

DIVISION OF WASTE MANAGEMENT,
PRODUCTION, AND REPROCESSING
PROGRAMS PROGRESS REPORT
FOR
JANUARY-JUNE 1977

Compiled by

R. E. Lerch

July 1977

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DIVISION OF WASTE MANAGEMENT, PRODUCTION, AND REPROCESSING
PROGRAMS PROGRESS REPORT

January-June 1977

R. E. Lerch

ABSTRACT

This is the eighth progress report on Division of Waste Management, Production, and Reprocessing programs being conducted at the Hanford Engineering Development Laboratory (HEDL) for the United States Energy Research and Development Administration. The report describes progress in the first half of 1977 on the following programs:

*Intermediate Level Liquid Waste Solidification
(KX-03-02-01)*

*Chemical Processing of Combustible Solid Waste
(KZ-03-04-02)*

*Application of Acid Digestion to Commercial Wastes
(KX-03-04-02)*



CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF ILLUSTRATIONS	vi
LIST OF TABLES	viii
OTHER REPORTS IN THIS SERIES	ix
I. INTRODUCTION	1
II. SUMMARY	2
III. INTERMEDIATE LEVEL LIQUID WASTE SOLIDIFICATION	3
A. PREPARATION AND TESTING OF IMMOBILIZED PRODUCTS	5
B. THERMAL STABILITY CHARACTERISTICS OF WASTES AND WASTE PRODUCTS	12
C. COMPARATIVE LEACH RATE MEASUREMENTS	20
D. LABORATORY TREATMENT OF ILW CONTAINING VOLATILE CONTAMINENTS	31
E. RESIN SWELLING IN CEMENT-RESIN IMMOBILIZATION SOLIDS	38
IV. CHEMICAL PROCESSING OF COMBUSTIBLE SOLID WASTES	41
A. RADIOACTIVE ACID DIGESTION TEST UNIT (RADTU)	45
B. ACTIVITIES RELATED TO RADTU	56
1. ACID RECYCLE	56
2. RADTU SAFETY ANALYSIS REPORT (SAR)	58
3. RADTU DOCUMENTATION	60
V. APPLICATION OF ACID DIGESTION TO COMMERCIAL SOLID WASTE	61
A. OFF-GAS CLEANUP AND RECYCLE ACID STUDIES	61
B. SAFETY STUDIES	66
VI. REFERENCES	68

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1.	Immobilization of Boric Acid Residues in Type II Cement Using Calcium Chloride to Accelerate the Set.	9
2.	Immobilization of Boric Acid Residues in Type II Cement Using Sodium Silicate to Accelerate the Set.	10
3.	Immobilization of Boric Acid Residues in Type III Cement.	11
4.	The Mettler Differential Scanning Calorimeter Used for Thermal Stability Measurements.	13
5.	The duPont Differential Scanning Calorimeter Used for Thermal Stability Measurements.	14
6.	A DSC Temperature Scan of a Sample of Nitrate Form Anion Resin.	18
7.	The Drying, Decomposition and Burning Characteristics of Nitrate Form Anion Resin Exposed to Heat.	19
8.	A DSC Temperature Scan of Nitrate Form Anion Resin-Bitumen Product.	21
9.	Leach Rate Testing Using an Orbital Shaker for Gentle Agitation.	23
10.	Conical Form Leach Specimens of Cement and Urea-Formaldehyde, and Pelletized ADTU Leach Specimen.	24
11.	Two-Inch Cube Leach Test Specimens (Bitumen, Urea-Formaldehyde and Cement).	25
12.	Cesium and Strontium Leach Rates in Simulated Cement-Waste Product Containing Anion Exchange Resin.	32
13.	The Leaching of Cesium from Bitumen as a Function of Sodium Nitrate Content.	34
14.	Ruptured Can and Pulverized Cement Due to Swelling of Dowex SAR Anion Exchange Resin.	39
15.	Closeup View of Ruptured Can and Pulverized Cement Due to Swelling of Dowex Anion Exchange Resin.	40
16.	Cement-Cation Resin Swelling Specimens.	42
17.	Cement Expansion Strength Measuring Device, California Type.	43

ILLUSTRATIONS (Cont'd.)

<u>Figure</u>	<u>Page</u>
18. Waste Digester Module with Equipment in Place During Unloading at RADTU Facility.	46
19. Waste Digester in Place at RADTU Facility.	47
20. Back Portion of RADTU Facility Showing Nonradioactive Caustic Scrubber (on left), Acid Scrub Tower (in center) Residue Separation Hood, and Liquid Transfer Glovebox.	48
21. Front Side of Waste Preparation Hood Showing Waste Feed Conveyor and Extrusion Feeder.	49
22. Front Portion of RADTU with Waste Preparation Hood (on left) Digester Module (in center) and Hydraulic Drive for Shredder (on right).	51
23. Acid Scrubber and Hood During Field Assembly.	52
24. Caustic Scrubber During Assembly in RADTU Facility.	53
25. Liquid Transfer Glovebox Containing Radioactive Solution Pumps in Place in RADTU Facility.	54
26. Closeup of Liquid Transfer Glovebox Showing Solution Transfer Pumps.	55
27. Process Control Instrument Panel in RADTU Facility.	57
28. Recycle Acid Reboiler.	63
29. Recycle Acid Fractionator.	64
30. Equipment Arrangement for Off-Gas Cleanup and Acid Recycle Studies in ADTU.	65

TABLES

<u>Table</u>		<u>Page</u>
1.	Boric Acid Immobilized in Type II Cement Accelerated with Calcium Chloride.	6
2.	Boric Acid Immobilized in Type II Cement Accelerated with Sodium Silicate.	7
3.	Boric Acid Immobilization in Type III Cement.	8
4.	Combustion Characterization for Bitumen, Resin and Bitumen-Resin Products.	15
5.	Flammability Data on Simulated Urea-Formaldehyde and Bitumen Waste Products.	16
6.	Leach Tests on Immobilized ADTU Residue Containing 10 wt% $\text{UO}_2(\text{NO}_3)_2$.	27
7.	Uranyl Nitrate Leach Rates from Immobilized Anion Resin Products.	28
8.	Leach Rates of Cesium and Strontium from Immobilized Boric Acid and Sodium Sulfate Products.	29
9.	Leach Rate of Cesium and Strontium from Immobilization Resin Samples.	30
10.	Cesium and Strontium Leach Rates Determined in a Simulated Ion Exchange Resin-Cement Waste Solid.	33
11.	Leach Rates of Cesium and Strontium from Immobilized Sodium Nitrate.	35
12.	Iodine Volatilization During Approximately Ten-Fold Concentration of Mercuric Nitrate-Nitric Acid Solutions.	37
13.	Expansion of Resin-Cement Test Samples.	44
14.	Summary of Risks Due to Potential Accidents at RADTU.	59
15.	Document Status.	61
16.	ADTU Acid Recycle System Performance.	62

