fluorinel Waste Glass

A glass frit to immobilize Fluorinel waste from which 80% of the fluoride has been removed is being developed by systematically varying frit components and waste residue to give optimum product properties. The systematic experimental procedure used to generate new formulations for optimization, the results of this study through the frit round of formulation testing, and a description of the desirability coefficient derivation have been previously described. The composition of second round formulations generated by the procedure is given in Table 4, Part A. The properties of the second round formulations, the desirability coefficients of each property, and the overall desirability coefficient of each new formulation are given in Table 5, Part A. Although products of the second round had improved overall desirability coefficients over those replaced, none of them produced translucent, homogeneous glasses. Thus, a third round of formulations (Table 4, Part B) was determined using the same calculations as for the second round. Products of two third round formulations had the highest overall desirability coefficients (Table 5, Part B), yet attained and produced the first translucent, homogeneous glasses of the study. A fourth round of formulations (Table 4, Part C) also produced two translucent, homogeneous products of high overall desirability coefficients. Products of these two formulations, Nos. 15 and 17, also attained some of the highest desirability coefficients attained in the study (Table 5, Part C).

TABLE 2

Mean Temperatures Recorded During Different Phases of Melter Operations (Degrees Centigrade)

Glass	10 Hours of Idling	Feeding	Dissolution
Frit glass	1072 ±5	-	-
Waste glass with as-received frit	1040 ±3	995 ±9	1026 ±2
Waste glass with ball-milled frit	1036 ±2	990 ±4	1027 ±2

TABLE 3

Product Characteristics of Frit 127 - Zirconia Waste Glass Prepared by Slurry and Solids (Calcine) Feeding

		Leach Test Results (Total Mass Loss, g/m^2 day)			
127 Glass	Viscosity (poise)	Soxhlet*	MCC-1** 3 Day	7 Day	X-Ray Diffraction Analysis Results
Slurry Fed Waste Glass					
Prepared with as-received frit	150-300	0.39	0.03	0.14	CaF_2, α-alumina
Prepared with ball-milled frit	150-300	0.99	0.14	-	CaF_2, α-alumina
Solids Feeding Waste Glass					
Frit glass	75-140	1.55	0.29	0.08	Amorphous
Crucible scale					
Radioactive***	150-300	1.7	4.42	3.78	CaF_2, α-alumina
Nonradioactive	150-300	3.1	1.59	3.10	CaF_2, α-alumina
Pilot scale melter		3.8	2.22	3.50	CaF_2, α-alumina

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* Performed at 95°C for 72 hours.

** Performed at 90°C with deionized distilled H_2O leachant.

*** Prepared with radioactive zirconia calcine retrieved from Bin Set 2.

TABLE 4

Candidate Second, Third, and Fourth Round Glass Formulations Generated for Product Property Optimization Study

A. Second Round Formulations

Formulation Number	Weight Percent SiO_2	Alkali Oxide	B_2O_3	Waste Residue
9	53.8	9.3	10.0	26.8
10	43.0	20.1	10.0	26.8
11	49.9	12.1	6.8	31.1

B. Third Round Formulations

12	46.4	17.2	10.4	25.9
13	42.4	20.7	5.5	31.6
14	54.0	8.3	6.8	30.9

C. Fourth Round Formulations

15	41.7	20.1	10.7	27.5
16	41.9	11.8	13.4	32.7
17	37.6	23.9	10.7	27.7

TABLE 5

Properties of Second, Third, and Fourth Round Fluorinel Glass Products

Formulation Number	Total Mass Loss Rate by Soxhlet Leach, g/cm^2 day	Desirability Coefficient	Viscosity, poise	Desirability Coefficient	Corrosion to Inconel® 690,* mils/month	Desirability Coefficient	Overall Desirabilit Coefficient
Part A - Second Round							
9	2.51	0.841	400	0.063	2.54	0.771	0.344
10	5.72	0.601	75	0.555	14.00	0.368	0.497
11	8.02	0.378	300	0.060	5.21	0.600	0.531
Part B - Third Round							
12	3.09	0.801	350	0.435	0.91	0.988	0.701
13	0.33	0.980	325	0.555	1.117	0.986	0.812
14*	-	-	>500	-	-	-	-
Part C - Fourth Round							
15	3.60	0.765	75	0.555	0.87	0.988	0.749
16	7.80	0.403	400	0.109	0.90	0.988	0.351
17	4.50	0.699	125	0.754	1.69	0.980	0.802

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* Did not produce a product with measurable properties.

Ceramic Formulation Development Studies

Hot isostatic pressed (HIPPed) forms developed in the study performed under subcontract by Rockwell Science Center show excellent potential for providing significant volume reduction in final HLW volumes over melter formed borosilicate glass. The highest loadings up to 75 wt % at 3.4 to 3.6 g/cm^3 density were obtained in laboratory-scale studies by conversion of low alkali content (50:1 Fluorinel liquid waste:sodium bearing waste) waste with yttria-silica additions to a ceramic form. With proper control over redox and chemical mixing conditions the product crystalline phases (zirconia, CaF_2, $NaYSiO_4$) will host all actinides while a durable interstitial high-silica glass phase will retain boron and host cesium and strontium. For the low alkali wastes, conversion with yttria and silica additives to a ceramic form also resulted in a product of the high leach resistance.

More development is required to define consersion of high alkali wastes (6:1 Fluorinel liquid waste:sodium bearing waste) to a product of high waste loading, density and leach resistance. Products formed through HIPPing after addition of yttria-silica, titania-silica-calcia, or with Frit 127 with waste are being studied. Frit-based products may offer a volume reduction of 3.2 over melter produced glass, while the yttria-silica and titania-silica-calcia forms may offer a volume reduction of about 3.4.

WASTE-FORM DEVELOPMENT AND CHARACTERIZATION

Waste-Form Compliance Test Method Development

At the request of the BWIP and in support of the BWIP task to develop waste acceptance requirements and specifications, the MCC has collected and developed a set of procedures for a materials interactions test method -- The BWIP Compliance Test on Radionuclide Release for Determining Acceptance of a Loaded Waste Form (MCC-14.4). The purpose of this test is to measure steady-state radionuclide concentrations in solutions after hydrothermal interactions of a synthetic basalt groundwater, basalt, and a radioactive waste-form material.

Measured portions of a crushed and sized waste-form material are combined with crushed and sized reference basalt and immersed in synthetic basalt groundwater solutions. The suspensions are agitated in relatively inert reaction containers at 150°C for up to 3 months. Selected elemental and radioisotopic analyses are performed on filtered and unfiltered solution aliquots from each container. To eliminate, as much as practicable, the effect of atmospheric oxygen on the solution redox potential, the deaeration of the synthetic basalt groundwater, loading and sealing of the reaction vessels, and final sampling of the test suspensions are conducted in an inert gas (argon) glove box.

The steady-state radionuclide concentrations determined in this test method do not, in themselves, indicate any equilibrium solubility-limited reaction, because steady-state concentrations include both solution and colloidal species and are not approached from both undersaturated and supersaturated conditions. Furthermore, the test method does not provide procedures for identifying stable or metastable solid phases.

Following review and concurrence by the SWIP, the MCC-14.4 Compliance Test Method was submitted, in July 1984, to the Office of the Chairman/Materials Review Board (OTC/MRB). An appendix to MCC-14.4 identifies the factors that will affect the approval status of MCC-14.4. These factors include the time necessary to reach steady-state conditions, quench effects, suitability of materials in high radiation fields, container decontamination, tolerance limits for solution analyses, and benchmark test data for determining the precision and accuracy of the method. An initial review of the test method and related issues was received from the OTC/MRB in August. In September, MCC staff met with members of the BWIP staff to discuss appropriate responses to the review of MCC-14.4 by the OTC/MRB. The changes and modifications recommended will be incorporated into a revised MCC-14.4 test method, which is to be resubmitted in December 1984, following review and concurrence by the BWIP.

During the current reporting period, modifications to the rotator ovens were completed and the oven hoods were fabricated and installed in the lab. A set of reaction vessel leak tests at 150 and 200°C using Teflon® (Du Pont Company) and aluminum/asbestos gaskets and synthetic (GR-4) basalt groundwater were completed for periods up to 1 month. None of the vessels using Teflon® seals leaked; however, two out of four vessels with aluminum/asbestos seals leaked noticeably (3 to 30 liquid weight percent loss over 3 weeks). The aluminum/asbestos seals were badly corroded and coated with a white precipitate. The precipitate was identified as a mixture of poorly crystallized boehmite (gamma-AlOOH) and calcite. Apparently the aluminum corroded easily in the alkaline GR-4 groundwater, and the corroded surface provided nucleation sites for the precipitation of calcite. No precipitation was observed in tests with Teflon® seals. These tests suggest that the synthetic GR-4 groundwater is supersaturated with respect to calcite at 150°C.

Washing of the Cohassett basalt and the crushed and sized plutonium-doped glass was completed. The results from the ultrasonic cleaning of the basalt indicate that ultrasonic cleaning was not really necessary to remove the fine material. The procedure adopted involved washing the basalt with distilled water on a 230-mesh sieve. The basalt was dried at 60°C for 24 hr and is stored in the argon chamber. The plutonium-doped glass was washed in distilled water in an ultrasonic bath for 5 min, the supernatant was decanted, and the glass was dried.

The first MCC-14.4 waste form compliance test was initiated in September. Ten titanium pressure vessels were loaded with a 1:1 mixture of ATM-4 (plutonium-doped 76-68 glass) and Umtanum basalt. The GR-4 synthetic basalt groundwater was added to obtain a solution-volume-to-solids-mass ratio of 10:1. The vessels were sealed with Teflon® gaskets and placed in a rotator oven at 150°C for durations of 3, 6, 9, 12, and 15 weeks. During the first 2 weeks, to determine that there was no leakage, the vessels were weighed on 3 different days; no significant weight changes were observed for any vessels. The first two vessels (duplicates) are to be dismantled and sampled during the first week in October.

Aliquots of the GR-4 groundwater made up for the MCC-14.4 test (discussed below) were submitted to two different analysts for ICP/IC analyses. The results from both analysts were in general agreement for all constituents except potassium. However, the concentrations of calcium and silicon were not within the 5% tolerance limit of their respective concentrations for the theoretical GR-4 composition. The cause of the calcium and silicon discrepancies is being investigated.

In addition to MCC-14.4 testing with plutonium-doped glass, experiments with uranium-doped borosilicate glass (PNL-76-68) have been conducted through FY 1984. The test matrix in some of these tests have been altered in order to measure the results of such changes on observed elemental solution concentrations.

Analyses from previously completed experiments using uranium-doped glass/basalt suspensions in deionized (DI) water (discussed in the prior report in this series) were compared with results from an MCC-3 glass-only test in DI water. In the glass/basalt test equal amounts of glass and basalt (of the same mesh size) were used; the total SA/V (670 cm^{-1}) was the same in both tests.

The pH values (at room temperature) of the glass/rock suspensions heated to 90°C for up to 91 days ranged from 9.4 to 9.6. Total uranium concentrations measured in 0.45-μm filtrates from the 90°C glass/basalt system were 3 ppm at 90 days. However, uranium concentrations in 1.8-nm filtrates were ~0.5 ppm and appeared to have reached steady state. The difference in measured uranium concentrations in the 0.45-μm and 1.8-nm filtrates suggests that the bulk of the uranium released from the waste glass is in colloidal form.

Several experiments using the uranium-doped 76-68 glass were begun during the second half of FY 1984. In one test, various ratios (1:1, 1:10, and 1:100) of uranium-doped glass and Untanum basalt were added to a synthetic GR-4 groundwater at 90 and 150°C. In addition, a rocking autoclave was set up containing a suspension of the uranium-doped glass and basalt in GR-4 groundwater at 150°C. These materials interactions tests were designed to test the effects of various conditions pertaining to the MCC-14.4 test method. They have been completed, and the data are currently being analyzed.

Preliminary analyses of solutions from the 150°C rocking autoclave containing uranium-doped glass, basalt and GR-4 synthetic basalt groundwater indicate that between 150°C and 25°C, the quench effect on the measured pH (a 0.3 pH unit increase) was similar to that observed in the glass/groundwater test. However, the addition of basalt to the system resulted in lower pH values (for solutions sampled at temperature and measured at room temperature) by 0.5 to 0.7 pH units. In the case of colloidal or dissolved silica, the presence of basalt lowered the pH (to about 9.6), which in turn reduced silica saturation relative to the glass-alone experiment. Quench effects of about 5% were observed for dissolved silica concentrations.

From the 150°C rocking autoclave experiment, uranium concentrations for nonfiltered aliquots and 0.45-μm filtrates were about 2 to 3 ppm and for 1.8-nm filtrates were 0.5 to 1 ppm. No significant quench effect was observed for uranium. The results infer that the bulk of the uranium released from the waste glass is in colloidal form (as observed in the 90°C glass/basalt test with deionized water) and that the uranium colloids are not affected by silica colloids under these conditions. Further detailed results will be forthcoming in reports to be prepared in FY 1985.

Development of Corrosion Test Methods

Test methods are being developed and validated for evaluating the corrosion of metallic container and canister materials in nuclear waste repository environments. The methods will be applicable to basalt, salt, tuff and crystalline rock repositories. The MCC program is emphasizing the development of methods that are consistent with the test plans of the waste package programs for the various repositories and will provide a basis for establishing reproducibility of corrosion tests and statistical statements on the precision of corrosion data.

The MCC began benchmark tests for corrosion in basalt earlier this year and has continued this testing. Tests for 30 and 120 days at 100°C were completed, and the MCC-105.1 Benchmark Test Report was prepared and will be reviewed by the BWIP in October 1984. This test report will provide supportive evidence for obtaining MRB approval of MCC-105.1.

MCC-105 Test Method for Long-Term Corrosion in Repository Environments

Test methods are being developed and codified for basalt, salt and tuff. Six test methods have been identified, MCC-105.1 through MCC-105.6, for application to three types of geologic media. Three of the test methods, two for basalt and one for salt, have been drafted and reviewed by BWIP and ONWI waste package investigators. Methods for tuff are still in a preliminary stage. The Office of Crystalline Repository Development (OCRD) program has not initiated any corrosion testing yet. The MCC has initiated benchmark testing for the basalt static test, MCC-105.5.

<u>MCC-105.1 Basalt Static System</u>. The benchmark tests according to initial drafts of this test method were completed for 30 and 120 days at 100°C. As a result of test results on the 30-day tests, the MCC revised the procedure for loading specimens to ensure better contact between the crushed basalt plus bentonite packing material and the specimen surfaces. The average penetration rate correlated with apparent area of contact; the change in loading procedure is expected to improve the precision of the test method. The data were analyzed for variations among specimens and among vessels. For the 120-day tests, the within-vessel specimen-to-specimen relative standard deviation (RSD) was about 10%, the vessel-to-vessel RSD was about 6%, and the overall specimen-to-specimen RSD was about 11%.

<u>MCC-105.3 Salt-Limited Reactants System</u>. Further development of this salt system static test is awaiting decisions by ONWI. The MCC purchased several titanium vessels in anticipation of later development of this test method.

<u>MCC-105.4 Basalt Flowby System</u>. The MCC codified this test method during the previous reporting period. Further development of the test method depends on initiation of experimental activities to prove out the concept of placing corrosion specimens in a packet that limits water access and simulates long-term, post-closure conditions in a basalt repository. The MCC plans to initiate testing in early FY 1985 and to submit the test method to the MRB in FY 1985.

MCC-105.5 Basalt Waste Vapor System. Investigators for the BWIP have requested the MCC to codify a test method wherein the corrosion specimens are placed in a slowly refreshed water vapor environment to simulate conditions in the operational period of the basalt repository. Westinghouse Hanford Company investigators have built a test apparatus for performing this type of testing, and the MCC will follow progress of their testing program in FY 1985. The MCC plans to initiate benchmark testing and submit the test method to the MRB in FY 1986.

Waste Form Characterization

Major emphasis will be placed in FY 1985 on the application of MCC and other test methods to waste acceptance specifications. A review of these specifications made this year showed that several MCC test methods are directly usable to demonstrate compliance. The need for two new MCC test methods was also identified in this review. In FY 1985 the MCC will prepare a draft plan on methods that should be employed to collect data that will show that a waste form complies with acceptance specifications.

A summary of recent progress in each major area of work is presented with a short description of work planned for FY 1985.

MCC-1P and MCC-2P Static Leach Test Methods

The major objectives in this work element were the submission of the two test methods to the MRB for full approval and the collection of data on ARM-1 (Approved Reference Material) glass. Both objectives were essentially met. MCC-1 was submitted to the MRB early in the year and was returned with comments. These comments were carefully incorporated into the test method and the appendix issue report. MCC-2 was submitted to the MRB in August with a report resolving the technical issues in the appendix. In these submissions the issues of Eh control, quench effects, and applicability to waste acceptance specifications were resolved by including them as limitations to the test method. The other issues were resolved either by changes in the test method or by presentation of data substantiating the MCC position. An important change in MCC-2 was the elimination of the 190°C test because of excessive leachant losses.

The testing on the ARM-1 glass is proceeding without any significant problems. The results are comparable with those from other glasses such as 76-68. The ARM-1 testing will continue into FY 1985, and after completion of the 1-year tests, the data will be collected into two data packages for review by the MRB. Once approved, the data will be distributed with the ARM-1 glass samples for use by investigators to verify the accuracy of their data.

MCC-3P Agitated Powder Leach Test Method

Extensive tests were conducted this year to help resolve several technical issues remaining on this test method. The test method itself was modified somewhat to keep it current with the changes made in MCC-1 and MCC-2. This test method was not submitted to the MRB because the test results did not sufficiently resolve some of the technical issues.

Tests were made using uranium-doped 76-68 glass to evaluate the effects of quenching on the final results. Samples of leachant were taken at 25°C intervals from 150°C to ambient conditions. Some small effects were noted that were judged to be relatively minor. However, as the MCC does not believe it is possible to rule out quench effects for all systems, a warning on quench effects will be included in the test method's limitations section. A revised version of MCC-3 will be submitted to the MRB in FY 1985.

MCC-3 tests were initiated using ARM-1 glass. The glass samples were placed in deionized water, silicate water, and brine at temperatures of 90 and 50°C. These tests will continue into FY 1985, and the final results will be compiled in a data package for submission to the MRB.

MCC-4S Low-Flow-Rate Leach Test Method

The MCC decided this year to rewrite the MCC-4 test method in FY 1985 before resubmitting it to the MRB. The test method is technically adequate, but the presentation of the material needs to be clarified. No work beyond this rewrite is planned for this test method.

MCC-7S Method for Preparation of Isothermally Heat-Treated Forms

The MCC-7 version that was submitted to the MRB was returned with comments. These comments were beneficial in improving the clarity of the test method and were incorporated. The test method will be resubmitted to the MRB early in FY 1985.

MCC-13S Recommended Practice of Determining the Microstructure of a Waste Form

A preliminary draft of the MCC-13 recommended practice was prepared and will be completed in FY 1985 and submitted to the MRB. This recommended practice will be directly useful in testing waste forms to show compliance with waste acceptance specifications.

MCC-15S Waste/Canister Accident Testing and Analysis

MCC-15 was developed this year to supply data required by the Transportation Technology Center (TTC) and by the draft waste acceptance specifications. The purpose of this method is to subject full-scale prototypic waste canisters to impacts that are required by regulations to simulate transportation and handling accidents. Data will be collected on the deformation of the canister and on the damage to the waste form inside the canister. Canister containment integrity will be determined by helium leak testing. The test method was drafted this year, and testing was performed to verify the soundness of approach and to provide data to the TTC. The method will be submitted to the MRB early in FY 1985 after it has been reviewed by the users of the data.

Two full-scale canisters were tested this year using the MCC-15 test method. The prototypic Savannah River Laboratory (SRL) canisters were dropped 9 m, with the center of gravity over the bottom corner. The glass was removed from the canisters and sieved into two size ranges: greater than and less than 6 mm. Representative samples of the smaller particles were taken and the size distribution was determined to 2 microns. The data were found to follow a log-normal distribution and were comparable to earlier data. The amount of respirable fines in one of the canisters was 80 g, which is a factor of about 150 below the proposed maximum limit for transportation of the reference high-level waste canister from SRL.

Thirty-six quarter-scale canisters were filled with SRL glass and tested under different conditions to determine what conditions cause the most damage to the glass and canister. Canisters were tested at -25°C and 85°C in four orientations: top, bottom, side, and slapdown. The glass from these canisters was removed and sized, and the data are being analyzed.

Development of MCC-15 will continue in FY 1985, and extensive testing of prototypic SRL canisters will be performed. A study is also planned that will use the canister deformation data to establish the ability of the SRL canister to maintain integrity after an impact.

Reference Materials and Handbook Data

A condensed version of Data Package MCC-D1 was published in PNL-3990. MRB approval of the complete data package was received.

Data Package MCC-D2 was revised according to recommendations received from the OTC/MRB and was resubmitted. The Data Panel of

MRB approved D2 and recommended additional changes. The MCC response to the Data Panel recommendations is in preparation. Data Package D2 has been published in PNL-3990.

Static leach tests are continuing on the ARM-1 in order to obtain calibration reference data for field applications of test methods MCC-1, -2, and -3. Tests up to 182 days duration have been completed for MCC-1 at 40 and 90°C, and to 91 days for MCC-2 at 150°C; both are continuing to 1 year. MCC-3 tests have been started at 90 and 150°C, and will continue to 91 days. Results for all ARM-1 tests are scheduled for publication in MCC Handbook Data Packages during FY 1985.

The BWIP project now requires that all MCC preparation and characterization of reference materials to be used in BWIP repository research and development (R&D) be conducted under terms of specific written procedures which have received prior BWIP QA approval. Nine such procedures have been written by MCC to cover the sequential tasks involved in production of approved testing materials. Use was made of existing QA procedures wherever possible, but reference materials production is mostly a unique activity requiring separate written formal procedures. Following iterative discussions with appropriate BWIP and PNL personnel, the final draft of these nine procedures has been submitted to PNL's MCC and QA management for approval. Concurrence by BWIP QA staff is expected by October 31, 1984. The procedures have been written so as to be applicable to all MCC materials preparation and generally will be applied hereafter regardless of which repository project or glass producer has requested the testing material.

ATM Glasses

Three new Approved Testing Materials (ATM) glasses have been completed, two others are in preparation or advanced planning, and one additional ATM glass is scheduled for FY 1985 (Table 6). The detailed characterization of existing glasses, planned for FY 1984, has been postponed until FY 1985 due to limited time and funding.

TABLE 6

MCC's Planned Preparation or Acquisition of Approved Testing Materials, April 1984 to September 1985*

Identification	Description	Radioactive Isotopes, g/g Glass	Status
New Materials			
ATM-1c	NNWSI** Glass-I (U-doped 76-68 type)	UO_2 (3.98E.2)	Complete
ATM-8	NNWSI Glass-II (Actinide-doped 76-68 type)	UO_2 (4.1E.2) NpO_2 (4.0E.3) PuO_2 (1.0-E.3) Tc_2O_7 (5.0E.3)	Complete
ATM-9	SRL Defense Glass: ONWI, BWIP	UO_2 (1.84E.3) PuO_2 (2.50E.3) Am_2O_3 (6.30E.4) NpO_2 (1.10E.2) Tc_2O_7 (1.00E.2)	Complete
ATM-11	SRL Defense Glass: BWIP	UO_2 (1.84E.2) PuO_2 (2.50E.3) Am_2O_3 (6.3E.3) NpO_2 (1.13E.2) Tc_2O_7 (1.05E.2) Sm_2O_3 (2.00E.2)	Advance Planning Completed
ATM-12	NWSI Glass-III (Actinide-doped "aged" 76-68 type)	UO_2 (4.00E.2) NpO_2 (2.30E.3) PuO_2 (4.00E.4) Am_2O_3 (1.20E.3) Tc_2O_7 (8.40E.3)	Glass In
ATM-10	West Valley	To be selected	Planned
ATM-102	BWR Spent Fuel	"Typical" Burnup	Planned
ATM-103	Spent Fuel	"Extreme" Burnup	Planned

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* Nominal values: analyses in progress.

** Nevada Nuclear Waste Storage Investigations.

INTERIM WASTE OPERATIONS - PROCESS DEVELOPMENT

TRANSURANIC (TRU) WASTE MANAGEMENT

"Technical Basis for Limits for the Disposal of Transuranic (TRU) Waste," DPST-84-226, has been transmitted to the Department of Energy, SRL, SRP, and Wilmington management. The final document now includes a compendium of SRP site-specific pathway analyses and scenario calculations including groundwater contamination, Savannah River site boundary analysis (drinking water, recreation, irrigation/food chain), and hypothetical future land occupation cases (Wilhite-Fauth Base Case, lysimeter release rates, elimination of biotic transport). Absolute and incremental environmental values have been calculated as a function of eight scenarios to illustrate that the Pu-239 disposal limit could be as high as 1000 nCi/g without an environmental impact exceeding current DOE regulations (5480.1A). It has been recommended to DOE that the 10 to 100 nCi/g fraction of TRU waste be handled by Greater Confinement Disposal.

DOE has been requested to transmit this document to the U.S. House of Representatives (Rep. Dingle, Michigan, Commerce and Energy Committee) and the U.S. Senate (Sen. Hollings, South Carolina) by October 15, 1984.

LLW Burial Ground Analyses

DPST-84-854 (draft) on "Savannah River Plant Burial Ground: Environmental Transport Studies/Annual Report for the National Low Level Waste Management Program for FY 84 is in circulation for approval to transmit to EG&G/Idaho and ORNL. Subjects covered include TRU waste analyses (10 nCi/g vs. 100 nCi/g), analyses of potential transport of mobile radionuclides (H-3, Tc-99, I-129), exposure reduction factors for improved burial operation, food chain scenarios for surface stream contamination and results of calibration of the transport code against the tritium plume and other data bases.

DP-MS-84-82 on "Radionuclide Migration Studies at the Savannah River Plant Humid Shallow Land Burial Site for Low-Level Waste" was presented at the Denver National LLW Meeting and will be published in the Proceedings.

Under the Office of Civilian Nuclear Waste Management (DOE-HQ), the Technical Working Group for the DOE Site Transfer Committee was formed and includes SRL participation. The committee is charged with analysis of the technical data base (monitoring, inventory, modeling) for the Sheffield, IL, Commercial LLW site (test case) to judge compliance with the Nuclear Waste Policy Act of 1982. The procedures to be established by this committee will be applicable to decommissioning of Defense LLW sites, including SRP.

SRP Hazardous and Mixed Waste Sites

Assistance has been provided to SRL Seepage Basin and CMP Pits custodians on analysis of severity of soil and groundwater contamination for each of those areas. Procedures used to evaluate permissible soil contamination limits for hazardous/mixed waste sites have been reviewed with the Environmental Advisory Committee (Patrick, Cairn, Kahn, and Davis).

DPST-84-709 on "SP Project S-2598/SRL 904 Trench Radioactive Silt" was transmitted to LSD management with cover letter in response to Wilmington management concerns. Discussions continue with LSD personnel on the 904 Trench Soil analyses and severity of soil contamination.

DEFENSE WASTE PROCESSING FACILITY

SITE CONSTRUCTION ACTIVITIES

Construction activities are summarized below:

- Following completion of the pouring of a six-inch-thick mudmat for the vitrification building, re-steel was installed. The vitrification building concrete basemat, which is about ten feet thick, will be poured in twelve segments. The first pour began September 13 and lasted about twenty-four hours. Approximately 1400 cubic yards of concrete were placed.

- Installation of dowels, anchor bolts, forms, embedded plate and No. 9 rebar continues in preparation for the second pour (approximately 1400 cubic yards) which is scheduled for October.

- The 704-S operations building is being constructed early to provide office space for operating personnel. Three segments of the floor slab have been poured. A total of eight segments are planned.

- An area of unstable soil at the railroad crossing over Tinker Creek hindered the installation of the drainage piping culvert. The culvert is being relocated approximately 200 feet north of the present location. Removal of the drainage piping is complete.

- The storm drain system in S Area consists of two approximately equal length systems (designated as A and B) draining to two separate outfalls. Approximately 70% of the B-Line system has been installed. Work on the catch basins is in progress. Installation of the A-Line system is approximately 10% complete.

- The sanitary sewer plant is approximately 80% complete. Most of the underground lines associated with the sewage plant have been installed. Installation of electrical conduit is in progress. The floor slab for the chemical building has been poured.

- Backfilling and compaction of areas for the sand filter, fan house, and interim glass storage building are in progress.

PERMITS

Permits for various DWPF service facilities are required from the South Carolina Department of Health and Environmental Control (SCDHEC). Major activities in this area are summarized below:

- In August, SCDHEC issued a permit to allow receipt of domestic water in a tank truck as a temporary measure. A new 150 gpm well is planned to provide water during the construction phase.
- A sewage collection system permit for the temporary construction facilities was issued by SCDHEC on July 26. This permit will allow sewage collection in a 18,000-gallon tank which will be pumped out, as needed, for processing in an offsite treatment facility.
- In September, SCDHEC approved an application for a permit to construct the sewage collection lines in the operations portion of S Area. This permit includes a temporary discharge line from the sewage treatment plant to Upper Three Runs Creek rather than the planned discharge to Four Mile Creek. This will eliminate the need to dispose of sewage treatment plant effluent by trucking until the permanent effluent line to Four Mile Creek is installed. The NPDES permit which currently authorizes discharge to Four Mile Creek has to be modified to reflect this flow.

PROJECT DESIGN STATUS

Major activities in the DWPF design are summarized below:

- Engineering design continued to be focused on the critical path portions of the vitrification building model and the structural design for the first level of the vitrification building.
- Design of the new glass waste storage building is under way. This single-tier, clear span facility is designed to accommodate approximately 2300 filled canisters, or five years production by the DWPF process.
- Conceptual design of the saltstone facility has been completed, reviewed, and approved. Final design is beginning.
- Model activity continues to be a top priority. The vitrification building model is 66% complete and the melt cell model 87% complete. The status of the engineering design models and percent complete are shown in Table 7.

TABLE 7

Design Models - Percentage Complete

Item	221-S Building 3/4"	Melt Cell 1-1/2"	Sample Cell 3"	Cold Feed Chem Stor 3/4"	Low Point Pump Pits 3/4"	Aux. Pump Pits 3/4"
Model tables w/building frames	84	80	80	70	78	78
Equipment and installation	67	95	71	70	51	51
Embedded and header piping installation	67	80	44	0	68	68
Jumper installation	80	80	74	NA*	10	10
HVAC duct installation	20	NA*	80	NA*	0	0
Electrical/controls trays, motor control center, panel installation, lighting	66	100	49	0	0	0
Total model	66	87	62	29	46	46
Last month (8/24/84)	62	80	57	29	44	44

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* Not applicable

Melter/Melt Cell

The current melter off-gas system design provides a film cooler in the primary off-gas system but does not contain a cooler in the backup off-gas system. The design is being changed to provide a film cooler in the backup system.

Canister Decontamination

Canisters of waste glass will be decontaminated by blasting with a glass frit slurry. An experimental canister frit blaster at SRL used seven individual pumps to supply the frit slurry to nozzles which direct the slurry at the canister. However, the design for the DWPF decontamination chamber provides for the slurry to be fed to the nozzles from a recirculation loop similar to that used for the melter feed. Verification of the DWPF concept will be performed during the operability testing of decontamination chamber No. 1 using a feed system similar to the DWPF design.

Contamination on the outer surface of a waste glass canister will be determined by smearing and counting of the smears. SRL tests of three types of smearing mediums (standard filter paper, Buehler Microcloth, and Buehler Texmet) indicate that each removes similar amounts of radioactive material. A throwaway smear holder will be specified in design.

Process Cell Tanks

The contract for fabrication of process cell tanks was awarded. These tanks will be fabricated with trunnions, nozzles, etc. installed to the dimensional tolerance required for the remotely maintained DWPF. In the past, these items were generally installed on the tanks after arrival of SRP. Representatives met with the vendor to discuss the tank design, specifications, inspection, shipping, etc. Tank fabrication facilities were toured. Prior to beginning the fabrication of DWPF tanks, the vendor plans to make improvements to building and equipment (temperature control, bench marks, etc.) to ensure that the tanks are properly fabricated.

Shielding Studies

Waste processing is performed behind a thick concrete shield wall to protect personnel from radiation. The criteria for design specified that the radiation through the wall should not exceed 0.5 mrem/hour. An analysis was initiated of the effect of wall penetrations such as embedded chemical addition lines on the shielding design. Currently, the study is complete for all of the weld test cell and up to the mezzanine level (elevation 302'-6") in the chemical process cell. Of the 428 penetrations analyzed, 158 have been identified as requiring additional shielding. The additional shielding ranges from less than 1 to 6-inch-thick steel plate or equivalent placed in the walls adjacent to horizontal legs of penetrations. Some plates are as large as 35 x 11 inches, but generally are about 15 x 10 inches. This study will be completed during October.

Distributed Control System

Design of the distributed control system (DCS) "primary" and "backup" host computers will be changed from the standard DEC PDP 11/44 to newer technology DEC VAX systems. The primary host will be a VAX 11/750 located in Building 221-S. The backup host will be a VAX 11/785 located in Building 210-S and will perform numerous management information functions for DWPF.

Many of the control operations presently defined in the process control descriptions (PCDs) and control logic diagrams (CLDs) require significant operator/supervisor action. Where possible (and desirable), these operations are being redefined to fully utilize the advantage of the distributed control system's decision-making capabilities. Process operating procedures (POPs) are being written to define this new control philosophy. The vendor will use the information in the POPs, PCDs, CLDs, and P&IDs to configure the Control System.

Materials of Construction

The Materials of Construction Composite Committee met to review corrosion test data. New test results and recommendations are listed below.

- Pumps - Tests to determine the effect of galvanic corrosion on various pump materials coupled with Alloy C-276 indicate that Stellite 6 has good corrosion resistance under these conditions. Tests are continuing to confirm the abrasion resistance of Stellite 6 for the most severe service. CW7M and HC 250 have been tested under simulated less severe service conditions, judged acceptable, and specified to the vendor. CW7M is a cast nickel base alloy similar to C-276; HC 250 is a cast iron base alloy with high Cr and C content for hardness. Pump material changes will not impact pump delivery dates.

- Quencher - Potential galvanic couples that could occur between the quencher and off-gas line have been tested and found not to accelerate corrosion. After extensive testing, it has been concluded that ALLCORR (a product of Teledyne-ALLVAC) and Alloy C-276 are acceptable for off-gas quencher service and are superior to any other alloys tested. Because both materials exhibited limited attack in some tests, the committee recommended the first quenchers installed be fabricated of ALLCORR and the spares be fabricated of Alloy C-276. Work by Bechtel confirmed that ALLCORR can be welded by standard welding procedures.

- Salt Precipitate Process - Test programs are being developed to identify materials of construction for salt precipitate process equipment and to evaluate effects of the new stream on designed DWPF equipment. Because sludge process corrosion test conditions anticipated the precipitate process stream to some extent, significant changes in DWPF material recommendations are not expected.

Interarea Transfer Facilities

A rheology of 200 dynes/cm^2 and 10 cp for sludge feed has been used as a design basis for waste transfer pumps. However, recently confirmed rheology data for salt precipitate waste feed to DWPF (300 dynes/cm^2 and 50 cp) makes it necessary to provide a pump with larger head capacity for pump pits in the interarea transfer line between H Area and S Area. Existing pumps in use at SRP are not adequate to meet the requirements for a pumping head of about 250 psi at 100 gpm. Specification and bid requests will be prepared and submitted to pump vendors for delivery of a prototype for testing. The pump is to be an overhung shaft type with design features to include a separately removable motor and bearing unit to permit replacement without removal of the pump portion of the assembly. Motor and bearing failure account for about 90% of failures in existing pumps in waste service.

Present design of pump pit tanks provides for two 38-inch openings to accommodate a pump and an agitator. The design is to be changed to provide an opening for a second pump in the tanks. Uncertainty of the characteristics of sludge at various compositions and concentrations, and concurrent frequency of flushing which may be required lead to this request.

Ventilation of the pump pits is to be provided when the pit covers are removed. The design is to provide a minimum air flow of 50 linear feet per minute into the pit with half the cell covers removed (approximately 200 ft^2 opening). Air for this purpose will be supplied and diverted from the building ventilation system previously included in the design. Air discharge from the building and pit will be filtered by HEPA units and monitored before release.

H-Area CCTV System

Operation of the 221-H hot canyon CCTV test was discontinued during June because of crane decontamination system. Following completion of this work, operation was resumed the week of September 10. Three of the six pan/tilt and camera units were reinstalled but the picture quality is erratic and fuzzy during crane movement. The problem is being investigated.

Two new unshielded camera enclosures are being modified and will be installed on the crane when scheduling permits.

Recommended modifications to reduce the starting torque on the pan/tilt units have been installed and are being checked out.

Three pan/tilt units were ordered from an alternate vendor for testing and they will be installed as soon as they arrive.

TANK FARM OPERATION

Tank 13 Cleanup

Construction continued to excavate contaminated asphalt and dirt from the area surrounding tank 13. Through June 20, 434 cubic yards containing an estimated 17.9 curies had been removed and transported to the burial ground.

Remote blast cleaning of the north side of tank 13 began June 2. Most of the northern half of the tank had two passes with the Blastrac® unit, each pass removing about 1/8 inch. Remote cleaning of the accessible areas on the north side is essentially complete. A radiation survey indicates the radiation levels have been significantly reduced. Radiation levels at 3 feet above the concrete are mostly 40-200 mR/hr. Several "hot spots" exist with rates up to 800 mR/hr. Lead shields have been installed around the feed pump riser and feed line to minimize operator exposure during manual blasting of the "hot spots".

A Von Arx® surface cleaning machine has been ordered. This device will remove contaminated concrete from areas inaccessible to the Blastrac®. Modifications will be made to the machine to allow cleaning under the feed line.

Tank 20 Monitoring

As reported last month, four additional groundwater monitoring wells have been drilled closer to tank 20 to determine if radioactivity is escaping (DPSP-83-21-5). Results of initial samples taken in May were not significantly different from data for the other wells surrounding the F-Area single wall tanks (Table I). However, the nonvolatile beta activity, 39 pCi/L in the well south of tank 20 was higher than for the other new wells, so the monthly results will be monitored closely for trends.

There has been no unusual increase in radioactivity in the tank 20 sump; in fact, radioactivity removed from the sump has leveled off since April 8 (Figure 1). Monitoring of the sump will continue on a weekly basis to determine if this trend holds.

INSPECTION PROGRAM

Inspection Summary

Inspection of tank 14 showed a very small increase in the waste in the annulus pan due to very slow seepage from the primary vessel since 1982. In tank 9 annulus a leak detection probe was improperly located. Inspection of the tank 27 cesium removal column revealed the column was in good condition.

Visual Imagery

Inspections in tank 14 showed a very small increase since 1982 in the dry solidified waste in the annulus. Annual inspections since the annulus was dewatered in 1972 have documented that a small amount of waste has seeped during the intervening years from the tank primary vessel into the annulus pan.

Inspection revealed the leak detection probe beneath the south riser annulus riser was not on the pan floor but atop the ventilation duct 20 inches above the floor.

Inspection made in the tank 27 cesium removal column revealed that the spent zeolite had been successfully removed and the screens were in good condition.

Beta-Gamma Incinerator Project 5-2424

Photographs were made during and after installation of new refractories in the combustion chambers. These photographs document the before service conditions of the chambers.

An inspection was made of the refractory in the exhaust gas line adjacent to the spray quench tank. The refractory appeared to be in good condition.

BURIAL GROUND OPERATIONS

Beta-Gamma Incinerator Project

The vendor has completed the installation of the refractory fire brick in both chambers of the incinerator. A new refractory was recommended by two consultants because the original refractory was not installed properly and was in very poor condition. It was decided to replace the refractory rather than perform extensive patching repairs during the radioactive demonstration. The new refractory is about 80% brick and 20% castable.

Hotworks Inc., contracted to cure the new refractory, used propane burners to heat the chambers to 1500°F. This cure is complete.

A Halon® fire suppression system has been installed in the feed lag area and control room to replace the original sprinkler system. The sprinkler system was converted to Halon® after it was determined that the water system would overfill the water collection tank and cause water to back up into Building 299-H. The new Halon® system alleviates this potential problem.

The Halon® system is presently charged with Freon® for its initial testing. It will be charged with Halon® and activated prior to the next box burning campaign.

Construction is modifying the solvent feed tank by adding top-mounted level detectors and installing a dike and lead shielding. Project is specifying a replacement recirculating pump for the tank.

The solids auger feeder was not effective in transferring calcium oxide into the solvent feed tank during the slurry test burn. The auger feeder was tested with the reference particle size calcium hydroxide. The auger did not work with the calcium hydroxide even though this material was originally used by the vendor to specify the auger. The vendor recommended modifying the auger tube with a central core. This part has been ordered and will be tested prior to the next run.

Two new spray nozzle locations were selected. One location makes use of the primary chamber's length to spray the slurry, allow the solvent to burn, and deposit ash in the hearth to be removed by the ash rams. The second nozzle location sprays vertically into the primary chamber hearth. The two new nozzles have been ordered from the vendor, Coen Spray Systems Co. To provide a cooler flame, the new nozzles will use steam rather than air to atomize the slurry. These changes will be tested to determine if they eliminate the unacceptable ash deposits that were produced in the earlier run.

Solid Waste Compaction Facility (SWCF)

A Basic Design Data is being prepared for an FY-85 cost-funded project. This facility will process low level beta-gamma and alpha waste. SRL is in the process of preparing a Technical Data Summary for this process. A meeting was held with Impell Corporation in Atlanta to discuss design of a remote material feeder.

Equipment Retirement and Reclamation (ERR)

A Basic Design Data is being prepared for a $70 million, FY-87 line item project. The facility, called the "TRU Waste Processing Facility" (TWPF), will house both the ERR and Plutonium-238 Waste Incinerator (PWI) processes. A sand filter for the TWPF will also be constructed on this project.

The TNX Equipment Cold Test Demonstration (ECTD) project is being prepared for an estimated $993,000. This cost project will cover purchasing and installing additional testing equipment, and a new building. The Shredded Metal Handling System was inspected at Machine Development Corporation. Fabrication is approximately 60% complete. The system is expected to be ready in August.

The purchase requisition for the Tele-Robot manipulator has been approved by Du Pont SRL management and is now being routed through DOE. Formal specifications were issued to seven vendors for bids. Also, specifications for the electric worktable have been issued for comments.

Experimental TRU Waste Assay Facility (ETWAF)

Site preparation is under way for construction of the ETWAF. The construction bid package has been issued for bid solicitation, and construction is expected to begin in late July. An assay system training session for WMT, WMO, and WMWE personnel at Los Alamos National Laboratory has been set up for early August. TFI Corporation is preparing prints for final approval of the Real-Time Radiography System.

Waste Certification Facility (WCF)

Funding for the WCF has been reduced from $880,000 to $470,000. The project cost was reduced by eliminating the change room, HEPA filtration of the building exhaust and spray painting equipment. Also, the overhead crane capacity has been reduced. The scope of work should be complete by the end of June for FY-84 authorization.

Retrieved Waste Preparation Facility (RWPF)

Informal discussions have begun with three concrete cutting tool manufacturers. Target Equipment and Norton Equipment offer adaptations of standard concrete cutting equipment that would be used to open the seven-foot-diameter culverts.

The third vendor, Bechtel, proposes an alternative to radial cutting; evenly spaced holes would be drilled around the culvert's circumference into the grout. The holes would be filled with an expansion compound which would crack the grout. The Bechtel proposal eliminates the maintenance and cooling water problems associated with radial saw concrete cutting.

Specifications for explosion tests required to determine the design basis accident for the RWPF are being drafted.

WASTE TRANSFER/TANK REPLACEMENT

Tank 17 Waste Removal

The leak in the tank 18 jet was repaired and the transfer from tank 18 to tank 27 was completed. A total of 488,000 gallons was transferred out of tank 18. Initial tank levels were: tank 18 - 366.3"; tank 27 - 210.3".

The southeast and west slurry pumps in tank 17 started up on 6/20/84 for batch #3A. The northeast slurry pump was not operated because of its proximity to the suspected crack site in the tank.

Batch #3B will proceed after batch #3A is complete. The suspected crack site in tank 17 at 315 inches will be inspected after batch #3B.

The decision was made to accelerate the installation of the telescoping transfer pump (TTP) into tank 18. The installation will begin at the completion of batch #3 in tank 17, after the material pumped from tank 17 to 18 has been decanted.

The TTP should increase the transfer rate out of tank 18 relative to the existing jet, and should be more reliable than the jet. The jet leaked the previous three times that a transfer was attempted. The TTP should speed up the waste removal programs from 17, 19, and 20, because all the waste from these tanks must pass through tank 18.

Oxalic Acid Cleaning of Tank 24

Preparations are continuing for oxalic acid cleaning of tank 24. The two slurry pumps were lengthened and reinstalled in the tank. The rotary spray riser plugs are being fabricated. Preparations are being made to remove the CRC from tank 24. The replacement CRC, which will be installed in tank 32, is expected to be delivered in July.

At the low tank levels planned during the oxalic acid cleaning there is some concern that the slurry pumps may vortex, causing air to be sucked into the pumps. This could damage the pumps. Plans are to test a clean pump at TNX to determine how fast the pump can be run in tank 24 without vortexing. Until data are available, the tank 24 slurry pumps will be operated at 1,000 rpm as a precautionary measure.

Interarea Dilution Facilities, Project 5-3663

Preparation of the CAC estimate continues. Design of facilities in F Area and 643-G continues.

The Nametre viscometer was received for testing at TNX. A test loop was set up to demonstrate jetting sludge slurries. This test will be completed in July. The results will be used to determine if a jet can be used as a secondary method to empty a pump tank.

In-Tank Precipitation

The Technical Data Summary written by SRL was issued in its final form on 6/7/84. It will be forwarded to the Engineering Department.

SRL completed a study of repeated oxalic acid cleaning of the filter bundles. It was concluded that the life of the filters will not be limited by the cleaning process.

The ED proposed an alternate filter bundle containment system that would house the filters in shielded "cans" above the tank top. This design was inadequate in that a filter changeout could not be completed in foul weather and maintenance of equipment inside the can could not be done remotely.

An attainment study of the precipitation process and the saltstone process was made by WMT. It was concluded that a filter feed pump or filter bundle failure in tank 48 could affect our ability to feed the saltstone plant. This reinforced the need for installed spare equipment and the ability to change filters remotely. It was also concluded that an installed spare feed pump in tank 50 (the filtrate feed tank to saltstone) is needed.

A preliminary study was done by WMO and WMT to determine the makeup of the first few batches of feed to the precipitation facilities and saltstone. Although the design of the saltstone plant was based upon 15-year aged feed, it was determined that this feed scheme was not possible. The types I, II, and IV tanks contain a total of 1.5 years of feed. The only other tank that will be equipped for salt removal is tank 41 and this tank will be aged about 4.5 years before it is processed and fed to saltstone. DWPF is currently reviewing the design of the saltstone plant to assess additional shielding requirements.

Sludge Processing

A WMT study to optimize the sludge processing program was completed. The volume of sludge to be co-washed, the volume of water per wash, and the degree to which the sludge will be allowed to settle after each wash were varied within the given constraints. The result was that a 400,000 gallon batch of sludge will be co-washed with a 300,000 gallon batch. About 19.2 washes and 455 days will be required. This strategy will allow WM to produce two years worth of sludge feed to DWPF while limiting wash water usage to 6.65 gallons wash water per gallon of washed and settled sludge. Aluminum dissolution will add slightly to each number.

WMO and WMT proposed a sludge removal/processing scheme to DWPF and SRL personnel. The constraints were getting out of Type IV tanks by 1986, feeding well blended sludge to the DWPF and having a two-year supply of washed sludge on hand at least one year prior to the startup of DWPF. There was no problem meeting the constraints. The findings will be documented in July.

Waste Management Effluent Treatment Facility (WMETF)

SRL has completed testing the leachability of hazardous materials from saltstone containing a synthetic formulation of concentrated waste from the proposed WMETF. The saltstone passed the EP toxicity test for chromium, mercury, copper, and lead by a factor of 25 and for nitrate by a factor of 5. Thus, it is non-hazardous with respect to these materials.

SRL experimental work on candidate WMETF process steps - filtration, reverse osmosis, ion exchange, and ultrafiltration (UF) is under way. Preliminary filtration results show a pH of 7 to be optimum for iron, aluminum, and silicon removal and the addition of a filter aid/flocculant improves silicon, Ce-144, Ru-106, and Cs-137 filterability. Reverse osmosis tests on contaminated cooling water samples, prepared by diluting actual F and H-Canyon samples, and H-Area trebler samples have been run and analysis is in progress to determine decontamination factors. Ion exchange columns are being set up and test runs should begin shortly. Preliminary UF runs at TNX using TNX process water, which is similar to 200-Area water, were made and results are being evaluated.

F- and H-Area Seepage Basin Closure

Woodward-Clyde Consultants (WCC) have completed their review of the proposed basin sediment characterization study. Their major recommendations are to postpone the work until the basins are out of service and can be drained. This will greatly simplify sample acquisition, and reduce the amount of sample analysis. WMT, SRL, and E&E met with WCC to review these recommendations. It was agreed that a preliminary characterization of sediment in all basins is needed now to provide data for evaluating closure options. This will be done as soon as possible and will consist of 3 to 5 shallow core samples (3 to 5 feet deep) from each basin. The detailed characterization study (deep cores down to the water table, shallow cores on a 50 ft x 50 ft grid), with a reduced analysis scope, will be deferred until after the basins can be drained.

FOURTH QUARTER

LONG-TERM WASTE MANAGEMENT TECHNOLOGY

HIGH-LEVEL WASTE TECHNOLOGY

Other Support

Modified Zirflex Laboratory-Scale Studies (ICPP)

The modified Zirflex fuel dissolution process is an alternative for ICPP high-level waste volume reduction to be studied for basic feasibility of reprocessing nuclear fuels. Preliminary laboratory studies were completed for the modified Zirflex process dissolution of Zircaloy coupons. This report provides a summary of recent additional laboratory studies which are ongoing and include laboratory studies on precipitation and precipitate settling.

Studies were conducted to determine the effects of surface oxide coatings on the dissolution of Zircaloy-clad fuel coupons in the modified fuel dissolution process. In this series of dissolution studies, the boiling modified Zirflex dissolvent (9.3M NH_4F - 0.5M NH_4NO_3) and added 0.93M H_3BO_3 did not penetrate the surface oxide coating in 8 hours. Hydrofluoric acid was added at 0.5M and 1.0M to the modified Zirflex dissolvent to attempt dissolution of the oxide. The results of these tests are shown in Figure 1. The dissolution curve of an unoxidized zircaloy coupon in the modified Zirflex dissolvent is shown for comparative purposes. The calculated material balance for the dissolution step agreed with experimentally measured quantities.

Studies were conducted to determine the settling rate of the precipitate produced by the addition of ammonia gas or ammonium hydroxide in one or two steps to the modified Zirflex process dissolver product. The settling studies were made using synthetic dissolver product containing five fission product simulants (Sr, Ru, Cs, Ce, and Ba), depleted uranium, and in some cases the nuclear poison boron and/or added HF. All studies used solutions containing about 30 g/L zirconium at 25-30°C. Figure 2 presents the range in height of the precipitate/supernate interface with respect to time. As several initial column heights were used, the abscissa has been normalized to 100. The limits shown in Figure 2 indicate the range of settling observed in this study for all solution compositions used.