OTHER REPORTS - THIS SERIES

1. Commercial Alpha Waste Program Quarterly Progress Report, March-June 1974, USAEC Report HEDL-TME 74-50, September 1974.
2. Commercial Alpha Waste Program Quarterly Progress Report, July-September 1974, USERDA Report HEDL-TME 74-61, November 1974.
3. Commercial Alpha Waste Program Quarterly Progress Report, October-December 1974, USERDA Report HEDL-TME 75-41, February 1975.
4. Commercial Alpha Waste Program Quarterly Progress Report, January-March 1975, USERDA Report HEDL-TME 75-87, October 1975.
5. Commercial Alpha Waste Program Quarterly Progress Report, April-June 1975, USERDA Report HEDL-TME 75-102, December 1975.
6. Nuclear Fuel Cycle and Production Programs Progress Report, July-December 1975, USERDA Report HEDL-TME 76-22, May 1976.
7. Division of Waste Management, Production, and Reprocessing Programs Progress Report, January-December 1976, USERDA Report HEDL-TME 77-40, April 1977.



DIVISION OF WASTE MANAGEMENT, PRODUCTION
AND REPROCESSING PROGRAMS

PROGRESS REPORT

JANUARY-DECEMBER 1976

I. INTRODUCTION

This is the eighth progress report issued on waste management programs at the Hanford Engineering Development Laboratory (HEDL) for the Waste Management, Production, and Reprocessing Division (WPR), USERDA. The report covers progress during the first half of 1977 on the following three programs: Intermediate Level Liquid Waste Solidification (KX-03-02-02); Chemical Processing of Combustible Solid Waste (KZ-03-04-02); and Application of Acid Digestion to Commercial Wastes (KX-03-04-02).

The program on Intermediate Level Liquid Waste Solidification was started in FY-1977 and has as its principle objective the development and demonstration of treatment and immobilization technologies for intermediate-level liquid and dispersible solid wastes generated in the nuclear fuel cycle. The program includes development of appropriate processes to treat various waste streams, development of acceptable test procedures for solidified product forms, verification tests of immobilized products, and development of recommended criteria for acceptable packaged product forms for storage. The program also includes treatment of some low level wastes (wastes that do not require shielding during waste treatment and disposal) because of the similarity of waste types and the lack of a sharp dividing line between low and intermediate level wastes.

The program on Chemical Processing of Combustible Solid Wastes was established to demonstrate the applicability of acid digestion for treating waste materials. Overall program objectives and descriptions of the program were discussed in detail in the first Quarterly Progress Report in this series.⁽¹⁾

The program on Application of Acid Digestion to Commercial Wastes was started to supplement the program on Chemical Processing of Combustible Solid Waste, which is developing acid digestion for ERDA wastes. Its primary objective is to support development of acid digestion technology to meet requirements for processing commercial nuclear fuel cycle combustible wastes, including licensability, process economics, recycling of acids, shielding/remote handling for β - γ wastes, fixation of residue for storage, and ability to accept appropriate waste forms. The program will ensure that the developed technology will be appropriate to industrial needs.

II. SUMMARY

Construction of the 100 kg/day Radioactive Acid Digestion Test Unit (RADTU) facility was completed in June, 1977 with the exception of the acid recycle mode, which is being added to the originally planned unit. The project was completed on schedule and within the authorized funds. Cold shake-down testing will commence during the next report period.

The Safety Analysis Report (SAR) on the RADTU facility was completed in June, 1977.

Engineering tests of the acid recycle flowsheet, using test equipment one-quarter scale of the proposed acid recycle addition to RADTU, confirmed the validity of the zero effluent flowsheet proposed for RADTU. Long lead time equipment was ordered for the acid recycle addition.

Studies were continued on immobilization of wastes in cement. Cement products containing up to 16 wt% boric acid were successfully made and tested for compressive strength.

The thermal characteristics of various waste products were determined using a differential scanning calorimeter (DSC). The ignition temperatures for bitumen and bitumen products containing salts, including sodium nitrate, were found to be approximately 400°C. There was no significant lowering of

the ignition temperature below that of bitumen itself upon incorporation of these salts into bitumen. Urea-formaldehyde products exhibited ignition temperatures around 300°C. Ignition temperatures of resins (anion and cation) were relatively high (400 to 600°C) except for anion exchange resin in the nitrate form which ignited about 250°C.

Leach tests were performed on various waste products immobilized in cement, urea-formaldehyde, and bitumen. The results indicated that cement solids exhibited the lowest leach rates for leaching of uranyl nitrate from immobilized anion exchange resin and from immobilized acid digestion residue. Leach rates of cesium and strontium from immobilized anion exchange resin were lowest for bitumen products.

Work is proceeding on development of a process to reduce the volume of mercuric nitrate - nitric acid off-gas scrub solution without loss of the iodine. Preliminary results are promising and indicate that volume reductions of at least 10-fold can be achieved with as little as 0.01% of the iodine being volatilized.

III. INTERMEDIATE LEVEL LIQUID WASTE SOLIDIFICATION (KX-03-02-01)

The program on Intermediate Level Liquid Waste Solidification was started at HEDL in October 1976. The purpose of the program is to develop and demonstrate immobilization technologies for liquid and particulate solid intermediate level wastes (ILW) within the nuclear fuel cycle. The program includes identification of sources and quantities of ILW, development of appropriate processes to treat the various waste streams, development of acceptable test procedures for solidified product forms, verification tests of immobilized products, and development of recommended criteria for storage, transportation, and disposal of immobilized ILW.

For the purposes of the HEDL Intermediate Level Liquid Waste program, ILW are defined as those liquid and solid radioactive wastes, other than high level wastes (HLW) and fuel cladding hulls, that, in packaged form, have

radiation dose readings greater than 200 millirem/hour at the packaged surface and 10 millirem/hour at three feet from the surface. The International Atomic Energy Agency (IAEA) value of 10^4 Ci/m^3 for ILW defines the upper limit. This level is the approximate dividing line above which some external cooling must be provided to prevent radionuclide heat buildup in the container.

Work during this report period on the ILW Solidification Program has centered on continuing immobilization studies, investigation of thermal stability characteristics of organic wastes and waste products, leaching characteristics of simulated waste products, and on treatment of waste solutions containing volatile contaminants. All of these activities are discussed in the following sections.

In addition to the research and development activities, two papers were presented at the Symposium on "Management of Low-Level Radioactive Wastes" held in Atlanta, Georgia May 23-27, 1977. Titles and authors of the papers were:

D. E. Clark and R. E. Lerch. Volume Reduction Options for the Management of Low-Level Radioactive Wastes, USERDA Report HEDL-SA-1235. May 1977.

R. E. Lerch, W. O. Greenhalgh, J. A. Partridge, and G. L. Richardson. Treatment and Immobilization of Intermediate Level Radioactive Wastes, USERDA Report HEDL-SA-1244. May 1977.

Another paper, resulting from a previous waste management program at HEDL on Commercial Alpha Wastes⁽¹⁾ was published in the June issue of Nuclear Technology. Title and authors were:

W. O. Greenhalgh and D. T. Ott, "A Reusable Frame Greenhouse that Saves Money and Erection Time and Reduces Waste Generation." Nuclear Technology, 34: 111-13 (June 1977).

A. PREPARATION AND TESTING OF IMMOBILIZED PRODUCTS

W. O. Greenhalgh

Boric acid waste solutions generated during routine operation of pressurized water reactors (PWRs) are normally evaporated and concentrated to about 10 wt% dissolved solids. Immobilization of these solutions in cement is difficult since boric acid and borates retard setting of the cement and tend to destroy the hydraulic setting characteristics of the cement. Testing of the immobilization of boric acid in cement showed that acceptable products can be made. The amount of boric acid immobilized in the cement was $\leq 16\%$ by weight, which indicates this process is applicable for solidifying a 10 wt% borate solution typical of the PWRs.

Immobilization of boric acid in cement was investigated using both Type II and Type III (high early strength) cement and using equal amounts of calcium chloride-sodium hydroxide or sodium silicate-sodium hydroxide set accelerators. Results, summarized in Tables 1 through 3 and in Figures 1 through 3, indicate that boric acid can be immobilized in Type II cement over a very narrow range of compositions. For example, the water content must be in the range of 30 to 37 wt%, and the boric acid content must be less than 8 wt% with an equal amount of set accelerator added (i.e., up to 8 wt% of either calcium chloride-sodium hydroxide or sodium silicate-sodium hydroxide). Compositions that produced acceptable sets exhibited lower compressive strengths [in the range of 7 to 70 kg/cm² (100 to 1000 psi) rather than the normal 70 to 280 kg/cm² (1000 to 4000 psi)] and required longer setting times (i.e., two to three weeks rather than one week) than those with other salts immobilized in HEDL studies. Type III cement, a high early strength cement, gave improved immobilization characteristics and a wider range of composition, but was still limited in its application.

TABLE 1

BORIC ACID IMMOBILIZED IN TYPE II CEMENT ACCELERATED WITH CALCIUM CHLORIDE

Sample Number	Water Boundary	Composition (wt. %)					Density (g/cm ³)	Compression Strength (kg/cm ²)	Abrasion ^(c) Losses (g/r)	Curing Time (wks)
		Cement	Water	Boric Acid ^(a)	Calcium Chloride	Sodium ^(b) Hydroxide				
1-control	min.	73	27	0	0	0	2.10	323	--	1
2-control	max.	63	37	0	0	0	1.68	44	--	1
3	min.	70	24	3	1.5	1.5	2.00	<2	--	1
4	min.	66	22	6	3	3	1.94	<2	--	2
5	max.	54	40	3	1.5	1.5	1.70	16	--	2
6	min.	60	30	5	2.5	2.5	2.09	68	7.2	2
7	max.	58	36	3	1.5	1.5	1.71	62	--	3
8	max.	53	35	6	3	3	1.69	62	4.3	2
9	min.	54	28	9	4.5	4.5	1.89	<2	41.8	2
10	min.	40	30	15	7.5	7.5	1.83	<2	>1000	2
11	min.	37	27	18	9	9	1.77	<2	--	2
12	max.	43	37	10	5	5	1.71	19	6.2	2
13	max.	41	32	16	5.5	5.5	1.91	<2	--	2
14	min.	65	23	6	3	3	1.94	39	1.9	2
15	min.	50	22	14	7	7	1.97	<2	47	2
16	min.	66	24	5	2.5	2.5	1.94	75	2.4	2
17	max.	50	34	8	4	4	1.75	32	3.8	2
18	max.	49	35	8	4	4	1.60	32	2.1	2
19	max.	45	33	11	5.5	5.5	1.73	35	1.3	2
20	max.	44	34	11	5.5	5.5	1.72	27	2.0	2

(a) Added as solid H₃BO₃.

(b) Added as solid NaOH.

(c) Grams lost per revolution using a Los Angeles Abrasion Machine.

TABLE 2

BORIC ACID IMMOBILIZED IN TYPE II CEMENT ACCELERATED WITH SODIUM SILICATE

Sample Number	Water Boundary	Composition (wt. %)					Density (g/cm ³)	Compression Strength (kg/cm ²)	Abrasion ^(c) Losses (g/r)	Curing Time (wks)
		Cement	Water	Boric Acid	Sodium Silicate ^(b)	Sodium Hydroxide				
1-control	min.	73	27	0	0	0	2.10	323	--	1
2-control	max.	63	37	0	0	0	1.68	44	--	1
3	min.	67	28.5	3	1.5	0	1.91	50	0.8	3
4	min.	55	15	15	7.5	7.5	2.01	<2	--	2
5	min.	67	22	5.5	2.7	2.8	2.03	72	4.0	2
6	min.	69	22	4.5	2.2	2.3	2.04	63	3.2	2
7	max.	50	34	8	4	4	1.70	57	2.1	4
8	max.	46	38	8	4	4	1.66	50	2.5	2
9	max.	45	33	11	5.5	5.5	1.63	<2	--	2
10	max.	43	37	10	5	5	1.61	<2	--	2
A ^(a)	min.	44.5	44.5	6	2	3	1.62	16	1.5	4
B	max.	42	45.5	5.5	4.5	2.5	1.58	5	5.0	4
C	max.	44	45	6	2	3	1.51	<2	--	4
D	max.	42	45.5	5.5	4.5	2.5	--	<2	--	4
E	max.	45	41	6	5	3	1.59	<2	--	4
F	max.	50	42	6	2	0	1.60	<2	--	4
G	max.	54	37	6	3	0	1.65	<2	--	4
H	max.	49	43	6	2	0	1.56	<2	--	4

(a) Samples A through F were made and tested but are not included in Figure 3 since samples had poor characteristics and since the ratio of boric acid to sodium silicate-sodium hydroxide was highly variable.

(b) Added as 40°Bé sodium silicate. Water fraction not included with water total.

(c) Grams lost per revolution using a Los Angeles Abrasion Machine.