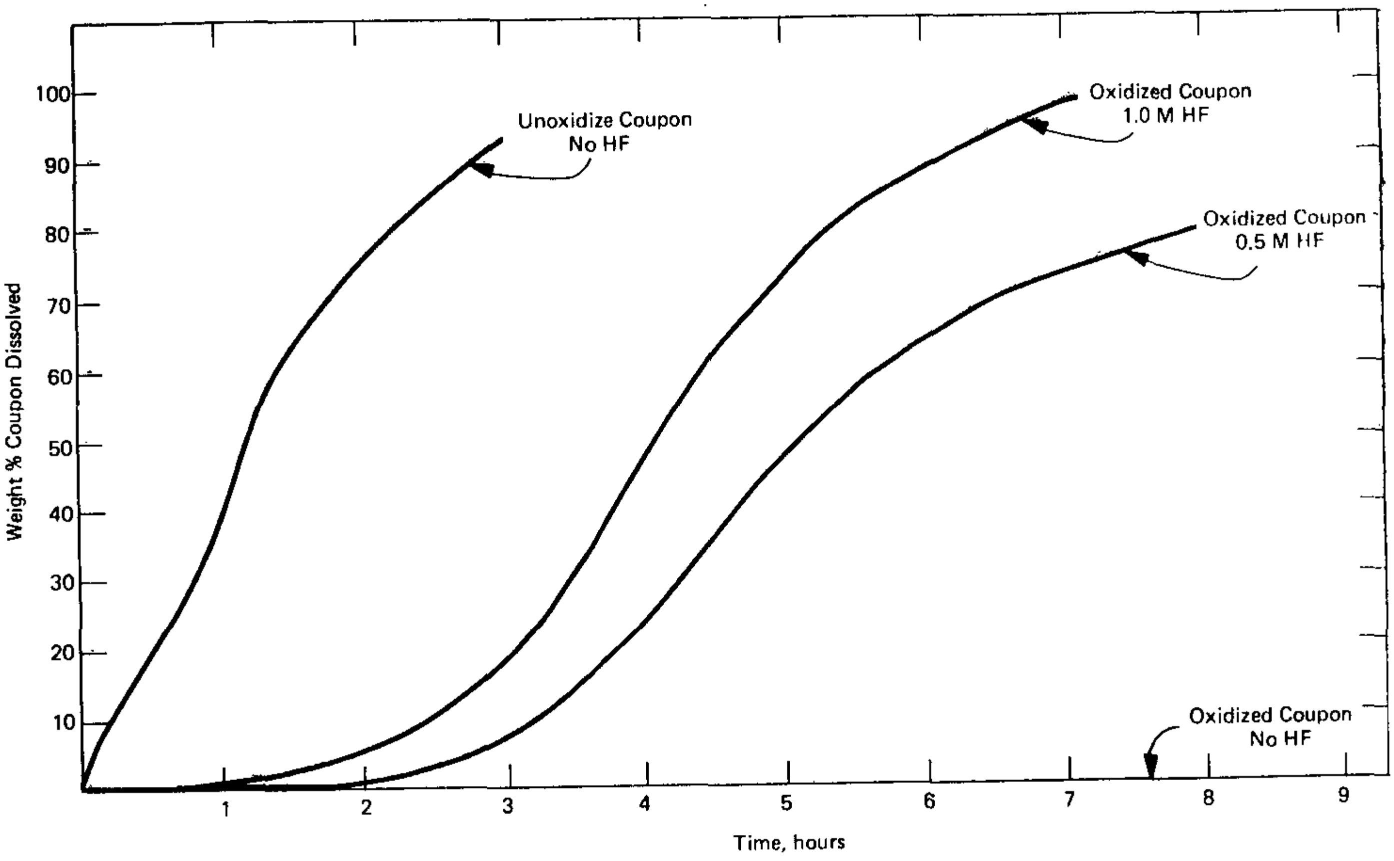

FIGURE 1. Dissolution of Zircaloy Coupons as a Function of HF Concentration and Time

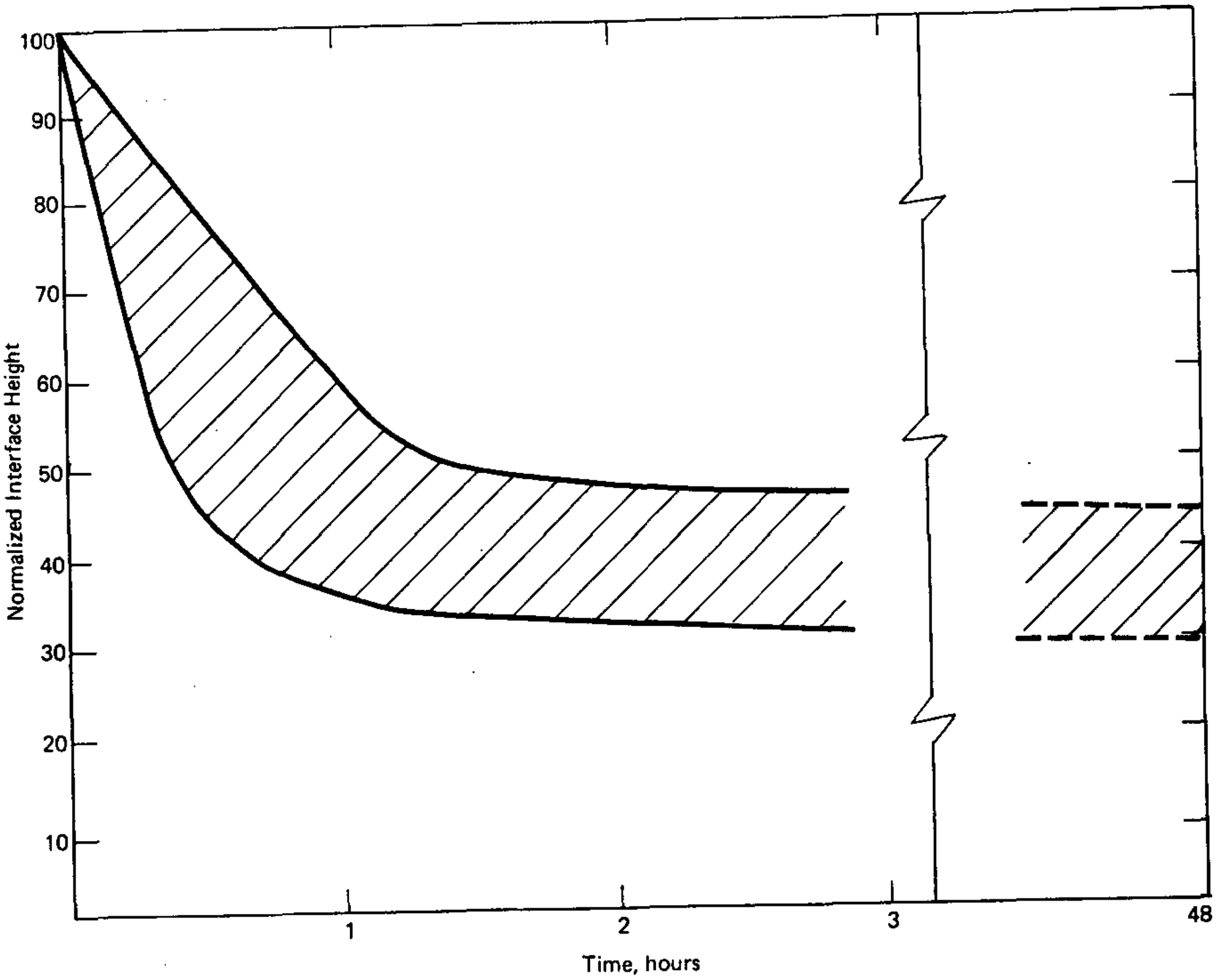

FIGURE 2. Range of Precipitate Interface Heights During Settling

All suspensions started with a solids content of about 4% by weight. After 2 hours of settling, the solids concentrated to 7-10% by weight. During an extended settling time (48 hours), the solids concentrated to 8-13% by weight. From a settling time of 2 hours, 50-65% of the original liquid volume could be decanted for recycle preparation.

Measurements have been made to determine the approximate size of the coagulated precipitate. These measurements are summarized in the following table.

Particle Size (micron)		Weight %
Greater than 180	less than 180	18.6
Greater than 90	less than 90	21.2
Greater than 43	less than 43	19.4
Greater than 38	less than 38	22.2

The size distribution indicated that the precipitate and supernate could be separated by mechanical methods such as filtration, gravimetric methods such as sedimentation (settling), or centrifugation.

Studies have been performed using both filtration and centrifugation to concentrate the solids and separate them from the liquid. The suspension was placed in centrifuge tubes and centrifuged at 8000 rpm for varying lengths of time. The solids can be concentrated to about 23% by weight after 15 minutes of centrifuging. This concentration would allow about 80% of the original liquid volume to be decanted for recycle preparation.

Filtration studies show that the precipitate can be easily filtered into a dense, moist filtercake with no blinding of the coarse (Whatman 41) filter paper. The solids are concentrated in the filtercake to about 28% by weight. This concentration would allow about 84% of the original liquid volume to be recovered for recycle preparation. Washing either the centrifuged solids of the filtercake would produce a dilute fluoride-bearing stream which could be concentrated for recycle preparation. This washing could reduce the fluoride content of the solids which would lead to a waste volume reduction.

WASTE FORM DEVELOPMENT AND CHARACTERIZATION

HLLW Neutralization Studies (ICPP)

Neutralization of ICPP acidic HLLW to separate radioactive components as precipitates from inert components may be a potential intermediate step in producing a reduced volume final waste form. Thus, a preliminary laboratory scale study was performed to determine the approximate volumes of precipitated HLW components and of inert wastes resulting from neutralization.

Liquid simulated Fluorinel waste of composition shown in Table 1 was used in this study. The waste was titrated into a strongly basic solution to keep the pH higher than 13.0 and to keep amphoteric aluminum mainly in solution while precipitating multivalent ions of actinides, fission products, and waste matrix elements. During neutralization, certain elements, including B and Cs are expected to remain in solution, while others including Na, K, Al, Sr, and F are expected to distribute between the solution and the precipitate. As in the SRP-proposed process, it is hoped that the volume of liquid waste contains reduced amounts of radioactivity, making the resulting solid potentially disposable as low-level waste.

TABLE 1

Composition of Simulated Fluorinel Waste Used in Neutralization Study

Component	Nominal Species Contribution, M
Zr	0.483
Cd	0.141
Al	0.312
Sn	0.005
Cr	0.056
F	3.610
NO_3	2.310
B	0.253
SO_4	0.087
H^+	1.820

An initial study was performed by titrating 100 mL of simulated fluorinel waste into 420 mL of 1.77M NaOH. The precipitate which formed was separated by centrifuging, scrubbed four times with 75 mL portions of 0.3M NaOH, then washed three times with deionized water to dissolve sodium fluoride and aluminum hydroxide. X-ray diffraction analysis of this precipitate determined the presence of no crystalline materials. The precipitate was mixed at 32 wt % with one of the test frits[1] developed for low-fluoride simulated HLW and vitrified at 1150°C and 20 hours to produce a homogeneous glass sample.

The supernate, precipitate, scrubs, and wastes were analyzed by inductively coupled plasma emission and atomic adsorption techniques. Elemental distribution in the precipitate, supernatant liquid, and washes resulting from neutralization are given in Table 2.

TABLE 2

Elemental Mass Balance from Neutralization of 100 mL of HLLW

Element	Concentration in HLLW Solution, mg/100 mL	Amount Precipitated from HLLO Solution, mg	Amount in Supernate (520 mL), mg	Amount in NaOH Scrub (300 mL), mg	Amount in H_2O Washes (225 mL), mg	Total Amount Recovered, mg	% Removed
Al	841.8	95.3	614	124.7	14.9	849	101
Cr	291.2	285.8	3.0	1.5	0.5	291	100
Zr	4406	4044	28.0	5.0	2.5	4080	93
Cs	50	0.9	39.1	7.3	0.5	47.8	96
Sr	50	1.2	3.4	2.0	-*	-*	-*
F	6859	78.3	4632	974.7	57.3	5742	84
B	273.5	2.4	236.5	98.3	3.3	339**	124**
Cd	2184	1593.4	13.2	32.6	6.5	1646**	75**

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* Inconclusive data for Sr, possibly due to matrix interference in analysis.

** Possible matrix interference in analysis.

The data indicate that most Cr, Zr, and Cd are precipitated, while most Al, F, B, and Cs remains in solution. Some Al, F, and B which precipitates are redissolved by the caustic scrubs and water washes. The data are incomplete for Sr, high in recovery for B, and somewhat low in recovery for Cd because of solution matrix interferences inherent in the chemical analysis techniques applied.

The precipitate remaining after scrubbing and washing weighed 8.98 ±0.05 g. The analyzed composition in the precipitate shown in Table 2 can be calculated to produce approximately 79 g/L of the equivalent oxides, which can potentially be formed into 250 g glass at 32 wt % loading. If the same quantity of simulated HLLW is not neutralized but calcined and vitrified, it would result in approximately 830 g of glass. This indicates that neutralization of Fluorinel HLLW may result in approximately a three-fold volume decrease in vitrified final product over that obtained by mixing the waste with frit components and calcium nitrate to complex all fluoride to form a slurry to feed a glass melter.

Approximately 8000 m^3/yr of solidified LLW could be generated by neutralization. The NaF formed initially is a hazardous waste and would have to be converted to CaF_2. The solidification step has not been tested and required a determination of the effects of Na, B, CaF_2, and other potential constituents on forming a durable grouted waste form for LLW disposal.

Low Volume Glass Development

Low volume glass development activities discussed in this report include slurry feeding and frit development studies. Feeding of the laboratory-scale melter was successfully performed with a slurry of the composition given in Table 3. The vitrified products from the feeding tests have characteristics similar to those of solids feeding, but are formed at a much slower rate because energy from the melt is required to vaporize the liquid waste. T 3

Frit-waste residue combinations resulting in potentially feasible low-fluoride, low-volume glasses of practical waste loadings, low melt viscosities, and low corrosivities have been developed on a laboratory-scale basis.

Low volume ceramic and glass ceramic waste forms were prepared using hot isostatic pressing (HIPPing) techniques with high sodium content and low sodium content simulated wastes of compositions shown in Table 4. T 4

The glass-ceramic products are prepared by mixing calcined waste with a glass frit and then densifying and crystallizing the product by HIPPing. Waste loadings of 80 wt % at densities of

TABLE 3

Composition of Frit 127, Simulated Liquid Zirconia Waste and Slurry Used to Produce Glass of 33 wt % Waste Loading

Component	Frit 127 wt %	Waste, M	Slurry, grams/liter*
SiO_2	70.4		220.7
Na_2O_3	13.0		40.7
B_2O_3	8.5		28.1**
Li_2O	6.0		18.8
CuO	2.1		6.6
Al^{+3}		0.83	14.0
B^{+3}		0.22	
Zr^{+4}		0.76	43.3
Ca^{+2}†		2.2	
F^-		4.0	97.6††
H^+		1.36	0.86
NO_3^-		1.6	62.01

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* Components are combined in the following proportions: 1000 mL Zr waste, 470 grams $Ca(NO_3)_2$, and 501 grams of Frit 127 to give 1600 mL slurry.

** Total from frit and waste.

† Added to simulated zirconia waste to immobilize all F^-.

†† As CaF_2, added as 427 g $Ca(NO_3)_2$ to form 97.6 g CaF_2 per liter of slurry.

TABLE 4

Compositions of Simulated Wastes Used in Ceramic and Glass-Ceramic Development Studies

Component	Low Na-Waste, wt %	High Na-Waste, wt %
ZrO_2	22.82	21.63
CaF_2	54.79	52.05
Al_2O_3	5.58	7.11
$CaSO_4$	0.61	1.01
Fe_2O_3	0.03	0.11
CdO	5.84	5.55
B_2O_3	4.33	4.18
Na_2O	0.47	3.75
K_2O	0.07	0.54
CaO	3.94	2.67
U_3O_8	1.00	1.00
Cs_2O	0.25	0.25
SrO	0.25	0.25

3.2 g/cm^3 have been achieved. The ceramic products are prepared by the addition of materials including titania, yttria, and calcia to calcined waste to produce the desired crystalline phases with the waste when densified by HIPPing. Silica is also added to produce a durable amorphous glass phase with the waste boron which will not form durable crystalline phases.

Typical compositions of these waste forms are shown in Table 5. Both types of products are as, or more, leach resistant than glasses and result in waste volume reductions of 55-65% compared to glass.

Table 6 compares the leach resistance of major elements in the most desirable glass-ceramic and glass waste forms tested with those in Frit 127 glass.

All of the forms appear to have potential to reduce ICPP waste volume. Of the sixteen different frit-based glass-ceramics prepared using both low-Na and high-Na waste, all showed similar behavior in terms of product density, crystalline content, and processability. The major differences were in leach resistance and the distribution of glass and crystalline phases at the highest waste loadings.

PROCESS AND EQUIPMENT DEVELOPMENT

Radiolysis of Tetraphenylborate (University of Florida Trip Report)

Summary

On October 4, 1984, the recent program and current plans relating to the tetraphenylborate radiolysis subcontract were discussed with Professor R. J. Hanrahan of the University of Florida, Gainesville, Florida. The new ISCO liquid chromotograph purchases as part of this subcontract was viewed during a tour of Professor Hanrahan's laboratory facility. The following report reviews the accomplishments of his work to date and lists the areas remaining to be investigated. In addition, an interview progress report submitted by Professor Hanrahan is attached. Based on the number of areas still to be investigated and the short time remaining on the present subcontract, a one year continuation of this work is recommended.

Results to Date

The major accomplishments on this subcontract are detailed in the attached report. Briefly, these have been:

TABLE 5

Typical Compositions of Candidate Glass-Ceramic and Ceramic ICPP HLW Forms

Candidate Waste Form	Typical Composition, wt %					
	Waste	Frit 127	CaO	TiO_2	SiO_2	Y_2O_3
Frit 127 glass-ceramic	70	30	-	-	-	-
Titania-calcia-silica	80	-	1	6	13	-
Yttria-silica	83	-	-	-	15	2
Pyrochlore-based	53	-	-	6	19	22

TABLE 6

Summary of Leaching Properties of Most Desirable Ceramic and Glass Ceramic Waste Forms Compared to Frit 127 Glass

	MCC-1 28-Day Leach Resistance, g/m^2-d		
High Na Waste	Ca	Sr	Cs
70% waste (Frit 127 glass-ceramic	0.09	0.29	0.33
80% waste (Na-free frit glass ceramic)	0.10	0.23	0.22
80% waste (titania-calcia-silica ceramic	0.18	0.82	ND
70% waste (yttria-silica)	0.06	<0.01	0.38
Low Na Waste			
70% waste (Frit 127 glass ceramic)	0.11	0.33	0.59
80% waste (Ti + Si + Ca ceramic)	0.23	1.60	1.15
80% waste (yttria-silica-ceramic)	0.14	0.30	ND
33% Frit 127 glass	2.71	0.43	9.28

ND = not detectable

The high leach resistance of the ceramic forms is directly attributed to the Zr content of the waste. The presence of a liquid amorphous phase during HIP consolidation enhances diffusion and reaction in the product, and near theoretical densities can be achieved at temperatures from 1000 to 1100°C.

- Analytical techniques have been established which are suitable for quantitatively measuring the hydrogen, benzene, phenol, and biphenyl produced during the radiolysis of tetraphenylborate solutions and slurries. Both gas chromatography and liquid chromatography are used. An ISCO liquid chromatograph with a variable wavelength detector was purchased as part of this project.

- Radiolysis of tetraphenylborate solutions produces hydrogen at the same rate as radiolysis of water alone. The hydrogen G-value of 0.46 molecule per 100 eV (of energy deposited in the solution) was determined on a 0.05 molar NaTPB solution. This value is the same as that determined for pure water. The implication is that little or no hydrogen is produced from the tetraphenylborate. This substantiates the assumptions made earlier in calculating the amount of hydrogen which will be produced during storage of the precipitate slurries.

- The pH increases during radiolysis of tetraphenylborate solutions. This result is important since it indicates periodic addition of more sodium hydroxide will not be required to maintain inhibitor levels in the slurry storage tank.

- During the radiolysis of KTPB slurries, most of the benzene is trapped by the solids and is not released. Subsequently, dissolving the solids frees the benzene. This phenomenon was observed during the full-scale in-tank demonstration when benzene levels in the tank exhaust increased during precipitate washing. Approximately 10% of the benzene produced was released promptly during radiolysis and 90% was released when the solids were dissolved in acetone. The G-values for both types of benzene production have been measured.

- A recent result indicates that the radiolysis product distribution may be influenced by the solvent used to dissolve the irradiated solids. In experiments so far, irradiated KTPB was dissolved in acetone or acetonitrile. When acetonitrile was used, less benzene was produced and other products (such as phenol and biphenyl) were observed. Further investigation of this point is under way.

- Radiolysis of a 10 wt % KTPB/water slurry produced the same amount of benzene (per 100 eV of energy deposited in the sample) as did radiolysis of a 25 wt % slurry. This is surprising since much of the radiolysis energy should be deposited in the liquid part of the slurry. As liquid is replaced by solid in the more concentrated slurry, one expects more benzene to be formed. This result implies that regardless of where the radiolysis energy is initially deposited, it is all eventually transferred to the solids. This point is to be investigated further using more dilute slurries.

Much of the first nine months of work was spent in obtaining equipment and establishing the analytical techniques. With these techniques in hand, the rate at which radiolysis data can be obtained should increase.

Future Work

Several aspects of the radiolysis of tetraphenylborate slurries still need to be investigated. Some of these can be accomplished in the time remaining on this subcontract. The following areas of concern were identified:

- Effects of dissolved salts on product yield and distribution. To date, all the radiolysis experiments have been done on solutions or slurries in distilled water. The presence of NaOH and salts such as $NaNO_3$ and $NaNO_2$ could produce new decomposition products and change the product distribution. The determination of these effects is a high priority objective during the remainder of the subcontract.

- Effect of solvent on product distribution. The solvent used to dissolve the slurry solids may change the decomposition product distribution. Previously, irradiated KTPH slurries were dissolved in organic solvents prior to analysis. In actual practice, water will be used to dissolve the excess NaTPB. Experiments using water as the dissolving medium for irradiated NaTPB slurries are a high priority objective during the remainder of the subcontract.

- Hydrogen production in slurries. The rate of hydrogen production from the radiolysis of a homogeneous solution of NaTPB was measured. Measurement of the hydrogen production rate in the presence of dissolved salts and slurry solids is still required. It is not expected that the rate will change significantly under new conditions.

- Effect of slurry concentration. As mentioned above, benzene production rates have been measured on 10 and 25 wt % slurries. Further work between 0 and 9 wt % is needed.

- Effect of oxygen on product distribution. All the work so far has been done in the presence of air. The impact of oxygen on the product distribution is important for a basic understanding of how the various products arise.

- Identification of minor decomposition products. With the availability of the liquid chromotograph, better separations and more sensitive detection are obtainable than with the gas chromatograph. This should allow the detection and identification of some of the minor products of the radiolysis. This is required for the long-term predictions on residue accumulation in the storage tank.

In the remaining two months of the subcontract, only the first two items in this list can be investigated adequately. The remaining items are sufficiently important and extensive to require a one year extension of the subcontract. Professor Hanrahan is amenable to an extension and it is possible the same postdoctoral fellow can continue the work.

The Radiolysis of Tetraphenylborate (Interim Report, September 1, 1984, University of Florida, Department of Chemistry)

Introduction

A detailed explanation of the preparation and properties of soluble and insoluble metal tetraphenylborate salts is given by Flaschka and Barnard.[2]

In 1967, Williams et al.[3] carried out the photolysis of aqueous solution of sodium tetraphenylborate with light of 2537 A° wavelength. In the presence of oxygen, biphenyl was the major product; and in the absence of oxygen, 1-phenyl-1,4-cyclohexadiene was the major product.

In 1982, Kilpatric and Lee identified and determined the rate of formation of gases and liquids by irradiating a mixture of Cs/K tetraphenylborate precipitate in a synthetic salt solution. The gases were hydrogen, carbon monoxide, and nitrogen; the liquids were benzene, nitrobenzene, and biphenyl.

The present investigation is to identify and determine the yield of the products in the radiolysis of soluble and insoluble tetraphenylborate salts using gas chromatography and high pressure liquid chromatography techniques.

Environmental Methods and Equipment

Reagents

Sodium tetraphenylborate: ACS grade (99.5% min) sodium tetraphenylborate was obtained from Eastman Kodak Company.

Potassium tetraphenylborate: This compound was prepared by the procedure described by Flaschka and Barnard.[4] Microanalysis report showed the following results:

Expected	% C:	80.4	% H:	5.6
Found:	% C:	79.9	% H:	5.6

Sample Irradiation

Radiation Source and Vessel: Irradiation of the tetraphenylborate solutions was carried out using a 300-curie ^{60}Co gamma source which is described in Reference 5. Figure 3 shows a cross-sectional view of the irradiator. Glass test tubes of 13 mm diameter, with ground-glass stoppers, were used as radiolysis vessels. A rigid aluminum sample holder was used to ensure reproducible positioning of the radiolysis vessel.

Dosimetry

Weiss, Allen, and Schwarz[6] have suggested a procedure for the preparation of Fricke dosimeter solution. Samples consisting of 5 mL and 1 mL, respectively, of the Fricke dosimeter solution were irradiated in 13 mm test tubes with ground-glass stoppers. Irradiations were carried out in the absence and presence of NaCl, used to diagnose possible organic contamination. Optical densities were measured on a Beckman spectrophotometer at a wavelength of 305 mm. Tables 7 and 8 give the optical densities of 5 mL and 1 mL solutions at various time periods. Figures 4 through 7 show plots of optical density versus irradiation time in the absence and presence of NaCl when 5 mL and 1 mL solutions were irradiated. The presence of NaCl does not affect the dose rates. The calculated dose rates when 5 mL and 1 mL of solutions were irradiated were 2.31×10^{19} eV $mL^{-1}hr^{-1}$ on February 27, 1984, and 2.18×10^{19} eV $mL^{-1}hr^{-1}$ on July 2, 1984, respectively. When the decay correction is applied, it is seen that the dose rate is the same irrespective of the amount of solution (1 mL or 5 mL) irradiated.

Analytical Equipment and Product Analysis

Gas Chromatograph Instrument: A Tracor Model 1500 gas chromatograph equipped with thermal conductivity and flame ionization detectors connected in series was used for the qualitative and quantitative analysis of the organic products. A 6 m long Carbowax-20M (polyethylene glycol) column was used with nitrogen carrier gas flow rate of 40 mL/min. A 10-inch-long SE-30 (silicone gum rubber) on a Chromosorb 60/80 mesh column was used as a pre-column; it was replaced by another after every two analyses. The oven compartment in which the column is situated was heated to 100°C. Programming was started 10 m minutes after injection of the sample into the column. The oven compartment was programmed at a rate of 25°C/min up to a temperature of 200°C. The output of the gas chromatographic detector was fed to a 1 mV potentiometric recorder. At the end of each analysis, the column was conditioned at 200°C for several hours.

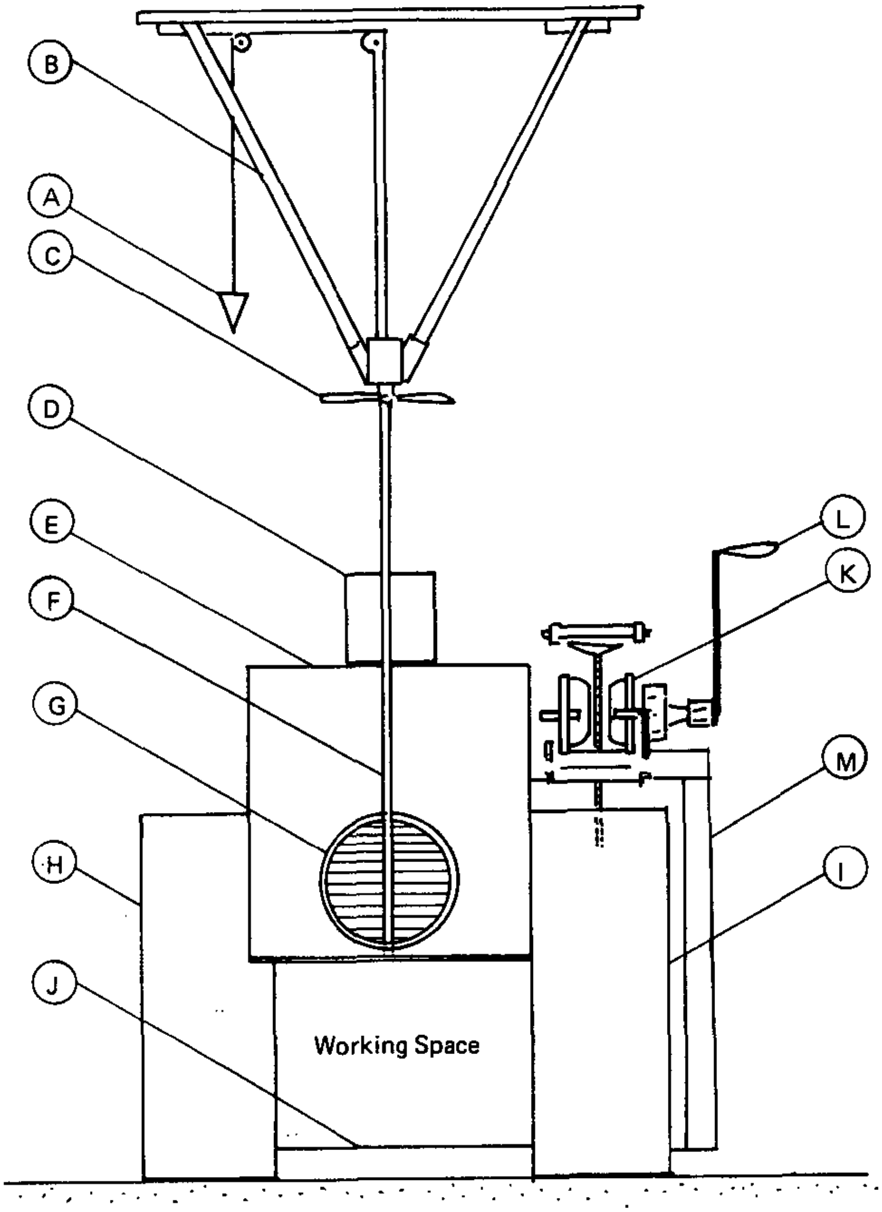

FIGURE 3. Cross Section of ^{60}Co Gamma Ray Source

Legend: (A) counterweight; (B) upper support; (C) control rod handle; (D) extra top shielding; (E) storage turret; (F) 300-curie ^{60}Co; (G) shutter shown open; (H) rear wall; (I) door; (J) downward shielding; (K) door carriage; (L) door crank; (M) door frame

TABLE 7

Fricke Dosimetry

Optical density of 5 mL solution at various time periods

	Optical Density	
Time/minute	No NaCl	With NaCl
0.5	0.118	0.110
1.0	0.227	0.211
1.5	0.342	0.329
2.0	0.446	0.440
2.5	0.547	0.553
3.0	0.659	0.637
4.0	0.855	0.873

TABLE 8

Fricke Dosimetry

Optical density of 1 mL solution at various time periods

	Optical Density	
Time/minute	No NaCl	With NaCL
0.5	0.146	0.137
1.0	0.229	0.223
1.5	0.351	0.321
2.0	0.438	0.436
2.5	0.521	0.524
3.0	0.644	0.631
4.0	0.819	0.835

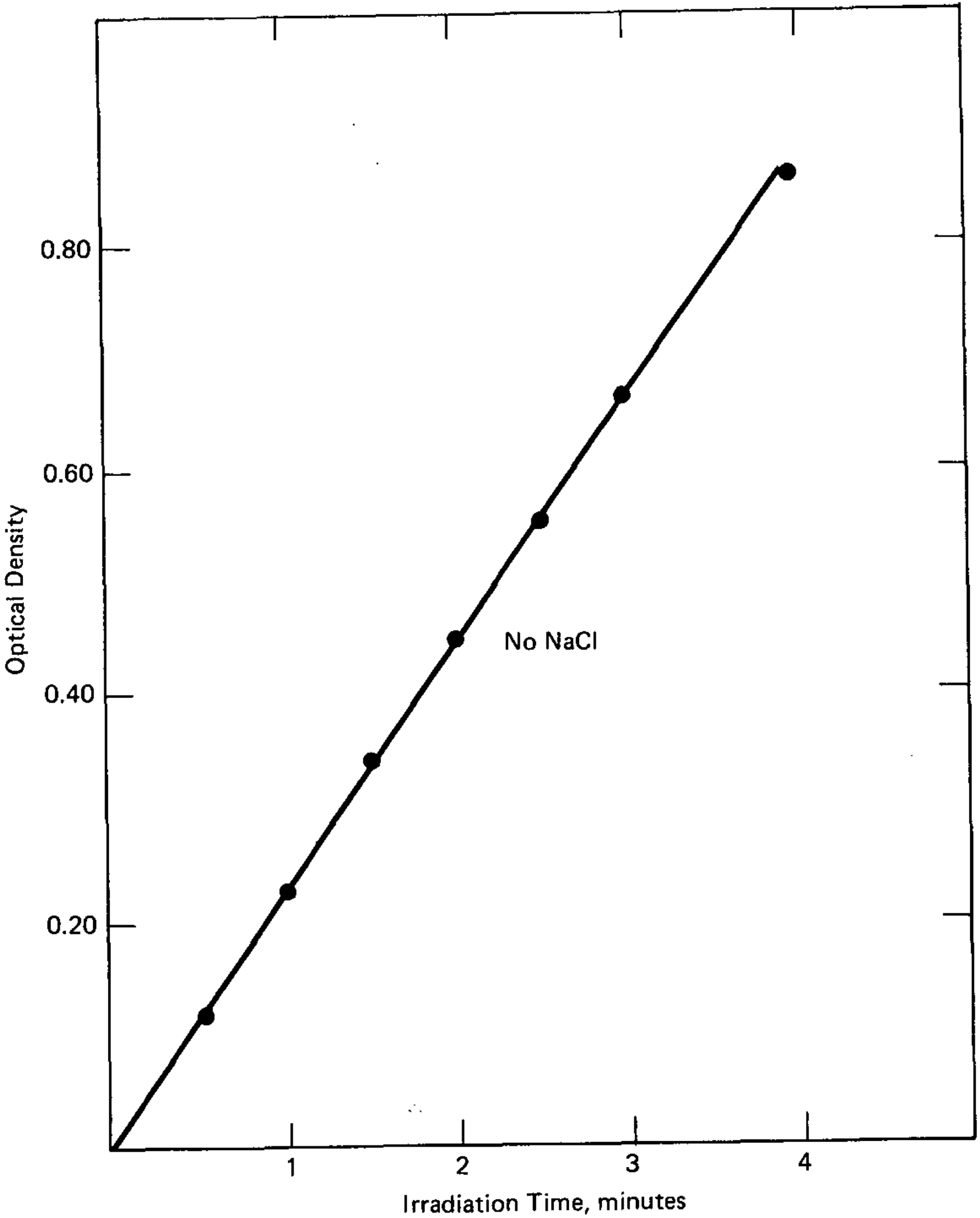

FIGURE 4. Dosimetry: Optical Density as a Function of Irradiation Time (5 mL of solution)

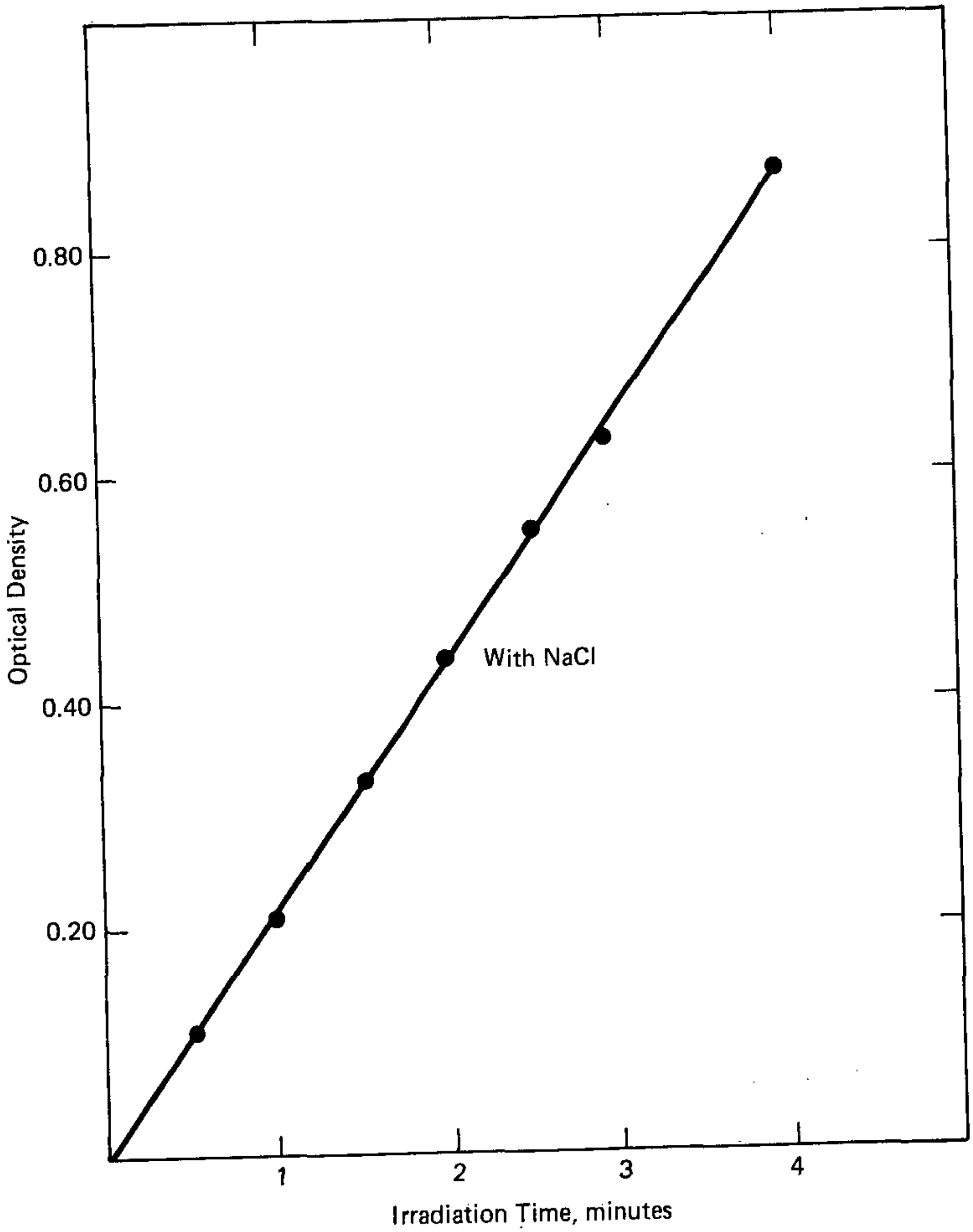

FIGURE 5. Dosimetry: Optical Density as a Function of Irradiation Time (5 mL of solution)

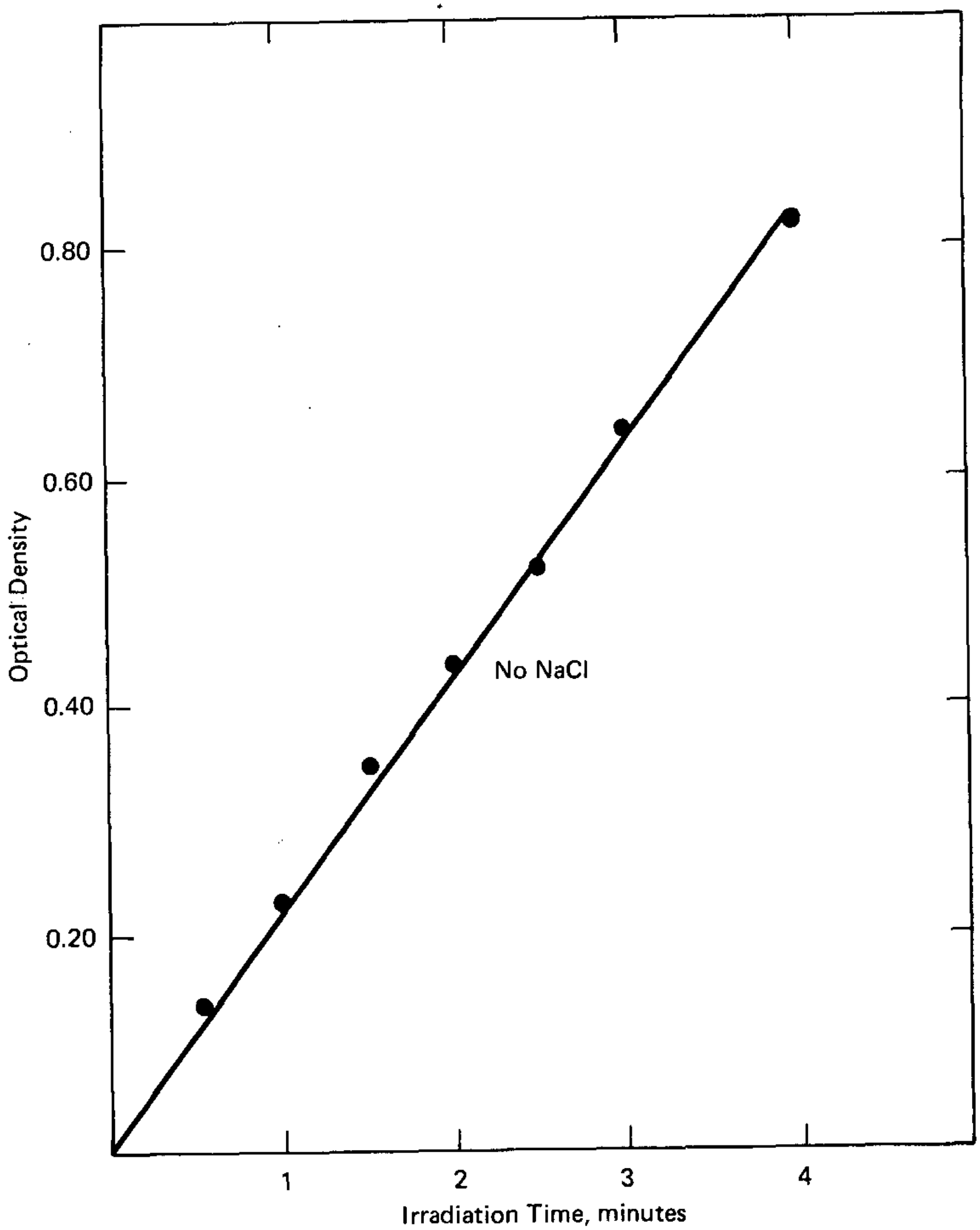

FIGURE 6. Dosimetry: Optical Density as a Function of Irradiation Time (1 mL of solution)

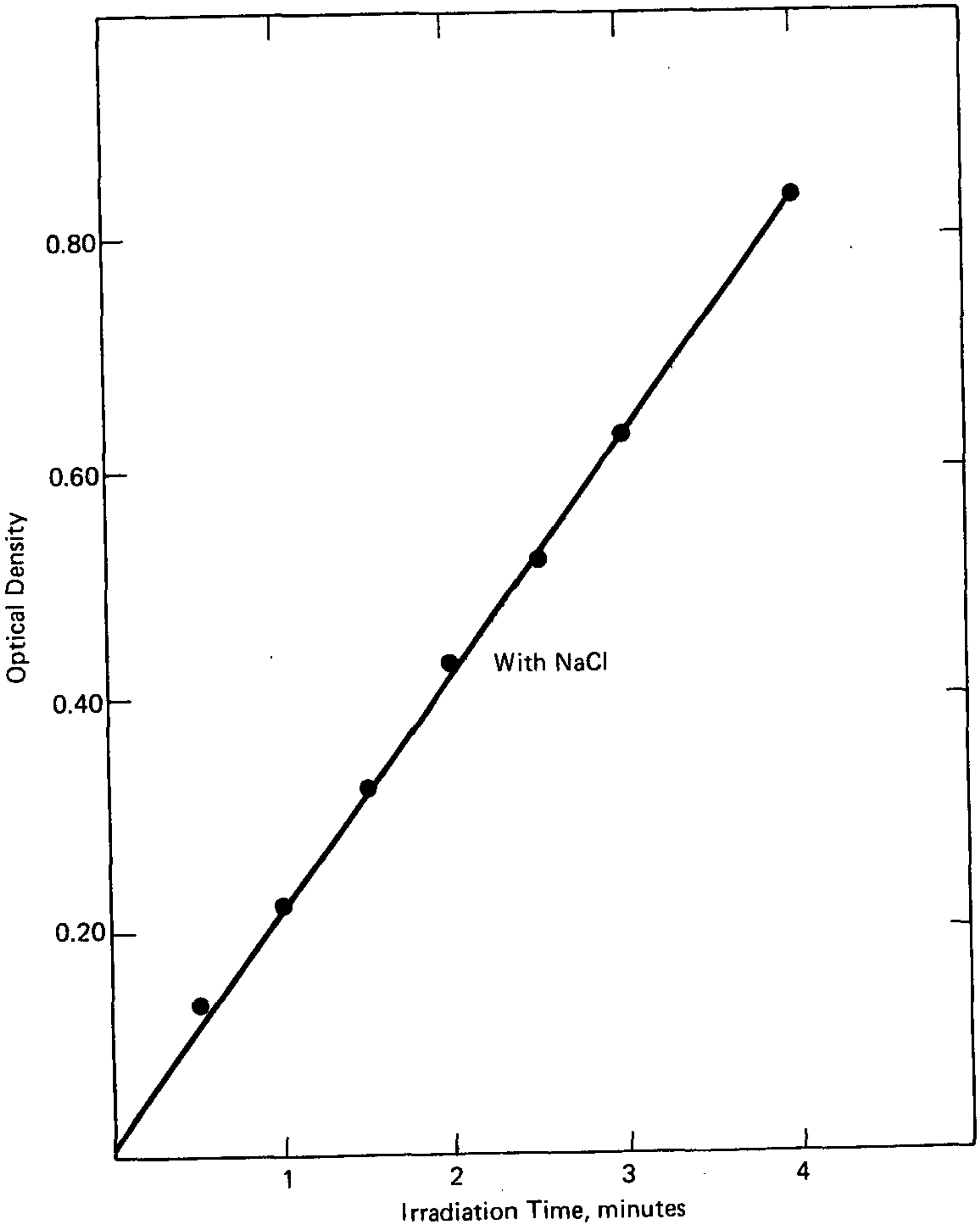

FIGURE 7. Dosimetry: Optical Density as a Function of Irradiation Time (1 mL of solution)

Analysis of Products Noncondensible at -196°C: Figure 8 shows the Toepler pump - McLeod gage apparatus. A submanifold was provided to attach the radiolysis vessel (at position X) to the input of the combined pump/gage system via a liquid nitrogen U-trap packed with glass helices. A special three-way stopcock allowed the Toepler pump to transfer the noncondensible radiolysis products either into a series of calibrated volumes (thus acting as a McLeod gage) or into sample loop S_2 for analysis by a gas chromatograph. An additional custom tubulation on the base of the vacuum stopcock allowed the evacuation of sample loop S_2. This system was equipped exclusively with Teflon stopcocks (T) and had a thermocouple vacuum gage (G_2) for monitoring sample transfer operations. The Toepler pump McLeod gage apparatus was attached to the main manifold of the vacuum system through V_2. The main vacuum system is of conventional design, with a mechanical forepump and liquid nitrogen traps preceding and following a mercury diffusion pump.

After a good vacuum was reached, the system was isolated from the vacuum pumps; the U-trap was immersed in liquid nitrogen and the break seal was broken using a magnetic hammer sealed in glass. The noncondensible fraction was collected and transferred in 12 Toepler pump cycles to the sample loop (shown in Figure 9). A completely new injection system constructed in this laboratory using several commercial components was fitted onto the gas chromatograph. This is shown in Figure 10. The input system included provision for the use of an external sample loop, connected via dual Swagelok fittings.

Since the flame ionization detector is not sensitive to hydrogen, it was measured using a thermal conductivity detector. Hydrogen and oxygen were separated by using nitrogen as the carrier gas and a 3.5 m molecular sieve (5A) column.

Results

Radiolysis of Sodium Tetraphenylborate Solutions

Samples consisting of 5 mL of air-saturated solutions of 0.05M sodium tetraphenylborate were sealed in 13 mm test tubes and irradiated for different time periods. In all, one gas phase product (H_2) and four organic products were observed. Three of the latter were identified by their retention times as biphenyl, benzene, and phenol. The fourth product has yet to be identified. Biphenyl and phenol were analyzed qualitatively and quantitatively by injecting 10 mL in the gas chromatograph from the aqueous layer. An experimental difficulty was encountered in the case of the benzene analysis, as detailed in this section.