TABLE 3
BORIC ACID IMMOBILIZATION IN TYPE III CEMENT

Sample Number	Water Boundary	Composition (wt. %)					Density (g/cm ³)	Compression Strength (kg/cm ²)	Abrasion ^(c) Losses (g/r)	Curing Time (wks)
		Cement III	Water	Boric Acid ^(a)	Calcium Chloride	Sodium ^(b) Hydroxide				
1-control	min.	73	27	0	0	0	1.91	149	--	1
2-control	max.	60	40	0	0	0	1.57	65	--	1
3	min.	63	31	3	1.5	1.5	1.98	40	3.0	3
4	min.	67	30	3	0	0	1.90	30	3.3	3
5	max.	56	36.5	2.5	2.5	2.5	1.74	70	1.0	2
6	min.	63	25	6	3	3	1.92	67	5.6	2
7	max.	52	38	5	2.5	2.5	1.72	56	1.2	2
8	min.	59	21	10	5	5	1.90	50	1.6	2
9	min.	49	23	14	7	7	1.80	9	2.7	2
10	min.	36	30	17	8.5	8.5	1.71	2	5.7	2.5
11	max.	43	37	10	5	5	1.64	36	1.3	2.5
12	max.	38	37	15	5	5	1.60	<2	--	2.5
13	min.	44	26	15	7.5	7.5	1.83	29	1.6	2.5
14	min.	66	25	6	0	3	1.91	9	2.9	2
15	min.	57	19	16	0	8	2.02	9	1.4	2
16	min.	68.5	24	5	0	2.5	1.97	66	2.5	2
17	max.	52	36	8	0	4	1.69	55	2.3	2
18	max.	51	37	8	0	4	1.70	53	2.2	2
19	max.	47	35	12	0	6	1.68	26	1.0	2
20	max.	46	36	12	0	6	1.66	30	1.6	2

(a) Added as solid H₃BO₃.

(b) Added as solid NaOH.

(c) Grams lost per revolution using Los Angeles Abrasion Machine.

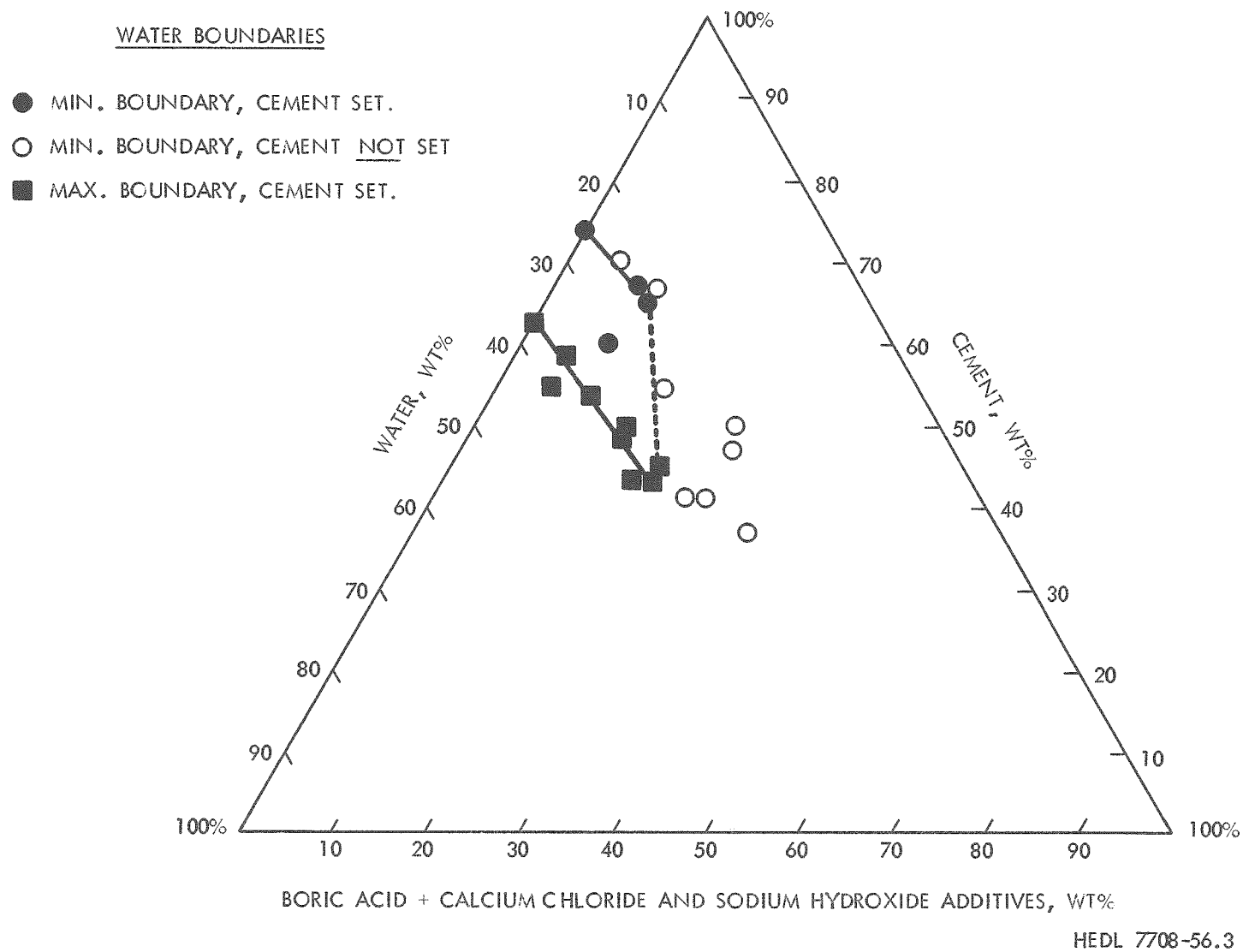


FIGURE 1. Immobilization of Boric Acid Residues in Type II Cement Using Calcium Chloride to Accelerate the Set.