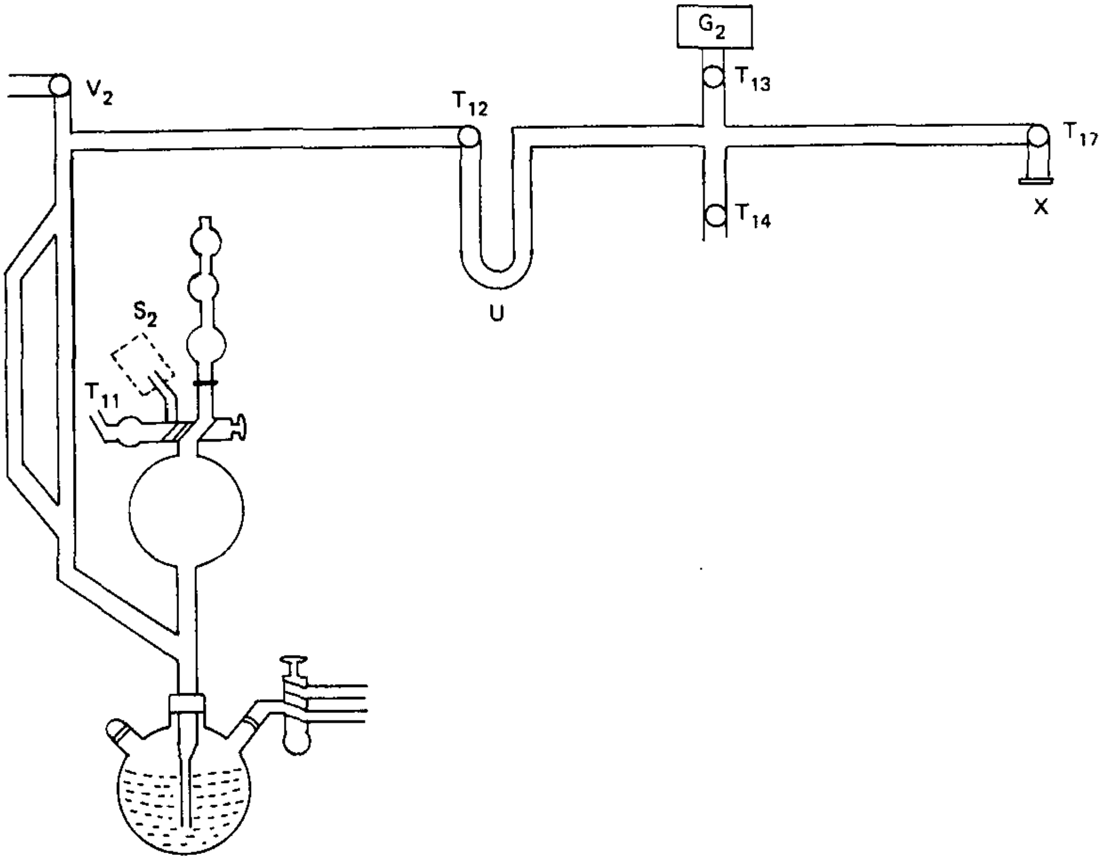

FIGURE 8. Toepler Pump - McLeod Gage Combination

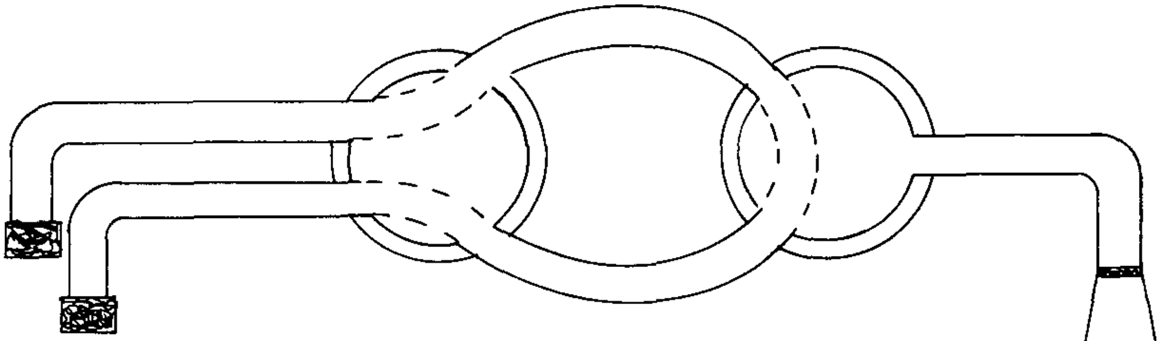

FIGURE 9. Sample Loop for Noncondensible Products

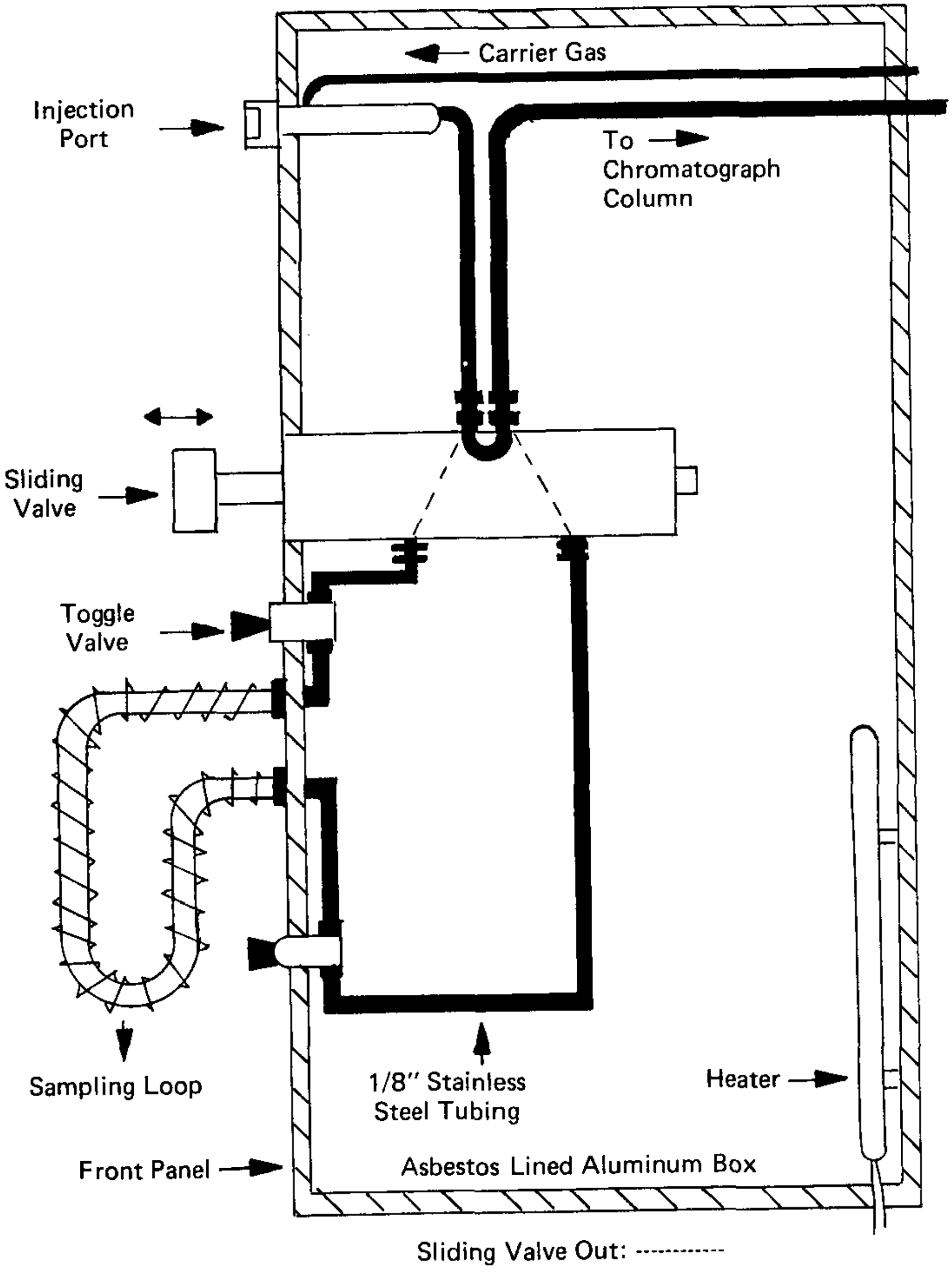

FIGURE 10. Gas Chromatograph Sampling Module

Initially, there appeared to be excessive scatter in yield-dose plots for the product benzene. In fact, the apparent yield of benzene showed little if any correlation with irradiation time. Accordingly, blank experiments were run to determine the validity of the benzene analysis under conditions identical to those used in the experiments. When an unirradiated blank solution of 0.05M sodium tetraphenylborate was injected into the gas chromatography, a peak for benzene was observed. This was apparently due to a reaction of the water in the sample with some residue of previous GLC analyses still on the column, since injection of pure water on a "used" column also gave a benzene peak.

Accordingly, it was necessary to devise a procedure for analysis of the benzene yield such that no water was present in the injected sample. The method selected was to extract benzene into a solvent which is immiscible with water; cyclohoxane was used for this purpose. A 10 mL sodium tetraphenylborate solution was shaken with 2 mL of cyclohexane and 10 mL of this solution was injected into the gas chromatograph. Benzene and biphenyl were analyzed from the cyclohexane extraction in this manner; the latter analysis duplicated data obtained by direct analysis of irradiated aqueous solutions.

Table 9 gives the yield of hydrogen at different time periods. Figure 11 shows a plot of hydrogen yield versus time of irradiation. The G-value of hydrogen calculated from data in Figure 9 is 0.46, indicating that the hydrogen evolved in the radiolysis of 0.05M sodium tetraphenylborate is essentially from the water that makes up the solution.

TABLE 9

Yield of Hydrogen at Different Time Periods in the Irradiation of Sodium Tetraphenylborate

Time/hour	Yield, micromoles/mL
1	0.16
2	0.30
3	0.50
4	0.66
5	0.86
6	1.02
12	2.10

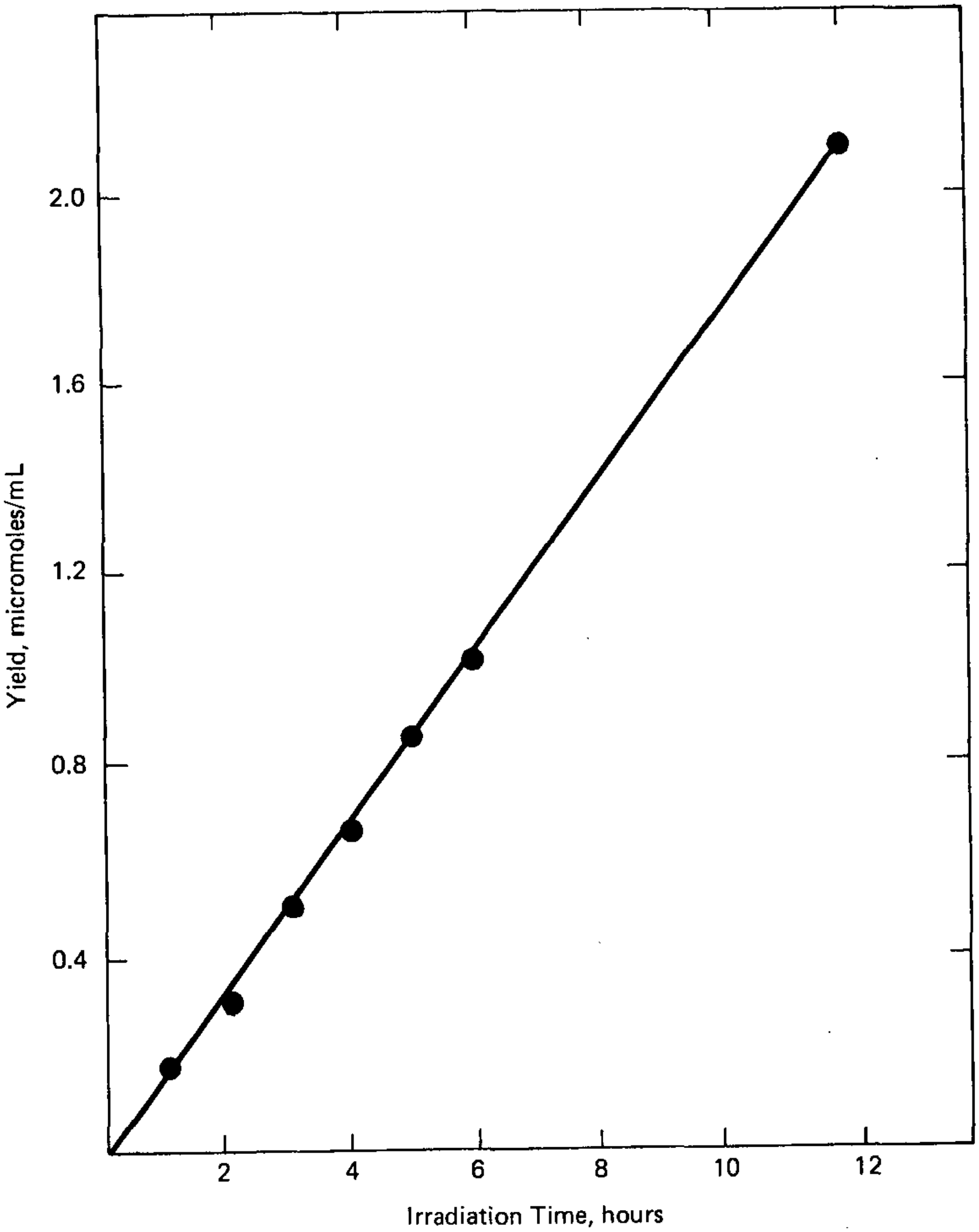

FIGURE 11. Production of Hydrogen as a Function of Irradiation Time in the Radiolysis of 0.05M Sodium Tetraphenylborate

Figures 12 and 13 show the yields of biphenyl, benzene, and phenol (analyzed from the aqueous layer and cyclohexane extraction as just explained) as a function of irradiation time. These yields are linear with absorbed dose, up to at least 4.4 Mrad. The G-values, i.e., the number of molecules changed for each 100 electron-volts of energy absorbed,[7] can be calculated from the slope of these lines. The G-values of various organic decomposition products along with that of hydrogen in the radiolysis of 0.05M sodium tetraphenylborate solution are listed in Table 10.

Effect of Radiolysis on the pH of Sodium Tetraphenylborate

After irradiation of the 0.05M sodium tetraphenylborate solution, the pH of the solution was measured on a pH meter. Table 11 gives the pH of the unirradiated and irradiated 0.05M sodium tetraphenylborate solutions. Figure 14 shows that the radiolysis of 0.05M sodium tetraphenylborate tends to increase the pH, i.e., the solution becomes more basic as the dose increases.

Radiolysis of Potassium Tetraphenylborate (KTPB)

Systems consisting of 10% and 25% solid KTPB in water were prepared as follows. To 0.1 g and 0.25 g of solid KTPB, 0.9 g and 0.75 g of water was added. These mixtures were then centrifuged until most of the solid settled at the bottom.

Samples consisting of 1 g of 10% and 25% of solid KTPH in water, respectively, were irradiated in a ^{60}Co gamma source for different time periods. After irradiation, 1 mL of water and 1 mL of cyclohexane were added to the mixture. The mixture was then shaken and 10 mL of the cyclohexane extraction was injected into the gas chromatograph for analysis. Benzene was the only product that was found in the cyclohexane extraction. When 10 mL of the aqueous layer was injected, no products were detected.

Since considerable accumulated experience at the Savannah River Laboratory suggested that additional benzene might be adsorbed or otherwise included in the solid potassium tetraphenylborate, a procedure was devised to investigate this possibility. After the aqueous layer and the cyclohexane layer were decanted from the solid KTPH, the (somewhat moist) solid was dissolved in 5 mL of acetone. This was done so that the trapped products would be released and could go into solution. The microliters of this solution was injected into the gas chromatograph for analysis. Again benzene was the only product that was detected. Blank experiments were also carried out because a false peak for benzene was observed when water was injected, as explained earlier. Exact duplicate pairs of heterogeneous water/solid KTPB samples were

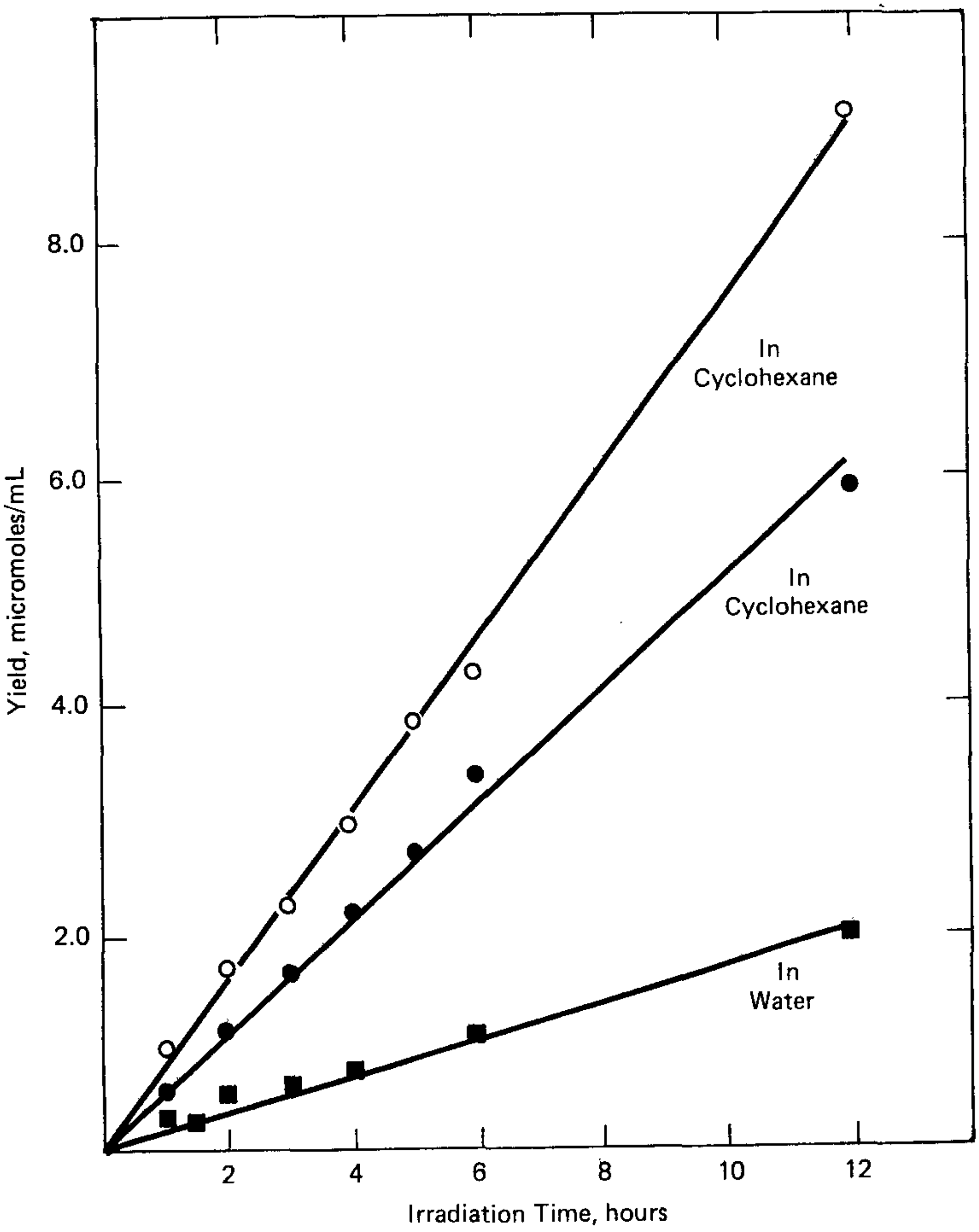

FIGURE 12. Production of Biphenyl, o; benzene, ●; and phenyl, ■; as a Function of Irradiation Time in the Radiolysis of 0.05M Sodium Tetraphenylborate

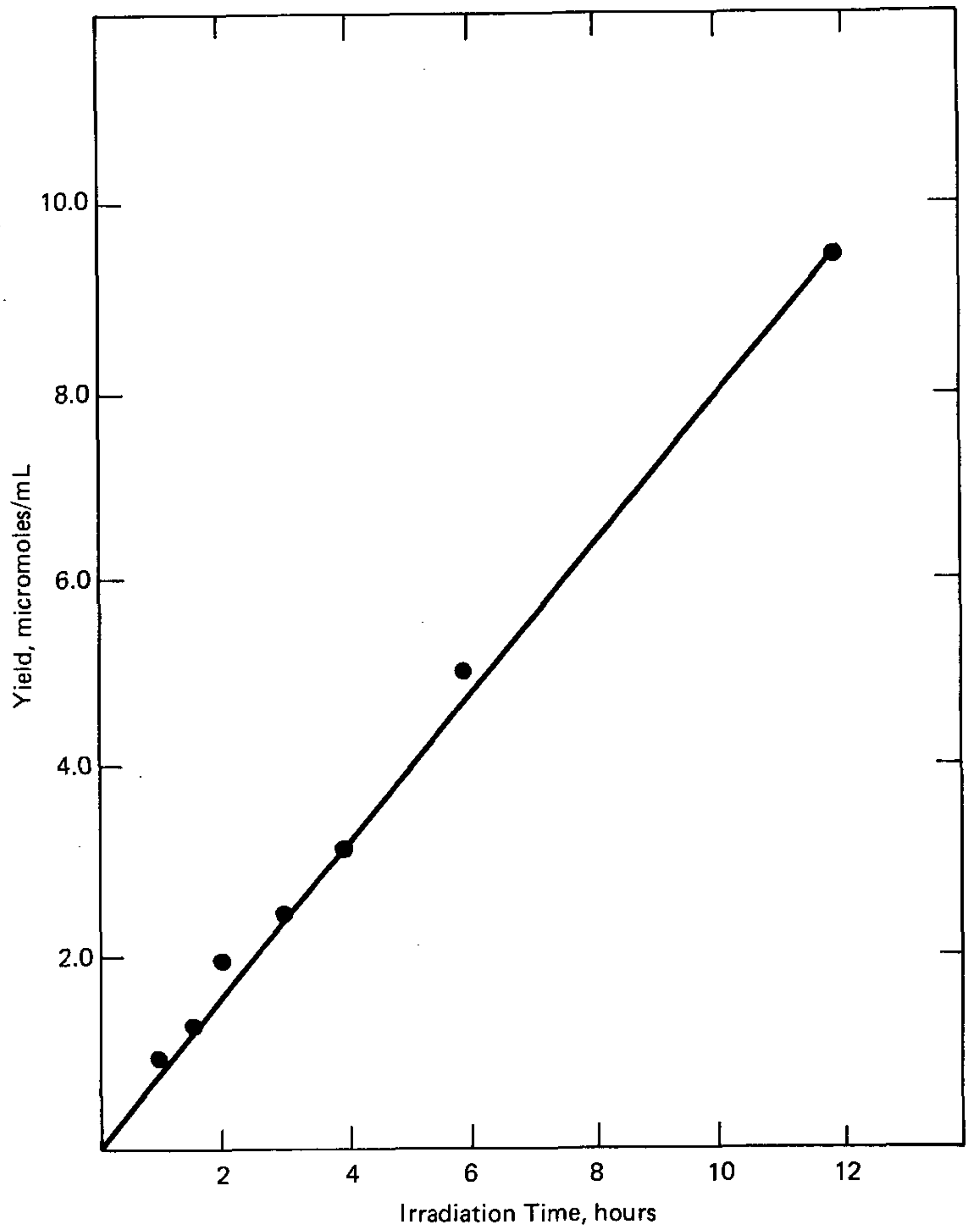

FIGURE 13. Production of Biphenyl as a Function of Irradiation Time in the Radiolysis of 0.05M Sodium Tetraphenylborate (biphenyl measured in water solution)

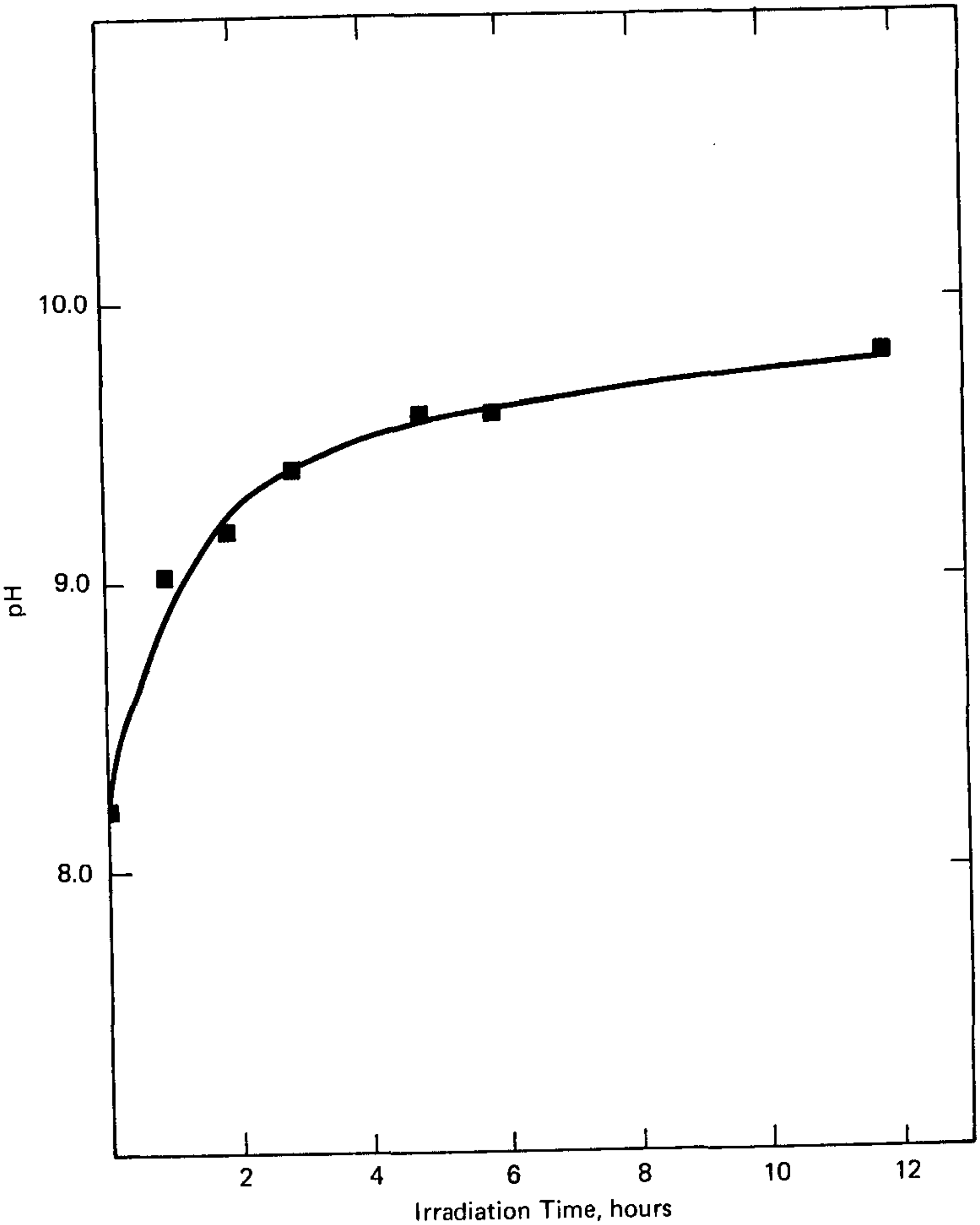

FIGURE 14. pH as a Function of Irradiation Time in the Radiolysis of 0.05M Sodium Tetraphenylborate

TABLE 10

G-Value of Products in the Radiolysis of 0.05M Sodium Tetraphenylborate

Product	G-Value
Hydrogen	0.46
Biphenyl*	1.94
Benzene*	1.28
Phenol**	0.41
Biphenyl**	2.03

---

* Measured after extraction with cyclohexane.

** Measured in water solution.

TABLE 11

pH of 0.05M Sodium Tetraphenylborate at Various Irradiation Times

Time/hour	pH
Blank	8.2
1	9.0
2	9.2
3	9.4
5	9.6
6	9.6
12	9.8

prepared, one of which was irradiated and the other reserved as a blank for the same length of time. In all cases, a substantial correction for an "extraneous" benzene yield was necessary, presumably because the KTPB sample was moist after separation of cyclohexane and water, and the resulting acetone solution contained some water (which is known to react with the "used" GC column to form benzene, as previously described. However, the magnitude of the blank correction is not dependent on the holding time of the KTPB-acetone solution.

This observation apparently precludes any major formation of benzene as a result of decomposition of KTPH in acetone solution under experimental conditions. Additional evidence for the assertion that the observed yield of trapped benzene is real is the fact that the net yield of benzene after subtraction of the (essentially constant) blank is linear with radiolysis dose. Figures 15 through 18 show plots of benzene yield (from cyclohexane extraction and from KTPB solid dissolved in acetone minus blank) and total benzene yield versus different time periods for 10% and 25% solid KTPB. The G-values for benzene (free, trapped, and total) in the radiolysis of 10% and 25% KTPB in water are listed in Table 12. It is seen that the total G-value of benzene is the same in the radiolysis of 10% and 25% KTPB in water. This result will be confirmed using an ISCO high pressure liquid chromatograph with a V^4 variable wavelength absorbence detector. A Whatman ODS-3 column will be used (along with a guard column) and the mobile phase will be 75% acetonitrile in water.

Experiments with 50% and 75% KTPB in water were attempted, but the water phase was not sufficient for the solid to settle at the bottom.

TABLE 12

G-Value of Benzene in the Radiolysis of Potassium Tetraphenylborate

	10% KTPB	25% KTPB
Free benzene	0.71	0.67
Trapped benzene	7.07	7.53
Total benzene	7.78	8.20

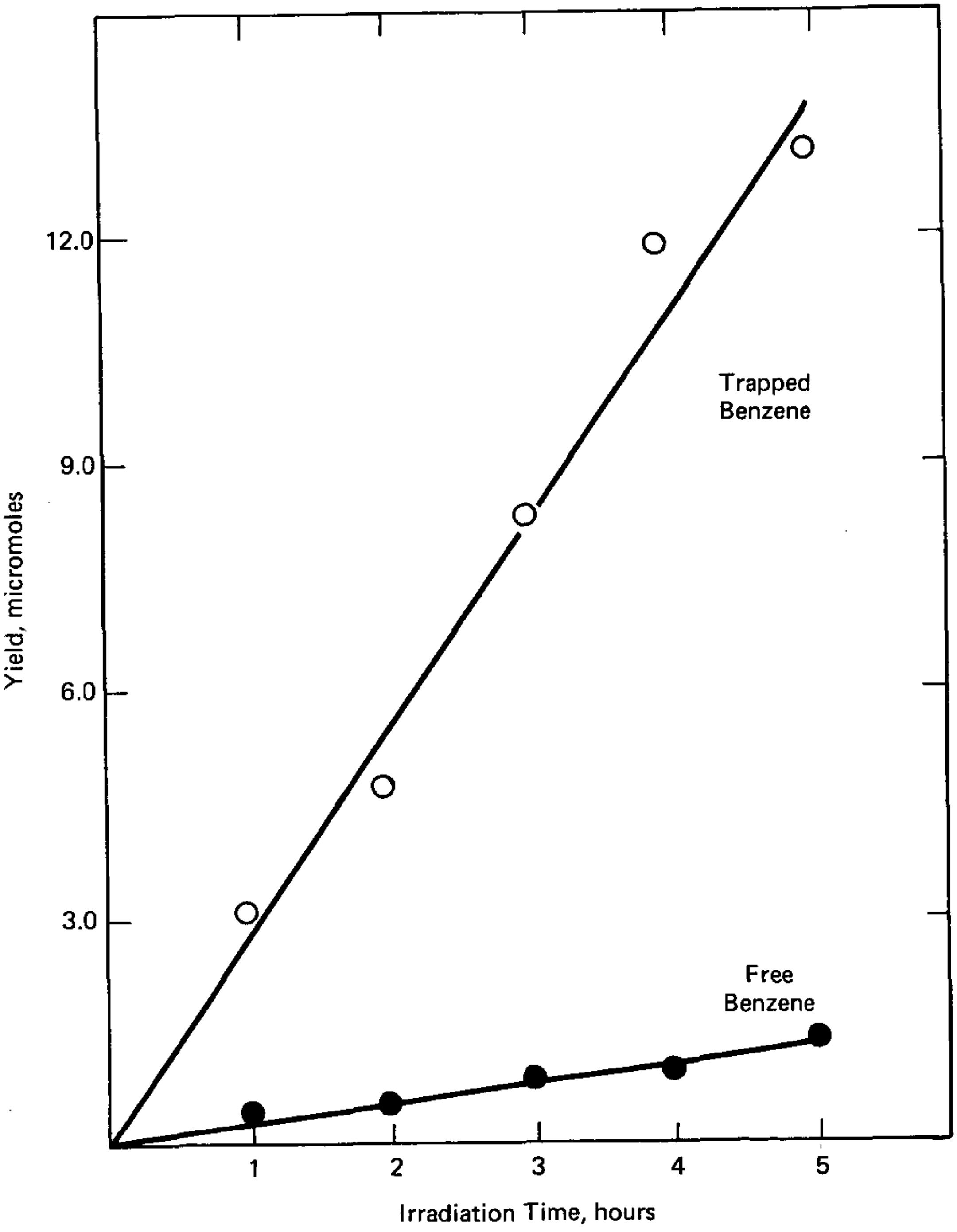

FIGURE 15. Production of Benzene Versus Irradiation Time in the Radiolysis of 25% Solid KTPB in Water

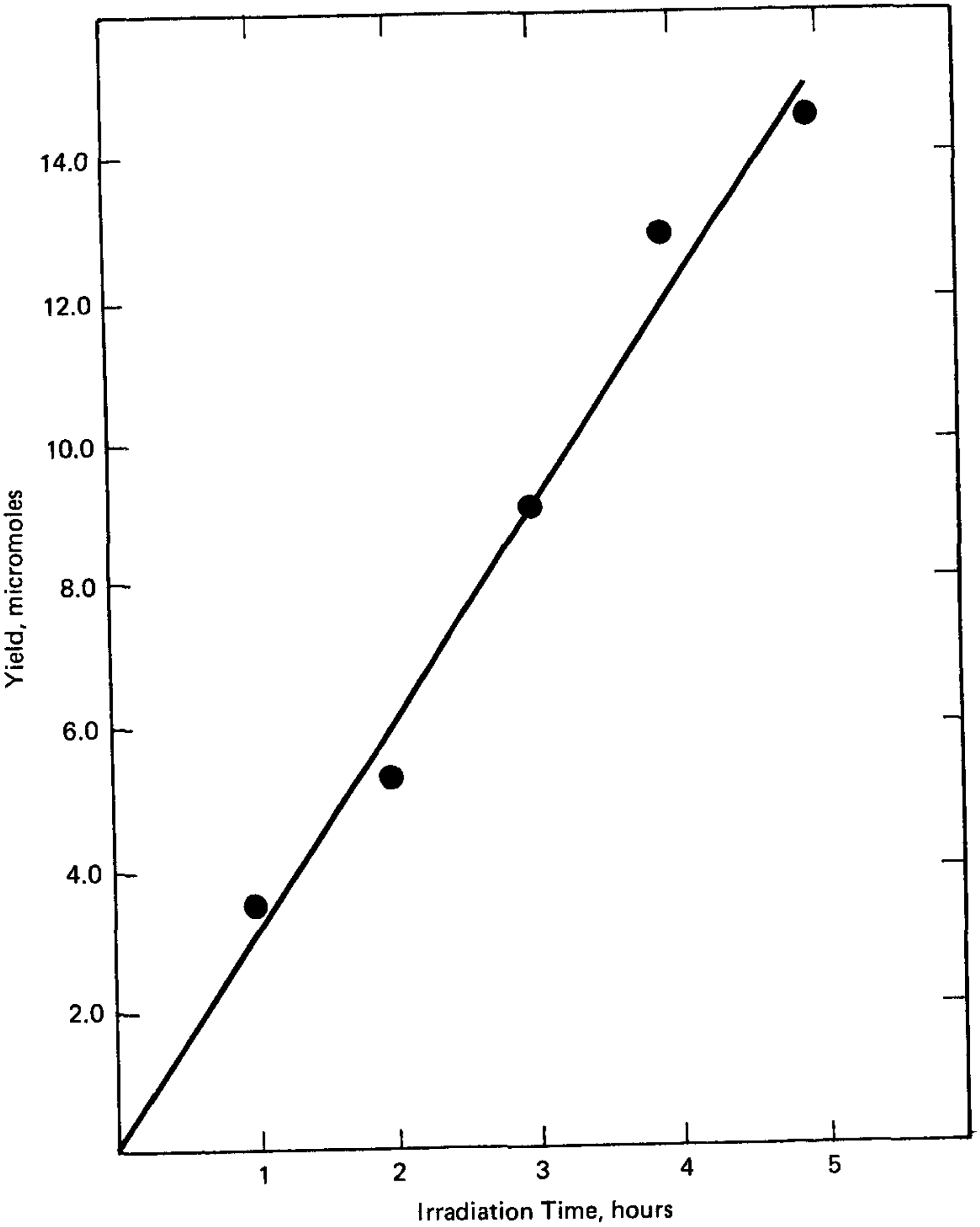

FIGURE 16. Production of Total Benzene Versus Irradiation Time in the Radiolysis of 25% KTPB in Water

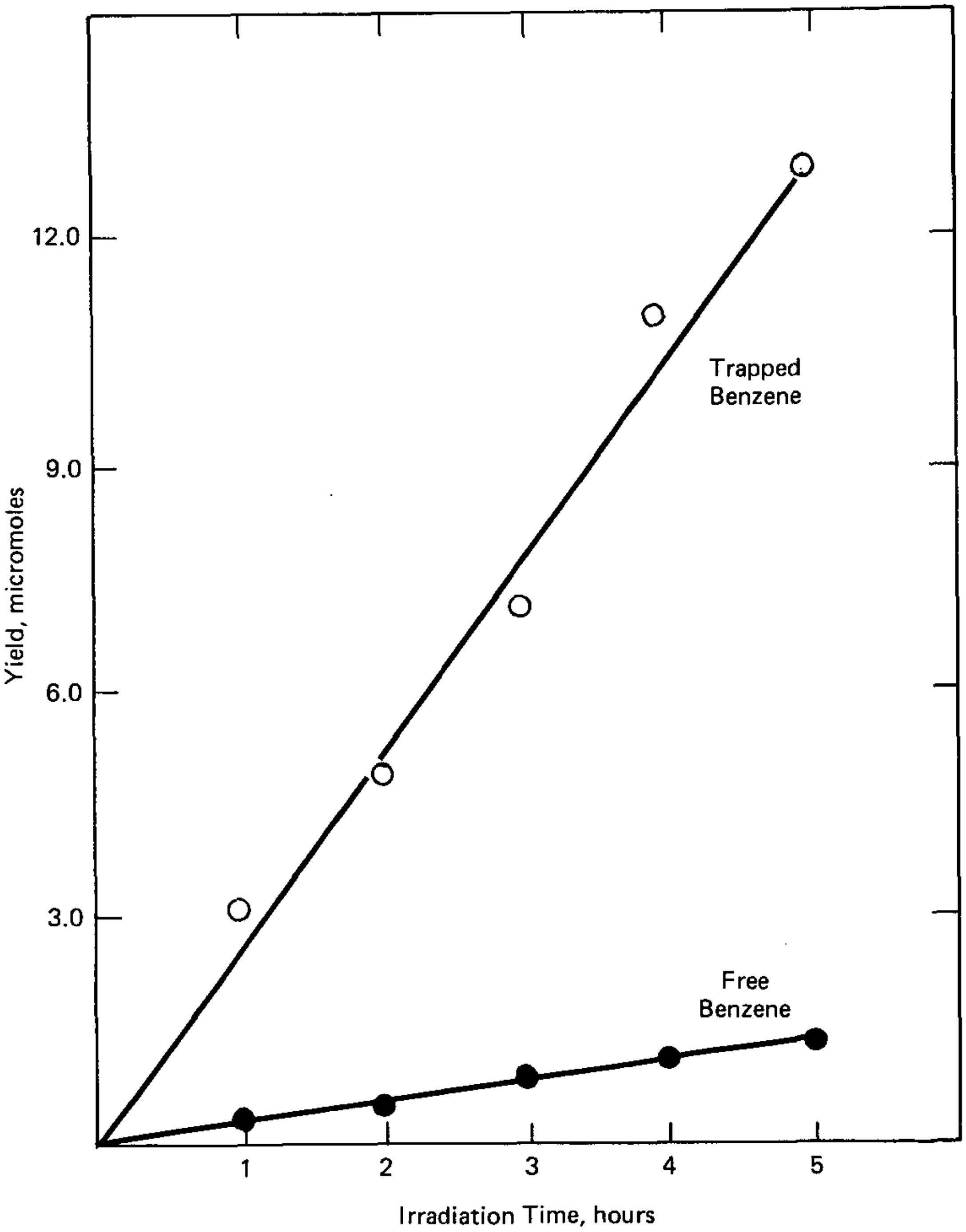

FIGURE 17. **Production of Benzene Versus Irradiation Time in the Radiolysis of 10% Solid KTPB in Water**

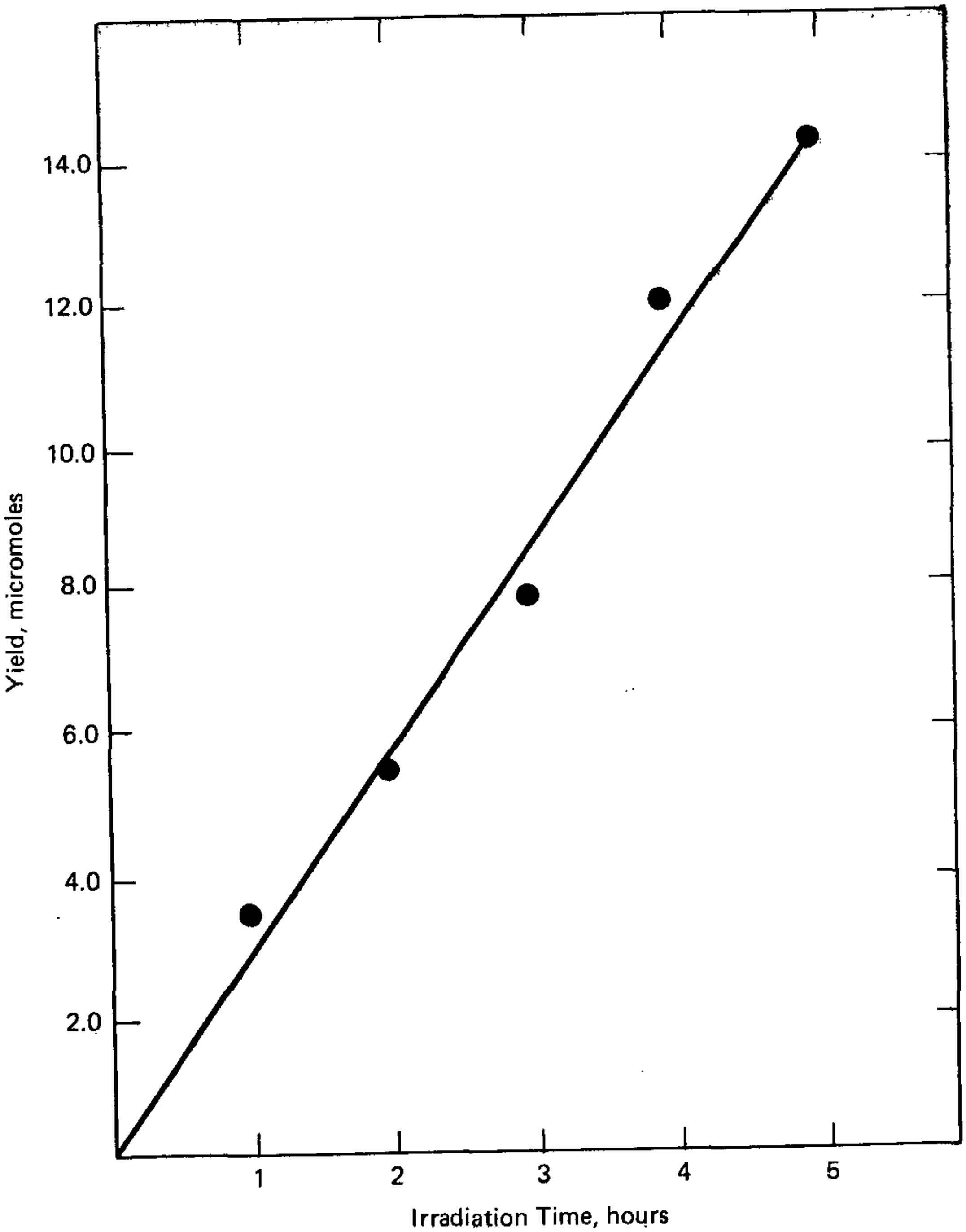

FIGURE 18. Production of Total Benzene Versus Irradiation Time in the Radiolysis of 10% KTPB in Water

Experiments with 50% and 75% KTPB in water were attempted, but the water phase was not sufficient for the solid to settle at the bottom.

SCM-2 Acid Hydrolysis Run Sampling Results

Summary

Slurry containing simulated acid hydrolysis product was fed to small cylindrical melter-2 (SCM-2) to determine its processability and to define off-gas chemistry. The blended feeds represented 82% to 100% conversion in the acid hydrolysis step. In the worst case for combustion, about 5% of the feed carbon exited the melter as organics. This occurred with the highest organic concentration in the feed and with the melter lid heaters off. The molar ratio of CO_2CO in the off-gas ranged from 3 at very low plenum temperatures to 50 at the high temperature (817°C).

Oxides of nitrogen were detected in the melter off-gas under all conditions. On average, 50% of the NO_3^- in the feed was converted to NO_x in the off-gas. The molar ratio of NO to NO_2 in the quenched off-gas was about 3 to 1.

Sampling results from the SCM-2 run were used to refine glass melter thermochemistry models. By extrapolating the results to DWPF melter conditions, melter off-gas stoichiometry was established for sludge feed coupled with precipitate hydrolysis product. The CPES material balance was updated to reflect the new feed and off-gas compositions.

Introduction

A special run was conducted on the SCM-2 to determine the processability of feed containing both sludge waste and acid hydrolysis products. The run began on February 13, 1984, with sludge-only feed as a baseline case and ended eight weeks later after testing various blended feeds. The blended feeds contained supernate representing 82% to 100% conversion in the acid hydrolysis step. Unconverted aromatics were simulated in the feed by phenylboric acid, phenol, and biphenyl.

A major objective of the run was to characterize the melter off-gas. This was accomplished by using online gas analyzers, bubbler/impinger sampling trains, and gas sample bombs. All sampling results, including off-gas, are contained in this report.

Background

Radioactive waste salt and supernate stored at SRP will be decontaminated by precipitating cesium with sodium tetraphenylborate (NaTPB) and adsorbing strontium and plutonium on sodium titanate ($NaTi_2O_5H$). Due to its high organic content, however, the washed precipitate is too reducing to add directly to DWPF glass melter feed. A high percentage of the aromatics must be removed. This is accomplished in the acid hydrolysis process where tetraphenylborate compounds are hydrolyzed to form primarily benzene. The benzene is separated from the aqueous stream which is then blended with sludge-only waste, treated with formic acid, and fed to the melter. The aqueous stream still contains a small fraction of aromatic compounds in the form of phenylboric acid, phenol, biphenyl, and trace benzene.

Slurry containing simulated acid hydrolysis product was fed for the first time to an SRL melter (other than the Building 773-A minimelter) during the acid hydrolysis run on SCM-2. The off-gas data generated during the run were used to refine glass melter thermochemistry models developed for the DWPF and to establish the DWPF material balance bases for vitrification of acid hydrolysis (sludge-supernate) feed. This required extrapolating the SCM-2 data to DWPF conditions. Some design differences between the melters affected the data interpretation (Table 13). Most important was the amount of oxygen available for cold-cap reactions. Because the DWPF melter is considerably more airtight than the SCM-2, there is less air inleakage and hence, less oxygen available for reaction in the DWPF melter on a pound of O_2 per pound of glass basis. Two steps were taken to bring SCM-2 oxygen concentration closer to that of the DWPF melter. First, the melter was operated at only a slight vacuum (1/4 inch to 1/2 inch H_2O) to minimize air inleakage, and second, the melter purges were switched from air to nitrogen.

TABLE 13

Melter/Off-Gas Operating Conditions (Sludge-Only Feed)

	SCM-2	DWPF
Melter feed rate, lb/hr	22	680
Waste glass, lb/hr	7.8	228
Melter vacuum, in. H_2O	0.5	6.0
Melter air inleakage, lb/hr	20	100
Melter purges, lb/hr	45	80
Quencher exit vapor, lb/hr	105	1572
Plenum temperature, °C	750-800	-
Off-gas temperature, °C	600-700	725

Sampling Techniques

Online Gas Analyzers

Continuous gas analyzers were installed adjacent to the off-gas processing equipment to measure concentrations of CO, CO_2, O_2, NO_x, and SO_2 in the melter off-gas (Table 14). Most gas samples were extracted through two sample probes in the off-gas condensate tank (Figure 19). Each probe assembly consisted of a shielded 20-micron filter element to remove particulates and a 1/4-inch Dekoron® (Du Pont) sample tube that was electrically heated to prevent condensation. Both probes were positioned in the vapor space near the off-gas exit line.

TABLE 14

SCM-2 Continuous Gas Analyzers

Gas	Range	Principle of Operation	Accuracy
CO	0-2000 ppm	Infrared radiation absorption	±1% FS
CO_2	0-6%	Infrared radiation absorption	±1% FS
O_2	0-1%, 10%, 25%	Electrochemical cell	±2% FS
NO_x	0-100,200,500, 1000,2000, and 5000 ppm	Photometric detection	±1% FS
SO_2	0-200 ppm	Photometric detection (UV)	±3% FS

Two probes were necessary to supply a gas sample to all analyzers at one time. One sample line was connected to the Du Pont Model 459 photometric analyzer for SO_2. This analyzer had an automatic control station which was set to periodically purge and blow back the sample line and zero the output meter. Upscale calibration was performed with a certified gas mixture (200 ppm SO_2 in N_2) about once a week. The entire sample system was heated to prevent condensation in the instrument. The second sample line was connected to a sample conditioner (Infrared Industries IR-1100) with air eductor, bypass filter, permeation dryer, and sample pump. The dry gas exiting the conditioner was distributed to the remaining analyzers.

An Infrared Industries Model IR-702, nondispersive infrared (NDIR) dual gas analyzer was used to monitor concentrations of CO and CO_2 in the sample stream. The O_2 concentration was determined by an Infrared Industries Model IR-2100 oxygen analyzer with

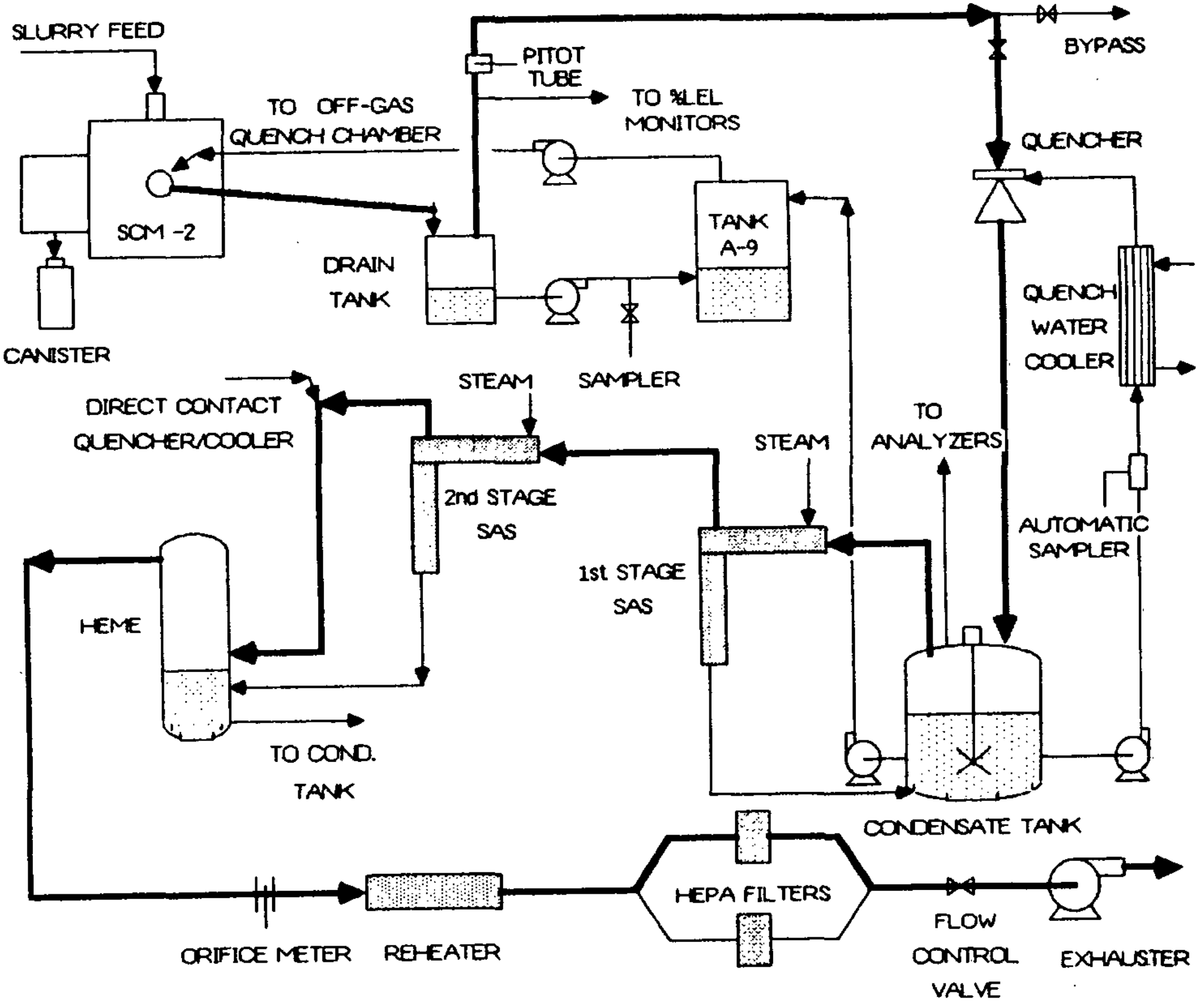

FIGURE 19. SCM-2 Off-Gas System

by an Infrared Industries Model IR-2100 oxygen analyzer with electrochemical cell. Both analyzers were calibrated at least once a week with UHP nitrogen as the zero gas and a certified gas mixture (1790 ppm CO, 5.00% CO_2, 22.00% O_2, balance N_2) for the upscale readings.

A Bendix Model 8102 analyzer was used to measure NO and NO_x concentrations in the off-gas. Measurements were by photometric detection of the chemiluminescence resulting from the flameless gas phase reaction of NO with ozone. This gave the nitric oxide (NO) concentration. When it was desired to determine the total oxides of nitrogen (NO_x or NO + NO_2), the sample was passed through a catalytic converter that changed the NO_2 to NO before it entered the reaction chamber. The gas phase reaction then represented total NO_x. The instrument was calibrated with a nitrogen zero gas and a certified gas mixture (0.45% NO, balance N_2).

All calibration and process gases were maintained in a closed system. Purge/vent lines from the analyzers were connected to a manifold which rejoined the off-gas line downstream of all processing equipment.

In addition to the two probes in the condensate tank, off-gas samples were also withdrawn through a probe in the melter plenum (Figure 20) to the continuous analyzers. The filter, impingers, and bubblers served to condition the sample by cooling the gas and removing particulates and water as described later.

Plenum Sample Train

A probe and sample train were used to obtain off-gas directly from the melter plenum (Figure 20). The stainless steel probe (Figure 21) was inserted through the top of the melter with the tip placed at the same height as the centerline of the quench chamber, about 15 inches from the melt surface. Plenum gas was drawn through the probe and sample train with a Research Appliance Company Staksamplr®, Model 2414. The gas passed through a heated filter where the solid particles were collected. The filter was heated above the dew point temperature of the gas to avoid water condensation on the filter. The gas was then passed through a water bath, two empty impingers, and silica gel to cool it and remove as much water as possible. The rate of gas flow was controlled by adjusting the amount of recirculation on the vacuum pump. The volume of gas sampled was measured with a dry gas meter. Noncondensible gas samples were taken at the exit of the silica gel and analyzed by mass spectroscopy in the Building 232-H laboratory at SRP.

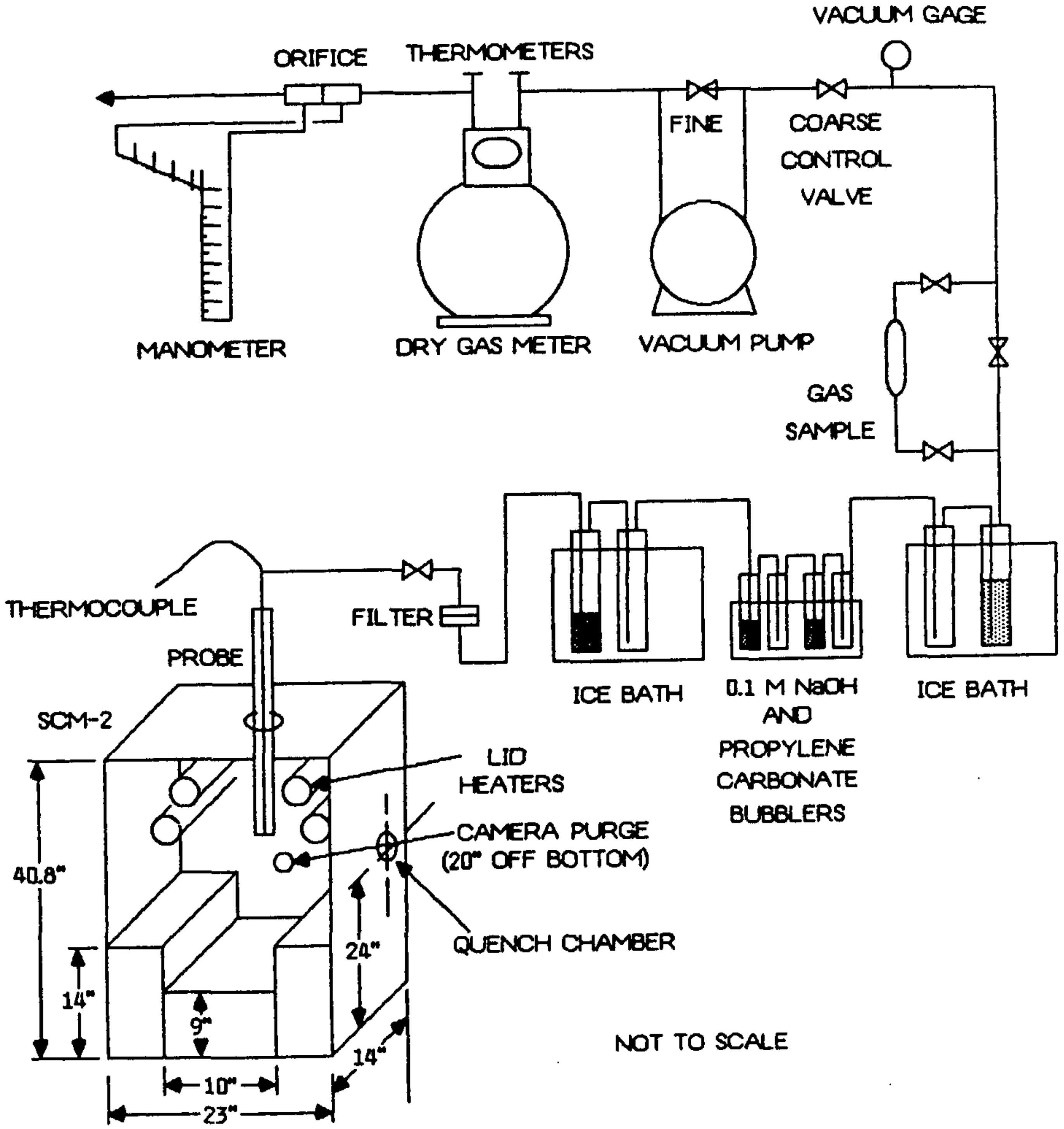

FIGURE 20. SCM-2 Melter Sample Train

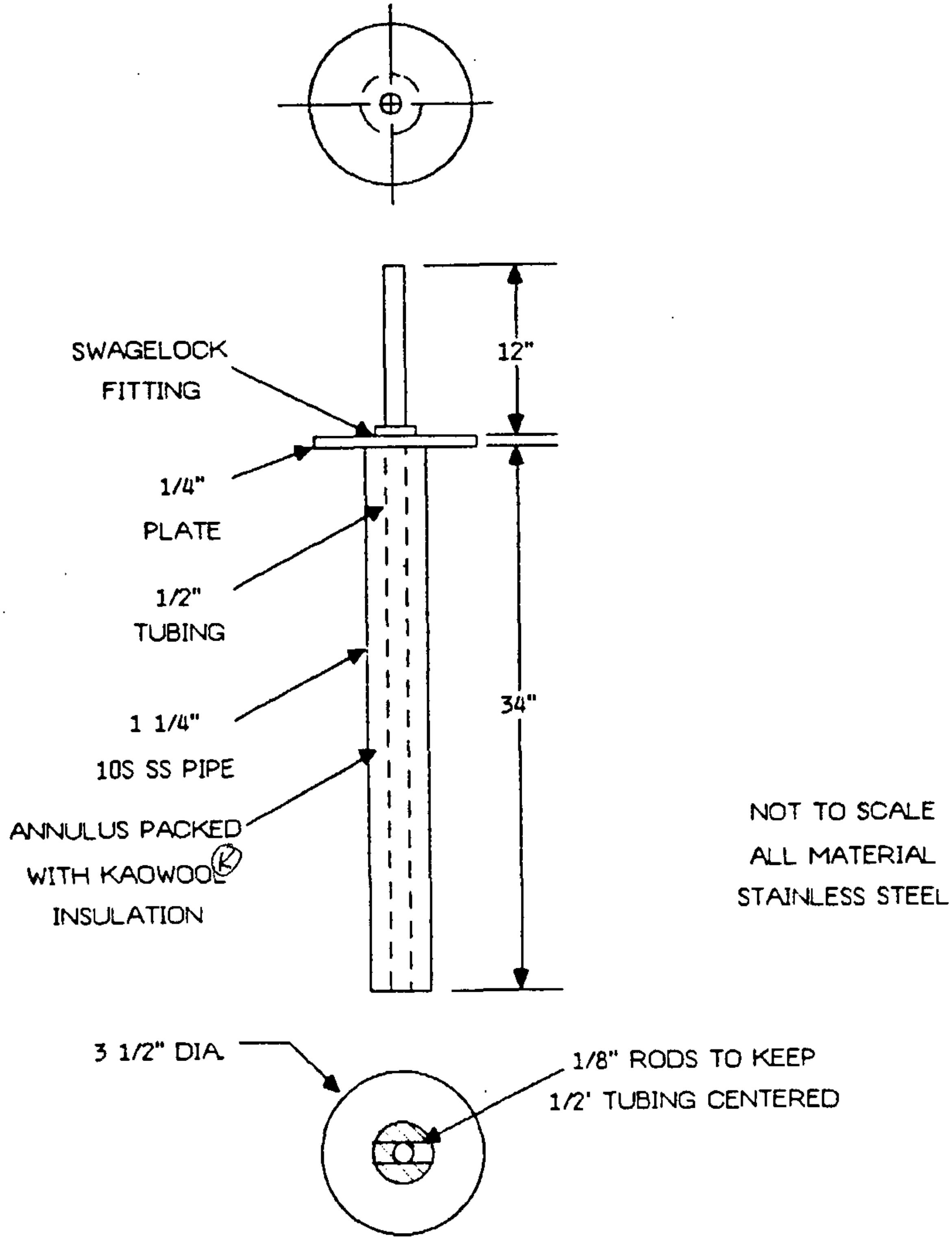

FIGURE 21. **SCM-2 Plenum Probe**

Bubblers were added to the sample train during feeding with slurry containing organics. The first bubbler contained 0.1M NaOH for the removal of phenylboric acid and phenol. The second bubbler contained propylene carbonate for the removal of benzene.

L.E.L. Monitors

Four lower explosive limit (L.E.L.) monitors were installed to continually monitor the combustibility of the quenched off-gas. The four sensors were placed in a metal box through which quenched off-gas from the drain tank was drawn. An alarm was set to sound at 50% of the L.E.L. A fifth L.E.L. monitor was positioned in the off-gas line just downstream of the second steam atomized scrubber.

Slurry, Glass, and Condensate

Slurry feed, glass, and condensate samples were obtained on a routine basis throughout the run. A stainless steel ladle was used to take dip samples from the slurry feed tank. Glass grab samples were obtained while the melter was tilt pouring. Condensate samples were collected from the small drain tank and the off-gas condensate tank through bottom drains.

Results and Discussion

Slurry Feed Preparation and Analysis

The acid hydrolysis slurry fed to the SCM-2 represented 82% to 100% conversion in the acid hydrolysis step (Table 15). Feed was first made up in a holding tank (A-5 in 678-T) and then transferred to the SCM-2 feed tank which held 150 gallons. Boric acid was added directly to the feed tank since its concentration decreased as the organic content increased. Phenol was added as a caustic solution.

Slurry samples from each batch were analyzed for physical properties in the 677-T laboratory (Table 16). Weight percent solids and density decreased as organic content increased. The thinner slurry caused more splattering and more frequent off-gas line pluggage. Yield stress for the acid hydrolysis blend was much lower than that of sludge-only feed.

Melter feed compositions were calculated for each batch, based on makeup data and the amount of heel left in the tank (Tables 17 and 18). Detailed descriptions of the sludge-only feed and Frit 168 are contained in Appendix A. Two sets of slurry samples were analyzed by Environmental & Chemical Sciences, Inc., of New Ellenton

TABLE 15

Melter Feed History for SCM-2 Acid Hydrolysis Run

Feed Batch	Dates Fed	Percent Conversion Acid Hydrolysis Step	Feed Description
1	2/13-3/1	-	Sludge-only
2	3/1-3/3	100	67 vol % (100% conv. slurry) 33% (sludge-only heel)
3	3/3-3/5	100	89% (100% conv. slurry) 11% (sludge-only heel)
4	3/5-3/9	100	96% (100% conv. slurry) 4% (sludge-only heel)
5	3/13-3/15	95	75% (93% conv. slurry) 25% (100% conv. heel)
6	3/26-3/29	91	75% (90% conv. slurry) 25% (95% conv. heel)
7	3/29-4/4	90	62% (90% conv. slurry) 38% (91% conv. heel)
8	4/4-4/6	84	61% (80% conv. slurry) 39% (90% conv. heel)
9	4/6-4/12	82	44% (80% conv. slurry) 56% (84% conv. heel)
10	4/13-4/16	-	Sludge-only

TABLE 16

SCM-2 Slurry Feed Characterization (677-T)

Feed Batch	Feed Type	Wt % Solids	Density, g/mL	Glass* Conversion, %	Yield Stress, dyne/cm^2
1	Sludge-only	38.7	1.34	94	11
2	100% conv.	36.2	1.29	-	4
3	100% conv.	37.4	1.30	91	2
4	100% conv.	37.6	1.30	94	2
5	95% conv.	36.7	1.30	91	2
6	91% conv.	38.5	1.31	85	1
7	90% conv.	36.5	1.28	80	2
8	84% conv.	34.9	1.28	90	2
9	82% conv.	29.0	1.23	84	1
10	Sludge-only	34.0	1.28	-	-

---

* Percent of feed solids converted to glass, based on crucible tests

TABLE 17

Calculated Concentrations of Acid Hydrolysis Feed Components

Component	Feed Batch 1	2	3	4	5	6	7	8	9
	(weight % of total solids)								
$NaNO_3$	-	1.02	1.44	1.56	1.60	1.60	1.60	1.60	1.60
NaCOOH	-	1.16	1.63	1.77	1.81	1.81	1.81	1.82	1.82
KCOOH	-	3.12	4.39	4.77	4.87	4.88	4.88	4.88	4.88
$B(OH)_3$	-	2.61	3.67	3.98	3.11	2.60	2.50	1.58	1.39
$NaTiO_5H$	-	0.89	1.25	1.36	1.39	1.39	1.39	1.36	1.35
$CsNO_3$	-	0.053	0.075	0.082	0.084	0.084	0.084	0.034	0.024
Na_2SO_4	-	0.13	0.19	0.20	0.21	0.21	0.21	0.09	0.06
$NaAlO_2$	-	0.22	0.31	0.33	0.34	0.34	0.34	0.14	0.10
$C_6H_5B(OH)_2$	-	0	0	0	1.32	2.36	2.56	4.38	4.77
C_6H_5OH	-	0	0	0	0.17	0.28	0.30	0.31	0.31
$(C_6H_5)_2$	-	0	0	0	0.13	0.13	0.13	0.13	0.13
Frit 168 (additional)	-	6.80	9.56	10.38	10.62	10.62	10.62	10.57	10.56
SME-33 sludge solids w/Frit 168	100	84.00	77.49	75.56	74.34	73.69	73.57	73.10	73.00

Weigh percents listed above for individual compounds are for the acid hydrolysis product and do not include contributions from the SME-33 sludge solids.

TABLE 18

Carbon Content of Melter Feed

Component	Feed Batch 1	2	3	4	5	6	7	8	9
	(weight % carbon of total solids)								
Acid Hyd. Prod.									
NaCOOH	-	0.20	0.29	0.31	0.32	0.32	0.32	0.32	0.32
KCOOH	-	0.44	0.63	0.68	0.70	0.70	0.70	0.70	0.70
PBA	-	0	0	0	0.78	1.39	1.51	2.58	2.82
Phenol	-	0	0	0	0.13	0.21	0.23	0.24	0.24
Biphenyl	-	0	0	0	0.12	0.12	0.12	0.12	0.12
Sludge									
	2.0	1.68	1.55	1.51	1.49	1.47	1.47	1.46	1.46
Total C (calculated)	2.0	2.32	2.47	2.50	3.54	4.21	4.35	5.42	5.66
Total C (E&CS analysis)	2.0	2.4	2.1	-	3.2	1.7	3.6	4.6	6.1

for total carbon and organic carbon. Due to some discrepancies in the results, the measured values were used only as a check. Calculated values of weight percent carbon were used to complete the carbon balance around the melter. The second set of slurry samples submitted to E&CS were generally lower in carbon than the first set, even for duplicate samples. This indicates a need for refrigeration and timely analysis of samples containing aromatic compounds.

Slurry samples were also submitted to ADD in SRL for elemental analysis (Table 19). Potassium and cesium concentrations were determined by atomic absorption and $SO_4^=$ by ion chromatography. The remaining elements were measured by ICP scans.

Glass Analyses

The Leach Rate Index (LRI) for glass made from acid hydrolysis feed was almost 20 times that made from sludge-only feed. This was caused primarily by the much higher concentrations of potassium and sodium in the acid hydrolysis slurry. Alkaline glass is known to have high leachability, so the results were expected. Frit 168 which was used throughout this run is relatively high in sodium and lithium. A new frit is being developed that compensates for the alkalinity of the acid hydrolysis product. By doing so the glass quality should be closer to that of sludge-only feed.

The same elemental analyses performed on slurry were performed on glass after dissolving it (Table 20). The glass composition reported for a given feed batch was the average of samples taken near the end of feeding that batch. This allowed time for flushing older glass through the melter. Glass residence time was approximately 40 hours.

Off-Gas Composition

One of the primary reasons for testing acid hydrolysis feed was to determine off-gas chemistry. The data were used to refine glass melter thermochemistry models and to establish material balance bases for vitrification of acid hydrolysis feed.

Off-gas was sampled in both the condensate tank and the melter plenum as described under "Sampling Techniques." Off-gas sampled through the plenum probe is considered most representative of conditions in the melt chamber (Table 21). Total noncondensible gas flow out of the plenum (lb mole diluent/lb glass) was determined from the amount of water in the feed, the slurry feed rate, the condensate collected per volume of noncondensible gas sampled, and the melt rate (see Appendix B). Multiplying concentrations by

T21

TABLE 19

Slurry Feed Elemental Analysis (ADD)

Element	Feed Batch							
	1	2	3	5	6	7	8	9
	---------------------- (Weight % of Solids) --------------------							
Al	2.33	1.99	1.57	1.74	1.68	1.79	-	-
B	3.30	3.58	3.49	4.01	3.88	3.45	5.59	3.44
Ca	1.23	1.04	0.84	1.11	1.79	1.07	-	-
Cr	0.03	0.04	0.03	0.02	0.01	0.01	0.03	0.03
Cs	0.04	0.05	0.06	0.08	0.09	0.08	0.12	0.10
Cu	0.08	0.07	0.06	0.07	0.07	0.07	0.13	9.99
K	0.08	1.07	1.57	2.15	2.68	2.02	3.08	2.89
La	<0.001	0.008	0.004	<0.001	<0.001	0.001	0.02	0.004
Li	1.49	1.39	1.06	1.56	1.37	1.32	2.32	1.14
Mg	0.46	0.42	0.34	0.42	0.31	0.41	-	-
Mn	1.60	1.37	1.18	1.48	1.63	1.34	2.64	1.84
Na	4.50	4.27	2.65	7.14	6.73	6.28	11.04	5.64
Ni	0.72	0.65	0.55	0.73	0.65	0.62	1.18	0.83
P	0.04	0.04	0.03	0.04	0.04	0.04	0.07	0.05
Pb*	0.08	0.07	0.06	0.09	0.08	0.08	0.14	0.09
Si	21.3	19.6	15.7	18.25	10.89	17.44	-	-
SO_4	0.16	0.26	0.32	0.37	0.29	0.29	0.34	0.38
Sr	0.03	0.02	0.02	0.02	0.04	0.02	-	-
Ti	0.02	0.10	0.12	0.15	0.15	0.15	0.21	0.12
Zn*	0.005	0.005	0.004	0.006	0.006	0.006	0.06	0.008
Zr	0.42	0.41	0.38	0.42	0.38	0.37	0.59	0.32
No. samples	6	3	1	4	3	4	2	6

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* Impurities - not added intentionally

TABLE 20

Glass Elemental Analysis (ADD)

Element	Feed Batch								
	1	2	3	4	5	6	7	8	9
	(Weight % of Solids)								
Al	2.50	2.03	1.98	2.17	2.22	1.87	-	-	-
B	4.53	4.37	4.12	4.96	4.01	3.97	4.43	4.54	4.23
Ca	1.44	1.11	1.10	1.23	1.28	1.12	-	-	-
Cr	0.11	0.10	0.10	0.10	0.08	0.09	0.13	0.12	0.12
Cs	0.04	0.07	0.08	0.10	0.06	0.09	0.10	0.10	0.09
Cu	0.11	0.09	0.08	0.09	0.07	0.07	0.09	0.08	0.09
Fe	9.58	8.64	7.86	8.07	6.54	7.92	8.60	8.10	9.06
K	0.63	1.37	1.07	2.53	1.75	2.49	2.45	2.79	2.82
La	0.01	0.01	0.01	0.01	<0.01	<0.01	0.01	0.01	0.01
Li	1.96	1.55	1.71	2.30	1.35	1.51	1.52	1.89	1.56
Mg	0.51	0.43	0.46	0.50	0.55	0.48	-	-	-
Mn	2.14	1.79	1.60	1.70	1.38	1.43	1.63	1.59	1.79
Na	5.87	3.83	6.18	8.80	5.16	6.38	6.78	8.50	7.00
Ni	0.95	0.82	0.76	0.80	0.65	0.68	0.85	0.79	0.80
P	0.04	0.05	0.05	0.05	0.04	0.04	0.05	0.05	0.05
Pb*	0.10	0.10	0.11	0.09	0.09	0.11	0.10	0.10	0.10
Si	23.2	19.0	19.9	22.75	23.83	20.05	-	-	-
SO_4	0.30	0.16	0.25	0.26	0.24	0.28	0.27	0.31	0.35
Sr	0.04	0.03	0.03	0.03	0.03	0.02	-	-	-
Ti	0.06	0.12	0.14	0.18	0.15	0.15	0.18	0.14	0.13
Zn*	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Zr	0.54	0.51	0.46	0.54	0.44	0.44	0.48	0.50	0.44
No. samples	3	2	2	2	2	1	2	2	4

Elemental concentrations reported above for a given feed batch are of glass samples taktn near the end of feeding that particular batch. This ensures that glass from the previous batch was flushed through the melter.

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* Impurities - not added intentionally

TABLE 21

SCM-2 Plenum Off-Gas Composition

Feed Type	Plenum Temp, °C	N_2	O_2	Ar	CO_2	CO	Organic Carbon	H_2	NO	NO_2	SO_2*
		(lb/M lb glass)									
Acid hydrolysis 90% conv.	769	6350	1874	104	258	13.0	0.03	ND	(0.2 lb mol NO_x)		0.9
	722	6840	1324	73	210	8.4	-	0.01	4.3	1.8	1.2
Acid hydrolysis 84% conv.	808	5460	1162	64	205	3.3	-	ND	(0.1 lb mol NO_x)		-
	805	5570	976	54	294	5.5	-	0.1	(0.1 lb mol NO_x)		-
Acid hydrolysis 82% conv.	817	8560	710	40	489	6.1	0.04	0.1	2.3	-	-
	801	4370	407	23	372	8.5	-	-	2.8	-	-
	781	<4650	186	10	320	>10.2	1.4	ND	7.7	-	-
	723	<7730	1328	73	318	>18.6	-	0.1	4.0	0.9**	4.1
	585	<6940	1082	59	316	>16.5	3.4	0.2	4.2	-	2.5
	555	<7020	1020	57	296	>16.5	3.4	0.5	3.9	1.6	3.4

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* Measured in condensate tank
** Caustic bubbler in use

ND = not detectable

the total noncondensible flow determined flow (lb/M lb glass) for individual compounds. Concentrations of CO_2, CO, NO, NO_2, O_2 of N_2, Ar, and H_2 were determined from bomb samples by mass spectroscopy. Since mass spectroscopy results were not always available, the argon flow was calculated from the oxygen analysis and the known % Ar in air. The balance of the total flow was assumed to be nitrogen. These assumptions agreed with the metered nitrogen flow and spectroscopy results. The organic carbon values were determined by analyzing sample train condensate. Carbon analysis was performed by Environmental and Chemical Sciences, Inc.

Off-gas was sampled on more continuous basis from the condensate tank (Table 22). Total flow in this case was measured directly with an S-type pitot tube. This flow was always higher than the corresponding flow calculated from plenum probe data. The oxygen flow was also higher, indicating that additional air inleakage occurred in the off-gas line between the melter and condensate tank - most likely at sightglasses upstream of the pitot tube. Although the oxygen flow was higher in the condensate tank than it was in the melter, flows for the other compounds in Table 22 should not have been affected.

A comparison between off-gas measurements in the plenum probe and in the condensate tank under very similar operating conditions exposes some differences (Table 23). As already mentioned, the total flow to the condensate tank was higher. This was due to eductor gas in the quench chamber and also to air inleakage between the melter and condensate tank. The mass flow of oxygen exiting the condensate tank was about three times that exiting the melter plenum. Stoichiometry was also affected. The molar ratio of CO_2/CO was always higher in the plenum probe. This was due to the gas in the probe passing very close to the lid heater sheaths (high temperature) and at the same time having a somewhat longer residence time in the melter. Both conditions promoted further oxidation of CO to CO_2. Residence times in the plenum were estimated to be about 3 to 4 seconds.

For all conditions tested, the combustion of organics in the plenum was nearly complete. In the worst case for combustion, about 5% of the carbon in the feed exited the melter as organics. This occurred at the end of the run when slurry with the highest organic content was fed to the melter with lid heaters off.

The molar ratio of CO_2/CO in the off-gas ranged from 3 in the condensate tank at low plenum temperatures to 50 in the plenum probe at the highest temperature (817°C). The CO_2/CO ratio in the condensate tank was higher at any given plenum temperature for sludge-only feed as opposed to acid hydrolysis feed. This indicates a more complete combustion of the formates than of the aromatic compounds.

TABLE 22

SCM-2 Off-Gas Composition in Condensate Tank

Feed Type	Plenum Temp, °C	O_2	CO_2	CO	NO	NO_2	SO_2	Carbon From $CO + CO_2$	Calculated* Feed Carbon
		(lb/M lb glass)							
Sludge-only	802	2716	78	1.4	-	-	-	20	22
	800	498	90	1.3	-	-	-	25	22
	421	3622	92	7.7	-	-	-	26	22
Acid hydrolysis 100% conv.	800	2729	149	2.7	-	-	-	40	28
Acid hydrolysis 95% conv.	798	5876	170	9.8	-	-	-	47	39
	892	3549	168	10.2	-	-	-	48	39
	759	4013	180	8.7	-	-	-	50	39
Acid hydrolysis 90% conv.	767	2377	168	14.7	4.8	2.4	2.7	51	48
	723	1278	180	14.0	-	-	-	54	48
Acid hydrolysis 84% conv.	810	2819	246	11.5	2.4	1.4	-	70	60
	758	3170	234	23.5	4.6	0.6	-	72	60
Acid hydrolysis 82% conv.	812	2241	329	27.3	-	-	-	100	63
	781	2578	244	28.8	3.8	-	3.7	77	63
	740	10,736	302	11.0	2.9	-	-	81	63
	655	3341	182	41.3	4.2	-	3.3	65	63
	544	2476	180	42.5	2.9	-	-	66	63

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* Corrected for CO_2 in air

TABLE 23

Off-Gas Composition — Plenum Probe Versus Condensate Tank for Same Operating Conditions

Source	Feed Type	Plenum, °C	Purge Gas	O_2	CO_2	CO
				(lb/M lb glass)		
Probe	Acid hydrolysis	817	N_2	710	489	6.1
Cond. tank	82% conv.	812	N_2	2241	329	27.3
Probe	Acid hydrolysis	781	N_2	186	320	>10.2
Cond. tank	82% conv.	781	N_2	2578	244	28.8
Probe	Acid hydrolysis	555	N_2	1020	296	>16.5
Cond. tank	84% conv.	544	N_2	2829	246	42.5
Probe	Acid hydrolysis	807	N_2	968	275	4.1
Cond. tank	84% conv.	810	N_2	2829	246	11.5
Probe	Acid hydrolysis	769	Air	1874	258	13.0
Cond. tank	90% conv.	772	Air	4812	174	13.1

Oxides of nitrogen (NO_x) were detected in the melter off-gas under all conditions tested (Table 24). An average 50% of the NO_3 in the feed was converted to NO_x in the off-gas. The molar ratio of NO to NO_2 in the quenched off-gas was about 3 to 1. No correction was made for NO_2 that may have been scrubbed out by the quencher or impingers. Condensate was analyzed for nitrate and nitrite, and it appears that an additional 2% to 7% of the feed nitrate may have been converted to NO_x and then scrubbed out.

TABLE 24

Oxides of Nitrogen in Melter Off-Gas

	NO_x		NO	NO_2
Feed Type	% Feed NO_3	lb/mol/M lb glass	lb/M lb glass	lb/M lb glass
Acid hydrolysis	53	0.18	4.3	1.8
90% conversion	61	0.21	4.8	2.4
Acid hydrolysis	49	0.17	4.6	0.6
84% conversion	32	0.11	2.4	1.4
Acid hydrolysis 82% conversion	48	0.16	3.9	1.6

The current CPES flowsheet for the DWPF assumes that all feed NO_3 converts to NO in the melter, and 10% of the NO then converts to NO_2. In the technical basis used to prepare the DWPF permit application for atmospheric emissions, the assumption was made that all nitrate in the feed exits the DWPF as NO_2. This results in a maximum projected atmospheric release of NO_x from melter off-gas of 22 tons per year as NO_2. In appears however, that the permit application and flowsheet are conservative in assuming all feed nitrate converts to NO_x.

Solids concentration of the plenum vapor was determined by filtering off-gas that passed through the plenum probe. The 7-day average for sludge-only feed was 14 mg/scf. By contrast the solids concentration in vapor space for acid hydrolysis feed averaged 30 to 40 mg/scf. The higher solids concentration was due at least in part to the lower weight percent solids and lower viscosity of the acid hydrolysis slurry. This tended to create more splatter at the cold cap.

Organic Analyses

Condensate and slurry samples were submitted to IT Analytical Services (Knoxville, TN) for analysis of organics using GC/MS. Samples were analyzed by EPA methods 624 and 625 for a quantitative determination of organic priority pollutants and an estimate of any other organics present. A complete tabulation of the results is contained in Appendix C.

Although numerous compounds were detected in the ppb range, only a handful equaled or exceeded 1 ppm (Table 25). Out of 88 organic priority pollutants the compounds that exceeded 1 ppmp in one or more samples were benzene, phenol, 2-nitrophenol and 4-nitrophenol. These four compounds were at their highest concentrations in off-gas condensate collected while feeding 82% conversion acid hydrolysis slurry to the melter with lid heaters off. The plenum temperature was below 600 °C. None of the four compounds were detected at a plenum temperature of 750°C for 91% conversion acid hydrolysis feed. In fact, when the plenum temperature was 750°C or 2,4-hexadiene) were present in the off-gas condensate in significant quantities. Based on these results and the total carbon measurements by E&CS, it appears that >99% of the organic carbon in the feed was converted to CO and CO in the off-gas when the plenum temperature was at least 750°C.

A slurry feed sample was analyzed to determine if any organic reactions took place prior to feeding. The only organic compounds added to the formated slurry were phenylboric acid, phenol and biphenyl. Although no benzene was added to the slurry, it was measured in the feed at a concentration of 1200 ppm. On a mole basis the amount of benzene formed was about equal to the amount of phenol added. The analysis also showed that the phenol that was added had all but disappeared. Biphenyl was not detected, and no method was available to analyze for phenylboric acid. Laboratory tests will be conducted to determine how the benzene was formed.

Applications to the DWPF

Sampling results from the SCM-2 were used to help establish the DWPF vitrification flowsheet for sludge feed coupled with precipitate hydrolysis product. Off-gas stoichiometry was determined by extrapolating the SCM-2 data to DWPF melter conditions.

A chemical equilibrium-based model was used to predict the gases released from the cold cap. A kinetic model which included steps for oxidation of benzene and phenol was used to predict vapor space chemistry. Both models were adjusted to fit SCM-2 results. Three cases were selected from the SCM-2 results to refine the kinetic model. They are the first three sets of (probe/condensate tank) data listed in Table 17. The O_2 concentration and reactor

TABLE 25

Organic Analyses for Condensate and Slurry

Compound	Slurry Feed 4/5/84 84% A.H. Conv.	Plenum Condensate 100% A.H. Conv. >800°C	Plenum Condensate 91% A.H. Conv. 750°C	Plenum Condensate 82% A.H. Conv. 555 to 585°C
Benzene	3.0 (1200 ppm)	ND	ND	5.6×10^{-3} (1.4 ppm)
Phenol	6.5×10^{-3} (2.6 ppm)	$<6.4 \times 10^{-5}$ (<0.02 ppm)	ND	8.0×10^{-1} (200 ppm)
2-nitrophenol	ND	ND	ND	1.2×10^{-2} (3.0 ppm)
4-nitrophenol	ND	2.9×10^{-4} (0.09 ppm)	ND	1.0×10^{-2} (2.5 ppm)
3-phenyl-2-propenal	ND	$<6.4 \times 10^{-5}$ (<0.02 ppm)	ND	4.8×10^{-3} (1.2 ppm)
1,5-hexadiene	ND	ND	2.9×10^{-3} (1.0 ppm)	ND
2,4-hexadiene	ND	ND	3.8×10^{-3} (1.3 ppm)	ND

ND = not detected
ppm = (milligrams per liter)

volume (2.5 ft^3) were based on interpretation of plenum probe data. The CO/CO_2 stoichiometry was based on condensate tank results.

As a result of these studies the DWPF melter stoichiometry will be updated as described below. Fifteen mole % of the carbon leaves the cold cap as CO and 85% as CO_2, and 25% of the hydrogen from nonaromatic sources leaves the cold cap as H_2 and 75% as H_2O. All aromatic compounds leave the cold cap as benzene. In the vapor space all of the benzene reacted to form H_2O and CO_2. All of the H_2 is combusted, and only 1% of the carbon remains as CO. Sufficient oxygen is assumed for total combustion in the plenum, and calculations are for the lowest vapor temperature expected. The off-gas composition was calculated for melter feed representing 90% removal of organics in the acid hydrolysis step.

The information above was used to update the CPES material balance for the DWPF melter and off-gas systems.

Conclusions and Recommendations

- Slurry containing acid hydrolysis product (82% to 100% conversion) was processable in a Joule-heated melter.
- Almost all organics fed to the SCM-2 were combusted. Even with the highest organic concentration and no lid heat, combustion was 95% complete.
- Off-gas contained only trace amounts of H_2, and the CO concentration was well below the design safety limit.
- The molar ratio of CO_2/CO in the off-gas ranged from 3 at low plenum temperatures to 50 at the highest temperature (817°C).
- An average of 50% of NO_3 in the feed was converted to NO_x in the off-gas.
- Glass quality for acid hydrolysis feed with Frit 168 was unacceptable due to high alkali content. A more suitable frit will be developed which compensates for the alkalinity of acid hydrolysis product.
- Off-gas results were used to update the CPES material balance after extrapolating the DWPF melter conditions.

APPENDIX A

TABLE A-1

Sludge-Only Feed Composition for SCM-2 Acid Hydrolysis Run

Alkaline Sludge	wt %	
$Fe(OH)_3$	42.13	
MnO_2	9.49	
$Ni(OH)_2$	3.53	
$CaCO_3$	5.90	
$Al(OH)_3$	17.39	Gibbsite
$Ca\ SO_4 \cdot 1/2\ H_2O$	0.45	Plaster of Paris
TCP	0.23	Tribasic Cal. Phosp. - $Ca_5(OH)(PO_4)_3$
$NaNO_3$	4.32	
NaOH	4.32	
NaI	0.03	
SiO_2	4.84	
Cr_2O_3	0.35	
CuO	0.34	
Coal	0.12	Anthracite 92 to 98% C dry basis
Zeolite	4.75	Linde IE - 95: SiO_2 - 54.4%
Na_2SO_4	0.27	Al_2O_3 - 15.6%
KOH	0.33	Fe_2O_3 - 2.8%
$SrCO_3$	0.15	CaO - 2.3%
$NaHPO_4$	0.03	MgO - 0.8%
$NaAl(OH)_4$	0.24	H_2O - 19.0%
$CsNO_3$	0.25	
Rare earth oxide	0.54	Primarily CeO_2, La_2O_3, Nd_2O_3

TABLE A-1, Contd

90% Stoichiometric HCOOH Added

@ 90%, conversions are:

Ca - 82%
Sr - 68%
Mn - 60%
Ni - 20%
Cu - 8%
Na, K - 100%

Stoichiometric HCOOH

Sludge Compound	Moles HCOOH per Mole of Compound
MnO_2	2
$Ni(OH)_2$	2
$CaCO_3$	2
NaOH	1
CuO	2
KOH	1
$SrCO_3$	2

Type 168 Frit added to alkaline sludge @ 66.8/33.2 ratio

Analysis Frit 168 (wt %):

61.75% SiO_2
16.37% B_2O_3
5.93% Li_2O
12.52% Na_2O
1.04% MgO
0.92% ZrO_2

SME-33 Characterization

ADD results (lb/100 lb solids) are shown below for duplicate samples. The "Expected" concentrations are based on the chemicals added. The "Goal" concentrations are based on the "Average" simulation adjusted for formic acid treatment. Processing includes reaction with 90% of the stoichiometric formic acid. Batch SME-33 includes use of frit Type 168.

Element/Compound	Computer Number 43731	 43732	Expected*,**	Goal**
Fe	7.7	8.2	6.66	6.88
Mn	1.6	1.6	1.78	1.42
Ca	1.0	1.1	0.79	0.78
Ni	0.83	0.83	0.66	0.66
Al	2.2	2.3	1.92	2.01
Si	21.0	21.5	19.06	19.15
Na	4.6	4.6	6.99	7.42
K	0.11	0.12	0.068	0.072
Cs	0.05	0.05	0.050	0.052
Sr	0.02	0.02	0.026	0.028
Mg	0.4	0.4	0.40	0.38
Li	1.6	1.7	1.72	1.73
B	3.5	3.5	3.18	3.29
Zr	0.47	0.48	0.43	0.46
SO_4	0.12	0.14	0.14	0.15
P	0.04	0.04	0.015	0.016
Ce	0.10	0.10	0.064	0.065
Zn	0.006	0.006	-	0†
Pb	0.07	0.09	0.019	0†
Cr	0.1	0.1	0.072	0.075
Cu	0.09	0.09	0.081	0.085

---

* Based on weights of chemicals added, and analytical results obtained from McMillan Research, Ltd., for AFF sludge and Ermhart Industries Glass Testing Laboratories for frit.

** Includes formic acid treatment.

† Impurities (not added intentionally). Both are believed near background of analytical technique used.

Note: Exceptions are that no HgO, RuO_2, or halides were added to Tank 0-12.

The frit-sludge slurry description in Tank 0-12 follows:

Volume, gal		2300
Slurry density at 25°C, g/cc		1.48
Wt % solids		51.3
Slurry rheology at 40°C		
Yield stress, dy/cm^2		200
Consistency, cp		40
Slurry pH		6.9
Frit type		168
Frit manufacturer		APEC
Frit AX No.		626326
Frit wt % of T.S.		62.5
Frit screen size (1):	wt % retained on 80 mesh	1.50
	wt % retained on 100 mesh	46.56
	wt % retained on 200 mesh	45.63
	wt % retained on 325 mesh	4.82
	wt % through 325 mesh	1.01
Avg. chemical oxygen demand, lb C/100 lb dry solids		0.88
Metal formation in open crucible		nil
Metal formation in closed crucible		nil

All of Batch SME-33 was transferred to Tank A-7 for slurry feeding the SCM-2.

APPENDIX B

TABLE B-1

Date Sampled	Condensate $\left(\frac{\text{lb H}_2\text{O}}{\text{lb diluent}}\right)$	Feed Water, lb/hr	Melt Rate, lb/hr	Off-Gas Flow rate $\left(\frac{\text{lb mole diluent}}{\text{lb glass}}\right)$	Total Organic Carbon, mg/L	Dilution Factor	Organic Carbon Rate $\left(\frac{\text{lb C}}{\text{M lb glass}}\right)$
2/25/'84	0.41	13	7.9	0.14	55.0	2.86	0.26
2.28	0.28	11	6.1	0.23	30.5	1.74	0.10
2/29	0.29	11	6.1	0.22	62.6	1.67	0.19
3/2	0.32	14	7.2	0.21	17.3	1.52	0.05
3/5	0.37	13	6.9	0.18	27.8	1.71	0.09
3/7	0.41	12	6.6	0.16	30.8	1.70	0.10
3/8	0.44	12	6.6	0.15	14.7	1.55	0.04
3/13	0.32	12	6.4	0.20	79.9	2.35	0.35
3/14	0.33	12	6.4	0.20	58.5	2.65	0.29
3/15	0.31	14	7.5	0.21	55.6	2.14	0.22
3/28	0.35	13	7.2	0.18	32.2	1.50	0.09
3/30	0.32	14	7.2	0.21	10.1	1.93	0.04
4/3	0.23	14	7.2	0.30	12.7	1.21	0.03
4/6	0.28	14	5.1	0.34	9.4	1.51	0.04
4/10,4/11	0.53	14	5.1	0.18	412	1.29	1.4
4/12	0.32	14	5.2	0.30	854	1.48	3.4

Sample calculation (2/29)

$$\left(\frac{11\ \text{lb H}_2\text{O}}{\text{hr}}\right)\left(\frac{\text{lb diluent}}{0.29\ \text{lb H}_2\text{O}}\right)\left(\frac{\text{hr}}{6.1\ \text{lb glass}}\right)\left(\frac{\text{lb mol dil.}}{28.5\ \text{lb dil.}}\right)=\left(\frac{0.22\ \text{lb mol dil.}}{\text{lb glass}}\right) \quad (1)$$

$$\left(\frac{62.6\ \text{mg C}}{1\ \text{liq.}}\right)\left(\frac{\text{lb C}}{454{,}000\ \text{mg C}}\right)\left(\frac{1\ \text{liq.}}{10^3\ \text{g liq.}}\right)\left(\frac{454\ \text{g liq.}}{\text{lb liq.}}\right)(167)\left(\frac{0.29\ \text{lb liq.}}{\text{lb diluent}}\right)$$

$$\times\left(\frac{28.5\ \text{lb dil.}}{\text{lb mol diluent}}\right)\left(\frac{0.22\ \text{lb mol dil.}}{\text{lb glass}}\right)\left(1000\ \text{lb glass}\right)=\left(\frac{0.19\ \text{lb C}}{\text{M lb glass}}\right) \quad (2)$$

APPENDIX C

TABLE C-1

Organic Analysis for Slurry Feed and Off-Gas Condensate

Compound	Slurry Feed 4/5/84 84% A.H. Conversion	Plenum Condensate 3/5/84 100% A.H. >800°C	Plenum Condensate 3/28/84 91% A.H. 750°C	Plenum Condensate 4/12/84 82% A.H. 555°-585°C	Quench Water Tank A-9 6/12/84	Quench Water Tank E-8 6/12/84
	(ppb)					
Volatiles*						
Acrylonitrile	-	-	13	820	-	-
Benzene	1,200,000	-	-	1,400	-	-
Chlorobenzene	310	-	-	<10	-	-
Tetrachloroethane	<50	-	-	-	-	-
Toluene	<50	13	280	41	-	-
1,1,1-trichloroethane	-	-	-	-	<10	<10
Acid Extractables*						
2,4-dinitrophenol	-	<20	-	-	-	-
2-nitrophenol	-	-	-	3,000	0	<10
4-nitrophenol	-	90	-	2,500	-	-
Phenol	2,600	<20	-	200,000	<10	<10
Base Neutral Extractables*						
Benzo(a)anthracene	-	-	-	-	<10	-
Benzo(a)pyrene	-	-	-	-	<10	-
3,4-benzofluoroanthene[1] and/or benzo(k)fluoranthene	-	-	-	<30	-	-
Bis(2-ethylhexyl)phthalate	-	46	-	-	<10	<10
Butyl benzylphthalate	-	<20	-	-	-	-
Chrysene	-	-	-	31	13	<10
Diethylphthalate	-	35	-	-	-	-
Di-n-butylphthalate	10	<20	<60	34	<10	-
Di-n-octylphthalate	-	-	<60	<30	-	-

APPENDIX C

TABLE C-1, Contd

Compound	Slurry Feed 4/5/84 84% A.H. Conversion	Plenum Condensate 3/5/84 100% A.H. >800°C	Plenum Condensate 3/28/84 91% A.H. 750°C	Plenum Condensate 4/12/84 82% A.H. 555°-585°C	Quench Water Tank A-9 6/12/84	Quench Water Tank E-8 6/12/84
	(ppb)					
1,2-diphenylhydrazine[2]	-	-	-	37	<10	<10
Fluoranthene	-	-	-	<30	-	-
Naphthalene	-	-	-	110	-	-
Nitrobenzene	-	-	-	-	<10	87
N-nitrosodiphenylamine[3]	57	-	-	400	-	<10
Phenanthrene	-	-	-	56	-	-
Pyrene	-	-	-	<30	-	-
Acetone	13	<10	240	370	-	-
2-propanol	280	-	-	-	-	-
Tetrahydrofuran	15	-	-	-	-	-
Bromobenzene	<10	-	-	-	-	-
Methoxybenzene	<10	-	-	23	-	-
1,1': 3',1'-terphenyl	1.9	-	-	-	-	-
(1-butylpentyl)-benzene	4.7	-	-	-	-	-
2-phenyl-1,3, 2-dioxaborolane	12	-	-	-	-	-
2-cyclohexen-1-ol	5.4	-	-	-	-	-
Terphenyl	7.8	-	-	-	-	-
Butanol	-	<10	<10	-	-	-
2-butyltetrahydrofuran	-	<10	-	-	-	-
Hexanol	-	11	-	-	-	-
4-methyl-1-pentanol	-	42	-	-	-	-
Piperidinone	-	<20	-	-	-	-
Hexanoic acid	-	<20	-	-	-	-
1-methyl-2-pyrrolidinone	-	84	-	-	-	-
1-(2-butoxyethoxy)-ethanol	-	<20	-	-	-	-
3-phenyl-2-propenal	-	<20	-	1200	96	37
Phthalate	-	59	<60	-	-	-
4,8,12 trimethyl-3,7,11-tri-decatrienenitrile	-	66	67	-	26	-
$C_6H_{12}O$	-	-	10	-	-	-
1,5-hexadiene	-	-	1000	-	-	-
2,4-hexadiene	-	-	1300	-	-	-
2-cyclohexen-1-one	-	-	<60	-	<10	-

APPENDIX C

TABLE C-1, Contd

Compound	Slurry Feed 4/5/84 84% A.H. Conversion	Plenum Condensate 3/5/84 100% A.H. >800°C	Plenum Condensate 3/28/84 91% A.H. 750°C	Plenum Condensate 4/12/84 82% A.H. 555°-585°C	Quench Water Tank A-9 6/12/84	Quench Water Tank E-8 6/12/84
	(ppb)					
1-methyl-2-pyrrolidinone	-	-	72	-	-	-
1,1-dichloro-cyclohexane	-	-	<60	-	-	-
1-chloro-2,4-hexadiene	-	-	<60	-	-	43
Oxirane	-	-	-	70	-	-
Trimethylborane	-	-	-	34	-	-
Nitromethane	-	-	-	170	-	-
2-methyl-2-propen-1-ol acetate	-	-	-	<10	-	-
3-buten-2-one	-	-	-	<10	<10	-
3-methyl-2-butanone	-	-	-	17	-	-
2,5-dihydrofuran	-	-	-	14	-	-
2-furancarbonitrile	-	-	-	<10	-	-
2-furancarboxaldehyde	-	-	-	<10	-	-
Benzonitrile	-	-	-	250	-	-
3-hydroxybenzaldehyde	-	-	-	310	-	-
1-phenyl-ethanone	-	-	-	470	-	-
Benzoxizole	-	-	-	300	-	-
Benzoicacid	-	-	-	200	-	-
C_9H_8O	-	-	-	140	-	-
1,1'-biphenyl	-	-	-	810	11	230
Benzofuran	-	-	-	230	-	-
Dibenzofuran	-	-	-	500	-	-
Benzo(c)cinnoline	-	-	-	150	-	-
5-methyl-benz(c)acridine	-	-	-	120	42	<10
2,3,-dihydro-1H-inden-1-one	-	-	-	-	-	-
Phenylpropenal	-	-	-	-	14	<10
Naphthacene	-	-	-	-	<10	-
1,5-hexadiyne	-	-	-	-	-	260
Ethenylcyclobutane	-	-	-	-	-	380
Nitrosobenzene	-	-	-	-	-	<10
3-chlorocyclohexene	-	-	-	-	-	<10
4-chloro,transcyclohexanol	-	-	-	-	-	<10
Iodobenzene	-	-	-	-	-	14
Phenylhydrazone benzaldehyde	-	-	-	-	-	<10
Number of Unknowns	15	7	7	5	9	4
Highest Conc. of an unknown (ppb)	20	200	190	440	60	<10

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* Organic priority pollutants
1 Isometric pairs
2 Detected as azobenzene
3 Detected as diphenylamine
Note: ppb = (micrograms per liter)

TABLE C-2

Organics in Off-Gas Based on Condensate Analysis

Compound	Plenum Condensate 3/5/84 100% A.H. Conversion >800°C	Plenum Condensate 3/28/84 91% A.H. Conversion 750°C	Plenum Condensate 4/12/84 82% A.H. 555°-585°C
	--------- (lb/MM lb glass)		---------
Volatiles*			
Acrylonitrile	-	0.04	3.27
Benzene	-	-	5.58
Chlorobenzene	-	-	<0.04
Toluene	0.04	0.82	0.16
Acid Extractables*			
2,4-dinitrophenol	<0.06	-	-
2-nitrophenol	-	-	11.95
4-nitrophenol	0.29	-	9.96
Phenol	<0.06	-	796.90
Base Neutral Extractables*			
3,4-benzofluoranthene[1] and/or benzo(k)fluoranthene	-	-	<0.12
Bis(2-ethylhexyl)phthalate	0.15	-	-
Butyl benzylphthalate	<0.06	-	-
Chrysene	-	-	0.12
Diethylphthalate	0.11	-	-
Di-n-butylphthalate	<0.06	<0.18	0.14
Di-n-octylphthalate	-	<0.18	<0.12
1,2-diphenylhydrazine[2]	-	-	0.15
Fluoranthene	-	-	<0.12
Naphthalene	-	-	0.44
N-nitrosodiphenylamine[3]	-	-	1.59
Phenanthrene	-	-	0.22
Pyrene	-	-	<0.12
Other Organics			
Acetone	<0.03	0.77	1.47
Methoxybenzene	-	-	0.09
Butanol	<0.03	<0.03	-
2-butyltetrahydrofuran	<0.03	-	-
Hexanol	0.04	-	-
4-methyl-1-pentanol	0.14	-	-
Piperidinone	<0.06	-	-
Hexanoic acid	<0.06	-	-
1-methyl-2-pyrrolidinone	0.27	-	-

TABLE C-2, Contd

Compound	Plenum Condensate 3/5/84 100% A.H. Conversion >800°C	Plenum Condensate 3/28/84 91% A.H. Conversion 750°C	Plenum Condensate 4/12/84 82% A.H. 555°-585°C
	--------	(lb/MM lb glass)	----------
1-(2-butoxyethoxy)-ethanol	<0.06	-	-
3-phenyl-2-propenal	<0.06	-	4.78
Phthalate	0.19	<0.18	-
4,8,12-trimethyl-3,7,11-tri-decatrienenitrile	0.21	0.20	-
$C_6H_{12}O$	-	0.03	-
1,5-hexadiene	-	2.92	-
2,4-hexadiene	-	3.79	-
2-cyclohexen-1-one	-	<0.18	-
1-methyl-2-pyrrolidinone	-	0.21	-
1,1-dichloro-cyclohexane	-	<0.18	-
1-chloro-2,4-hexadiene	-	<0.18	-
Oxirane	-	-	0.68
Trimethylborane	-	-	0.14
Nitromethane	-	-	0.68
2-methyl-2-propen-1-ol acetate	-	-	<0.04
3-buten-2-one	-	-	<0.04
3-methyl-2-butanone	-	-	0.07
2,5-dihydrofuran	-	-	0.06
2-furancarbonitrile	-	-	<0.04
2-furancarboxaldehyde	-	-	<0.04
Benzonitrile	-	-	1.00
3-hydroxybenzaldehyde	-	-	1.24
1-phenyl-ethanone	-	-	1.87
Benzoxizole	-	-	1.20
Benzoic acid	-	-	0.80
C_9H_8O	-	-	0.56
1,1'-biphenyl	-	-	3.23
Benzofuran	-	-	0.92
Dibenzofuran	-	-	1.99
Benzo(c)cinnoline	-	-	0.60
5-methyl-benz(c)acridine	-	-	0.48
Number of Unknowns			
Highest Concentration of an unknown	0.64	0.55	1.75

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* Organic priority pollutants

[1] Isomeric pairs

[2] Detected as azobenzene

[3] Detected ad diphenylamine

Durability of an Initial Acid Hydrolysis Waste Glass

Introduction

In the reference DWPF process, cesium and potassium are removed from radioactive salt solutions by in-tank precipitation as cesium and potassium tetraphenylborate (TPB) salts. This process results in two streams: one consisting of decontaminated salt and the other stream composed of concentrated radioactive cesium and potassium tetraphenylborate, as well as sodium titanate. The decontaminated salt will be incorporated into "saltstone" and stored onsite, while the radioactive stream will be slurry fed to the ceramic melter, along with the radioactive sludge, and immobilized in borosilicate glass in the Defense Waste Processing Facility (DWPF).