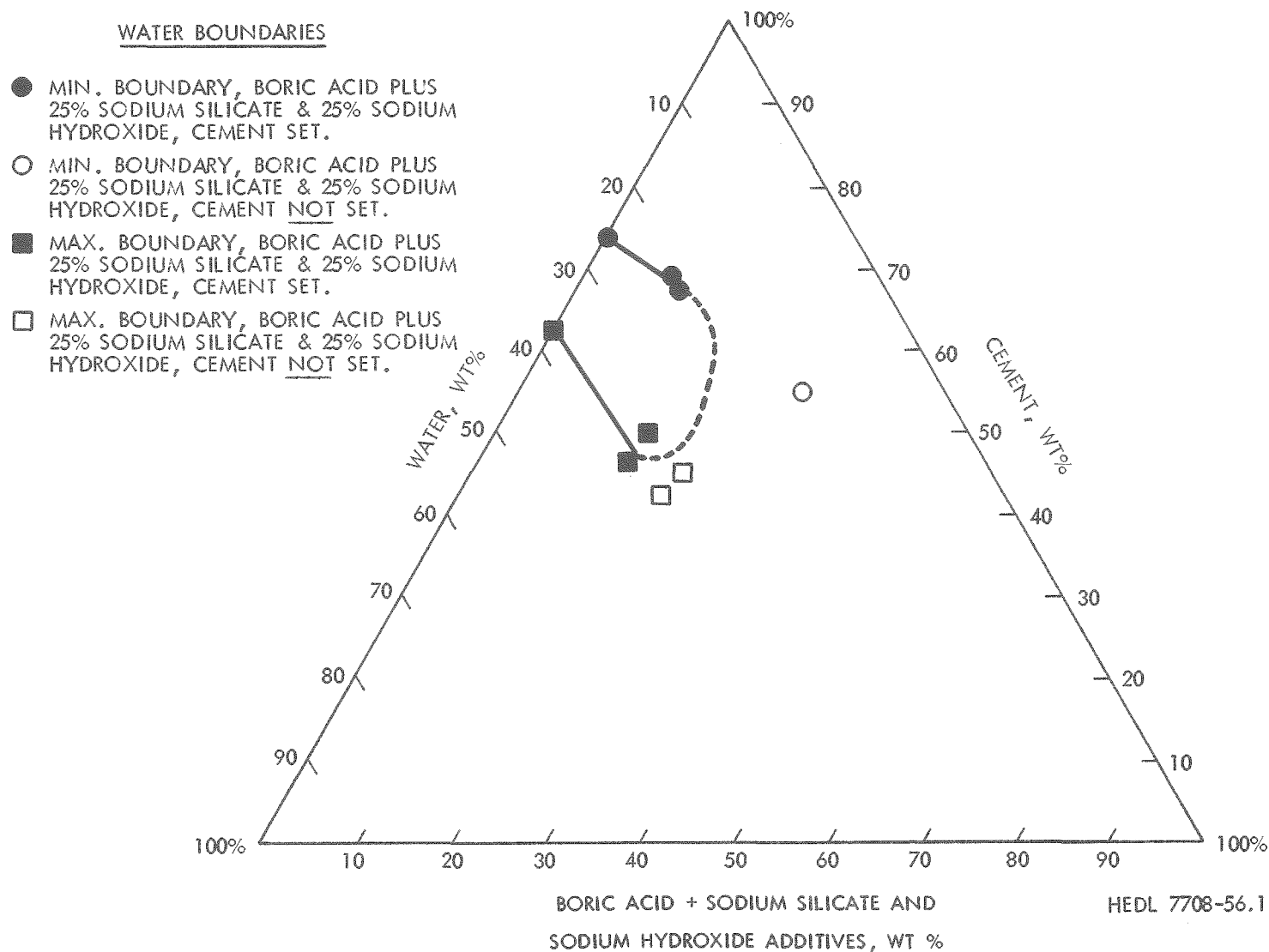
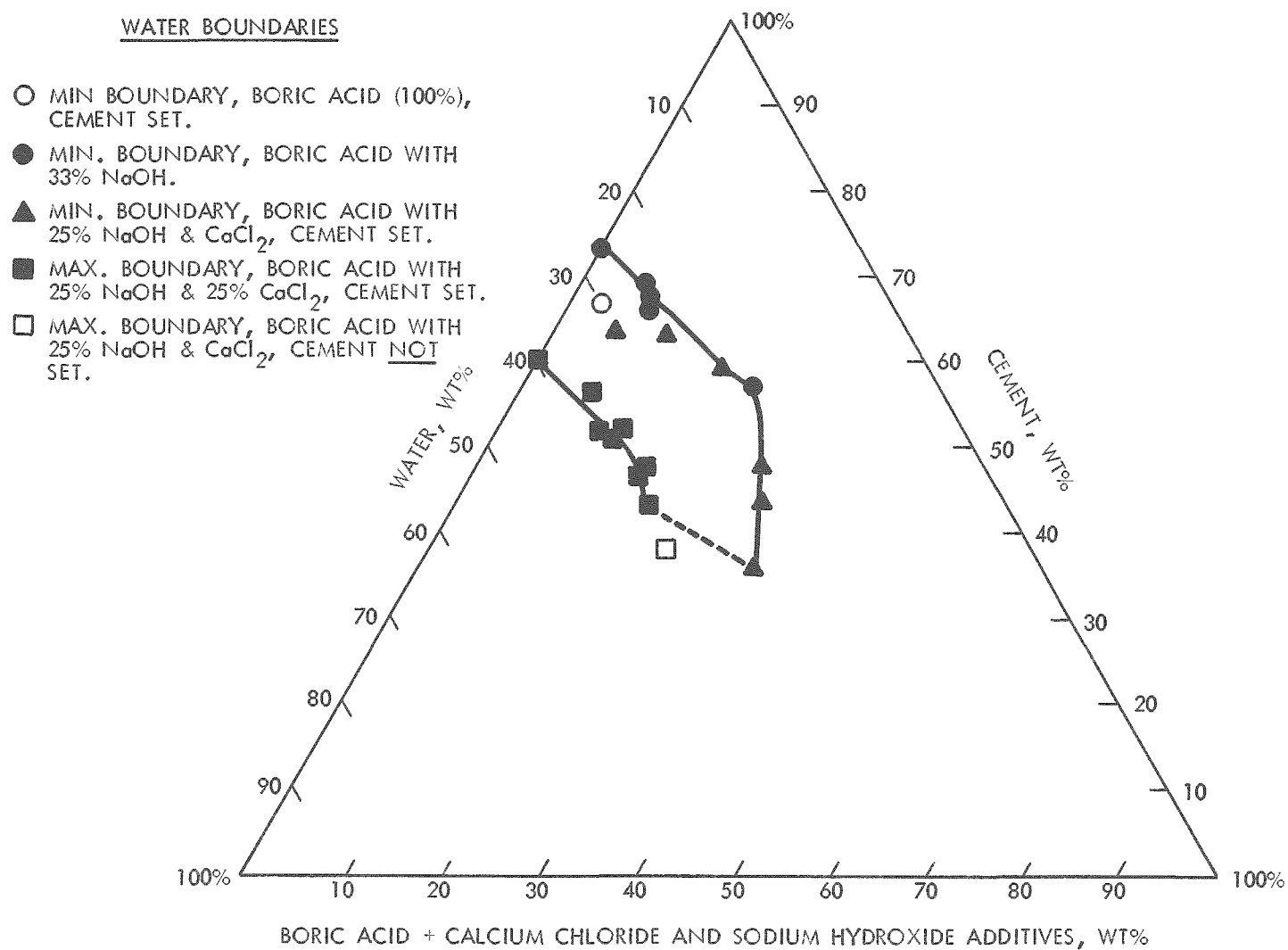


FIGURE 2. Immobilization of Boric Acid Residues in Type II Cement Using Sodium Silicate to Accelerate the Set (40° Baume Sodium Silicate Solution).



HEDL 7708-56.2

FIGURE 3. Immobilization of Boric Acid Residues in Type II Cement.

B. THERMAL STABILITY CHARACTERISTICS OF WASTES AND WASTE PRODUCTS

W. O. Greenhalgh, J. A. Partridge, and G. P. Bosuego

The thermal stability of nuclear wastes, particularly wastes containing organics, is of interest in assuring safe handling, storage, and disposal techniques. Samples of various organic-containing waste solids were analyzed by differential scanning calorimetry (DSC) and manual thermographic methods to determine decomposition temperatures, flame ignition temperatures, combustion temperatures, and heats of combustion.

A Mettler TA2000 thermal analysis system (DSC) on trial loan from the Mettler Instrument Corp. and a duPont 990 Differential Thermal Analyzer (DTA) equipped with a DSC cell were used for the bulk of the work. The Mettler instrument is shown in Figure 4 and features both programmed heating and cooling. The duPont instrument is shown in Figure 5 complete with the basic programmer, controller, and recorder.

The decomposition temperatures, ignition temperatures, and combustion temperatures were obtained with the Mettler and duPont DSC instruments, and by manual methods. The results are given in Tables 4 and 5. The ignition temperatures for bitumen and bitumen products containing salts, including up to 44 wt% sodium nitrate, were found to be approximately 400°C, i.e.; there was no significant lowering of ignition temperature below that of bitumen itself after these salts were incorporated into the bitumen. These results were obtained with the Pioneer-221 bitumen used as a waste-immobilizing agent in this country and agree with measurements carried out in European nuclear operations on Mexphalt-15 bitumen.⁽²⁾ Urea-formaldehyde exhibited an apparent ignition temperature of 300°C, but as reported in an earlier document⁽³⁾ urea-formaldehyde is resistant to burning and this is probably best reflected in these tests by the small partial heats of combustion. Ignition temperatures of the resins tested are comparatively high also (400 to 600°C) with the exception of the nitrate form anion resin, which is about 250°C. The nitrate form of this resin burns readily.

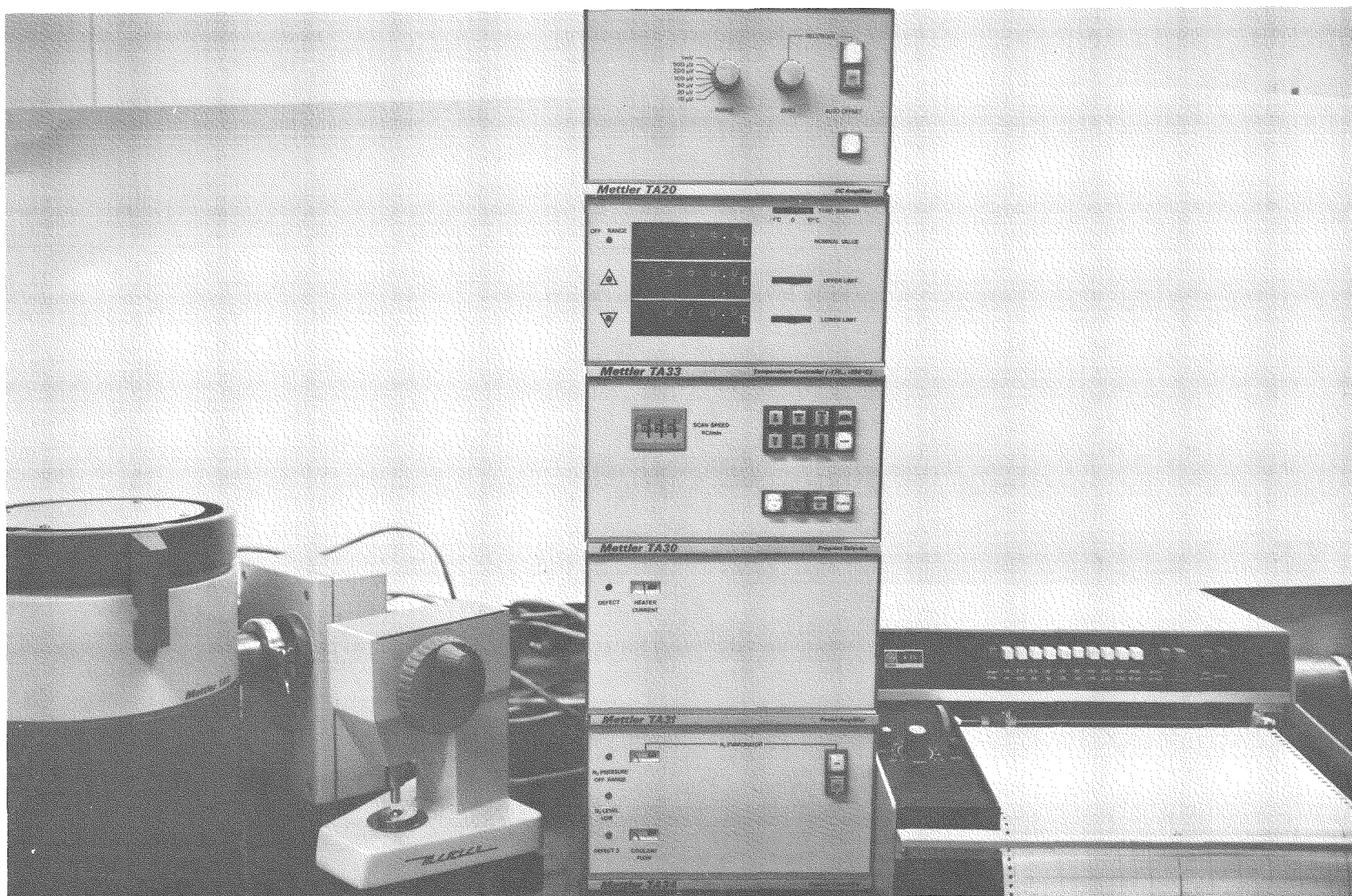


FIGURE 4. The Mettler Differential Scanning Calorimeter Used for Thermal Stability Measurements
Neg. No. 773503-8 CN