The organic part of the tetraphenylborate salts might produce overly reducing environment during melting, and could reduce some waste components to their respective metals. Thus, removing the organic part of these salts is highly desirable. The process which has been developed to remove the organic is hydrolysis of the concentrated tetraphenylborate slurry by formic acid. This removes the phenyl groups (organic part of the slurry) from the boron, yielding benzene and an aqueous solution. Separation of these two immiscible components produces an organic-free aqueous solution containing virtually all the radionuclides, which can then be fed to the ceramic melter safely.

The objective of the present study is to evaluate the durability of one glass containing simulated acid hydrolysis products, and to compare its durability to sludge-only glasses and to an ARM reference glass. The acid hydrolysis glasses were based on Frit 168.

Summary

The single most important conclusion resulting from this study is that the 168-based glass containing acid hydrolysis products is significantly less durable than either a LSFM 11 sludge-only waste glass or a 165-based sludge-only waste glass. Based on boron extraction, the acid hydrolysis glass was about seven times more leachable after 28 days in deionized water at 90°C. This does not mean that an acid hydrolysis based glass will not perform as well as a sludge-only glass, but that reformulation of the glass is necessary to produce a more durable glass product.

Experimental Procedures

Glass Characterization

Glass samples were characterized by chemical analysis and by a variety of bulk and surface techniques. The composition of the solid was determined analytically and used in subsequent leachability calculations. The glass was analyzed on a relatively macroscopic scale by optical microscopy (50X) and on a microscopic scale by scanning electron microscopy or SEM (476X). Potential crystallinity was assessed by wide-angle x-ray diffraction (WAXD). Leached glass surfaces were also examined chemically and microscopically by electron microprobe analysis. Direct comparisons were then made between the macro and micro-structures of the standard MCC glass, the LSFM 11 sludge-only waste glass, and the three SRL 168 based glasses that contain acid hydrolysis products.

MCC-1 Static Leach Test Method

The MCC-1 Static Leach Test Method is designed to evaluate the relative chemical durability of solids and is especially useful for studying nuclear waste forms. In the current study, samples that were leached include: (1) MCC ARM-1 glass standard, (2) 168/28% sludge-only waste glass, and (3) three 168/28% waste glasses that were produced under various acid hydrolysis conditions (8% acid hydrolysis products as defined by an independent analysis. The MCC standard glass was obtained from PNL and all waste glass samples were produced in the SRL small-scale ceramic melter. The leaching matrix and a summary of the glasses used along with relevant characteristics are given in Tables 26 and 27. Data from these tests were used to calculate normalized elemental mass losses and leach rates from specimens after being exposed for 28 days to deionized water at 90°C. The volume of deionized water used as leachant was 40 mL with a glass surface area of 400 mm^2. This achieved the standard surface area of glass to volume of leachant ratio of 0.1 cm^{-1}. A specimen support made of Teflon® was used which maintained the glass samples near the centroid of the leachant in each Teflon® vessel. New leach containers and supports were heated in a 200°C oven for one week prior to cleaning, and all containers and specimen supports were cleaned following MCC-1 procedures.

The testing procedures used during the experiments were as follows:

1. Determine the pH of the leachant.
2. Determine the volume of the leachant to be used based on measured geometric surface area of the specimen. (The surface area ratio must be 0.0100 ±0.0005 mm^{-1}).

TABLE 26

Leaching Study of Tetraphenylborate Waste Glass

(MCC-1 Leach Tests, 90°C, 28 Days, Deionized Water Leachant)

Glass Form	Sample ID	Simulated Acid Hydrolysis	Lid Heat	Can Number	Melt Rate	Number of Samples Leached
ARM (SAR-std)	ARM-1 ARM-2	-	-	(MCC)	-	2
LSFM-11 Sludge-only	SAR-1A SAR-1B SAR-1C	No	No	46	8.2	3
168/AH Waste	SAR-2A SAR-2B SAR-2C	Yes	No	57	5.7	3
168/AH Waste	SAR-3A SAR-3B SAR-3C	Yes	No	66	10.8	3
168/AH Waste	SAR-4A SAR-4B SAR-4C	Yes	Yes	87	9.8	3
Blanks		-	-	-	-	2

TABLE 27

Glass and Waste Glass Compositions

(wt % oxides of major components)

Oxides	ARM-1	SAR-1	SAR-2	SAR-3	SAR-4
SiO_2	48.86	43.94	53.77	52.22	47.98
B_2O_3	11.03	12.27	13.72	12.70	13.27
Na_2O	8.47	10.51	8.13	9.81	11.63
Al_2O_3	6.18	4.47	4.21	4.26	4.04
Fe_2O_3	3.35	14.18	10.64	9.93	10.29
MnO_2	0.02	3.75	2.21	2.00	2.15
MgO	0.10	0.76	0.93	0.87	0.82
LiO_2	4.11	4.09	3.46	3.58	3.94
CaO	2.93	2.04	1.81	1.64	1.61
NiO	0.47	1.17	0.90	1.07	0.92
ZrO_2	1.39	0.66	0.64	0.71	0.61
Total: Major oxides	83.92	97.82	100.42	98.79	97.26
Total: Minor oxides	16.73				
Total %:	100.65	97.82	100.42	98.79	97.26

3. Place volume into a clean container. Support the specimen near the centroid of the leachant volume. Completely submerse the specimen in the leachant. Weigh the leach container with contents; then within 30 minutes place it into the environmental chamber, which has been preheated to the test temperature. (The testing period begins when the container is placed into the chamber. Record that time.)

4. Retighten the leach container lids 24 hours after the start of the test to ensure a good seal. Therefore, avoid any movement of the container that could disturb a surface film.

5. At the end of testing, record exact time. Remove containers and weigh each container with leachant and specimen in it to determine leachant loss. If loss is <10%, remove specimen from hot leachant, replace the container lid immediately, and allow leachant to cool.

6. Rinse specimen in high-purity water for 5 seconds. Discard rinse water.

7. Measure the pH of an aliquot of the cooled leachant. Discard aliquot.

8. Inspect leachate and container for precipitation or solids. If none then move to next step. If solids are present, remove them by 0.45 micron filtration and return clarified leachate to container for acidification. The separated solids are then weighed, analyzed, and reported.

9. Except for brine leachant where HCl would be used, add concentrated HNO_3 equal to 1% of the original leachate volume less the aliquot to the leachate in the leach container taken earlier. For the brine leachant, if the volume of final leachate is between 90% and 99% of the original leachant volume, add high-purity water to return it to the original volume less the aliquot taken earlier. Allow it to stand for at least 12 hours at 90°C before chemical analysis.

10. Submit the acidified leachates for analysis.

11. Calculate normalized elemental mass loss (NL) and leach rates (LR) and plot results.

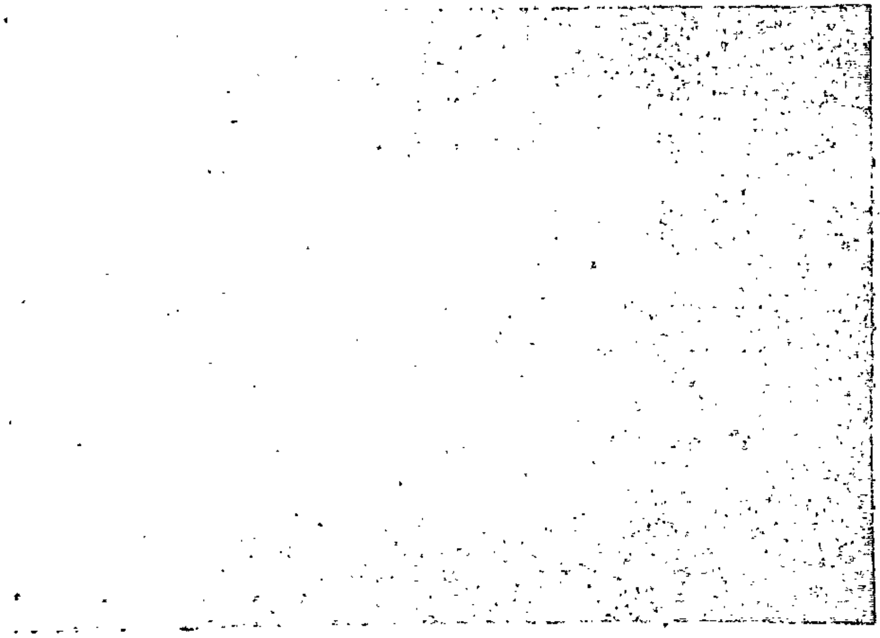
Results and Discussion

All glass samples, including the standard ARM glass, sludge waste glass, and each of the acid hydrolysis (AH) glasses, appeared homogeneous. This observation is based on optical microscopy, scanning electron microscopy (SEM), and wide-angle x-ray diffraction (WAXD). WAXD is sensitive in observing crystallinity of about 5% or greater. Representative microstructures are shown in Figure 22 and x-ray profiles given in Figures 23 through 25.

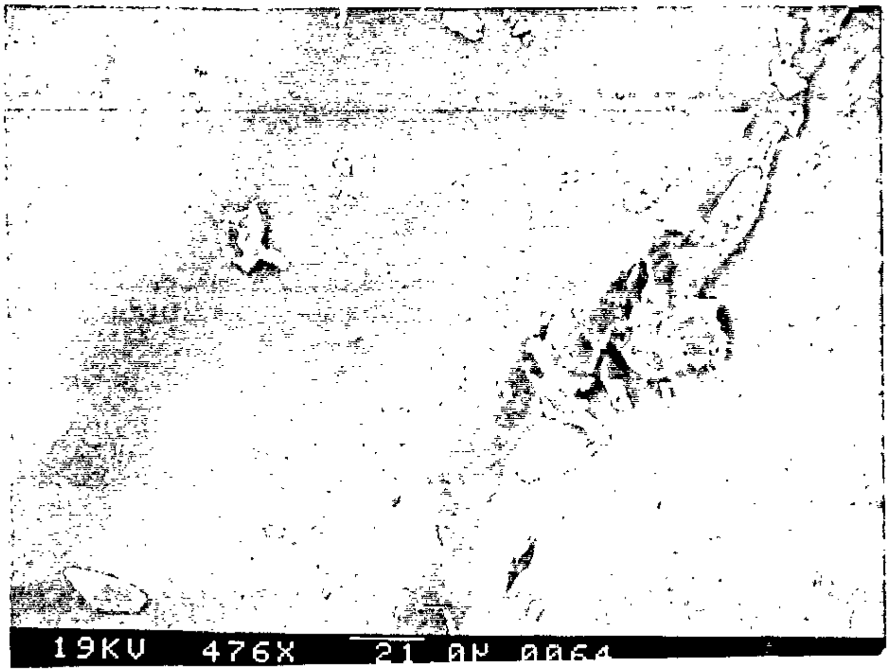
The chemical durability of each of the glasses was assessed by weight loss measurements and by extraction of Si, B, Na, Al, Fe, Mn, Mg, Li, Ca, Ni, and Zr. In general, the most durable composition was the standard ARM glass with the LSFM 11 sludge-only waste glass being only slightly more leachable. The SRL 168 acid hydrolysis glasses were significantly less durable. Weight losses, solution concentrations, and all leachability calculations are summarized in Appendix D. Normalized elemental mass losses and leach rates are graphically depicted in Figures 26 and 27.

One of the best elements to assess glass leaching is boron because it is the least likely to form insoluble precipitates and complicate leaching behavior. Based on boron extraction, the "relative leachability" of the acid hydrolysis glass was about 7X greater than the sludge glass. This trend of higher leachability for the acid hydrolysis glasses was also noted based on weight loss measurements and was consistent with slightly higher solution pH values.

Surface analyses were also performed on the glass samples. Differences in morphology were observed between the sludge glass versus the acid hydrolysis glass. From cross-sections of the sludge glass, discrete surface layers about 5 microns in width formed while for the AH glass, a thinner layer formed with a very large sublayer about 12 microns in width. This layer contained sharp protrusions penetrating into the matrix. The chemical profiles of major components were similar for both glasses, exhibiting a general deficiency in silicon and enhancements in iron, manganese, and magnesium compared to the bulk glass. These results are shown in Figure 28.



Optical Microscopy [50x]



Scanning Electron Microscopy [476x]

{Fractured Surface}

FIGURE 22. Microscopy of Acid Hydrolysis Glasses

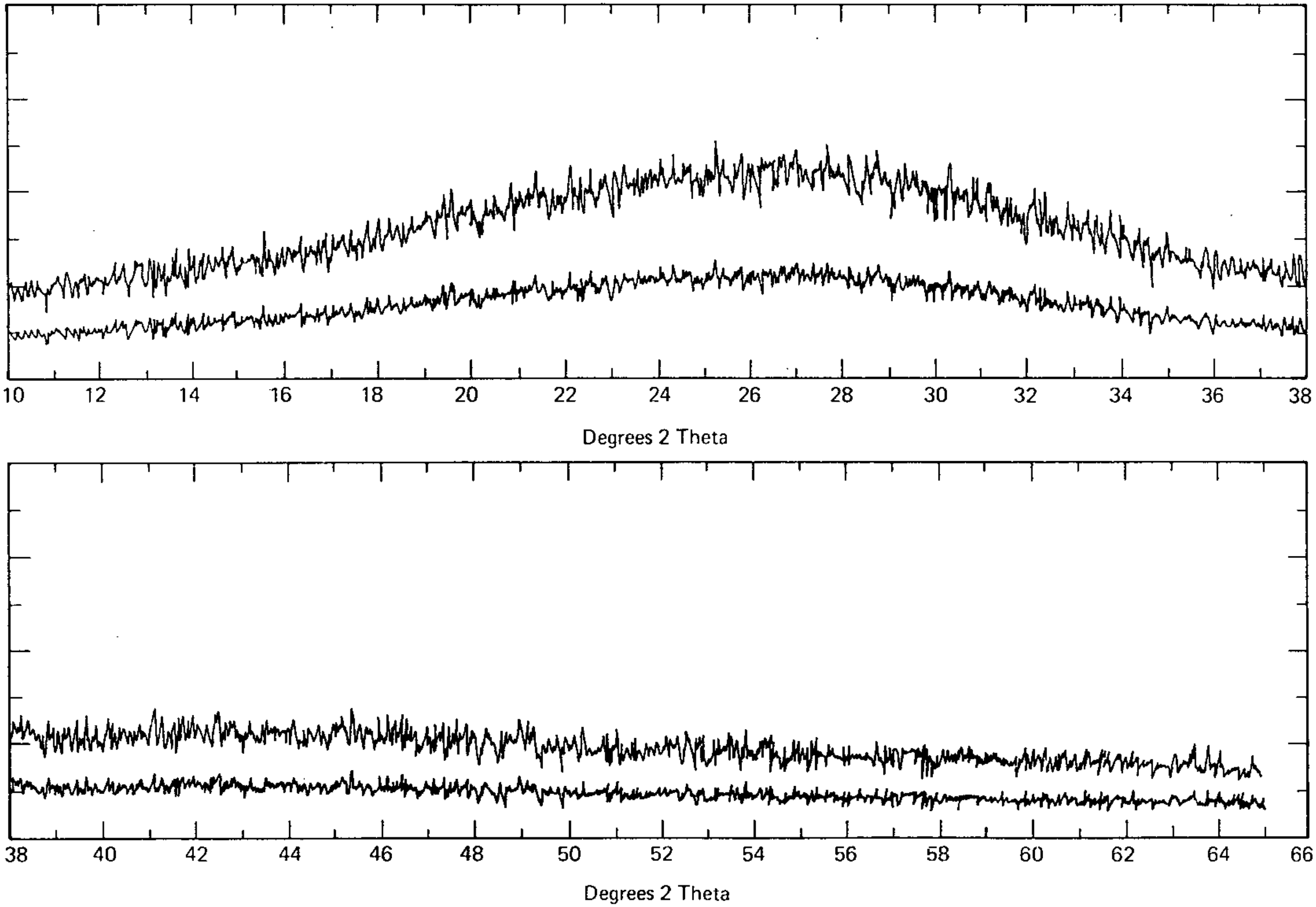


FIGURE 23. Wide Angle X-Ray Diffraction (ARM-1 Standard Glass)

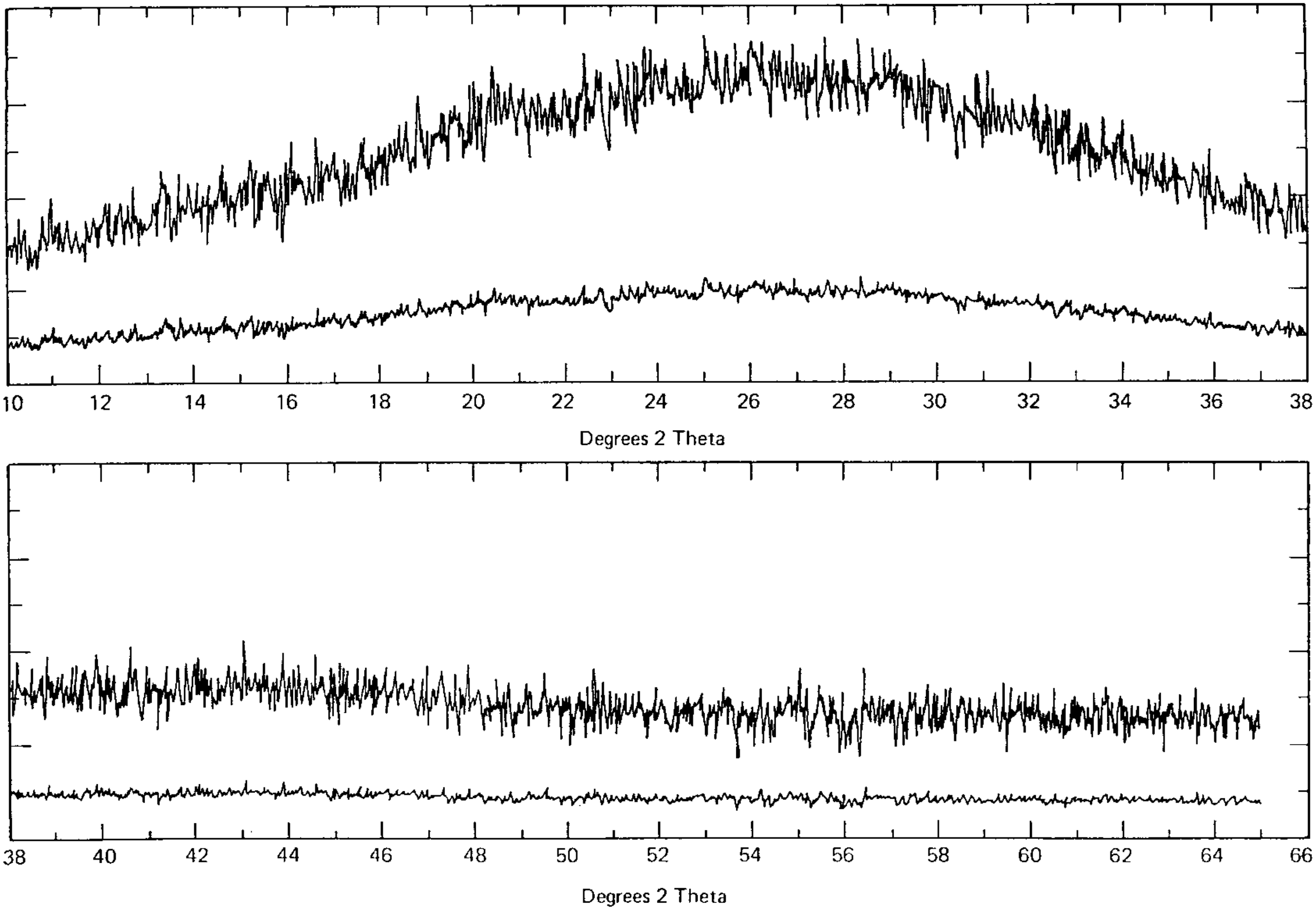


FIGURE 24. Wide Angle X-Ray Diffraction (165/TDS; Sludge Waste Glass)

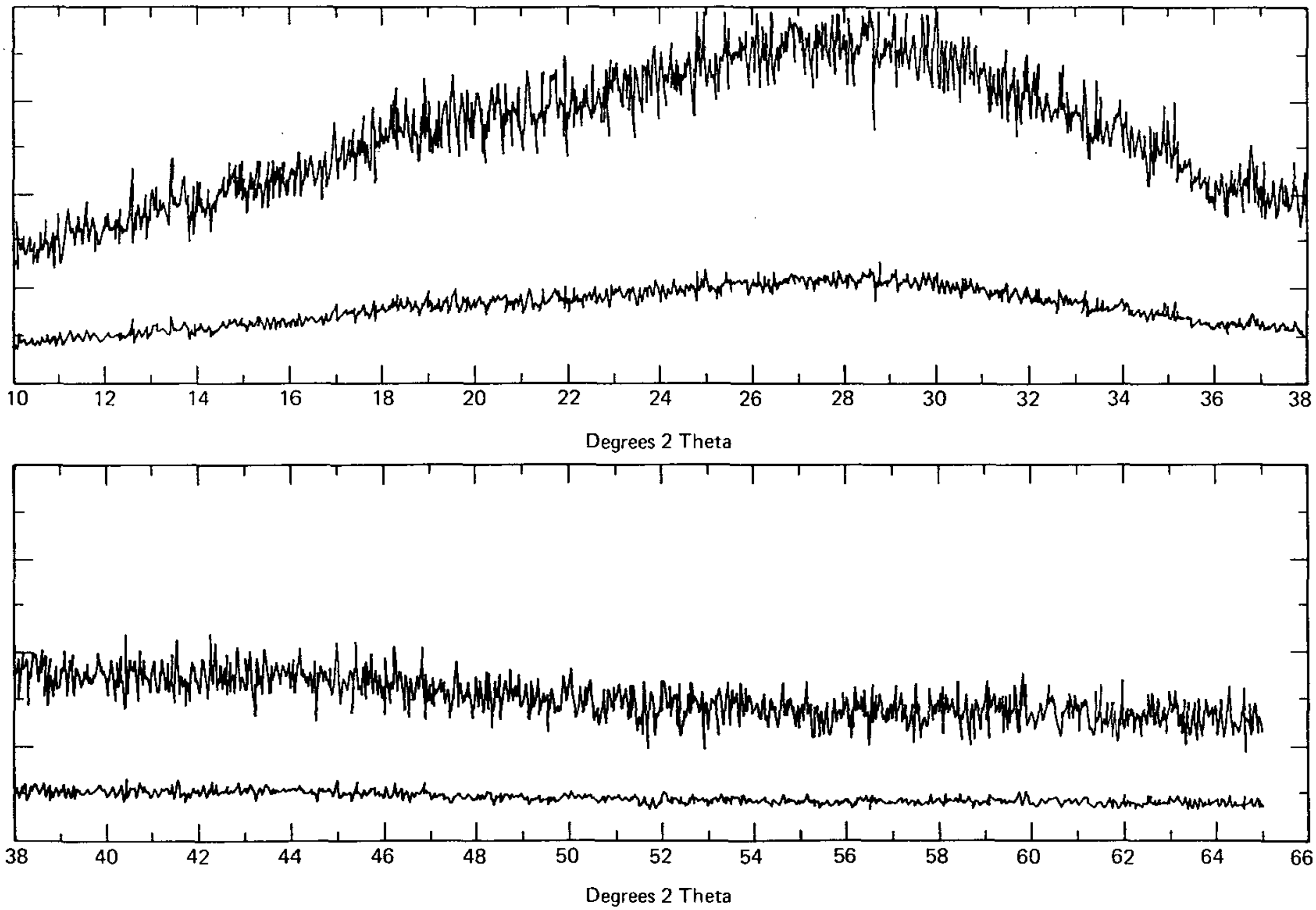


FIGURE 25. Wide Angle X-Ray Diffraction (Acid Hydrolysis Glass)

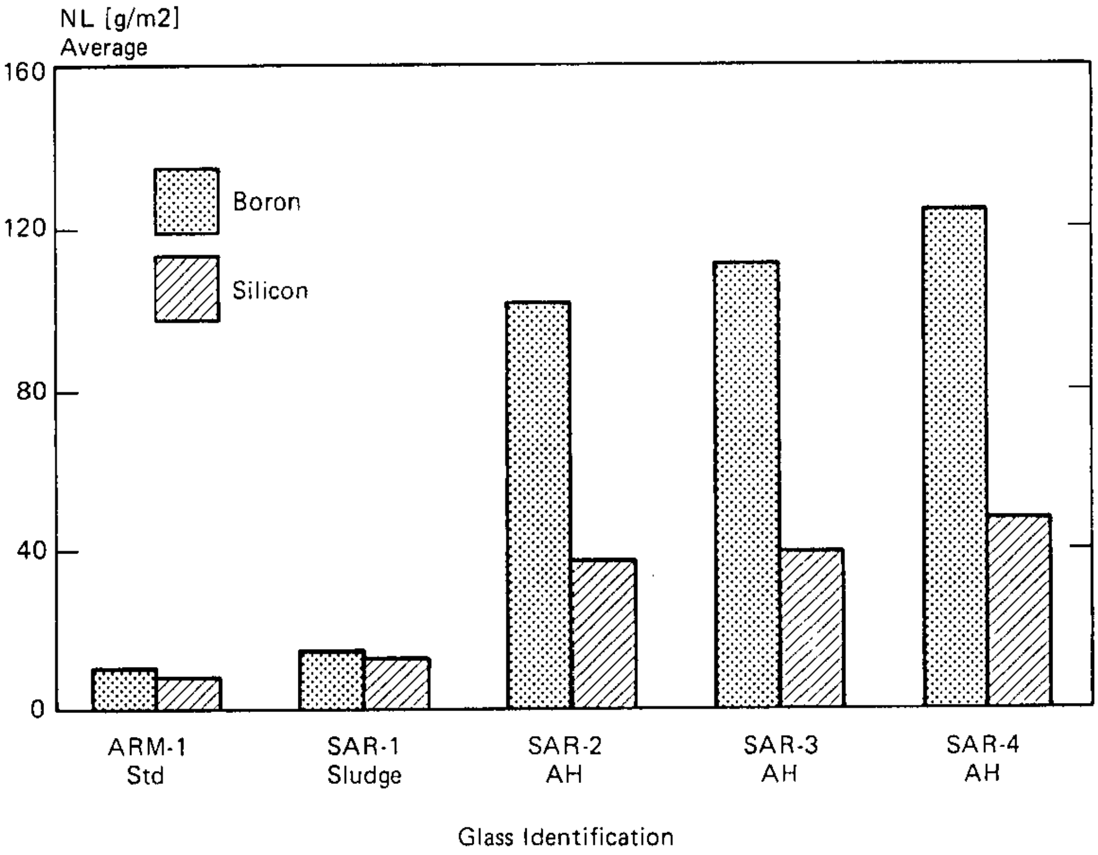


FIGURE 26. Normalized Elemental Mass Loss
Acid Hydrolysis vs. Sludge-Only Glass

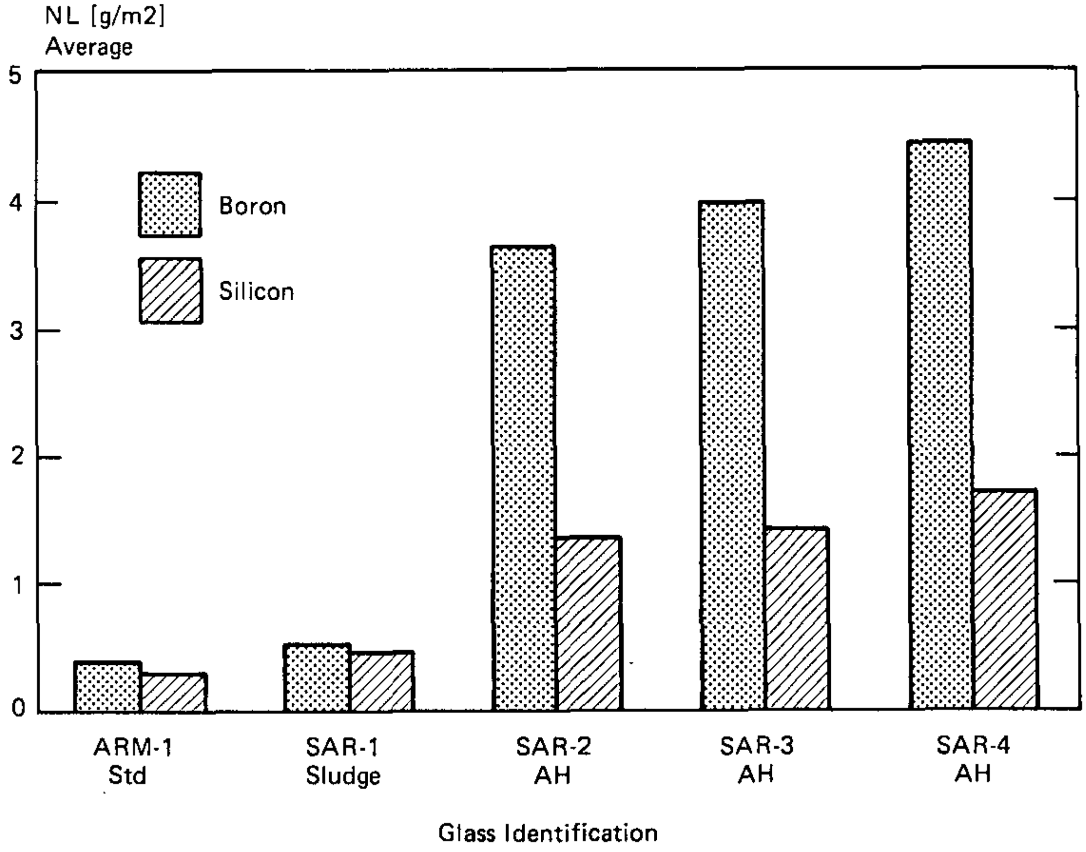
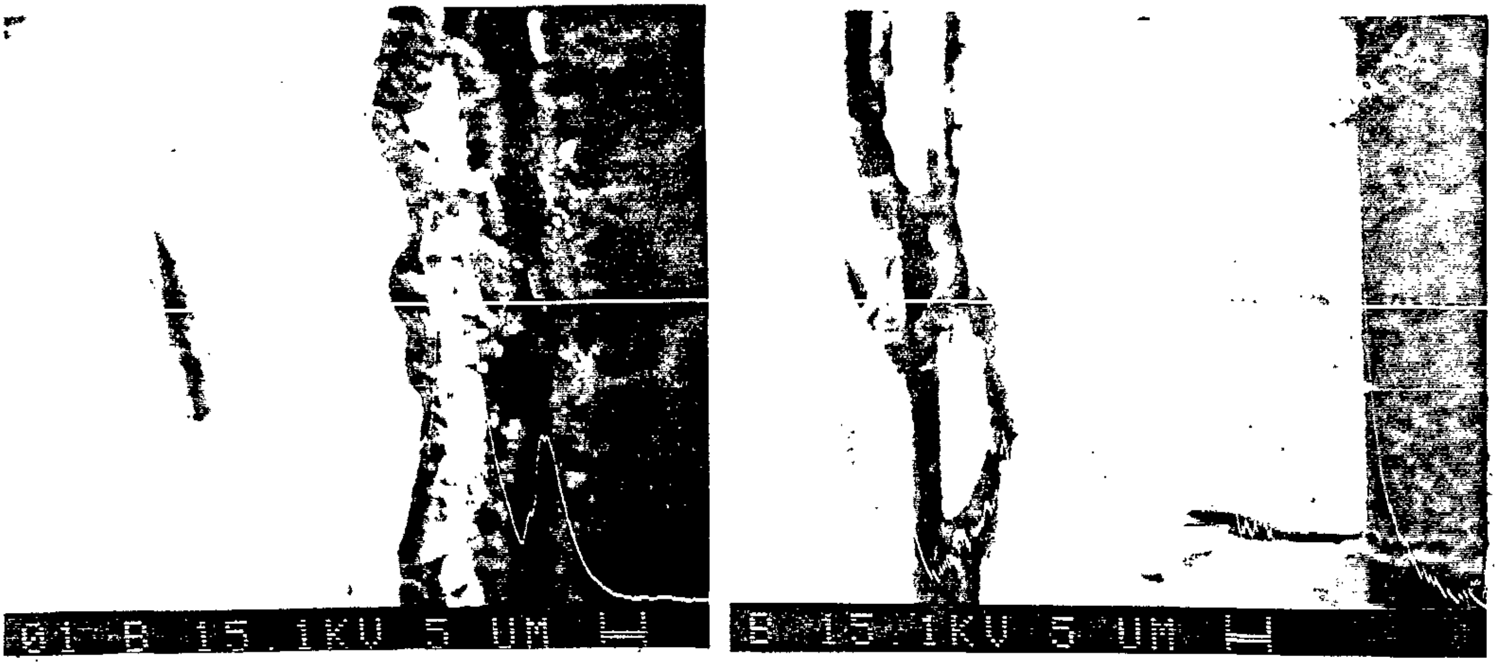
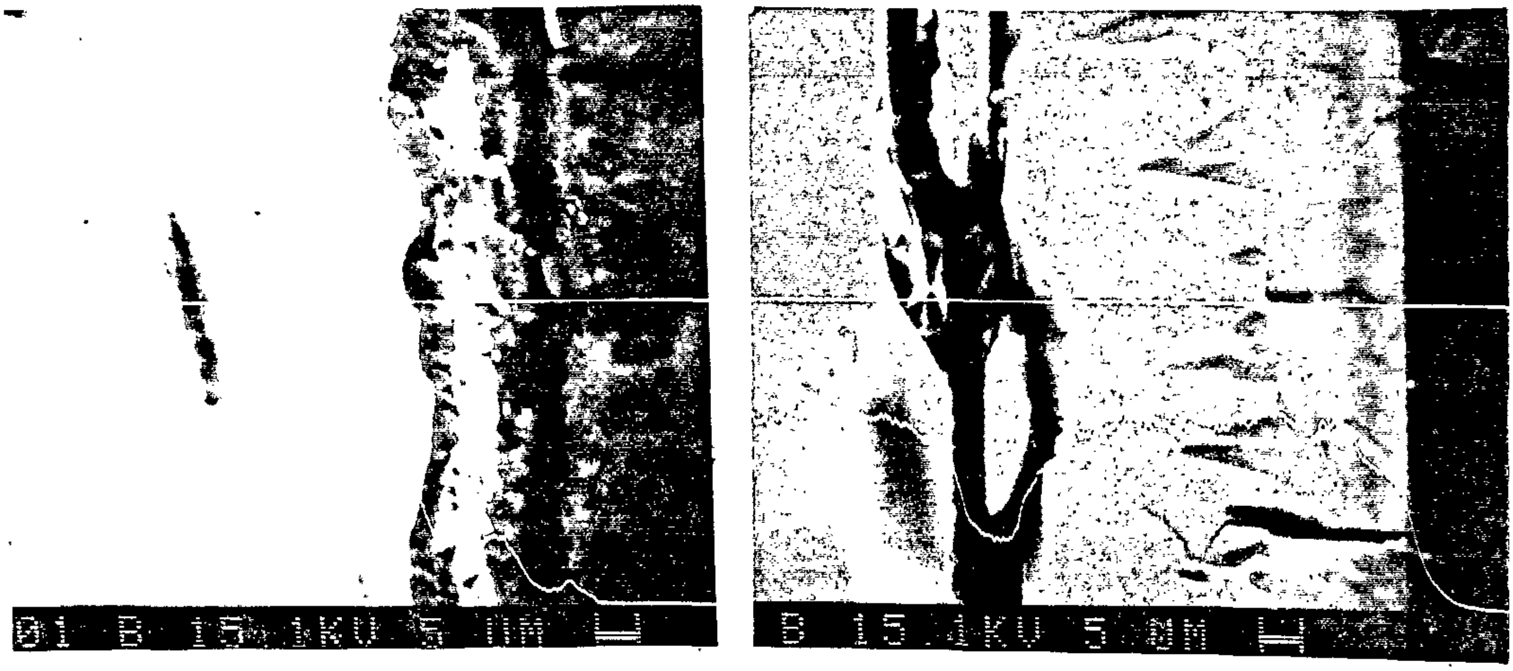


FIGURE 27. **Leach Rate**
Acid Hydrolysis vs. Sludge-Only Glass



Sludge Glass [Fe, Mg, Mn]

AH Glass [Fe, Mg, Mn]



Sludge Glass [Si]

AH Glass [Si]

FIGURE 28. Electron Microprobe Analyses
(Sludge vs. Acid Hydrolysis (AH) Glass)

Test Results of the Experimental Canister Frit Blaster Impacting the Canister Decontamination Chamber Design

Introduction and Summary

The Experimental Canister Frit Blaster (ECFB) has been installed in Building 672-T at the Equipment Test Facility (ETF). The ECFB is capable of frit slurry blasting full-size canisters and is similar to the Canister Decontamination Chambers (CDC's) that will be installed in the Defense Waste Processing Facility (DWPF).

The ECFB was tested with water only in April and May 1984. It was then tested with frit slurry in June, July, and August 1984. These tests have confirmed the adequacy of the basic concepts and design of the CDC and the associated equipment. Also, minor design modifications and additions have been identified that will improve the operation, efficiency, and reliability of the CDC and associated equipment. A list of these recommended modifications and additions is shown in Table 28. Recommendations for nozzle locations are shown in Table 29. Some concerns developed over the ribbon jet, chamber rinsing, and canister rubbing during rotation and are listed in Table 30.

Discussion

During the water only tests a canister was run through the complete blasting cycle over ten times. During the slurry blasting tests canisters were blasted during seven complete cycles. Oxidized canisters were used for three of these slurry blasting tests and a canister fitted with coupons was used for the remaining four tests. The appearance and oxidation removal on all three oxidized canisters were excellent. In all the coupon tests, the weight losses produced by the cylindrical nozzles were well above the 5 mg/in.^{2} required for decontamination. In the early tests, weight losses produced by the ribbon jet were marginal. However, with a modified ribbon jet in the last test, adequate weight losses were produced.

The recommendations for design changes or additions to the CDC and associated equipment are listed in Table 28.

Following are comments on each of these items.

1. Lubricated air is recommended by the manufacturer for operation of the diaphragm pumps. On a few occasions when a lubricator ran out of oil on the ECFB the diaphragm pump eventually stopped operating.

TABLE 28

CDC Recommendations

1. Lubricators required on all diaphragm pump air lines.
2. Oil lubricators should have visible oil level, and visible and adjustable oil flow.
3. Ribbon nozzle and the cylindrical nozzle pointed up should be flushed after all slurry blasting.
4. Prevent manual shutoff of nozzles during blasting without rinsing.
5. Canister guide opposite nozzles not required.
6. Use slow speed transducer for rotation and translation output.
7. Use low pressure or reservoir for rinse water through pumps.
8. Install one pressure gauge downstream of nozzle air solenoid (for pressure drop).
9. Change taper on CMM alignment pins or eliminate pins.
10. Provide travel limits for grapple open/close.
11. Provide independent motor speed readout.
12. Slurry lines to be sloped and without pockets to allow self draining.
13. Position of canister full down cam must not exceed stroke.
14. Provide self-relieving air pressure regulators.
15. Consider trash screen for sump pumps during run-in.
16. Rotate No. 3 nozzle 90 degrees do not rebound slurry towards cameras.
17. Provide means of determining when recirculation pump is pumping liquid.
18. Provide positive indication that grapple is rotating during all slurry blasting.
19. Prevent grapple bearing failure from allowing canister to be dropped.
20. Control flow rate from diaphragm pumps not pump air pressure.

TABLE 29

Recommendations for CDC Nozzle Locations

1. A 2-inch stream length is best but a 4-inch stream length for increased canister clearance produces less than 10% loss in efficiency.
2. The top canister nozzle is best at a 45 degree angle from the surface. Thirty-five degrees from horizontal would be a good compromise for the different surface angles involved.
3. The center-to-center distance of the nozzles can be as much as 0.5 inch greater than the stroke while blasting.
4. The nozzle for cleaning under the canister flange should allow the canister to raise for overlap with the top canister nozzle.

TABLE 30

CDC Concerns

Ribbon Jet

- Plugging
- Cleaning distribution

Chamber Rinsing

- Locations
- Rotating vs. stationary
- Water volume

Canister

- Run-out while suspended

2. The lubricators on the ECFB have opaque bowls so oil level could not be easily checked. Also, the oil flow into the air stream is not visible and is not adjustable. Some of the pump exhausts had an excessive amount of oil and were a housekeeping problem.

3. During slurry blasting a sheet of slurry from the side of the canister falls directly into the upward facing ribbon nozzle. Some slurry also splashes into the one upward facing cylindrical nozzle. A short water flush of these jets after slurry blasting would prevent frit from accumulating.

4. An interlock to immediately flush nozzles if they are shut down manually would remove frit from interior passages.

5. A semi-circular guide was initially installed on the ECFB in case the nozzles started to canister swinging. No swinging was ever observed and the guide was removed.

6. The original speed transducer on the rotation motor was a high speed transducer and lost its signal below 25% speed. A speed transducer that can read down to at least 10% speed (the drive capability) would be better.

7. With full plant water pressure used for flushing, the water flow could not be controlled by the diaphragm pump and the water flow was much higher than desired. By using a water pressure regulator or a water reservoir the pumps can control flow and the desired flow rate can be attained.

8. Slurry pressure is measured at the diaphragm pump outlet on the ECFB and not at the nozzle about 40 feet downstream. A pressure measurement at the nozzle, at least during the cold run-in, would indicate pressure drop in the pipe.

9. The small clearance and small taper on the CMM alignment pins caused occasional binding.

10. There are no travel limits or travel indications on the grapple open/close mechanism. The grapple was opened or closed until the torque limiter started slipping. This would eventually cause excessive wear on the torque limiter.

11. Speed readout directly from the drive was not directly proportional to actual speed and if the torque limiter was slipping it was not accurate. Readout from the shaft being turned (not the motor shaft) would be best.

12. The ECFB had flexible slurry lines to the nozzles to allow adjustment. These create loops that trapped liquid that would sporadically feed water to the nozzles during the air drying stage and could also trap frit.

13. The cam to indicate the canister full down position exceeded the stroke and was adjusted by 1/2 inch on the ECFB.

14. Nonrelieving air pressure regulators bleed through and indicate header pressure, so they must be adjusted with equipment operating. Self-relieving regulators may be adjusted to set pressure without equipment operating.

15. A rag was wrapped around the ECFB recirculating pumps impeller reducing flow rate by 90%. It required removal of the pump to correct. A trash screen would have prevented this problem.

16. Present CDC design has the camera port located about 90° from the upward facing nozzle. Some rebounding frit enters this camera port location. Nozzle placement in front of the camera port would reduce the amount of frit entering the camera port area, if it doesn't restrict viewing.

17. The recirculation pump will not pump liquid with the inlet blocked, or if it is not properly primed. When the ECFB pump was running and not pumping it pulled about 60 watts. When the pump was pumping liquid it pulled over 400 watts.

18. It is extremely important that the canister is rotating while slurry blasting to prevent removal of more metal than desired.

19. A grapple bearing failure on the ECFB allowed the grapple cam to drop. Friction between the canister and grapple prevented the canister from dropping. A design to prevent the cam from dropping if the bearing fails is desirable.

20. Because of differences in pipe runs, equal pump air pressures produce different liquid flow rates to nozzles. Flow rate should be directly controlled and different flow rates available for slurry and water would be advantageous.

Recommendations for the CDC nozzle locations are presented in Table 29. Since the nozzle locations in the CDC are not adjustable, it is important that these recommendations be followed closely.

Concerns developed during testing of the ECFB in the three different areas outlined in Table 30. The first ribbon jet had a 0.040 inch slot width and continuously plugged in varying locations in the slot. This ribbon jet produced erratic and marginal weight losses in the coupon tests. The second ribbon jet had a 0.060 inch slot width and produced better weight losses, but the low slurry flow rates allowed made the design questionable. A third ribbon jet is being designed with a constant area transition piece that may resolve the problem. Approximately 2 to 5 times more metal is removed by the ribbon jet in the center of the canister bottom than toward the outside of the canister bottom. However, this additional weight loss is only on a relatively small area of the canister and is probably acceptable.

Some concern also exists over the proper locations of the chamber rinse nozzles to assure all areas of the chamber are properly rinsed. If the inside of the CMM protective shield is not completely rinsed, some frit drops onto the cleaned canister. Two types of rotating rinse nozzles were used on the ECFB. The rotating fan nozzle stopped rotating after a few weeks of slurry blasting and the rotating stream nozzle developed a small leak of one of the rotating joints. A stationary rinse nozzle has been used but it produces a fine spray that doesn't seem to rinse as thoroughly as the powerful stream from the rotating stream nozzle. However, the rotating stream nozzle uses a large volume of water that may be a burden for the slurry mix evaporator.

A final concern is canister run-out. Canisters to date have been made a few at a time in small job shops. They have not met the tolerances expected for DWPF canisters. The flanges on these canisters are not exactly perpendicular to the canister axis and therefore hung at a slight angle from the CMM grapple. When these canisters are rotated by the CMM at the bottom of the vertical stroke, they bump the bottom centering guides in the chamber and abrade the canisters. This can cause recontamination problems in the DWPF. It is planned to build two canisters to DWPF tolerances and fill them with simulated waste glass to assure they will have acceptable run-out in the blast chamber.

Decontamination of Impacted Surfaces-1 Maximum Crane Speed Impact Study

Summary

In the current design of the canister decontamination chamber (CDC) for the DWPF, air-injected water cleaning is used to remove radioactive contamination from the guides and cradle that supports the canister. To facilitate this cleaning, an overlay of harder Stellite Multipass alloy #4 on these stainless steel surfaces has been proposed to prevent embedding of contamination. The test results reported here show that water blasting (no frit) will not decontaminate the CDC cradle if it is struck by a contaminated canister lowered at maximum crane speed (20 ft/min). A single specimen coated with CoCrAlY did show promise for water-only contamination.

Test Procedure

Type 304L stainless steel test specimens with or without a Stellite Multipass alloy #4 weld overlay and one specimen with a CoCrAlY coating were contaminated. Specimen radioactivity was determined by a Cutie Pit survey meter held directly over the specimen. A weighted curved surface was then dropped on to the contaminated spot. The impact force was designed to simulate a 5000 lb canister contacting the cradle at the maximum crane speed of 20 ft/min. The impacted specimen was subjected to successive washes with air-injected water (45 psi water, 90 psi air). After each water wash, the specimen was measured both directly with a Cutie Pie and by smearing the surface with filter paper which was subsequently examined for radioactivity while in a lead enclosure. The initial specimen radioactivity was compared with the radioactivity retained after each wash.

Results

Results of the first study shown in Figure 29 are repeated in Figure 30 with a reduced dependent variable scale to permit direct comparison with the second study. The figures depict successively the initial contamination levels of the stainless steel, Stellite Multipass alloy #4, and the stainless steel and Stellite controls which were contaminated but not subjected to impacting by the simulated canister. These are compared with the contamination levels of the same specimens after various air-injected wash times, one-half and five minutes in the first study and five and ten minutes in the second. Contamination levels are first shown for Cutie Pie measurements and then for measurements on filter paper smears. The amount of contamination applied in the second study (Figure 31) was reduced by an order of magnitude to be more representative of anticipated CDC conditions. Figure 32 represents a lone CoCrAlY surface which was decontaminated to very low levels after a five minute wash as determined by direct reading and after a ten minute wash as determined by smearing. These results show that:

- The amount of initial radioactive contamination had a minor effect on the amount of contamination retained after the same amount of water washing.
- Stellite and stainless steel retain contamination to the same degree.