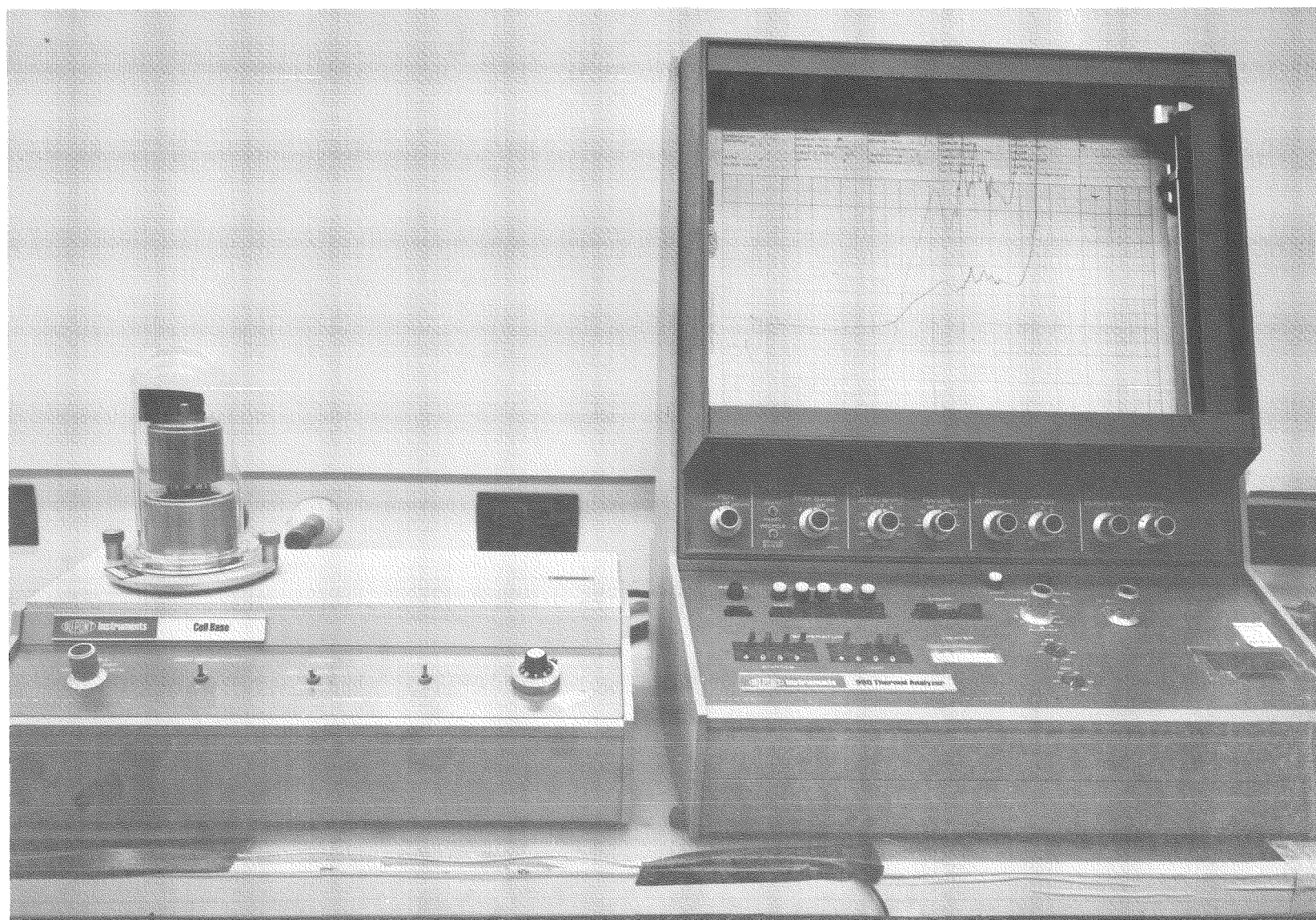


FIGURE 5. The duPont Differential Scanning Calorimeter Used for Thermal Stability Measurements

Neg. No. 773583-1 CN

TABLE 4

COMBUSTION CHARACTERISTICS FOR BITUMEN, RESIN, AND BITUMEN-RESIN PRODUCTS (METTLER DSC ANALYSES)

Sample Number	Sample Composition	Resin ^(a) Content (wt%)	Sample Weight	Partial Heat of Combustion (cal/gm)	Exotherm Initiation Temp (DSC)			Flame Ignition Temperature (visual), °C	Combustion Temperature, °C
					1	2	3		
1	Anion Resin Chloride Form	100	10.5	1869	420	--	--	500	550
2	Anion Resin Chloride Form	100	6.4	2007	420	455	--	500	540
3	Bitumen with Chloride Type Resin	31	5.7	3389	405	--	--	--	530
4	Bitumen with Chloride Type Resin	31	11.3	1933	360	475	--	--	525-555
5	Anion Resin Nitrate Form	100	5.3	2830	230	420	--	260	>500
6	Anion Resin Nitrate Form	100	9.8	3240	220	420	--	260	550
7	Bitumen with Nitrate Type Resin	47	4.4	3481	230	425	--	250	>500
8	Bitumen with Nitrate Type Resin	47	6.7	3434	230	450	--	250	535
9	Anion Resin Hydroxyl Form	100	6.6	2187	400	460	--	--	545
10	Anion Resin Hydroxyl Form	100	11.7	2169	400	425	--	--	550
11	Bitumen with Hydroxyl Form Resin	42	5.6	3487	340	435	--	--	540
12	Bitumen (Pioneer 221)	-0-	5.5	3901	365	420	--	415	540
13	Bitumen (Pioneer 221)	-0-	10.4	2824	350	390	--	415	540
14	Bitumen (Pioneer 221)	-0-	N.A.	10,200 ^(b)	N.A. ^(c)	N.A.	N.A.	N.A.	N.A.
15	Cation Exchange Resin (Sodium Form)	100	5.9	12,600	340	430	500	610	545
16	Cation Exchange Resin (Sodium Form)	100	7.4	10,700	340	450	515	610	>550

(a) Dowex SAR, except samples 15 and 16 which used Amberlite 200 macroreticular cation resin. Bitumen binder is Pioneer-221 asphalt.

(b) Bomb calorimeter used for this sample.

(c) Not applicable.

TABLE 5

FLAMMABILITY DATA ON SIMULATED UREA-FORMALDEHYDE AND BITUMEN WASTE PRODUCTS
(duPONT DSC ANALYSES)

<u>Sample Number</u>	<u>Product Material</u>	<u>Waste Additive</u>	<u>Percent Additive</u>	<u>Partial Heat of Combustion (cal/gm)</u>	<u>Ignition Temp (°C)</u>	<u>Combustion Temp (°C)</u>
UF-1	Urea-Formaldehyde	-0-	-0-	1610	300	360
UF-2		Water	50 vol%	731	295	390
UF-3		Water	67 vol%	353	300	345
UF-4		Boric acid	24 wt%	233	325	~400
UF-5		Boric acid	48 wt%	218	325	~390
UF-6		Boric acid	58 wt%	137	310	~390
UF-7		Boric acid	48 wt%	115	315	~390
UF-8		Sodium nitrate	31 wt%	380	310	350
UF-9		Sodium nitrate	23 wt%	273	305	345
UF-10		Sodium nitrate	47 wt%	291	305	345
UF-11		Sodium nitrate	32 wt%	307	300	335
AS-(a)	Bitumen	-0-	-0-	2074	400	455
AS-2 ^(b)		-0-	-0-	2067	400	465
AS-3		Boric acid	31 wt%	1443	400	465
AS-4		Boric acid	46 wt%	1139	425	495
AS-5		Boric acid	19 wt%	1697	415	500
AS-6		Boric Acid	31 wt%	1213	410	490
AS-7		Sodium sulfate	30 wt%	1427	420	500
AS-8		Sodium sulfate	48 wt%	1429	430	505
AS-9		Sodium nitrate	19 wt%	1297	470	520
AS-10		Sodium nitrate	27 wt%	1893	425	515
AS-11		Sodium nitrate	33 wt%	746	395	475
AS-12		Sodium nitrate	39 wt%	816	380	455
AS-13		Sodium nitrate	44 wt%	809	420	455

(a) Blackote brand roofing asphalt containing thinning solvent.