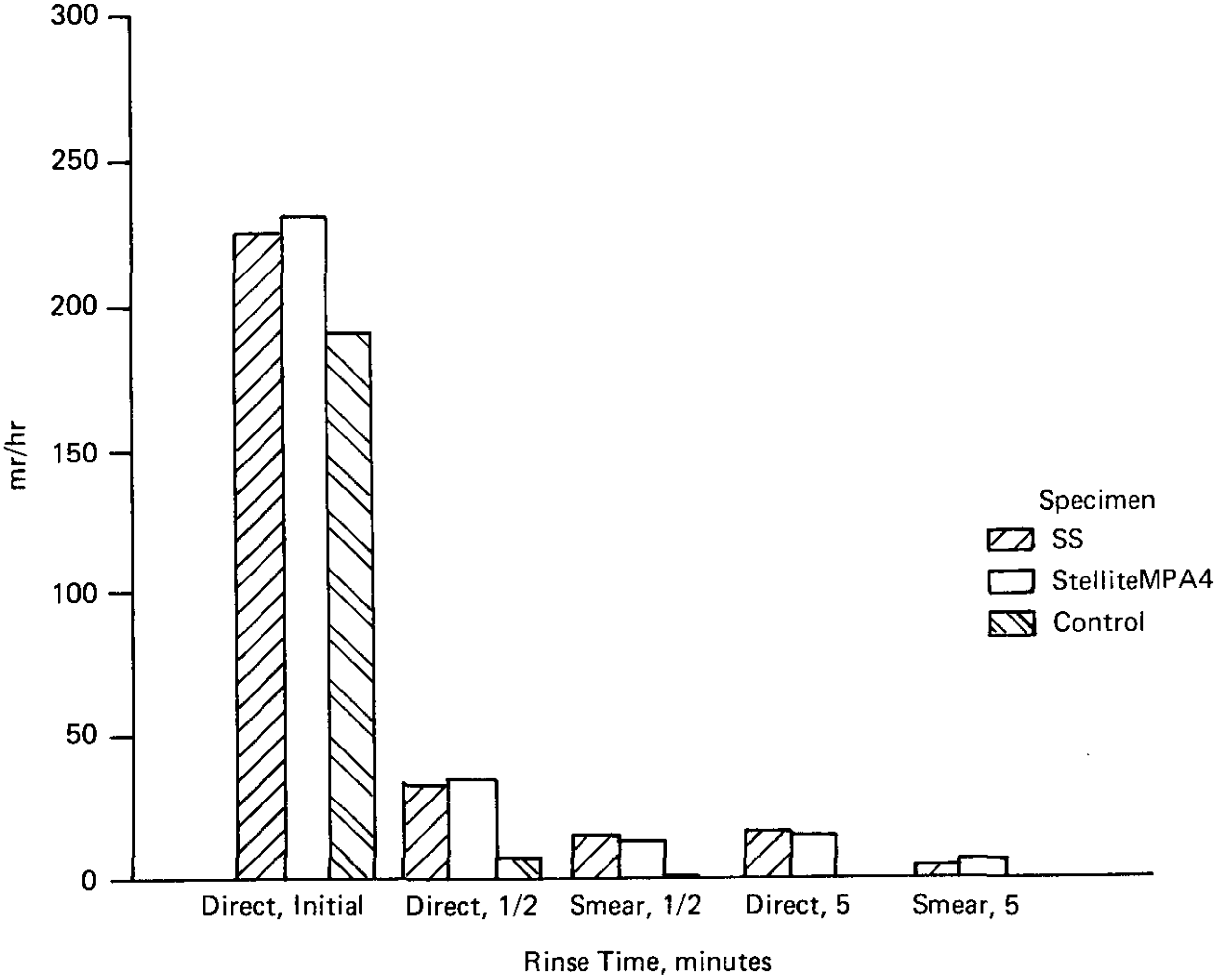


FIGURE 29. Impact Study-I

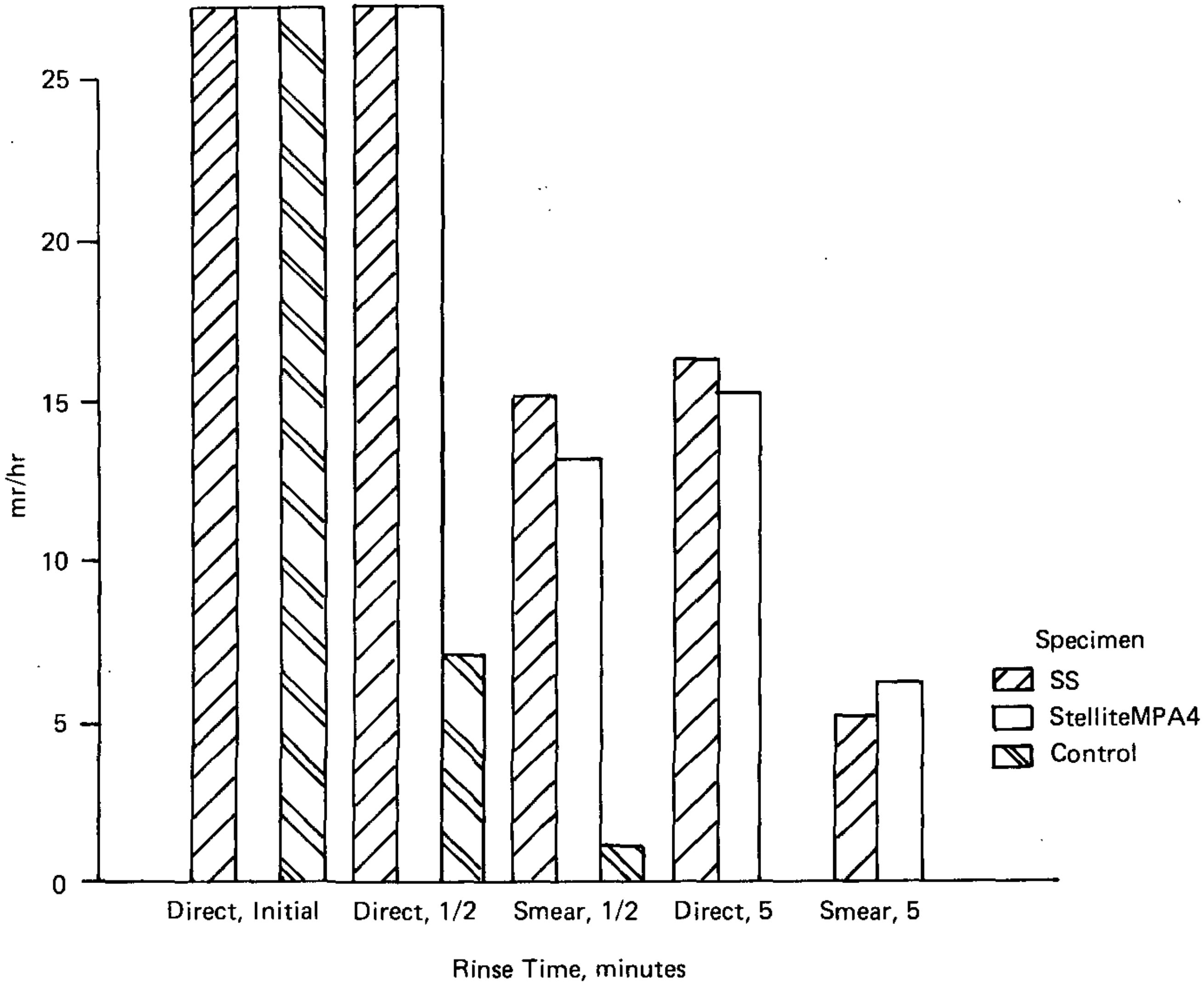


FIGURE 30. Impact Study-I

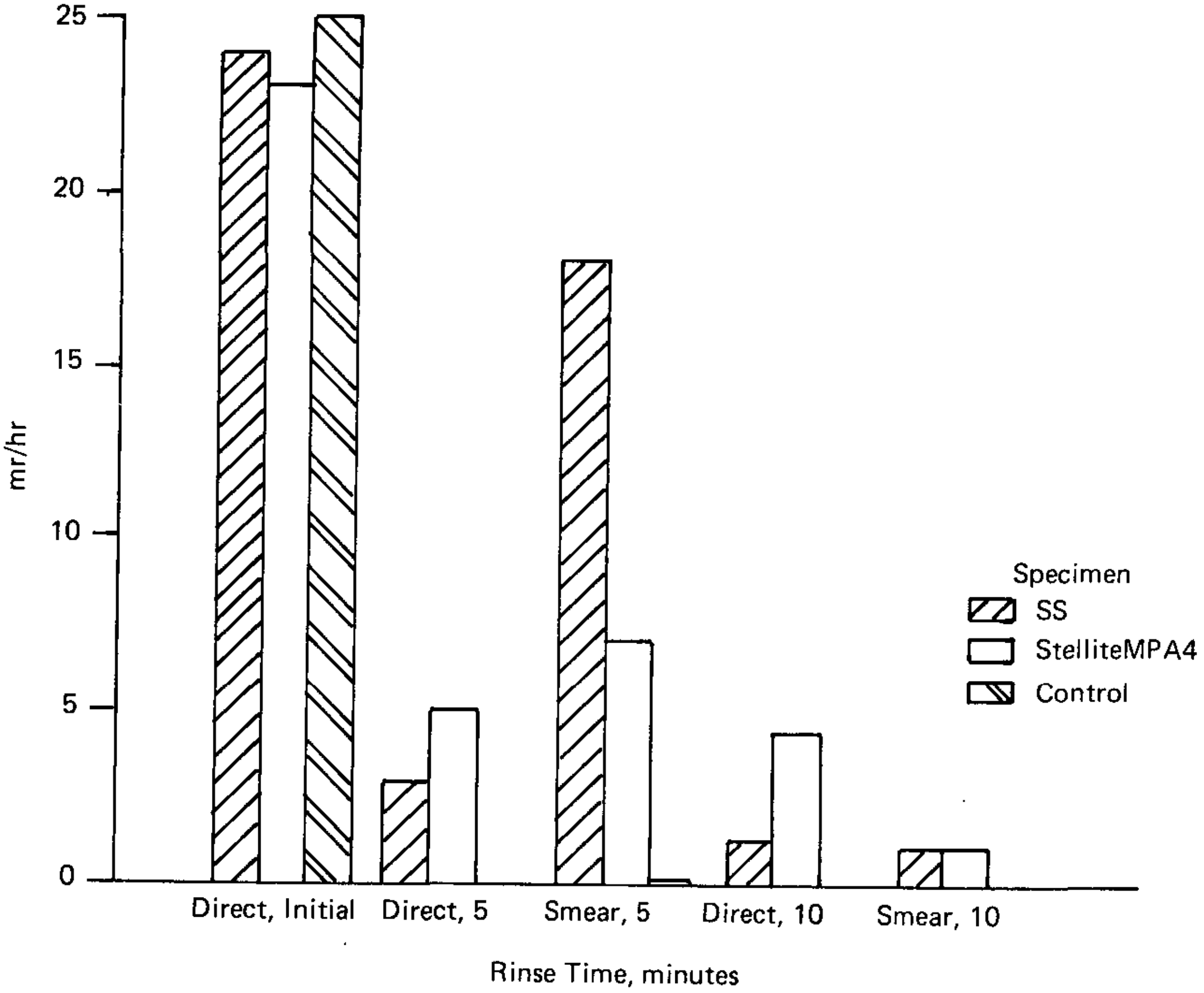


FIGURE 31. Impact Study-II

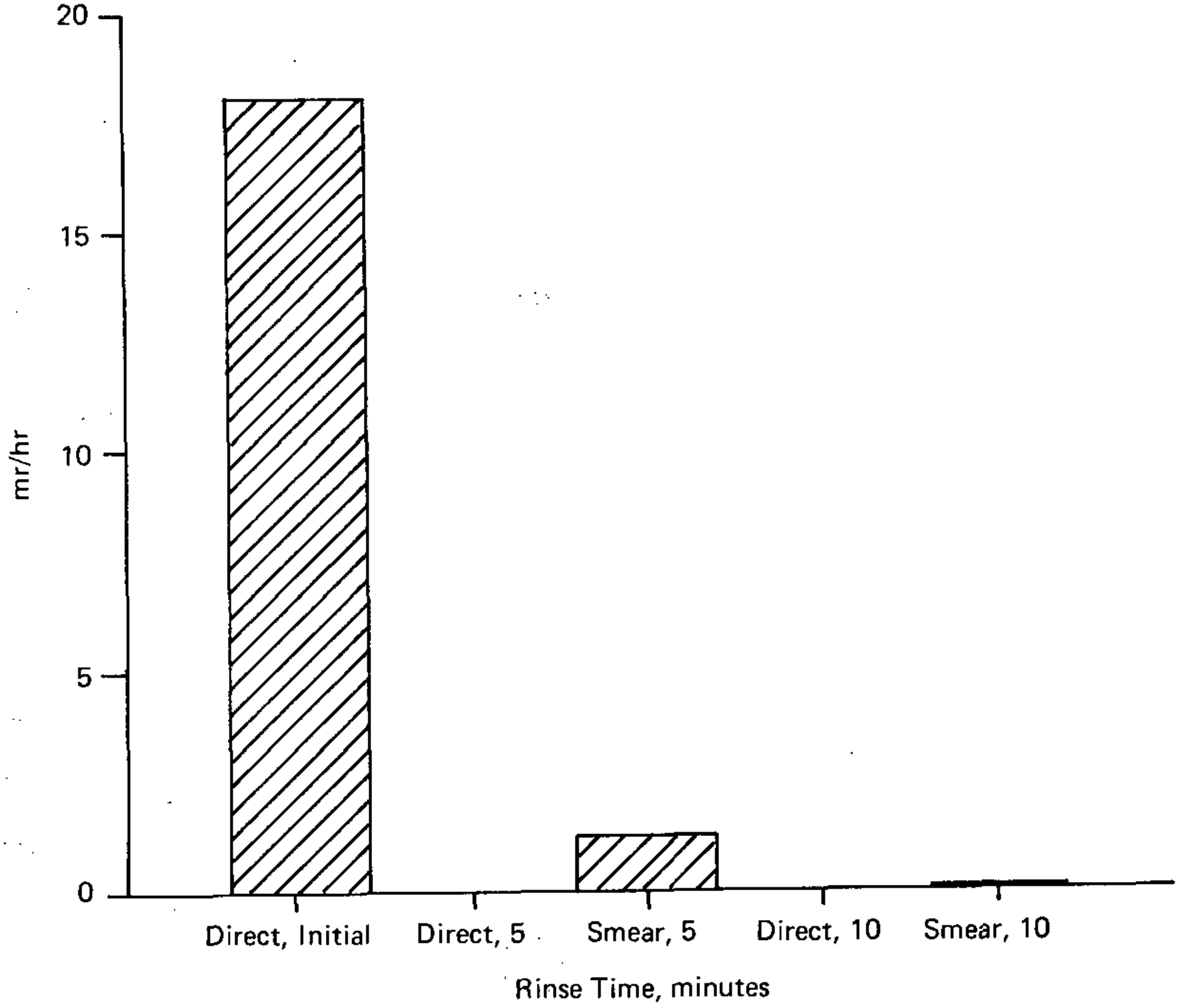


FIGURE 32. CoCrAlY Impact Study

- Air-injected water washing is insufficient to decontaminate surfaces impacted by a canister lowered at 20 feet/minute.
- CoCrAlY shows promise for achieving water only decontamination but was not tested extensively enough to establish confidence.

Mercury Removal From Supernate Using Ion Exchange

Introduction

An estimated 80-90M lb of mercury are present in existing SRP waste that will be processed in the Defense Waste Processing Facility (DWPF). About one-fifth of that amount will be present in soluble high-level waste (HLW supernate), representing 70% of the total mercury going to the melter. Although materials of construction for the melter and melter off-gas system have been carefully selected to resist mercury-induced corrosion, the potential for such corrosion can be further minimized by removing as much mercury as possible before arrival in that system. Tests on simulated and actual HLW supernate indicate effective mercury removal by Duolite® ES-465 cation exchange resin. Removal of Hg from the salt before it even reaches the DWPF would be of additional benefit because it would eliminate the generation of diphenylmercury and phenylmercuric formate during the reference processes of NaTPB precipitation followed by acid hydrolysis. These organomercurials are not as easily removed as the inorganic form, Hg^{2+}, found in HLW supernate.

Summary

The chelating cation exchange resin, Duolite® ES-465 has been demonstrated efficient and effective in removal of mercury from both simulated and actual diluted Tank 30H supernate, indicating that a properly designed column of this resin should be able to remove essentially all of the mercury from that stream. There is no apparent negative physical or chemical reaction by the resin to the substantial hydroxide concentration in supernate; the high concentration of sodium actually has a beneficial effect in that it preferentially displaces cesium and strontium from the resin. There is no significant retention of plutonium or ruthenium by the resin.

ES-465 and Simulated Supernate

The demonstrated effectiveness of Duolite® ES-465 in the removal of mercury from dilute solutions led to experiments that tested its efficiency at the high sodium and hydroxide concentrations present in supernate waste systems. First, batch tests using simulated supernate containing mercury showed that the resin performed well in removing the mercury at those concentrations and that there was no apparent degradation of the resin. Initial concentrations of 34.5 ppm were reduced to 0.10 ppm when 15 mL of simulated supernate were allowed to equilibrate with 0.21 g of the sodium form of the resin (Table 31). A small column of ES-465 was tested with simulated supernate to determine whether the resin would perform well in a column mode. Not only was the integrity of the column maintained during operation, but greater than 99% of the mercury was removed by the resin (Table 32).

TABLE 31

Simulated Supernate Batch Experiments

Sample No.	Resin, g	Supernate, mL	Initial µg Hg/mL	Final µg Hg/mL	Kd*
1	0.2159	15	34.5	0.13	1.84E+4
2	0.2167	15	34.5	0.11	2.16E+4
3	0.2109	15	34.5	0.10	2.45E+4

---

* Kd relates the concentration of Hg on the resin per gram of resin relative to the concentration of Hg per mL remaining in solution at equilibrium.

$Kd = [Co/C - 1]\,(V/m)$ where Co = the initial Hg concentration in solution, C = the concentration of Hg in solution at equilibrium, V = the volume of solution used in the solution, and m = the mass of resin in grams.

TABLE 32

Hg Removal from Simulated Supernate Using a 2 mL Column*

Sample	Column Volumes	Hg Concentration
Feed	-	21.3 ppm
Effluent fr. 1	2	0.50 ppb
Effluent fr. 2	10	0.10 ppb
Effluent fr. 20	20	<0.10 ppb
Effluent fr. 57	114	<0.10 ppb
Effluent fr. 80	160	0.70 ppb
Effluent fr. 100	200	0.20 ppb

---

* Pump rate through the 2 mL column was at mL/hr or 4 column volumes per hour. Four milliliter fractions were collected every 30 minutes.

ES-465 and Tank 30H Supernate

Mercury Removal

Batch tests run in the high level cells (HLC) on Tank 30H supernate, diluted to 5.4M Na^+ and to which mercuric nitrate had been added to bring the mercury concentration to 10.0 ppm, also resulted in mercury removal of greater than 99% to a final concentration of 13.8 ppb (worst case).

Radionuclide Uptake

Other analytical results of the experiments with Tank 30H supernate indicate that plutonium is not sorbed on the resin from supernate. In addition, ^{90}Sr and ^{137}Cs are not present in any significant amount on the resin after reaction. Thus, it appears that the high sodium ion concentration already present in the supernate acts as protection from Cs and Sr sorption. One wash of the resin with 2M $NaNO_3$ was sufficient to remove residual ^{137}Cs from the resin to a level of 0.60 µCi ^{137}Cs/mL of resin. This value is below the 1 µCi ^{137}Cs/mL allowed for classification as a Class A waste[6] (see Appendix D).

Experiments concluded earlier using Tank 50 decontaminated supernate show that ruthenium is not sorbed by ES-465 resin from that solution (Table 33). It is reasonable to expect similar behavior toward the resin by ruthenium in supernate originating from other tanks.

TABLE 33

Ruthenium Studies with ES-465 Cation Exchange Resin

Sample	Resin, g	Ru-106/mL*, µCi	Fraction of Ru on Resin
Tank 50 supernate	0.0000	9.79 E^{-2}	–
Ru-1 (25°C)	0.2005	1.21 E^{-1}	<0**
Ru-2 (25°C)	0.2000	1.00 E^{-1}	<0**
Ru-3 (25°C)	0.2003	1.00 E^{-1}	<0**
Ru-4 (80°C, 1 hr)	0.5003	1.05 E^{-1}	<0**
Ru-5 (80°C, 3 hr)	0.5003	9.43 E^{-2}	0.037

---

* All gamma counting was done on 3 mL aliquots of the reaction solution at 622 keV.

** Apparently, Ru does not sorb into the resin. Negative values reflect counting statistics.

Projected Resin Requirements for Removal of Mercury from SRP Supernate

Appendix E outlines calculations based on projected annual processing, intended to determine the amount of ES-465 resin required for proposed treatment of SRP supernate for Hg removal before in-tank precipitation was outlined. Our very conservative estimate is that 306 cu ft of ES-465 would be needed per year to remove the approximately one ton of mercury that will be in the volume of supernate projected for annual processing. In addition to the 306 cu ft of spent resin generated each year as waste, as much as two tons of $NaNO_3$ could be added to the soluble waste as a result of washing Cs from the resin before disposal.

That amount is minimal, representing an increase of less than 0.10% in the total amount of $NaNO_3$ which will be processed annually in the DWPF. The fate of spent resin has not been decided, but is has been determined that resin incorporated in grout meets EP-toxicity test standards for storage as a nonhazardous waste.

APPENDIX D

Batch Experiments with Tank 30H Supernate Mass Balance Calculations

Pu Mass Balance (all samples are 15 mL)

Pu in supernate = 1.10E+4 dpm/mL

Pu in supernate after resin	= 6.49E+3 dpm/mL
Pu in one water wash of the resin	= 1.71E+3 dpm/mL
Pu in one $NaNO_3$ wash following water wash	= 1.92E+3 dpm/mL
Total	= 1.01E+4 dpm/mL

Sr Mass Balance (all samples are 15 mL)

^{90}Sr in supernate = 1.62E+6 dpm/mL

^{90}Sr in supernate after resin	= 1.84E+6 dpm/mL
^{90}Sr in one $NaNO_3$ wash of resin	= 8.04E+4 dpm/mL
Total	= 1.92E+6 dpm/mL

^{137}Cs Mass Balance

^{137}Cs in 15 mL supernate = 1.77E+4 μCi

^{137}Cs in 15 mL supernate after resin	= 1.80E+4 μCi
^{137}Cs in 0.20 g dissolved resin after 2M $NaNO_3$ wash	= 0.222 μCi

To find μCi ^{137}Cs/mL resin:

$$(0.222\ \mu Ci/0.20\ g\ resin) \times (0.54\ g\ resin/mL\ resin) = 0.60\ \mu Ci\ ^{137}Cs/mL\ resin$$

APPENDIX E

Calculation of Hg to be Removed

Conservative estimates based on the latest available flow rates and concentrations for supernate indicate that 4.33E+3 moles of Hg^{2+}/yr will be sent as feed to the precipitation process. This represents 8.66E+3 gram equivalents Hg^{2+} to resin/yr. The computation for this is:

NaHg(O(OH)) in feed to process = 0.2789 lb/hr

[0.2789 lb NaHg (O(OH))/hr] x (454 g/lb) x

[200 g Hg/256 g NaHG(O(OH)] = 98.9 g Hg/hr

(98.9 g Hg/hr) x (24 hr/day) x (365 day/yr) = 8.66E+5 g Hg/yr

(8.66E+5 g Hg/yr) x (1 mole Hg/200 g Hg) = 4.33E+3 mole Hg/yr

(4.33E+3 mole Hg/yr) x 2 g eq. Hg/mole Hg) = 8.66E+3 g eq. Hg/yr

Calculation of Resin Needed

K_d as Predictor

There are two approaches for the computation of the volume of Es-465 resin needed to remove 8.66E+3 g eq. Hg/yr. The first of these uses the experimentally determined Hg equilibrium distribution constant for Es-465. That constant is 5.43E+4 mL/g for Tank 30H supernate which has been diluted to a sodium ion concentration of 5.4M.

$$K_d = (Co/C-1) \times (\text{mL solution/g resin}) = [(10.0\ \mu g/mL/0.0138\ \mu g/mL)-1]$$

$$\times\ (15\ mL/0.20\ g) = 5.43E+4\ mL/g$$

Theoretically, the number of column volumes of solution that can be processed by a given volume of resin before 50% breakthrough is achieved can be approximated by multiplying the K_d by the bulk density of the resin, p_B. For this system, the expected volume at 50% breakthrough would be

$$K_d = p_B = (5.43E+4\ mL/g) \times (0.54\ g/mL) = 2.93E+4$$

The expected flow per year for supernate is:

(2 cycles/yr) x (2.27E+6 gal feed/cycle) = 4.54E+6 gal feed/yr

(155 gal resin/yr) x (1 cu ft/7.48 gal) = 20.7 cu ft resin/yr

Saturation as Predictor

The K_d equation and value are useful as a predictor only if the system is far removed from saturation. In a practical situation, columns of resin for treatment would be maintained at least to near saturation conditions. Therefore, a second approach is to calculate how much resin would be needed based on saturation of the resin by mercury. We have demonstrated that the capacity of this resin for mercury is about 1.5 g eq. Hg/L resin for mercuric nitrate solution. For supernate, a very conservative estimate of the capacity would be more in the region of 1.0 g eq. Hg/L resin. Since 8.66E+3 g eq. Hg/yr are expected to be processed

(8.66E+3 g eq. Hg/yr)/(1.00 g eq. Hg/L resin) = 8.66E+3 L resin/yr

(8.66E+3 L resin/yr) x (1 cu ft/28.32 L) = 306 cu ft resin/yr

Waste Resin Generated

The second approach is probably the more realistic one for the determination of the annual volume of resin that will be required. Hence, a value of 306 cu ft/yr represents the estimate of the waste resin that will be generated. This is because it will probably be more desirable to retire columns slightly before total saturation.

Radionuclide Uptake

ES-465 has been demonstrated to sorb ^{137}Cs and ^{90}Sr in the presence of Hg^{2+}. Batch experiments with supernate, however, have shown that the high sodium ion concentration in supernate keeps these elements from collecting on the resin. Further, plutonium and ruthenium are not apparently sorbed by ES-465. The only radionuclide remaining in any significant concentration on the resin is ^{137}Cs. Experiments have shown that about half of the residual amount can be washed off with water and essentially all of it can be removed by washing with 2M $NaNO_3$. The K_d of ^{137}Cs under supernate conditions is found by the following computation from experimental data.

$$K_d = [(C_{Cs} \text{ on resin})/(C_{Cs} \text{ in solution})] \times (V\ NaNO_3 \text{ solution})/$$

$$(g \text{ resin}) = (0.22\ \mu Ci/843\ \mu Ci) \times (15\ mL/0.20\ g)$$

$$= 1.9E-2\ mL/g$$

The small value of K_d suggests that, at most, two column volumes of 2M $NaNO_3$ should effectively remove any ^{137}Cs still sorbed on the resin and most of that element on the inside walls of the column and held interstitially between resin beads. This represents

(2 cv) x (5.77E+3 L/yr/cv) = 1.15E+4 L of 2M $NaNO_3$/yr

to be used for washing purposes. This would generate an additional 2.30E+4 moles of $NaNO_3$/yr waste, or

(2.30E+4 moles $NaNO_3$/yr) x (85 g/mole $NaNO_3$) = 1.96E+6 g $NaNO_3$/yr

(1.96E+6 g $NaNO_3$/yr) x (1 lb/454 g) = 4.14E+3 lb $NaNO_3$/yr

This amount represents an increase of less than 1.10% in the total amount of $NaNO_3$ which will be processed annually.

Removal of Mercury from Sludge Using Ion Exchange

Introduction

Recent studies at Savannah River Laboratory (SRL) have determined that Duolite® ES-465 chelating cation exchange resin is a very efficient resin for removing dissolved mercury from Savannah River Plant (SRP) waste streams. Approximately 90% of the mercury in SRP waste is found in sludge. In the reference process for the Defense Waste Processing Facility (DWPF), a steam stripping procedure following reduction of mercuric ion with formic acid will remove, at most, 80% of the mercury from sludge as the metal. Remaining mercury will proceed with the sludge to the melter and ultimately to the melter off-gas system. In the event that it should become necessary to remove this last fraction of mercury, a resin-in-sludge process has been demonstrated effective in mercury removal using ES-465 resin with both formated sludge and steam stripped formated sludge.

Summary

Laboratory scale batch tests and fluidized bed column tests show that ES-465 cation exchange resin removes >90% of the mercury from formated simulated sludge and formated high-level radioactive sludge. Similar experiments using formated simulated sludge which has been steam stripped indicated that the resin is capable of removing about 75% of the mercury from that system in the same time 90% could be removed from sludge which has not been steam stripped. The percent removed can be improved by operating at higher temperatures.

Early batch experiments showed that abrasion from vigorous stirring of the sludge/ES-465 mixture caused the resin to degrade into particles too small to separate from the slurry after reaction. To protect the resin from abrasion, a resin-in-sludge mode of operation was designed wherein the sludge slurry contacts the resin by flowing through a bed retained between two screens in a column. The process has been demonstrated using both a 0.5 inch internal diameter upflow column containing two milliliters of resin and a 6.4 inch internal diameter stirred bed downflow column containing one liter of resin.

Discussion

Removal of mercury found in SRP sludge is a more difficult problem than removal of mercury from other waste streams and must be addressed differently. First of all, there is a much greater quantity of mercury to be removed from sludge than from dilute streams or supernate. Second, sludge is a very concentrated slurry, not a neat solution, and the nature of the slurry serves to hinder the sorption process by protectively coating both resin and the mercury particles in suspension. Third, chemical processes carried out on the sludge, primarily to effect removal of mercury by steam stripping, reduce the mercury to forms (Hg metal, Hg_2^{2+}) which are not soluble and, hence, more difficult to remove by ion exchange than the mercuric ion. Preliminary batch experiments, where ES-465 was shaken vigorously with solid mercuric oxide and aqueous solutions adjusted from pH 4 through 7, showed that the resin was capable of effecting dissolution of the solid and sorbing the resulting mercuric ion (Table 34). Encouraged by this result, subsequent experiments have been done demonstrating the ability of the resin both to sorb mercuric ion and to effect dissolution and sorption of initially undissolved mercury species from the sludge matrix.

TABLE 34

Removal of Solid HgO by ES-465, mg/Hg*

Sample	pH	g Resin	g HgO	Initial**	Final†
1	4	0.1026	0.0037	3.43	0.24
2	5	0.1025	0.0037	3.43	0.25
3	6	0.1011	0.0031	2.87	0.28
4	7	0.1025	0.0039	3.61	0.28

* All samples had 15 mL total volume of solution. All samples were shaken for 12 hours to achieve equilibrium.

** Based on solid added.

† Determined in solution. No solid HgO was visible with a magnifying glass after reaction.

Mercury Removal from Formated Sludge, Simulated and Real Batch Experiments

Measured amounts of mercuric nitrate and mercuric oxide were mixed well with samples of simulated sludge and formic acid. Aliquots of this mixture were used in batch equilibrium experiments with ES-465 resin. As illustrated in Table 35, the resin was effective in removing mercury, probably present as mercuric ion, from the slurry. Batch experiments were then done in the high-level cells (HLC) using formated Tank 42H aluminum dissolved, washed sludge. Analyses for mercury content before and after treatment with ES-465 indicate that 99.6% of the mercury was removed from the sludge in 12 hours. Rather an introducing a shaker into the HLC, the reactions were mixed by stirring with a magnetic stirrer. After reaction, attempts to separate the resin from the slurry with a wire screen (40 mesh) were unsuccessful because the abrasive action of the magnetic stirrer had ground the resin into fines. This apparent fragility of the resin precluded a simple, stirred batch operation and required development of a less destructive method of contacting the slurry with the resin.

TABLE 35

Percent Hg Removed from Formated Simulated Sludge vs. Time Using ES-465*

	Batch**		Column†	
Time (hr)	Hg (ppm)	% Hg Removed	Hg (ppm)	% Hg Removed
4	96.0	61.5	90.0	93.3
12	2.0	99.2	104	92.2

---

* All reactions were done at 24°C. Analyses are reported in ppm which implies µg Hg/mL of wet slurry.

** 2.67E-2 g resin/mL of slurry; initial Hg concentration = 256 ppm.

† 1.08E-2 g resin/mL of slurry; initial Hg concentration = 1340 ppm.

Mercury Sorption in Fluidized Beds

Recovery of mercury from a concentrated slurry such as sludge cannot be accomplished with a normal ion exchange column operation. Technologies have already been developed for ion exchange recovery of uranium from unclarified feed solution using a resin-in-sludge concept. For any of the variations of this method, the mixture containing the species of interest is reacted in a fluidized bed with resin which is ultimately separated from the mixture by screening after sufficient contact has been made for sorption and resin loading to occur. Laboratory experiments with simulated and actual Tank 42H aluminum dissolved, washed formated sludge used a fluidized bed contactor of column design as represented in Figure 33. The resin is contained between an upper and lower screen that is sized to allow sludge but not resin to pass through. The resin bed is fluidized by an upflow stream of feed sludge that is circulated through the system several times.

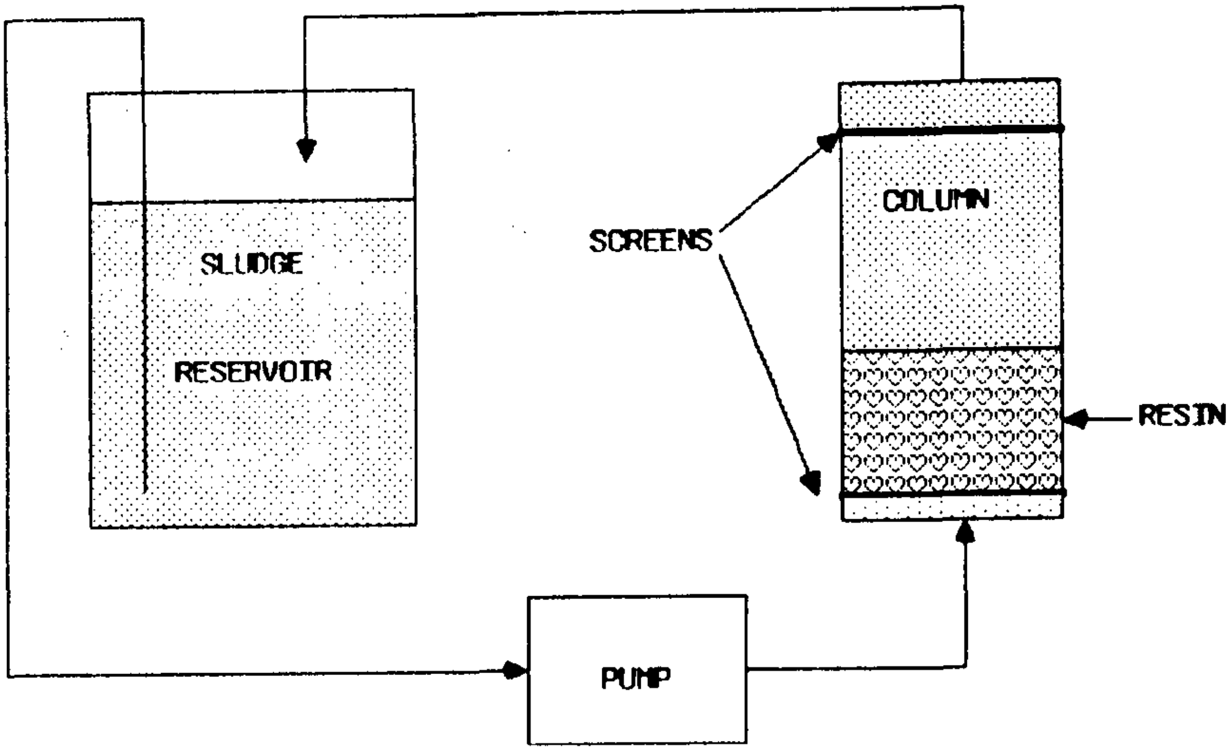


FIGURE 33. Column Apparatus for Sludge

In the laboratory experiments it was necessary to pretreat the sludge by passing it through a 200 mesh sieve to remove large particles that would plug the screens in the column. The resin was also presieved through a 40 mesh sieve to remove small resin beads that could plug the screens. A 0.5-inch inner diameter upflow column of this design has been used to demonstrate 87% mercury removal from both simulated sludge (Table 36) and high-level radioactive sludge (Table 37) by ES-465. With presieving as described, this column has operated without plugging, the longest consecutive period of operation being 24 hours. Results were the same for formated simulated sludge regardless of whether the mercury was added as solid mercuric oxide or as mercuric nitrate solution.

TABLE 36

Mercury Removal from Formated High-Level Radioactive Sludge

Sample	Hg (ppm) Initial*	Hg (ppm) Final*	% Hg Removed
Batch	1285**	4.81	99.6
Column	4884**	633	87.0

---

* ppm here refers to μg Hg/mL of wet slurry.

** Differences in initial concentration for the same Tank 42H aluminum dissolved sludge are presumed to be due to the difficulty associated with obtaining uniform samples of sludge.

TABLE 37

Mercury Removal from Steam Stripped Simulated Sludge at 25°C

Time (hr)	Hg ppm* (batch)	Hg ppm* (column)
0	63.4	63.4
1	46.7	31.7
2	46.0	32.7
3	43.7	26.7
4	39.2	28.7
5	27.0	20.0
6	22.7	13.0
7	22.3	17.0

---

* ppm here means μg Hg/mL wet slurry. (Obtaining uniform and representative samples for analysis is difficult.) Both batch and column runs used 6.7 μg resin/mL wet slurry.

Mercury Removal from Formated, Steam Stripped Simulated Sludge

When formated sludge is heated and steam stripped, mercury is reduced to Hg and Hg_2^{2+}. Both of these oxidation states are less soluble than Hg^{2+}, but earlier laboratory studies had shown that ES-465 could sorb dissolved metallic mercury and mercuric ion from aqueous systems. It was of interest then, to determine whether the resin would be effective for mercury removal from steam stripped sludge. Batch experiments and resin-in-sludge column experiments were conducted using steam stripped sludge containing mercury. Results of these experiments are tabulated in Table 38. In general, percent Hg removal was less in the same time for both modes of operation than that for sludge which had merely been formated. This was expected because of the less tractable nature of mercury species in steam stripped sludge. Nevertheless, ES-465 was successful at removing mercury from the sludge. A 6.4-inch inner diameter stirred bed downflow fluidized bed column of ES-465 was recently tested with mercury-containing steam stripped sludge. After initial sieving of the sludge, that column operated for seven hours, constituting two passes of the sludge through the resin. Preliminary analyses indicate that about 80% of the mercury was removed.

TABLE 38

Mercury Removal Temperature Studies*

T, °C	% Hg Removed
25	38.0
45	59.5
90	98.5

---

* All experiments were 4-hour batch runs using 0.01 g. ES-465 resin and 15 mL of steam stripped simulated sludge.

Temperature Studies

Because the sorption of mercury from formated and steam stripped sludge was less efficient than from formated sludge, batch temperature studies were done to determine the effect of increased temperature on the reaction. The results for similar four hour tests at three different temperatures are reported in Table 38. An increase in temperature made a significant improvement not only on the kinetics of reaction but also on the total amount of mercury that could be removed from sludge.

Quality Assurance

Mercury analyses were done by cold vapor atomic absorption using a Varian Model 64 atomic absorption spectrophotometer and a Perkin-Elmer Model 50A mercury analyzer. All mercury analyses were verified against standard solutions.

Demonstration of In-Tank Sludge Processing, Part III: Effect of Processing on Minor Waste Components

Introduction

The scope and cost of the Defense Waste Processing Facility (DWPF) has been significantly reduced by adding in-tank sludge processing to the process flowsheet. A demonstration of in-tank processing was completed in April 1983. The achievement of the major goals was described in a previous memo. This memo describes the effect of in-tank sludge processing on the minor nonradioactive elements in the waste. Halides will not be discussed due to lack of an effective analytical method at the time of the demonstration. The memo will also identify those areas that will require further work both before and during the next scheduled in-tank sludge processing batch.

Summary

The most significant minor waste component observably affected by the in-tank aluminum dissolution process was mercury. The net amount of soluble mercury increased, which would increase the mercury load on the tank farm evaporators. Due to the inconsistency in the mercury analysis on sludge solids no net decrease in insoluble mercury was found. Minor variations in the solubility of other waste components was observed by the impact of these variations should be minimal.

Discussion

The key processes relative to the minor waste components are aluminum dissolution and sludge washing. Each of these will be discussed after a review of the sample analyses procedures is given. Included with each discussion will be chronological tables of the measured results.

Experimental Procedure

The only procedures that shall be described are related specifically to chemical analysis. The dissolved samples and the samples liquids are analyzed by either atomic absorption spectroscopy (AA) or by inductively coupled argon plasma spectroscopy (ICP) for the metals. The results are reported in milligrams per liter of solution. The sludge samples are then corrected for the amount of solids dissolved to produce the solution.

Experimental Results

Aluminum Dissolution

The major goal of the demonstration was to dissolve 75% of the aluminum present in the sludge. At the same time, as many of the minor waste elements as possible were monitored for any change in waste composition. The minor elements monitored were Na, Fe, Mn, Ni, Hg, Ca, and some trace elements. Tables 39 and 40 give the results for soluble and insoluble compounds, respectively.

The only trends visible in the data on the minor components during aluminum dissolution are an increase in the amount of soluble mercury, uranium, chromium, and an increase in insoluble silica. Figure 34 displays the level of soluble mercury as a function of tank volume during aluminum dissolution. The increase in soluble mercury occurred at about the same time that the tank was heated to aid aluminum dissolution. After allowing the sludge solids to settle and decanting the aluminate rich supernate, the supernate remaining in the tank contains more soluble mercury than before aluminum dissolution as shown in Figure 35. The data for insoluble mercury does not reveal a corresponding decrease due to the extreme scatter as shown in Figure 36.

The variation in the insoluble mercury could be caused by nonrepresentative samples, loss of mercury during insoluble solids drying or loss of mercury during sample dissolution. During both aluminum dissolution and sludge washing only one sample dissolved by sodium peroxide fusion was higher than the same sample dissolved by acid bomb treatment. Such consistently smaller results definitely indicates that loss of mercury vapor during the peroxide fusion is occurring. The degree of loss probably reflects how much sludge solids were exposed on the surface or how badly the mixture cracks before fusing. In any future study mercury analyses in sludge solid should be based on acid bomb dissolutions and not peroxide fusions.

TABLE 39

Soluble Waste Components During Aluminum Dissolution

Sample	Mercury, lb	Calcium, lb	Chromium, lb	Iron, lb	Potassium, lb
5a-1	-	-	-	-	-
5a-2	-	-	-	-	-
5b	140	1.40	79.2	7.43	506
5d	-	-	-	-	-
5d	605	-	-	-	825
5e	148	2.95	153	10.3	865
5e	591	-	-	-	865
5f	639	-	166	13.3	935
5f	639	-	-	-	935
5g	816	0.326	190	9.09	954
5g	816	-	-	-	954
5h	1730	-	18	14.5	1010
5h	1730	-	-	-	1010
5i	1810	-	188	15.2	1060
5i	1810	-	-	-	884
5j	1880	-	195	13.1	1100
5j	1880	-	-	-	1100
5k	951	-	197	10.6	927
5k	1900	-	-	-	1110
5l	1950	1.95	203	13.6	952
5l	1950	-	-	-	1140
5m	1940	0.388	202	10.8	1140
5m	1940	-	-	-	947
5n	1990	7.97	207	11.1	972
5n	1990	-	-	-	972

TABLE 39, Contd

Sample	Sodium, lb	Silicon, lb	Manganese, lb	Zinc, lb	Nickel, lb	Uranium, lb
5a-1	-	-	-	-	-	-
5a-2	-	-	-	-	-	-
5b	227000	98.3	0.577	16.0	2.05	2.61
5d	-	-	-	-	-	11.7
5d	735000	339	-	-	-	10.2
5e	585000	-	-	24.1	8.65	10.4
5e	576000	-	-	-	-	12.4
5f	769000	559	0.219	51.1	4.68	19.8
5f	714000	224	-	-	-	16.5
5g	664000	34.3	-	13.3	-	11.8
5g	701000	571	-	-	-	20.1
5h	566000	-	-	14.1	7.61	13.8
5h	546000	-	-	-	-	13.9
5i	582000	-	1.49	11.8	10.6	13.6
5i	572000	-	-	-	-	9.73
5j	572000	-	1.55	12.3	8.26	17.8
5j	636000	-	-	-	-	16.8
5k	556000	-	1.30	12.4	8.35	21.5
5k	611000	-	-	-	-	16.2
5l	571000	-	1.61	15.9	11.4	19.9
5l	616000	-	-	-	-	17.2
5m	613000	-	1.60	15.8	11.4	17.3
5m	601000	-	-	-	-	17.7
5n	629000	69.8	1.09	13.0	8.76	19.1
5n	594000	-	-	-	-	10.6

TABLE 40

Insoluble Waste Components During Aluminum Dissolution

	Mercury		Calcium		Chromium	
Sample	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
5a-1	2550	-	-	-	-	608
5a-2	4360	5580	56.6	-	142	538
5b	4950	22800	-	-	258	487
5c	-	-	-	-	-	-
5d	5020	13500	2860	-	-5820	5820
5e	43.9	13000	2570	-	-725	725
5f	7000	24700	3160	-	-577	577
5g	340	4900	-	-	-	-
5h	16900	20500	1530	-	103	82.8
5i	5960	16100	1300	-	232	71.4
5j	8130	12000	1700	-	81.1	203
5k	965	8290	1590	-	138	68.9
5l	1590	10000	16 10	-	90.2	72.1
5m	129	-	4530	-	193	-
5n	6830	-	2670	-	86.1	-

TABLE 40, Contd

Sample	Iron		Potassium		Sodium	
	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
5a-1	12700	-	-	-	-	-
5a-2	11400	13500	-	56.6	-	16600
5b	12200	15800	-	57.2	-	24700
5c	-	-	-	-	-	-
5d	9600	21000	-	16300	-	25000
5e	15600	18700	-	22900	-	15900
5f	17700	20600	-	31200	-	18600
5g	20400	20400	-	48.5	-	19000
5h	17000	16400	-	20.7	-	13100
5i	14800	15800	-	17.8	-	10100
5j	18900	20300	-	28800	-	17200
5k	15800	18100	-	17.2	-	10000
5l	19900	18300	-	180	-	15000
5m	40500	-	-	-	-	-
5n	17700	-	-	-	-	-

TABLE 40, Contd

Sample	Silicon Na_2O_2, lb	Silicon Acid, lb	Manganese Na_2O_2, lb	Manganese Acid, lb	Zinc Na_2O_2, lb	Zinc Acid, lb
5a-1	1800	-	4430	-	57.9	-
5a-2	1560	-	4160	4020	28.3	56.6
5b	1830	-	4950	3410	57.2	28.6
5c	-	-	-	-	-	-
5d	1260	-	3110	4650	-	30.8
5e	-	-	5070	4720	-	901
5f	-	-	5040	4860	-	1930
5g	-	-	6360	2740	-	461
5h	2300	-	5300	4700	-	869
5i	1690	-	5990	4690	-	589
5j	2310	-	6360	6630	-	3180
5k	2500	-	5190	6430	-	620
5l	3910	-	6960	6490	-	848
5m	8660	-	14700	-	-	-
5n	15900	-	5510	-	-	-

TABLE 40, Contd

Sample	Nickel		Uranium	
	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
5a-1	-	-	170	-
5a-2	-	1020	104	107
5b	-	143	125	181
5c	-	-	-	-
5d	-	1290	308	665
5e	-	1230	218	419
5f	-	1180	295	652
5g	-	485	195	321
5h	-	786	257	308
5i	-	660	169	245
5j	-	750	282	173
5k	-	844	293	212
5l	-	1190	108	287
5m	-	-	111	-
5n	-	-	60.5	-

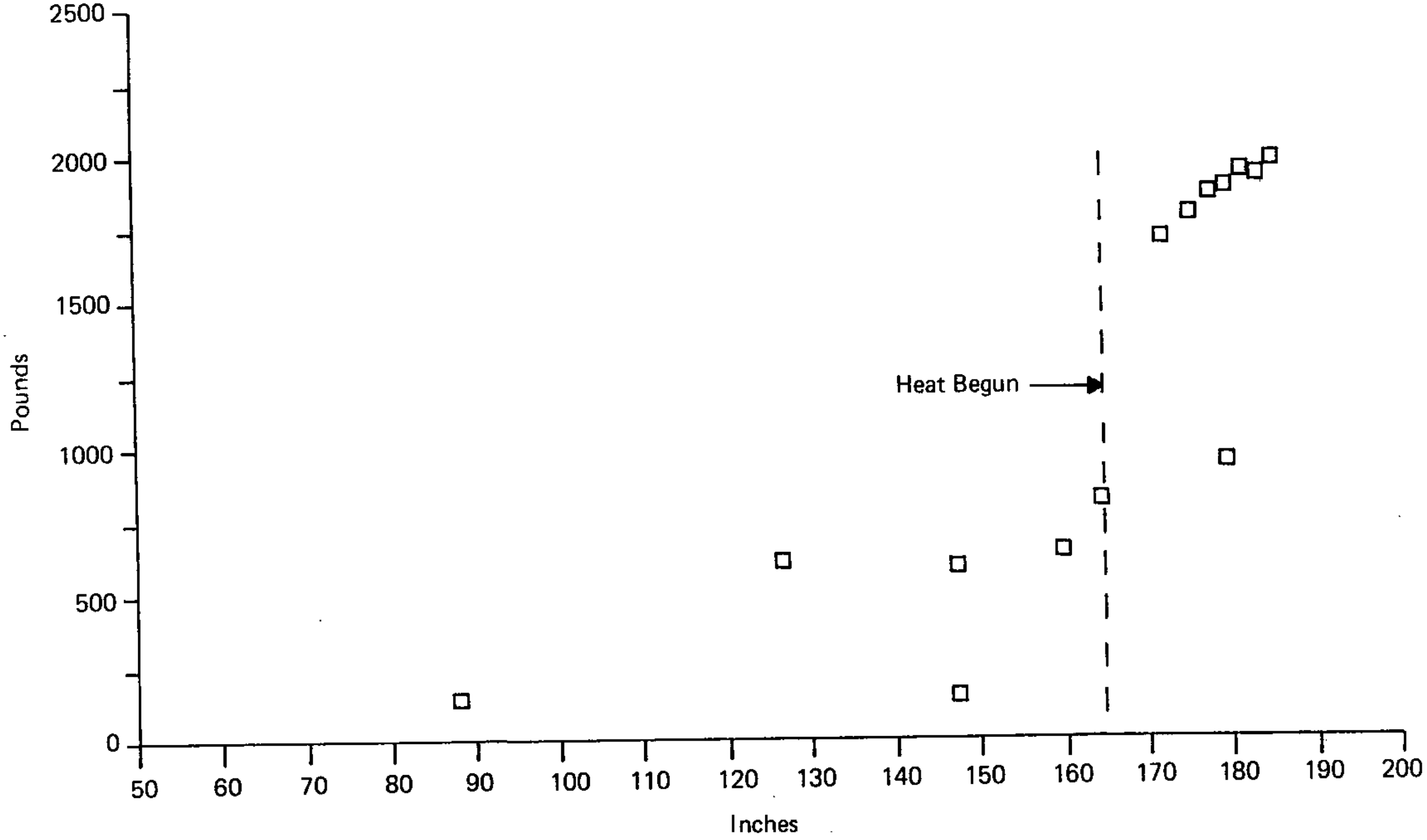


FIGURE 34. Soluble Mercury During Al Dissolution

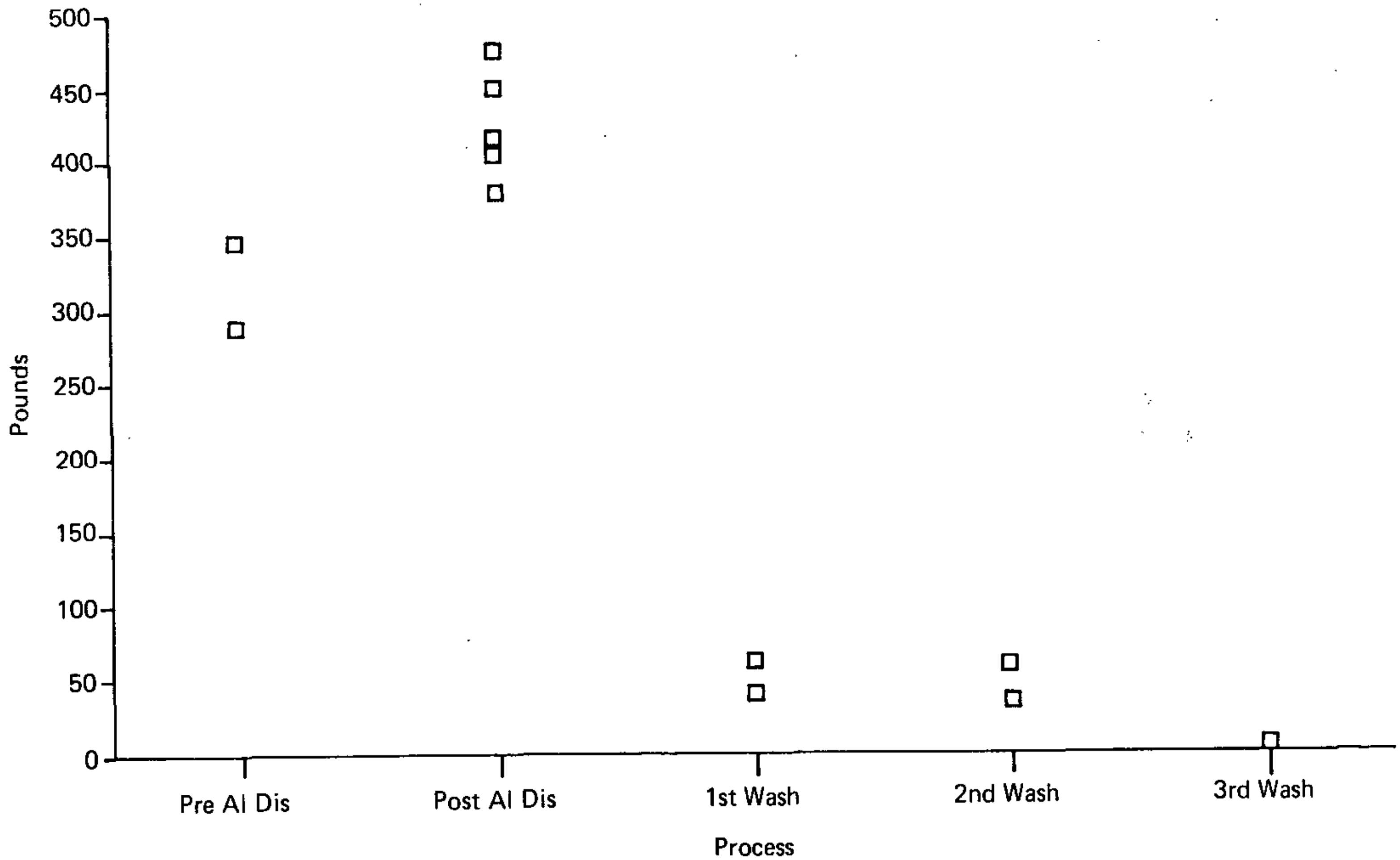


FIGURE 34. Contd

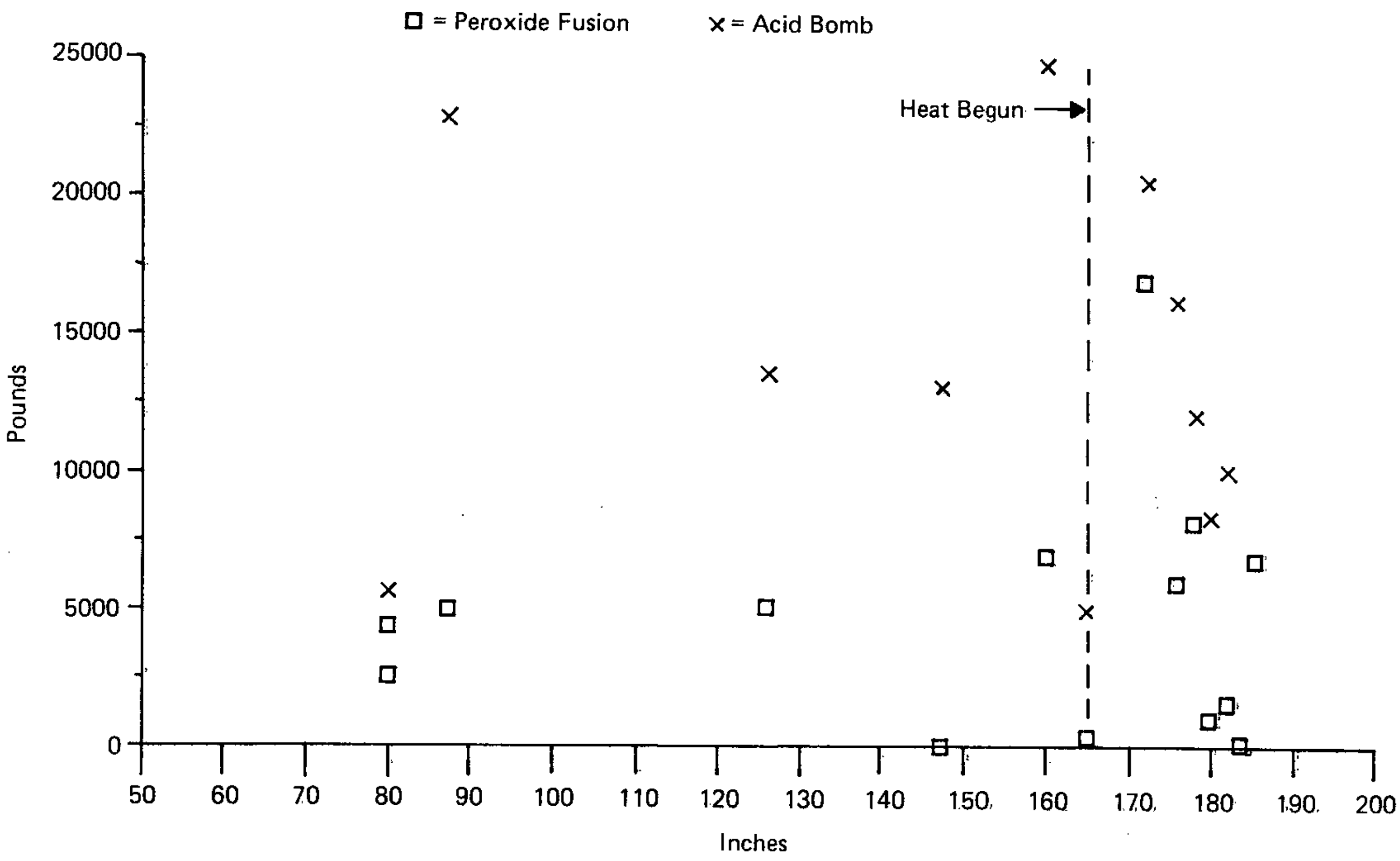


FIGURE 34. Contd

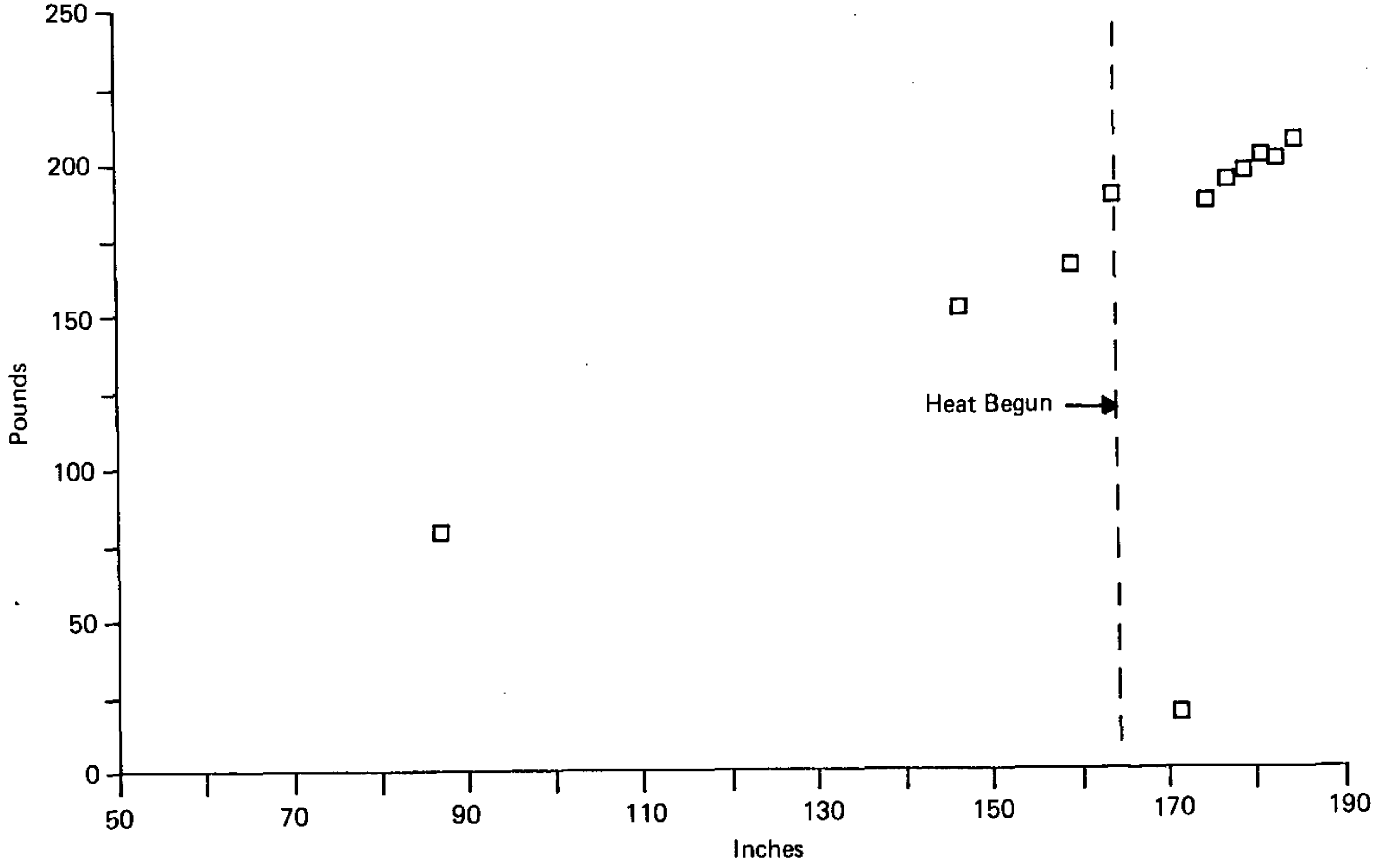


FIGURE 35. Soluble Chromium During Al Dissolution

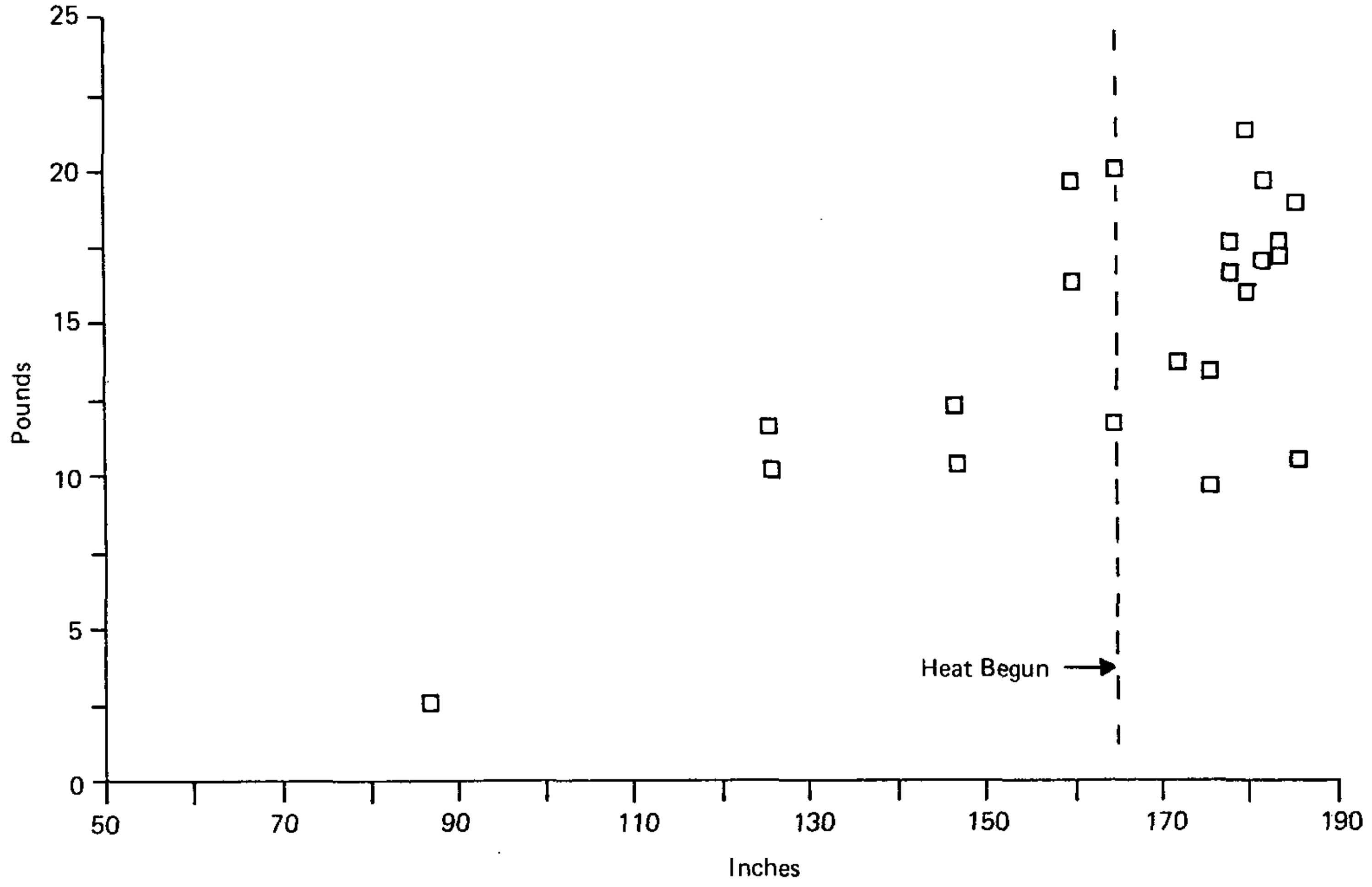


FIGURE 36. Soluble Uranium During Al Dissolution

The impact of additional soluble mercury will possibly affect three different processes. The supernate from the aluminum dissolving step is transferred to an evaporator feed tank and then to the evaporator. If the mercury remains soluble, the evaporator overheads could have higher than normal mercury levels and the salt concentrate would also contain high mercury levels. Eventually the salt concentrate would enter the precipitation process and produce increased levels of diphenyl mercury. If mercury does not remain soluble on cooling the aluminum-dissolved supernate, then the sludge solids in the salt tank would be high in mercuric oxide.

The increase in soluble chromium is very consistent throughout the aluminum dissolution process as shown in Figure 35. Since the soluble chromium varies directly with tank volume, the additional chromium is probably not dissolving out of the sludge but is coming in with the additional liquid or is produced as a systematic error by the inability of the analytical method used to detect the dilution that occurred during aluminum dissolution. The net impact of additional soluble chromate, if the increase is real, should be small.

One unexpected result is an apparent increase in the amount of soluble uranium based on Figures 36 and 37. The net increase in soluble uranium does not match the net decrease in insoluble uranium. Since the solids results vary widely, only the general trend can be relied upon. More careful sample preparation in the high level cells and sampling the tank farm should clarify the results. Another unexpected result was a sudden increase in the amount of insoluble silica during the last stages of the heating cycle. Figures 38 and 39 display the drop in soluble silica and increase in insoluble silica. Since the data is not based upon a large number of data points, drawing specific conclusions is unreliable. Silicates are normally soluble in alkaline solutions; however, certain aluminosilicates such as sodalite are insoluble and can be formed during aluminum dissolution. An increase in the insoluble silica should, therefore, be matched by a corresponding decrease in the soluble aluminum which was not observed during the demonstration. The source of the increased insoluble silica is the CRC column installed on top of Tank 42H. A batch of the zeolite was dumped on the last day of the aluminum dissolution process which corresponds with the increase in insoluble silica. As a result the dip sample was not representative of the bulk slurry and the 10,000 pound increase is a calculation artifact.

One expected result which was not observed was the dissolution of insoluble zinc. Zinc is an amphoteric metal similar to aluminum that reacts with sodium hydroxide as follows:

$$ZnO + NaOH \rightarrow Na_2ZnO_2 + H_2O$$

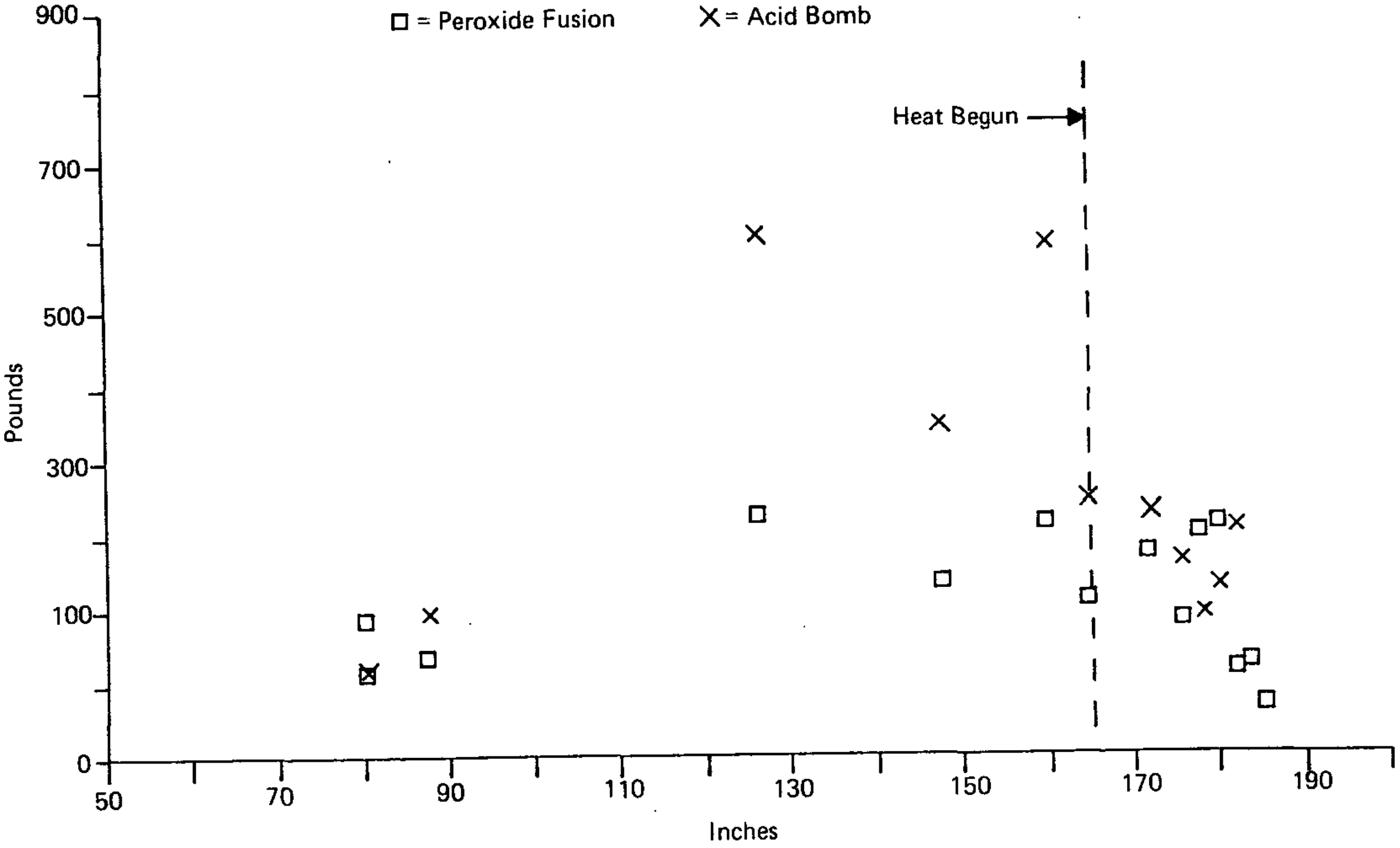


FIGURE 37. Insoluble Uranium During Al Dissolution

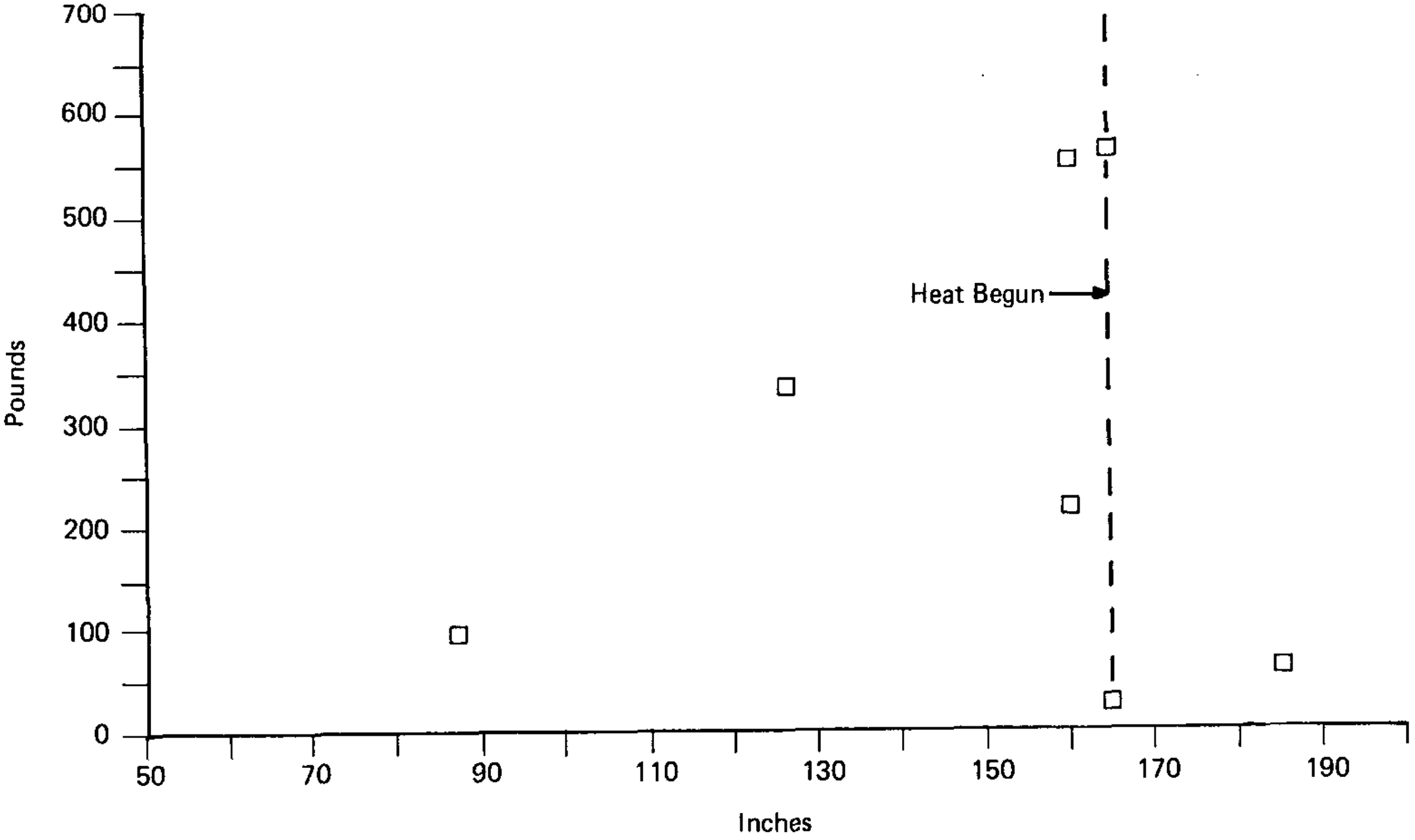


FIGURE 38. Soluble Silicon During Al Dissolution

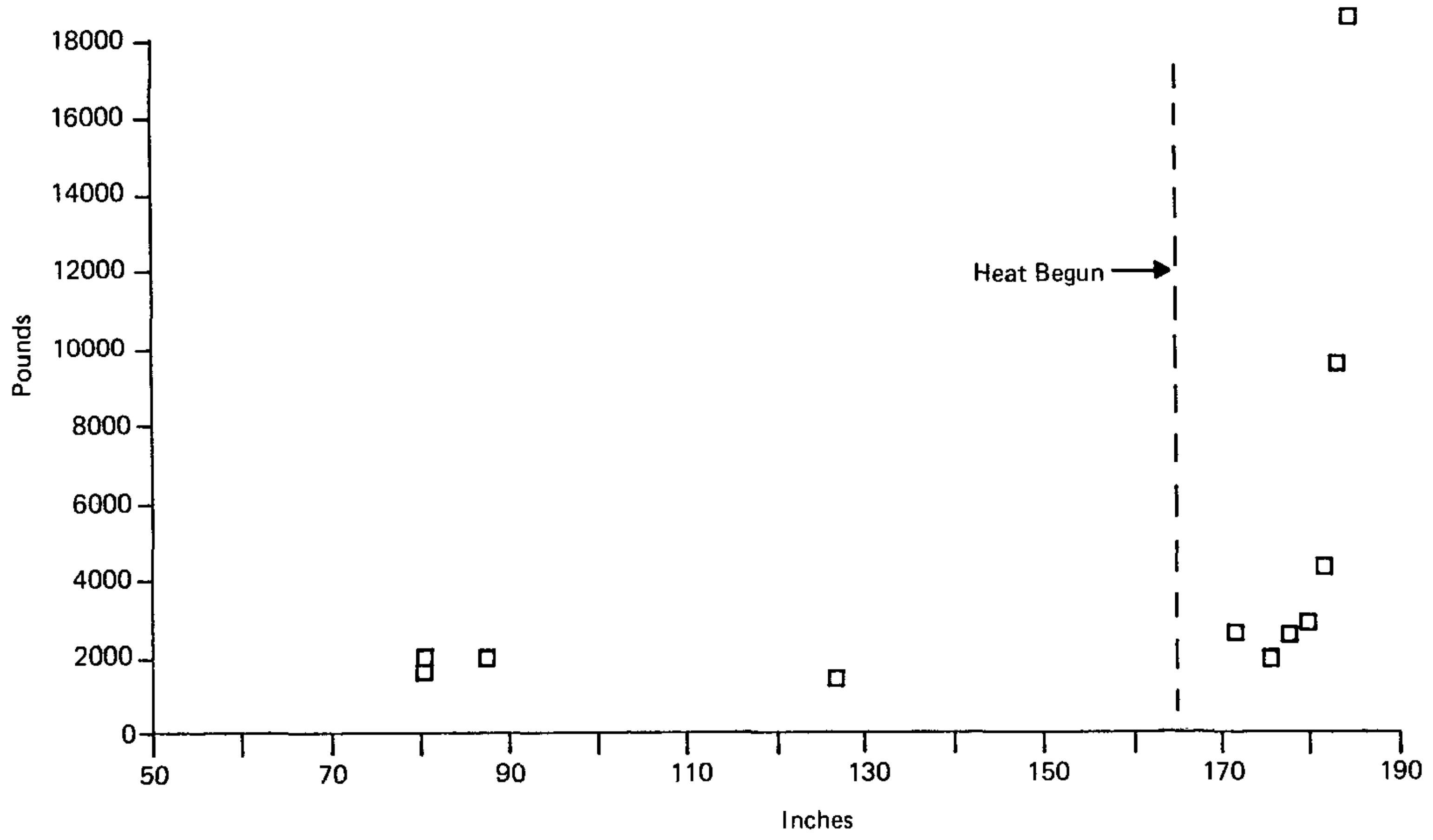


FIGURE 39. Insoluble Silicon During Al Dissolution

where the sodium zincate formed is a soluble compound. Figures 40 and 41 do not show a decrease in insoluble zinc or an increase in soluble zinc. The lack of dissolution suggests that the zinc is contained in an insoluble compound that will not react with the sodium hydroxide.

Washing and Settling

After aluminum dissolution the sludge was washed to remove the soluble salts and ^{137}Cs. The goal was to reduce the soluble salts to less than 2% of the sludge on a dry weight basis. During this process there is a potential for transferring other minor nonradioactive waste components to supernate and then on to a salt tank. The results of monitoring the minor components are given in Tables 41 and 42 for soluble and insoluble compounds, respectively.

The effectiveness of sludge washing can be obtained by monitoring the concentration of sodium during each step. Figure 42 compares the log of the pounds of sodium to the predicted log based upon dilution of soluble sodium present at the end of the aluminum-dissolved supernate decant. The only deviation is on the third wash when the sludge is washed with inhibited water which adds additional sodium.

The dilution model works successfully for those compounds that are very soluble and have not reached their solubility limit. For those compounds present in supernate at their solubility limit and also present in sludge, the dilution model will not predict the proper concentrations. As the compound is diluted below the solubility limit, additional compound will dissolve out of the sludge to maintain the solubility equilibrium. The time required for the sludge solids to settle versus the rate that equilibrium is attained will determine how close to equilibrium the solution will be.

During sludge washing the total amount of insoluble chromium dropped as shown in Figure 43, while the soluble chromium reached an equilibrium value greater than dilution would predict, Figure 44. The minor impact is increased chromate in saltstone and less chromium in the sludge feed to the DWPF. The mercury trend during washing is less clear as shown in Figure 45. It may be that the soluble mercury in the final wash had not yet reached equilibrium, 20-30 ppm, when the supernate was decanted. Minor waste components that are in sludge and are solubility limited are iron, calcium, and silicon. Figures 46, 47, and 48 show very little dilution on these metals. The impact should be small for all except mercury.

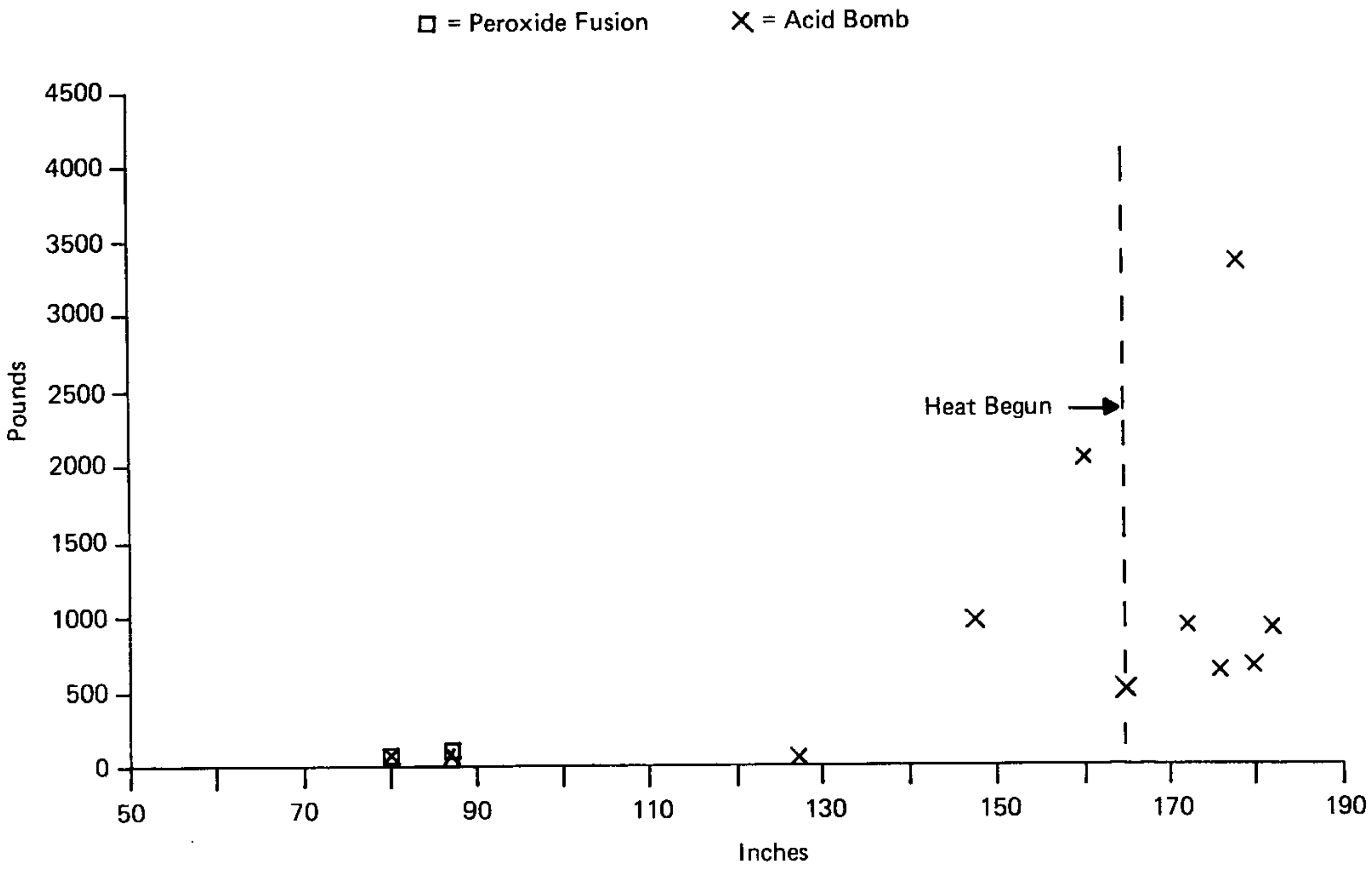


FIGURE 40. Insoluble Zinc During Al Dissolution

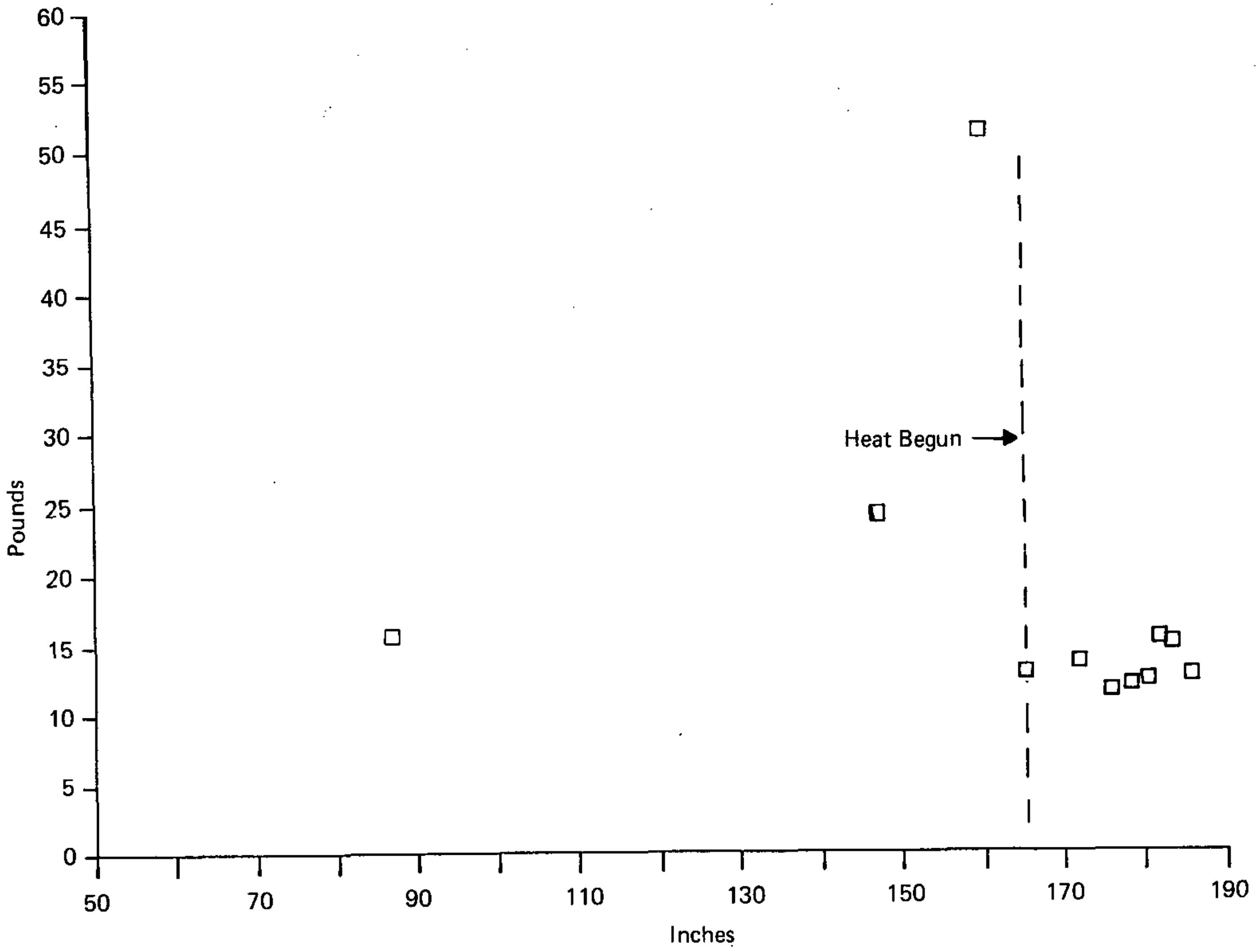


FIGURE 41. Soluble Zinc During Al Dissolution

TABLE 41

Soluble Waste Components During Sludge Processing

Sample	Mercury, lb	Calcium, lb	Chromium, lb	Iron, lb	Potassium, lb
4-T1	347	-	105	-	451
4-T-1	289	-	-	-	451
4-T2	347	-	-	-	450
4-T2	-	-	-	-	450
7-A	380	1.29	-	14.4	339
7-A	451	-	-	-	364
7-ASA-7A	413	-	71.4	3.84	349
7-ASA-7A	475	-	-	-	336
7-ASA-7B	407	-	71.4	1.92	363
7-ASA-7B	413	-	-	-	336
10	40.8	3.85	3.33	-	68.9
10	62.0	0	0	0	7.45
13	60.2	1.08	1.64	1.76	13.6
13	34.8	-	-	-	10.5
18-B	3.29	-	-	-	14.1
18-B	2.59	-	-	-	13.9
18-R1	4.19	0.728	2.59	3.27	9.16
18-R2	4.44	0.183	-	-	12.9
18-R2	-	-	-	-	-

TABLE 41, Contd

Sample	Sodium, lb	Silicon, lb	Manganese, lb	Zinc, lb	Nickel, lb	Uranium, lb
4-T1	113000	-	0.158	-	-	1.64
4-T-1	113000	-	-	-	-	1.18
4-T2	106000	-	-	3.77	-	18.3
4-T2	113000	-	-	-	-	1.54
7-A	230000	36.1	3.53	8.40	5.47	25.3
7-A	205000	90.2	-	-	-	25.0
7-ASA-7A	220000	64.6	-	6.74	2.02	17.6
7-ASA-7A	224000	28.9	-	-	-	18.6
7-ASA-7B	240000	64.6	-	6.74	2.02	17.6
7-ASA-7B	215000	35.7	-	-	-	17.9
10	35100	-	-	1.05	0.188	1.79
10	30300	14.4	-	-	-	1.54
13	5260	17.1	0.694	1.34	-	0.379
13	7410	17.1	-	-	-	0.332
18-B	2910	-	-	-	-	-
18-B	2520	2.59	-	-	-	0.431
18-R1	2310	-	-	-	-	0.557
18-R1	2480	9.55	-	-	-	0.492
18-R2	2380	10.7	-	-	-	0.674
18-R2	-	-	-	-	-	0.621

TABLE 42

Insoluble Waste Components During Sludge Processing

Sample	Mercury		Calcium		Chromium	
	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
4a	3400	17100	-	-	-	-
4b	3320	15200	-	-	-	-
4c	2530	18100	-	-	-	-
4-T1	2970	14100	212	-	-	-
4-T2	4840	11500	712	-	148	208
4-AD-A	879	13200	1140	-	117	-
4-ASA-42A	1050	0	2170	-	-	-
4-ASA-42B	4980	-	1790	-	-	-
7	1510	9240	1500	-	-	-
7-ASA-7A	1840	-	1470	-	-	-
7-ASA-42B	3160	-	1890	-	91.3	-
7-42AW	1080	7830	966	-	183	130
7-42BW	1160	10600	784	-	235	91.3
10	15200	8300	1610	-	-	-
13	3900	8360	1700	-	65.9	-
13	4080	8540	1600	-	65.9	-
18-B	272	3850	774	-	43.6	32.7
18-R1	5460	-	985	-	43.8	-
18-R2	4340	10000	794	-	55.1	-

TABLE 42, Contd

	Iron		Potassium		Sodium	
Sample	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
4a	15500	16900	230	20100	-	-
4b	13700	14900	217	13400	-	-
4c	12900	16800	246	20800	-	-
4-T1	16500	16100	182	-	-	10400
4-T2	15100	15800	356	29.7	-	18800
4-AD-A	15400	4340	-	87.9	-	14500
4-ASA-42A	18500	-	-	-	-	-
4-ASA-42B	19700	-	-	-	-	-
7	16800	17200	-	26.1	-	6970
7-ASA-7A	15300	-	-	-	-	-
7-ASA-42B	15000	-	-	-	-	-
7-42AW	16700	17700	-	26.1	-	4720
7-42BW	15900	13900	-	13.0	-	4960
10	12600	16700	-	10.2	-	4630
13	14200	15000	-	11.0	-	4260
13	14600	15100	-	11.0	-	3360
18-B	13400	17600	-	43.6	-	3280
18-R1	-	16400	-	-	-	-
18-R2	15700	17100	-	4.41	-	3110

TABLE 42, Contd

Sample	Silicon		Manganese		Zinc	
	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb	Na_2O_2, lb	Acid, lb
4a	3510	3770	4860	4600	3080	12500
4b	-	2720	4350	4100	924	8340
4c	-	3850	4040	4960	3200	14200
4-T1	2090	-	5300	4930	60.5	121
4-T2	2970	-	6620	4750	59.3	326
4-AD-A	2930	-	5830	5130	-	2670
4-ASA-42A	-	-	5040	-	-	-
4-ASA-42B	-	-	5210	-	-	-
7	2510	-	4910	4370	-	887
7-ASA-7A	1230	-	4660	-	-	-
7-ASA-42B	-	-	4290	-	-	-
7-42AW	1060	-	5040	4740	-	65.2
7-42BW	2040	-	4370	4070	-	52.2
10	-	-	3840	4030	-	61.4
13	2750	-	4130	3800	-	-
13	2870	-	4460	3890	-	-
18-B	2760	-	4040	4290	-	142
18-R1	2730	-	4740	-	-	-
18-R2	3030	-	4630	-	-	110

TABLE 42, Contd

Sample	Silicon Na_2O_2, lb	Silicon Acid, lb	Manganese Na_2O_2, lb	Manganese Acid, lb
4a	-	-	83.6	200
4b	-	-	125	181
4c	-	-	102	211
4-T1	-	968	223	168
4-T2	-	2460	177	124
4-AD-A	-	1170	2229	339
4-ASA-42A	-	-	-	-
4-ASA-42B	-	-	81.8	-
7	-	1000	227	404
7-ASA-7A	-	-	63.4	-
7-ASA-42B	-	-	-	-
7-42AW	-	1290	142	355
7-42BW	-	809	127	632
10	-	788	94.3	184
13	-	714	234	295
13	-	714	300	263
18-B	-	588	127	343
18-R1	-	-	162	291
18-R2	-	573	3470	348

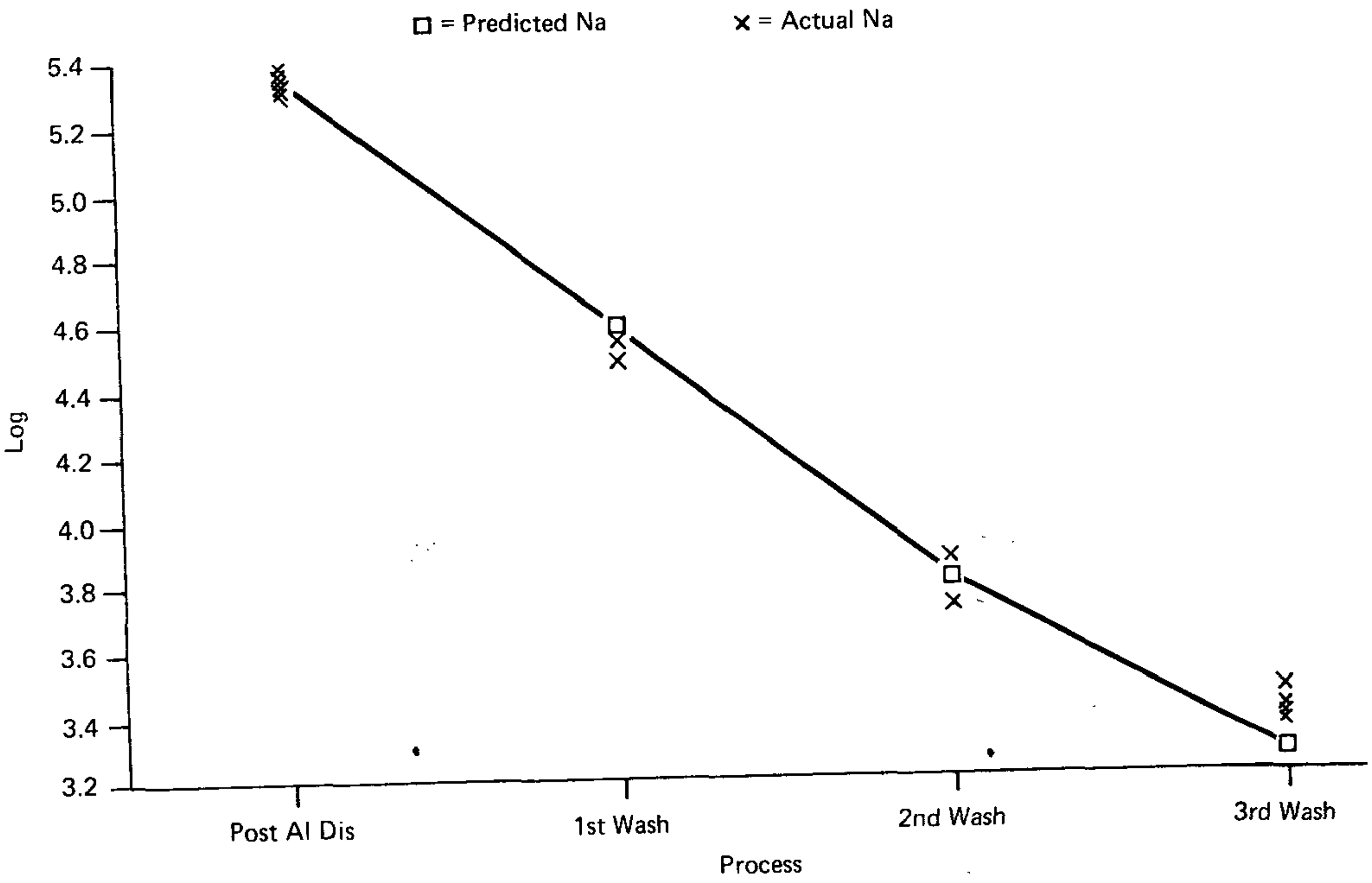


FIGURE 42. Soluble Sodium During Sludge Washing

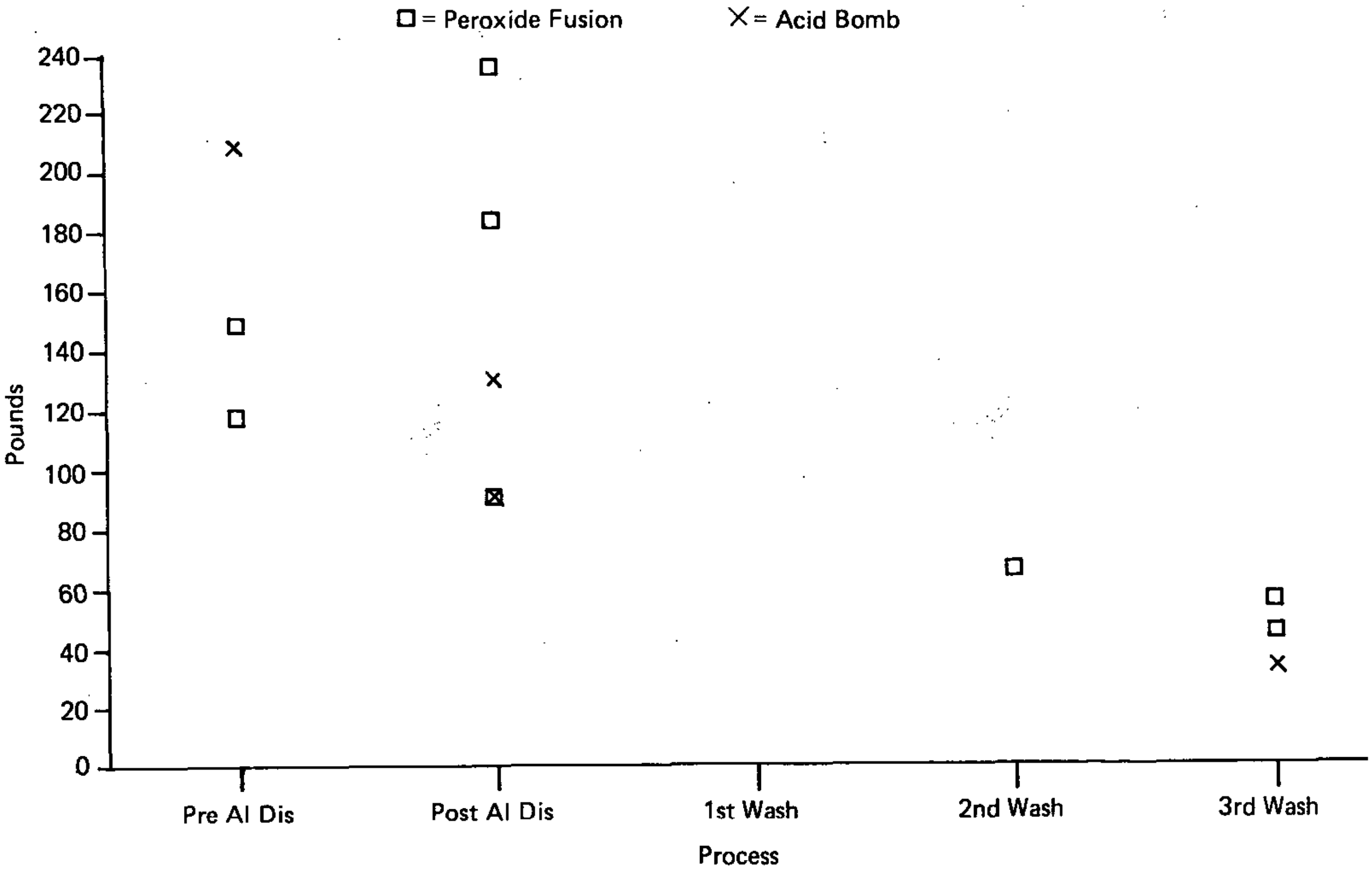


FIGURE 43. Insoluble Chromium During Sludge Processing

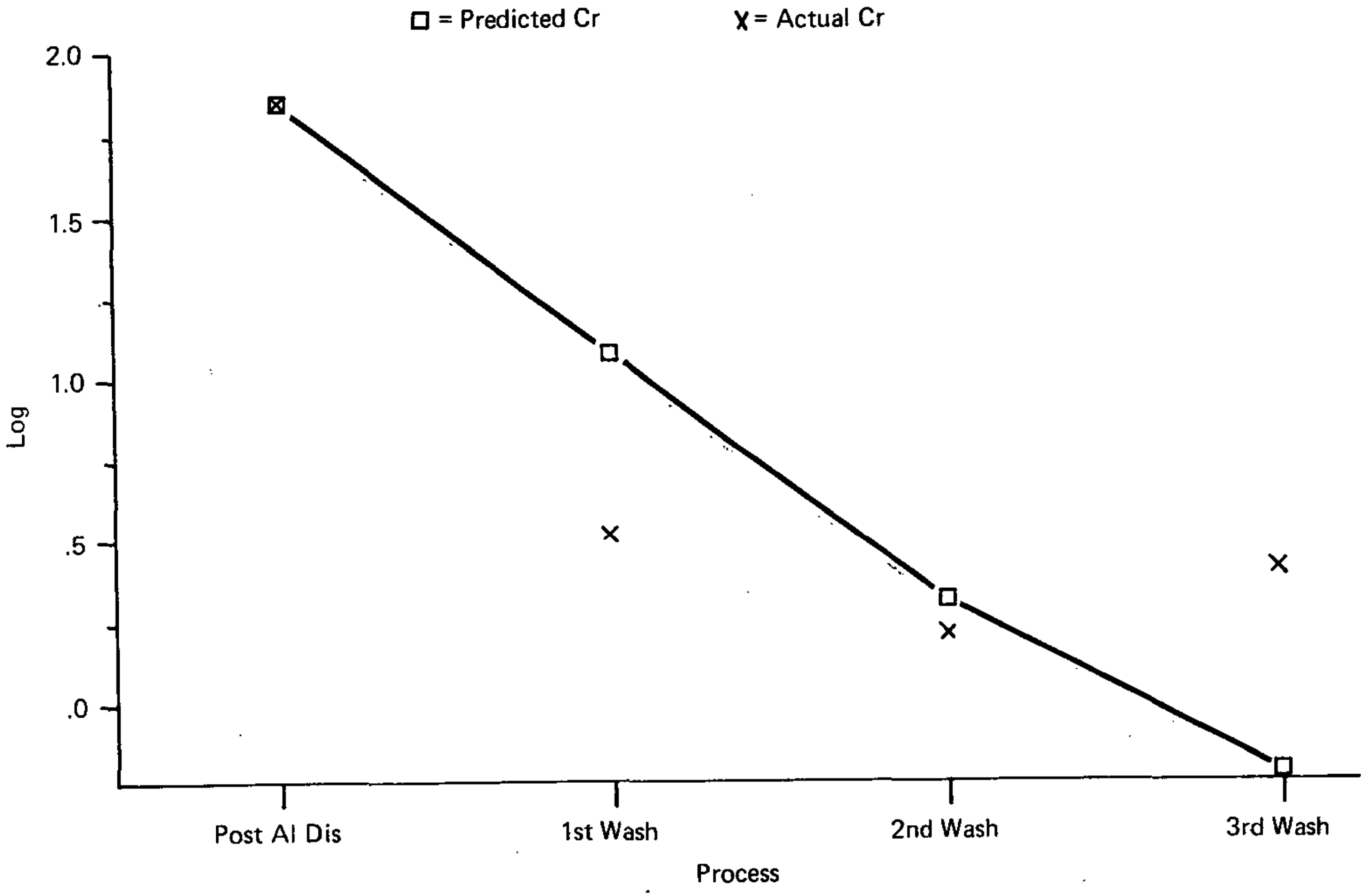


FIGURE 44. Soluble Chromium During Sludge Washing

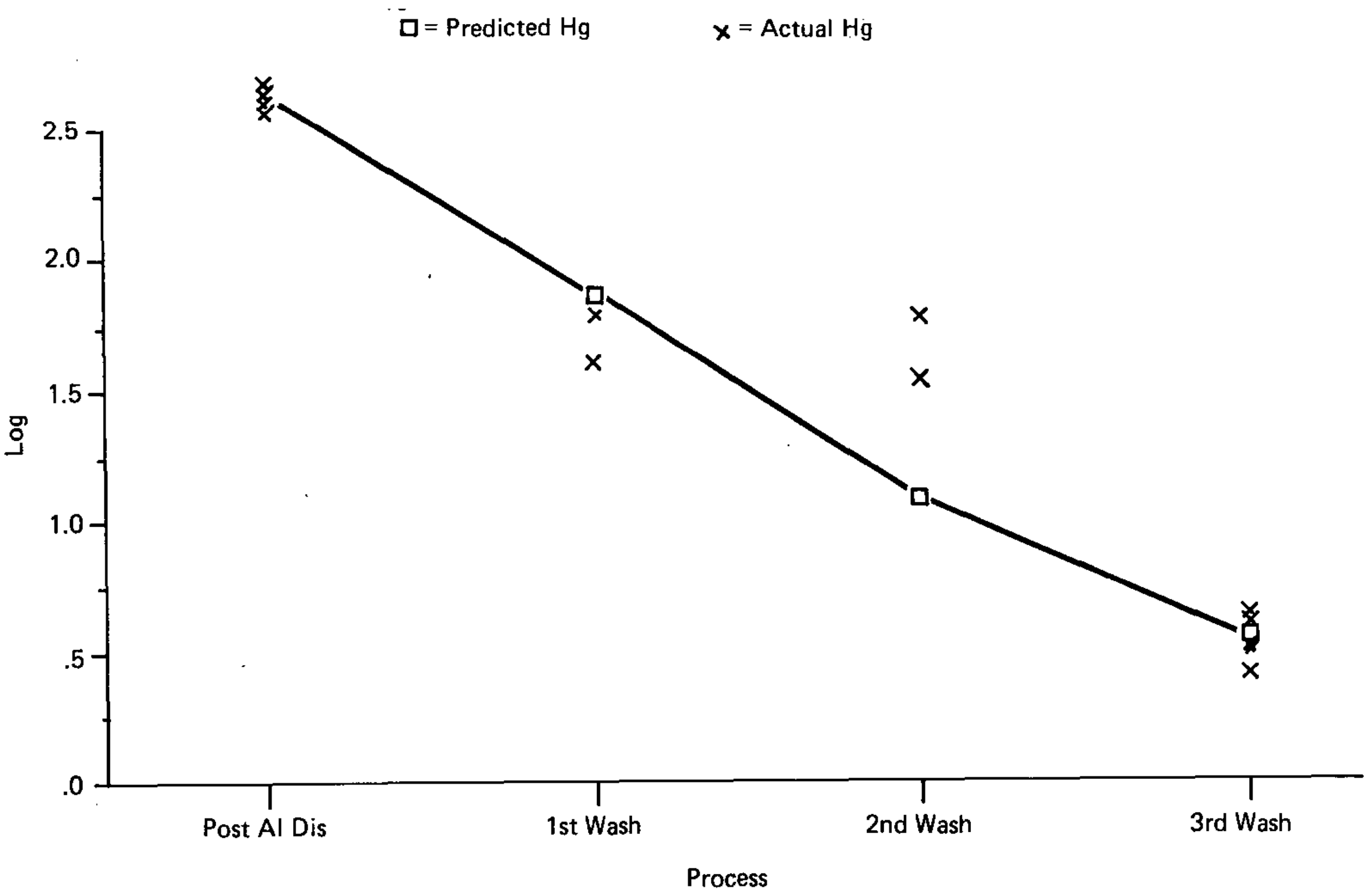


FIGURE 45. Soluble Mercury During Sludge Washing

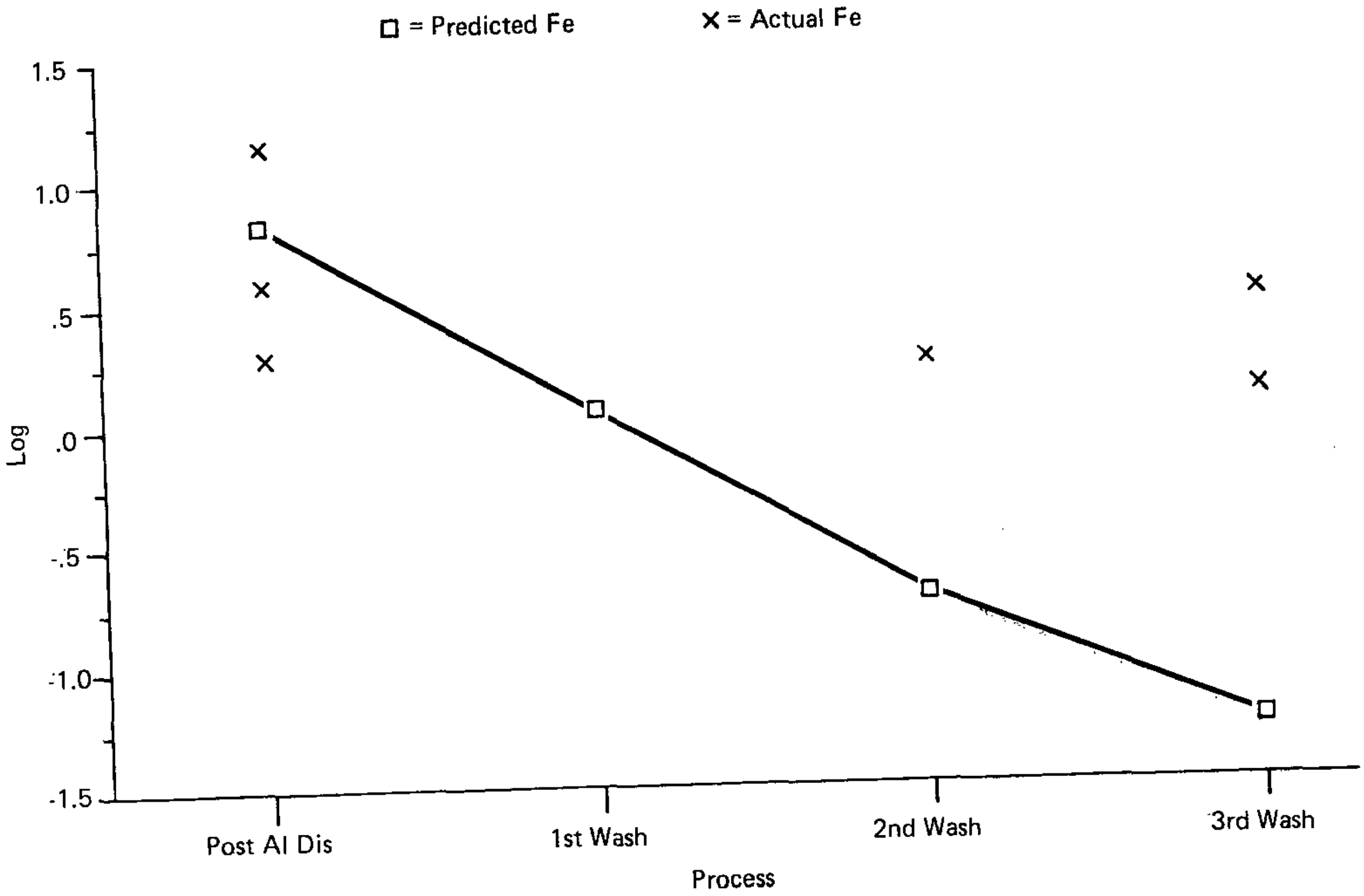


FIGURE 46. Soluble Iron During Sludge Washing

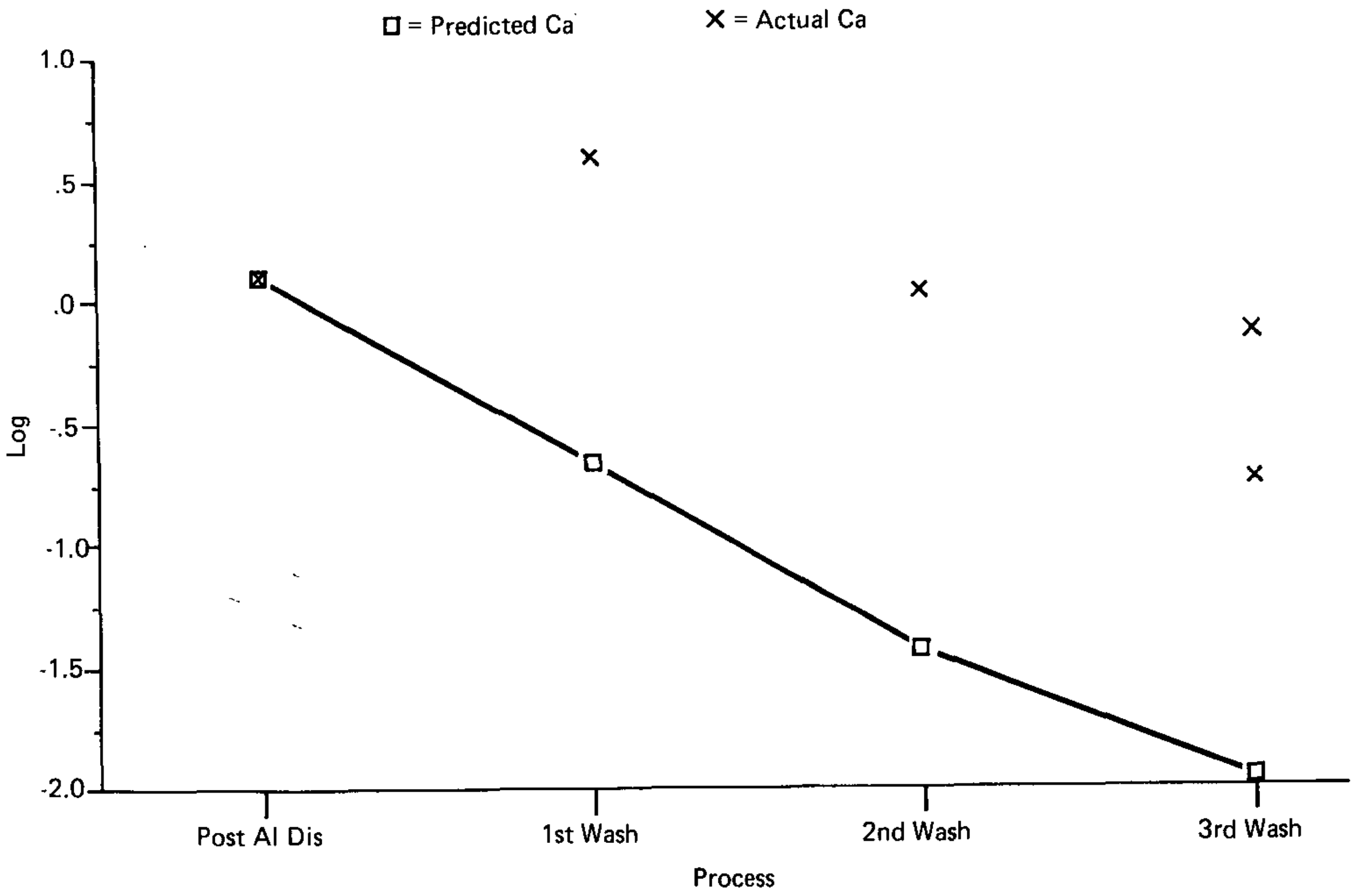


FIGURE 47. Soluble Calcium During Sludge Washing

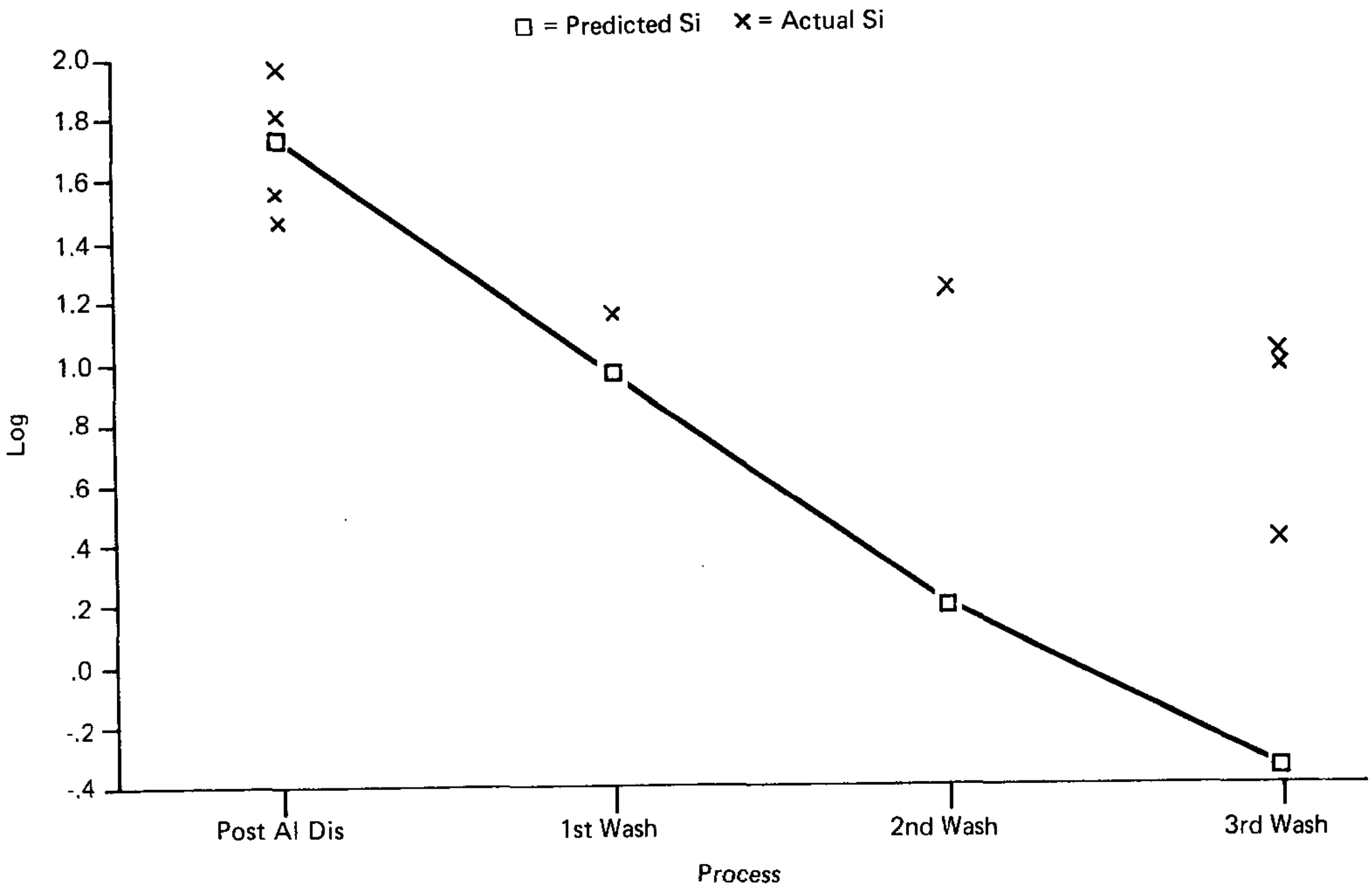


FIGURE 48. Soluble Silicon During Sludge Washing

Demonstration of In-Tank Sludge Processing, Part IV: Decanted Supernate Composition

Introduction

The in-tank sludge processing demonstration verified that processing SRL high-level radioactive sludge in a waste tank will remove 75% of the insoluble aluminum and wash the soluble salts from the sludge to produce Defense Waste Processing Facility (DWPF) feed material. Such a process significantly reduces the scope and cost of the DWPF. Previous memos described the process, sample handling, and analysis. The composition of the decanted supernate solutions will be described in this memo. Due to problems with the analytical method, chloride results are not available for the decanted supernate.

During the demonstration a total of 3,473,000 gallons of supernate were decanted from the sludge and transferred to the evaporator feed tank, 43H, for waste concentration. A total of five transfers were made with the composition of the supernate determined for each transfer. Table 43 is the supernate decanted after waste transfer and before aluminum dissolution step. Table 44 is the aluminate-rich supernate from the aluminum dissolution step. Tables 45, 46, and 47 are the dilute supernates from each of the three washes.

TABLE 43

Prealuminum Dissolution Decanted Supernate

Supernate Volume 642,000 Gallons

Ion	Average mole/liter
Free hydroxide	0.64
Total hydroxide	0.80
Aluminate	0.064
Carbonate	0.11
Nitrate	1.39
Nitrite	0.55
Sulfate	0.0486
Calcium	-
Chromium	0.0017
Iron	-
Manganese	0.0000024
Mercury	0.0138
Nickel	-
Potassium	0.0097
Silicon	-
Sodium	4.07
Uranium	0.0000051
Zinc	0.000049
Fluoride	0.000014
Chloride	-

TABLE 44

Post Aluminum Dissolution Decanted Supernate

Supernate Volume 424,000 Gallons

Ion	Average mole/liter
Free hydroxide	3.01
Total hydroxide	3.88
Aluminate	0.612
Carbonate	0.152
Nitrate	1.35
Nitrite	0.285
Sulfate	0.047
Calcium	0.00002
Chromium	0.00087
Iron	0.000027
Manganese	0.000041
Mercury	0.00134
Nickel	0.000034
Potassium	0.0057
Silicon	0.0012
Sodium	6.14
Uranium	0.000054
Zinc	0.000071
Fluoride	-
Chloride	-

TABLE 45

First Wash Decanted Supernate

Supernate Volume 937,000 Gallons

Ion	Average mole/liter
Free hydroxide	0.536
Total hydroxide	0.784
Aluminate	0.088
Carbonate	0.011
Nitrate	0.235
Nitrite	0.036
Sulfate	–
Calcium	0.00006
Chromium	0.00004
Iron	–
Manganese	–
Mercury	0.00016
Nickel	0.000002
Potassium	0.0006
Silicon	0.00032
Sodium	0.888
Uranium	0.0000044
Zinc	0.00001
Fluoride	–
Chloride	–

TABLE 46

Second Wash Decanted Supernate

Supernate Volume 942,000 Gallons

Ion	Average mole/liter
Free hydroxide	0.0875
Total hydroxide	0.117
Aluminate	0.0157
Carbonate	0.039
Nitrate	0.17
Nitrite	0.0533
Sulfate	0.000023
Calcium	0.000017
Chromium	0.00002
Iron	0.00002
Manganese	0.000008
Mercury	0.00015
Nickel	-
Potassium	0.0002
Silicon	0.00039
Sodium	0.174
Uranium	0.00000095
Zinc	0.000013
Fluoride	-
Chloride	-

TABLE 47

Third Wash Decanted Supernate

Supernate Volume 526,500 Gallons

Ion	Average mole/liter
Free hydroxide	0.0875
Total hydroxide	0.117
Aluminate	0.0157
Carbonate	0.039
Nitrate	0.17
Nitrite	0.0533
Sulfate	0.000023
Calcium	0.000017
Chromium	0.00002
Iron	0.00002
Manganese	0.000008
Mercury	0.00015
Nickel	-
Potassium	0.0002
Silicon	0.00039
Sodium	0.174
Uranium	0.00000095
Zinc	0.000013
Fluoride	-
Chloride	-

DEFENSE WASTE PROCESSING FACILITY

SUMMARY

Design activities of the DWPF continued on schedule. The percent design completion advanced to approximately 72% by the end of the quarter and the physical construction to 4% complete.

Site Construction Activities

Status of construction activities at the S-Area site are summarized below.

Vitrification Building 221-S

Placement of concrete for the vitrification building basement was completed during the quarter.

A total of approximately 18,000 cubic yards of concrete were placed in the basement. Currently, repairing of surface defects in the basement, damp-proofing and backfilling are in progress.

Fabrication of the stainless steel wall liner for the east side of the canister decontamination cell continues. The first wall pour is scheduled for late January 1985.

Operations Building 704-S

Installation of exterior wall boards, HVAC ducts, electrical conduit, roofing material, and plumbing continues.

Outside Facilities

The sanitary sewage treatment plant is approximately 98% complete. Installation of electrical wiring and building equipment is in progress. The facility is expected to be completed in late January 1985.

The vendor arrived onsite December 17 to begin fabrication of the neutralized/fire water tank. The work should be complete by mid-March 1985.

Installation of the fire water lines in the operations portion of S-Area is approximately 50% complete.

Installation of the A-Line section of the storm drain system is approximately 40% complete. Approximately 73% of the B-Line section of the storm drain system has been installed. Work on the catch basins continues.

The railroad contractor is presently laying out material for the rail spur into S-Area. One switch has been assembled. This job is scheduled to be complete in late April 1985.

Hydroseeding continues in all areas where fine grading has been completed.

A 410-foot-deep, 8-inch water well was drilled northwest of the 221-S Building. This well will supply water for temporary construction facilities.

Permits

Various DWPF facilities require construction permits. Progress in obtaining the permits is summarized below:

- SCDHEC verbally approved the permit application for two emergency diesel generators.

- Approval was also obtained from appropriate federal agencies to utilize the requested frequencies for the remote controlled main process cell crane.

- An application for a permit to construct two 1000 gpm wells was transmitted to DOE. It is expected that this permit will be forwarded to SCDHEC early in January.

- Treatment and disposal of decontaminated salt solution in Z-Area will require permits. Drafts of a hazardous waste treatment permit for salt solution and an industrial landfill permit for saltstone have been prepared and reviewed. These permit applications should be transmitted to DOE early in 1985.

Design Status

Design status is summarized below:

- Engineering design continued to be focused on the structural design of the vitrification building above the first level.

- All engineering, procurement, and construction activities on or near the critical path are on or ahead of schedule. December saw the completion of the vitrification building basement milestone, two months early.

- The project analysis and master schedule was approved on December 28, 1984. The mechanical completion date has been set as 3Q88.

- Status of design models and percent complete is shown in the following table.

Design Models — Percentage Complete

Item	221-S Bldg. 3/4 inch	Melt Cell 1-1/2 inch	Sample Cell 3 inch	Cold Feed Chemical Storage 3/4 inch	Low Point Pump Pits 3/4 inch	Auxiliary Pump Pits 3/4 inch
Model tables with bldg. frames	87	100	80	80	78	78
Equip. & installation	75	100	80	75	53	52
Embedded & header piping installation	81	NA	79	70	68	68
Jumper	79	80	80	0	80	80
HVAC duct installation	47	NA	80	0	0	0
Electrical/ controls - trays, motor control center, panel installation, lighting	87	100	49	70	0	0
Total model	77	96	76	73	55	55

Note: NA - not available

Melter/Melt Cell

A viewing study is being conducted with the 1/2-scale wood model of the melter head. This study will show the viewing available from the main cell crane cameras when the impact wrench is over the most congested areas on the melter head. Preliminary results indicated that the viewing is satisfactory.

An existing melter is being modified to simulate the design of the DWPF melter. This scale melter was received and set in place at the SRL Equipment Test Facility in December. Installation of the melter lid, electrodes, heaters, etc. is expected early in 1985. The scale melter is expected to provide confirmation of the DWPF melter design.

Canister Decontamination

SRL has developed data from the experimental decontamination of canisters. These data were transmitted to AES for continuing use in the design of the canister blasting, decon chamber sump recirculation, sump transfer, feed recirculation, and graphics interface display. This document will be the basis for the programmable logic controller and graphics system procurement and system programming.

Weld Test Cell

With an experimental upset resistance welder, SRL has demonstrated that plugs can be welded into the five-inch-diameter canister opening. Based on these tests, specifications for a process welder for the DWPF were developed.

Some improvements that were included in the DWPF welder design as compared to the experimental welder are listed below.

- Reduction of the number of shield wall penetrations for the bus bars by a factor of two.
- Incorporation of four power packs into two enclosures makes the bus bar system much shorter by symmetrically centering two enclosures on the welder.
- Improved diode set design.
- Analysis of the problems encountered with the SRL experimental welder has allowed more realistic design of circuit components with increased certainty that the new welder will deliver 400,000 amperes.

Salt Precipitate Processing

The soluble salt solution will be decontaminated in the tank farm by precipitation of cesium as the tetraphenylborate. After filtration this precipitate will be transferred to the vitrification building. In the vitrification building, the organic precipitate is hydrolyzed to an organic liquid (primarily benzene) and an aqueous liquid containing the cesium. Progress in the salt precipitate hydrolysis design are summarized below.

- Firm design of the salt precipitate processing was begun. A current appraisal of cost (CAC) will be prepared by mid-1985. A final sludge/supernate material balance was completed and issued by SRL.
- To reduce crowding on top of the precipitate reactor, the decanter and reactor condenser will be combined into one unit for mounting on a frame within the salt process cell.
- Small-scale testing to develop data on three types of incinerator off-gas treatment methods will precede small-scale testing of a selected method at the Engineering Test Center. The current plan for the DWPF incinerator is to provide for two-phase (aqueous and organic) incinerator feed. Test burns of the DWPF incinerator feed stream are scheduled for December 1984, and January 1985.
- A preliminary draft of the Technical Data Summary for benzene incineration was reviewed. The draft of the SCDHEC regulations for storage, handling, and incineration of hazardous wastes is being reviewed. These data will be assessed in locating the site for the incinerator.

Materials of Construction

Progress in tests designed to assist in the selection of materials of construction was reviewed. Test results and programs are summarized below:

- Most of the current and future tests are directed toward selecting materials for salt precipitate cell equipment. Preliminary tests designed to determine the effects of free ions indicate that chlorides in 10% formic acid solutions at 60°C are corrosive to 304L. Addition of mercuric chloride has little effect, but copper sulfate triples the general corrosion rate and at least doubles pitting and crevice corrosion. There appear to be no interactions between mercury and copper. Addition of nitrates and nitrites inhibited corrosion. Alloy C-276 was not attacked in identical tests.

- Future tests to determine materials for salt cell equipment will be directed toward confirming that Alloy C-276 can be used for all equipment. Because of uncertainties in compositions of various process streams, less resistant materials will only be recommended where conditions are not corrosive.

- Additional test results indicate that if recycle solutions to the tank farm have NaOH added to an excess of 0.5M, the solutions will result in acceptably low corrosion rates for carbon steel tanks and 304L stainless steel evaporators.

- Additional tests will be performed to confirm that the recycle solutions meet all requirements of the interim waste management technical standards.

Distributed Control System

Process Control of the DWPF will be performed by a distributed control system (DCS). The vendor will use control logic diagrams, piping and instrumentation diagrams plus process operating procedures to develop the distributed control system.

It is important that all documents be in agreement when they are transmitted. All the documents needed to configure a field operating station (FOS) will be transmitted at one time. Documents will be sent to the vendor in the order that the facility will need the DCS for equipment startup.

A plan is being developed with the DCS vendor to deliver all FOS hardware and software before it is needed for equipment startup. Normally, the entire DCS would be assembled and tested with special configuration software at the vendors factory before delivery. This plan will make it possible to test and deliver the FOS's when they are needed even if the configuration for the entire system is not complete.

Plans are being developed for a DCS training system that can be delivered in advance of the DCS. This training system will be used for the following:

- To download and revise configuration software to Buildings 980 and 292 for early equipment startup before the DCS computer is delivered.

- To familiarize operators with DCS operation before the system is delivered. It will be used to train new operators after the DCS is installed.

- To develop and test configuration changes offline.

Shielding Studies

An analysis was completed of the effect on shielding design of approximately 1350 penetrations (embedded piping, etc.) of the vitrification building wall. A total of 235 penetrations (17%) were found to require additional shielding to meet personnel radiation exposure criteria. Assuming that steel plate is used, typical dimensions are about 2 inches and 3 inches thick and about 1 ft^2 in area. The largest plate identified will be 6.5 inches thick, 11 inches wide, and 36 inches long in the melt cell wall.

Floor Drain Catch Tank

Floor drains from both regulated and nonregulated personnel areas of the vitrification building drain to a catch tank (FDCT) located in the lower level of the building. After vitrification of the absence of radioactivity in any liquid collected in the tank, the tank contents will be transferred to chemical and industrial waste treatment prior to discharge to the environment. Presently only one tank is provided. To ensure that the tank contents do not change while waiting for analysis an additional tank is being provided. The catch tank area is presently designed to hold the tank.

Safety and Fire Protection

A review of the DWPF safety and fire protection features was conducted.

Significant changes are summarized below:

- Salt Cell Fire Protection - The specification on wire, motors, and instruments is class 1, division 2, group D; Hanford connectors will meet this specification and will be used for electrical services. Ultraviolet fire detectors will be used in the cell in addition to the thermal detectors. A benzene detector will be provided in the salt cell exhaust duct. Flame arrestors will be provided for vent lines on salt cell tanks.

- Benzene Incinerator - A basic plan was developed for the incinerator. The tanks will be in a diked area. A dry pipe foam applicator system will be used for fire protection in the diked area.

- Manipulator Repair Shop Glove Boxes - The fire hazards of these boxes were reviewed and a plan developed. Thermal detectors (rate of rise) will be provided. Fire protection will be provided by manual Halon bayonet extinguishers (9 lb. size) and backup pressurized water extinguishers outside the boxes.

- Fire Water System - The fire water loop plan was reviewed. A sleeve will be provided for the 10-inch fire water line where it passes under a roadway used by the heavy shielded canister transporter. This will allow the line to be repaired without tearing up the concrete roadway.

Saltstone

Decontaminated salt solution will be mixed with cement and fly ash to form a pumpable grout which will be disposed of in trenches in Z Area. Activities are summarized below:

- Process operations and data management will be controlled by a programmable computer.
- The operations building floor plan will be modified to accommodate an adjacent building containing the process facilities (mixer, grout pumps, etc.), the electrical control room - instrument control room, and the maintenance facilities.
- The site plan will be rearranged to make optimum use of the new building arrangements.
- Basic data revisions will be completed by late 1984. Preparation of a current appraisal of cost (CAC) is scheduled for 2QCY85.

H-Area CCTV System

Operation of the 221-H hot canyon CCTV test continued during the quarter. The picture quality of the cameras was rated from fair to very good.

Unshielded camera enclosures are being installed and tested to determine if the lighter weight will reduce pan/tilt failures and perform satisfactory.

The three pan/tilt units ordered from an alternate vendor have been received and checked out in 717-F. Modification to the electrical connectors is required before they can be installed on the H-Area crane which is presently scheduled for February 1985.

At the request of DOE, a presentation was made to the Inter-Departmental Radio Advisory Committee (IRAC) in Washington, DC on December 11, 1984, requesting spectrum support for the radio frequencies presently being used in the H-Area CCTV test and for the remote control and viewing system being designed for the S-Area main process cell crane. A waiver of the time restrictions of the

National Telecommunications and Information Administration (NTIA) low power rules was verbally granted. This waiver allows continued operation of the H-Area CCTV system and design of the DWPF radio controlled crane. Conditions of the waiver will officially be transmitted to DOE.

Failed Equipment Storage Vault

Design of the DWPF melter provides the capability for draining the melter in the event the melter has to be replaced. However, complete removal of the glass is not possible. The facility is required to provide temporary storage for the glass melter assembly and other DWPF equipment which cannot be sent to the burial ground. The storage method is required to protect the environment and permit retrieval for final disposition. The storage vaults will be located in S Area south of the 221-S Building. A venture guidance appraisal cost estimate of $10 million for the failed equipment storage vault was developed.

The preliminary scope includes the items listed below:

- A melter transport box. The box is sized to contain a melter assembly filled with glass. It has steel walls to limit the radiation rate at the box surface. The equipment will stay in the box during transport and temporary storage in the vault.
- A railroad flatcar to transport the box from the vitrification building to the vault.
- A gantry crane to unload the storage box from the flatcar into the vault.
- An underground concrete storage vault capable of storing six transport boxes in individual cells. The vaults are equipped with sumps and a common collection tank. There is room at the site for vaults to contain at least twelve more melters.
- Miscellaneous site facilities such as additional railroad equipment, perimeter fencing and lighting, and a gantry crane storage building.

Prestartup Activities

Planning for startup of the DWPF is under way. The status of the activity is summarized below.

- DWPF Turnover - Operating personnel will accept custody of the DWPF from Construction personnel in small segments. Review of drawings indicate that there will be approximately 530 turnover segments for the DWPF project. Each segment is being defined to show its relationship with other segments of the project in preparation for computerization of the turnover sequence by the end of 1Q85. Currently, 243 of these 530 (46%) interrelated segment requirements packages have been drafted.
- Remotability - A letter, outlining the remotability test requirements, has been drafted and issued for review and comments. After receipt and review of comments this document will be developed and formalized as the "Remotability Test Plan."
- Shielding Wall Integrity Test - The integrity of the 221-S Building shielding walls will be evaluated prior to introduction of radioactive waste into the facility to verify adequate personnel radiation protection. Preliminary discussions with SRL indicate sufficient ^{60}Co will be available during the 2Q88 to perform these tests. A container will have to be designed and fabricated to permit remote crane handling of the ^{60}Co slugs.

New Waste Transfer Facility

A project to provide a new waste transfer facility (NWTF) is being developed. Design completion is expected in September 1985 with some site preparation beginning in June 1985. Mechanical turnover is projected for August 1988.

The project consists of four pump tank cells and a diversion box located south of the 241-H waste farm and providing pipe connections between 241-F, 221-S, and 241-H facilities. The 241-H facilities will be connected and interarea lines serving 241-F and 221-S. Piping connections between NWTF and HDB-5, 6, and 7 will provide transfer capability within the 241-H facility. Operational control of the NWTF equipment will be from the 241-82H control room to be provided in Project S-2033, In-Tank Precipitation.

Because of similarity with the pump pits required for DWPF, considerable available design will be directly applicable to the NWTF. It is expected that use of some existing design will speed preparation of overall design of the NWTF and provide a firmer basis for the CAC estimate than might otherwise be available.

Truck Shipping Cask

A project for delivering a truck shipping cask to the DWPF by 2QFY88 is on schedule.

Highlights of current activities are as follows:

- The cask product specifications were updated to reflect the latest versions of 10CFR71, 49CFR173, and the structural design criteria of the ASME code.
- Preliminary designs were completed for the cask lifting yoke, guide fixture, closure handling tool, canister guide funnel, and the trailer-mounted supports and tie-downs.
- Cask structural analyses have been completed by Sandia National Laboratories (SNL) and will be evaluated by General Atomics (GA) 4QCY84.
- A half-scale model cask procurement package has been transmitted from GA to SNL so procurement can be initiated.

Material Characterization Center Test Procedure

Seventeen persons from nine organizations met at Sandia National Laboratory (SNL) on November 8 to review the Materials Characterization Center MCC-15 proposed test procedure for evaluating the performance of defense high-level waste (DHLW) canisters containing borosilicate waste glass, under transportation accident conditions.

The specific purpose of the MCC-15 test procedure is to demonstrate that the DHLW canister, when subjected to transportation accident conditions, does not generate more than 20 curies of plutonium respirable fines. If this is the case, the DHLW canister can be shipped with single containment and will meet the requirements listed in the Code of Federal Regulations 10CFR-71.63 under transportation accident conditions described in 10CFR-71.73.

The licensing status of MCC-15 is uncertain. Since the shipment of 40 canisters from DWPF to WIPP involves only DOE, MCC-15 can be used in the DOE cask certification process. However, future transport to a federal repository will involve NRC, so additional tests may be required. To avoid this possible future conflict, the MCC-15 procedure will relate to the existing code of federal regulations as described in 10CFR-71.75 - 71.77.

The DWPF five-year sludge - 15-year supernate canister contains approximately 210,000 curies of which 2,530 curies are plutonium isotopes. To exceed the 20 curie limit, about 29 lb of <10-micron fines would have to be present in the canister after the transportation accident condition. To simulate the accident condition, a canister is dropped 9 meters onto an unyielding surface. Previous drops indicate the canister would generate less than 4 lb of <10-micron fines, so the reference canister should easily pass the test.

SRP recommends that PNL drop seven canisters after filling at ETF during 3QCY85. A successful seven canister drop will ensure that with 95% confidence at least 95% of all canisters will contain less than 0.8% material below a 10-micron size following the hypothetical accident.

The plan is to incorporate the comments into a revised draft and forward a copy to the Materials Review Board for evaluation. Assuming approval, the copy would circulate within DOE and eventually become part of the Safety Analysis and the DOE Certificate of Compliance. This work is to be accomplished before completion of cask fabrication in 4QCY87.

Inhibited Water for Evaporators on Standby

In response to an EED recommendation for prevention of tube bundle pitting in evaporators on standby, inhibited water is being maintained in the 242-H and 242-F evaporator pots until their operation is resumed. Eleven gallons of 50% NaOH was added to each evaporator pot on October 26. To maintain an OH^- concentration of 0.015M, six gallons of 50% caustic will be added to each evaporator pot every 30 days to compensate for steam dilution from specific gravity instrument dip tubes.

F-Area Reel Tapes

F-Area reel tape problems accounted for a significant reduction in waste volumes again in November. Changes in Tanks 1, 2, and 3 reel tapes indicated a loss of 4000 gallons of waste. However, there is little, if any, liquid in these tanks. Salt is evidently building up on the reel tapes causing a false reading. Then, when the reel tapes are flushed, water puddles under the reel tape riser. As this liquid evaporates, the level apparently declines. The surfaces of these tank contents are irregular salt mounds and the volume must be estimated. Also in November, the reel tape motor on Tank 20 was replaced. When the reel tape was reset, the level indication was 1.3 inch lower than before. The reading has been steady at this new level for two weeks. WMO is investigating this problem.

VOLUME REDUCTION OF STORED WASTE

F-Area Waste Evaporators

The 242-F evaporator remained down this month pending relocation of the feed pump and the CRC to Tanks 26 and 25, respectively. Construction work is scheduled to be completed in January 1985. Startup is planned for later that month.

The 242-16F evaporator operated 700 hours this month with a space gain of 232,000 gallons. The majority of the downtime was for desalt/descale and to repair the cash regulator of the tube bundle. The feed rate increased more than 25% this month following the installation of the new steam trap on the tube bundle exit.

The new trap is a Yarway series 40 lever trap. These traps feature higher capacity, a small constant control flow for quick response, and reliability over a wide range of temperatures and pressures. The Yarway 40 replaced three Yarway piston traps which had been used in parallel. The new trap has a rated capacity of 6000 pph steam compared to 3000 pph each for the piston traps. Under actual operating conditions steam flow has increased from about 6000 to 6600 pph. Operations plans to continue to use the lever trap until evaluation of a proposal for a condensate collection pot is completed.

F-Area Cesium Removal Column Performance

Since its extensive cleaning in May 1984, the 2F Cesium Removal Column (CRC) has operated satisfactorily. The cleaning removed degraded zeolite that had been plugging the column. To avoid future pluggage problems, two steps have been taken. First, the 20 x 50 mesh zeolite has been replaced with 14 x 30 mesh. The 14 x 30 mesh contains fewer fines initially and produces larger particles as it degrades. Second, the zeolite bed is discharged after six weeks. SRL tests have shown that pH greater than 10 degrades the zeolite over a period of time. Tank farm experience shows a definite increase in CRC P and dF four to six weeks after the zeolite is charged. Operating with 14 x 30 mesh for six weeks per charge has yielded approximately 5000 bed volumes processed per charge compared to less than 1000 bed columns earlier this year. The improved performance is considered adequate and no further actions are planned at this time.

INSPECTION PROGRAM

Inspection Summary

Inspections revealed that seals on three process piping penetrations of the annulus of Tank 44 had failed. The pipe penetrations are about five feet below grade and their failure allowed groundwater to leak into the annulus. No other unusual conditions were observed.

SEEPAGE BASINS

F-Area Seepage Basins

The level of the F-Area No. 3 seepage basin increased 17 inches to 85 inches in November. The increase was due to the receipt of 2.4 million gallons of contaminated cooling water from the 221-F canyon. WHO will proceed with the oxalic acid addition to kill algae in the No. 3 basin after basin sediment sampling is completed. Sediment samples are being obtained for a soil characterization study. No nitric acid was added to the basins for pH control this month.

H-Area Seepage Basins

The level of the H-Area No. 4 seepage basin increased eight inches to 25 inches. Cooling water from the tritium facilities remains diverted to the seepage basins. There were no additions of nitric acid for pH control this month.

SOLID WASTE OPERATIONS

Beta-Gamma Incinerator Demonstration

Installation of the primary chamber firestep is complete. Piping to provide 100 lb/hr of steam cooling was included to protect the steel work from excessive temperatures.

The final solids campaign test burn was completed this month. Over 600 boxes of simulated wastes were incinerated over a four-day period. Volume reduction is estimated to be 150:1.

Two difficulties were encountered during the test burn which slowed the rate of burning.

(1) A primary chamber thermocouple failed which, by interlock, shut down the feed system. The thermocouples was replaced the same day and the burning continued.

(2) High temperatures in the primary chamber necessitated a reduction of the rate at which boxes were fed to the incinerator. Air leaking into the primary chamber under the charging door caused the high temperatures.

Preparations are being made to begin burning radioactive solid waste. Waste Management is discussing waste packaging requirements with the waste generators. An incineration slip similar to the Waste Management burial slip has been developed and will be available to generators as an OSR form. A computer program is also being developed to compile waste data.

Preparations for the final solvent test burns are in progress. Solvent piping modifications are near completion. Auger feeder modifications are complete and will be tested.

A short solvent test burn using an alternative fixative has been incorporated into the test schedule. The test will follow the solvent campaign test burn. The fixative, Tyzor® TBT (Tetrabuytltitanate) is in order. The Test Authorization has been approved by SRP and SRL and is being routed for Wilmington approval.

Experimental TRU Waste Assay Facility (ETWAF)

Building design drawings were received from R. B. Wright and were reviewed and approved. Work on the ETWAF foundation has begun and is expected to be complete by December 20. The prefabricated metal building is scheduled to be installed by January 15. The building should be complete by February 15, 1985.

During November, information on a suitable scale and a forklift for the ETWAF was received. The digital scale will be used to weigh the 55-gallon TRU waste drums and will have a capacity of 1000 lb. Also, a draft of the ETWAF Safety Analysis Report was received and comments were returned to SRL.

Design changes for the x-ray system are being resolved with TFI. All problems should be resolved by mid-December.

A meeting has been scheduled with Los Alamos National Laboratories (LANL) for November 29 to discuss the system's performance and changes to the software. The system acceptance test is scheduled for mid-January and system delivery is scheduled for late February. The decision was made that the system will be operated by WMO technicians.

Waste Certification Facility (WCF)

Preliminary prints for the WCF concrete and architectural details and equipment arrangement were received and reviewed. Final check prints are to be issued in late December.

Transuranic Waste Facility (TWF)

The final revision of the TWF Basic Data Report (BDR) was transmitted to the Engineering Department at the end of November. Major revisions included:

- Inclusion of the Retrieved Waste Preparation (RWP) process basic data.

- Revamping of the Plutonium Waste Incineration (PWI) process basic data. The new basic data specifies PWI process requirements, rather than process equipment.

The Basic Data Report (BDR) will serve two purposes. For the TWF FY87 design-only project, the BDR will be used for a CAB-quality estimate. The BDR will also be the basis for a BGA estimate for the FY88 TWF construction project.

Alpha Decontamination and Disassembly (ADD)

DOE is reviewing a $990,000 project to fund construction of the ADD material handling demonstration at TNX. With DOE approval, the project will be authorized in the second quarter of 1985.

EED has completed certification tests on the Drath and Schrader transfer system drums. Before the drums can be DOT-approved, EED must complete a safety analysis on the drums. This documentation will be completed in three to four months.

Plutonium Waste Incineration (PWI)

Construction of the PWI feed prep system at TNX is complete. Testing of the system will begin in December.

Automation technology (ATI) of Mobile, Alabama has completed Modicon software for the PWI process controller. WMT personnel will attempt process control training at ATI in early December, preparing for shipment of the software to TNX in mid-December.

WASTE TRANSFER/TANK REPLACEMENT

Tank 17 Waste Removal

Work continues in preparation for restarting waste removal in Tank 17. The TTP for Tank 17 was removed from Tank 48 on 10/24/84. However, installation of the TTP in Tank 17 has been delayed because of high radiation rates found around the pump transport container. Plans have been formulated to flush the container and install the pump into Tank 17.

After the Tank 17 installation is complete, waste removal will continue with batch #4 in Tank 17.

Tank 20 Waste Removal

The northwest riser was probed on 10/25/84. Probing revealed an obstruction approximately 70 inches from the tank bottom. The obstruction is probably caused by a jet assembly which broke off and dropped into the tank in 1975. The broken jet assembly was encased in a large mass of salt, which is probably supporting it upright in the tank.

The new transfer jet planned for this riser will be shortened by 7 feet. Most of the waste removal from the tank can be accomplished with the jet at this level, although it will result in more water being added to the tank. Near the end of salt removal the jet will be removed and the riser probed again for obstructions. The broken jet assembly beneath the riser should have fallen when the salt supporting it was dissolved. The transfer jet will then be extended with a spool piece which will allow it to reach to the bottom, and waste removal from the tank will be completed.

Tank 22 Waste Removal

Waste removal from Tank 22 to Tank 51 is expected to begin early 1986 (original startup date was January 1985). Tank 22 waste removal will be delayed to permit construction of the DWPF valve box on the uncontaminated transfer line from HDB7 to Tank 51. This transfer line has not been placed in service. Previous plans were to proceed as soon as possible with waste removal, and subsequently have construction work on the contaminated transfer line. By delaying transfers to Tank 51, radiation exposure is eliminated, and the cost of construction is reduced. Current schedules indicate this work will be completed in early 1986.

Waste removal can start as early as July 1985 if construction on the DWPF valve box can be expedited. Prior to starting waste removal, about 1.1 million gallons of supernate in Tank 22 must be fed to the 2H evaporator. This should be complete about July 1985. Waste removal can commence after that date immediately upon completion of the DWPF valve box work.

Transferring the contents of Tank 22 to Tank 21 was considered as an option to speed up waste removal, but was rejected because of delays which would be caused in finishing construction on the south riser of Tank 21. The down-comer used for transfers into Tank 21 could not be cut to permit TTP installation in the south riser. The delay is a problem for construction, and would not significantly speed up Tank 22 waste removal because an additional 500,000 gallons of supernate would have to be evaporated to make space in Tank 21.

Inspection of Tank 48, Salt Decontamination Tank

A periscopic inspection of Tank 48 showed no significant corrosion in the vapor space or in the precipitate-coated portions of the tank. Tank 48 contains the washed precipitate from the In-Tank Salt Decontamination Demonstration. However, more work by SRL is needed to determine if corrosion will be a problem with long-term salt decontamination.

The inspection was prompted by evidence pointing to possible vapor space corrosion in tests run at SRL. In these tests, coupons of carbon steel were partially immersed in solutions representative of washed precipitate. The purpose of the tests was to determine if corrosion at the air/water interface would be a problem for long-term storage of washed precipitate. No significant corrosion was found at the interface in any of the coupons, but some of the coupons showed significant pitting-up to 0.17 inches in the vapor space. No pitting was found in similar tests run without the STPB used in the precipitation processes. The hypothesis is that some corrosive breakdown product of the STPB (such as phenol) is vaporizing from the liquid surface and condensing on the metal.

The inspection of Tank 48 confirmed the SRL test observation that no pitting occurred at 0.2M nitrite, the nitrite concentration presently in Tank 48. However, for long-term salt decontamination the nitrite concentration is expected to be 0.03 to 0.04M; significant pitting was found at these levels in the SRL experiments. However, the results are not conclusive because the tests were designed to examine interface corrosion, not vapor space corrosion. SRL is planning experiments which more accurately simulate the tank vapor space conditions to determine if there really is a problem and what corrective action needs to be taken if there is.

Tank 42 Supernate Outside of Technical Standards

Analysis of Tank 42 waste supernate sampled September 29, and confirmed by resample of November 7, showed the concentration of free hydroxide was less than Technical Standard minimum. Tank 42 was the tank used for the In-Tank Sludge Processing Demonstration, and is planned for long-term sludge processing. No adverse effects are expected because previous SRL tests with simulated Tank 42 supernate indicated that the inhibitor concentrations observed cause negligible corrosion. 220 gallons of 50 wt % sodium hydroxide have been added to the tank to bring the free hydroxide level above the standard. Plans are to lower a slurry pump into the liquid, agitate the tank contents to thoroughly mix the hydroxide, and then resample to confirm that the inhibitors are within limits.

The cause of the drop in hydroxide is not known at this time. But the incident points out that tanks containing washed sludge should be sampled more frequently than typical inactive waste tanks, because washed sludge contains very low inhibitors. The previous sample of Tank 42, January 26, 1983, showed 0.016M free hydroxide. The technical standard is 0.10M hydroxide minimum. The samples of September 20 and November 7, 1984 were below the detection limit for hydroxide with a pH of 9.5; the hydroxide level can be estimated from the pH to be 0.00003M. This is a drop of only 0.016M, which would not have caused a problem in other waste tanks with much higher hydroxide concentrations.

NONRADIOACTIVE HAZARDOUS WASTE

Pilot-Scale Mercury Removal Column

A pilot-scale mercury removal column has been installed in the 2H receiver cell to test the mercury removal effectiveness of Duolite® ES-466 polystyrene resin on evaporator overheads. Column operating procedures have been approved and startup is scheduled for the first week in December.

Soil Characterization of F- and H-Area Seepage Basins

Woodward-Clyde Consultants and Alsay, Inc. have started the collection of soil cores from beneath the H-Area seepage basins. The 3 to 5 foot samples are being collected by driving the sample tube into the clay with a 140 pound hammer attached to a tripod on the barge. Soil cores have been collected from H-Area Basin 1, and the collection of samples from Basin 2 is in progress. The samples are processed at a trailer next to H-Area seepage basin 4 and will be sent to an outside laboratory for analysis at 6-inch intervals. Once the H-Area basins are completed, soil cores will be collected from the F-Area seepage basins.

SCDHEC Part B Permit Application

The preparation of the SCDHEC Part B permit application for existing hazardous waste management facilities remains on schedule. The second draft of the container storage volume is due to Du Pont for review on December 17. The first drafts of the F- and H-Area seepage basin volumes was given to Du Pont for review on November 19. Meetings will be held the first week of December to discuss the F and H seepage basin drafts with Dames and Moore and with DOE.

A progress review meeting for the entire Part B permit application has been scheduled with SCDHEC on December 6.

Waste Management Effluent Treatment Facility (WMETF)

Following discussions with SRL and WMO, the three top WMETF treatment process alternatives were ranked as follows:

1. Tubular precoat filtration (TPF) and cartridge filtration followed by reverse osmosis (RO) and mixed bed ion exchange (MBIX) was chosen because of the high decontamination factor (DF) that results in a minimal offsite radiological impact and low nonradioactive hazardous material releases that can easily satisfy SCDHEC requirements.

2. Ultrafiltration followed by RO-MBIX was chosen second because, while it has the same high DF as the first alternative, but it is more costly.

3. TPF followed by zeolite polishing was the least costly alternative but was ranked third because increases offsite releases certain radionuclides.

Visits were made to inspect TPF and RO systems at the following locations:

- TPF at RBOF in H-Area used to treat water from the fuel receipt basins.

- TPF at Florida Power and Light's nuclear power plant at Turkey Point, Florida used to treat steam condensate.

- TPF-CF-RO at DOE's Rocky Flats Plant used to treat sewage treatment plant effluent.

- RO at the city to Denver's water treatment pilot plant used as part of a process to purify sewage treatment plant effluent for reuse as drinking water.

Experience with TPF has been good both at RBOF since startup of their TPF system in the early 1960's and at Turkey Point for the last two years after minor design and construction problems were resolved. Rocky Flat's experience has been mixed, but their problems were mostly due to design and operational inadequacies which will be avoided in the WMETF and to feed stream upsets from their sewage treatment that will not exist in WMETF feed. Denver's experience with RO was good in bench scale tests, but their pilot RO unit has not yet started up.

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