(b) Pioneer-221 steep roof asphalt used for samples AS-2 through AS-13; contained no thinning solvent.

It was not possible with the ordinary DSC instrumentation of either instrument to obtain complete heats of combustion due to partial volatilization or pyrolysis of the samples. Because the DSC crucibles are vented to provide oxygen, the heat given off by the burning volatilized fraction is not completely detected by the DTA, thus yielding only partial heats of combustion. This was verified by determining the heat of combustion for bitumen in a bomb calorimeter and comparing it to the heat of combustion of bitumen as determined by the DSC runs.

A typical DSC curve for a strong base anion resin in the nitrate form is shown in Figure 6. The curve shows two temperature regions of exothermic reaction; the first beginning at about 230°C and the second beginning at about 420°C. Gravimetric combustion analysis tests, shown in Figure 7 and discussed below, show that thermal decomposition of this resin in the nitrate form begins at about 200°C, producing volatile decomposition products and a solid residue.

The first exotherm on the DSC curve is apparently an oxidation reaction occurring with the volatile products from this decomposition. As discussed previously, the vented DSC crucibles resulted in incomplete measurement of this heat release and, possibly, incomplete combustion of the volatile fraction. The incomplete measurement of this heat of combustion is indicated by the data in the manual thermogram shown in Figure 7, since the heat of combustion in a temperature region should be proportional to the weight loss. A large loss of weight is observed just above 200°C, which is much larger than the weight loss observed in the temperature region above 400°C. The second exotherm in Figure 6 is thought to be due to the burning of the solid residue. The latter exotherm increases with temperature until it peaks at 530°C, the combustion temperature for this sample. The sample was held at 550°C (the limit for this instrument) until the burning was complete.

A manual gravimetric combustion analysis of Dowex SAR in the nitrate form is shown in Figure 7. Samples of the resin were heated one hour at the indicated temperatures and the resulting sample weight recorded and compared

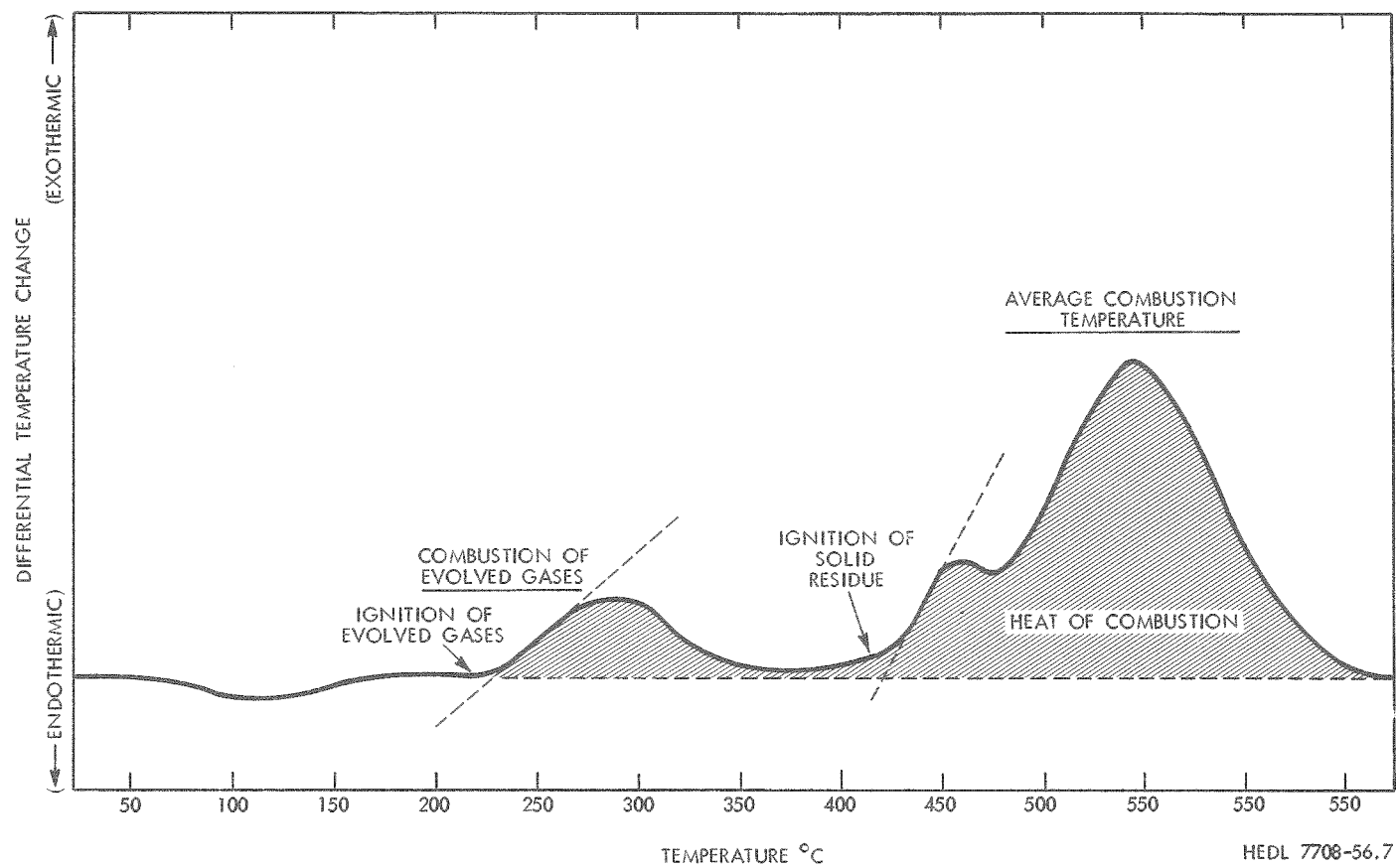


FIGURE 6. A DSC Temperature Scan of a Sample of Nitrate Form Anion Resin.

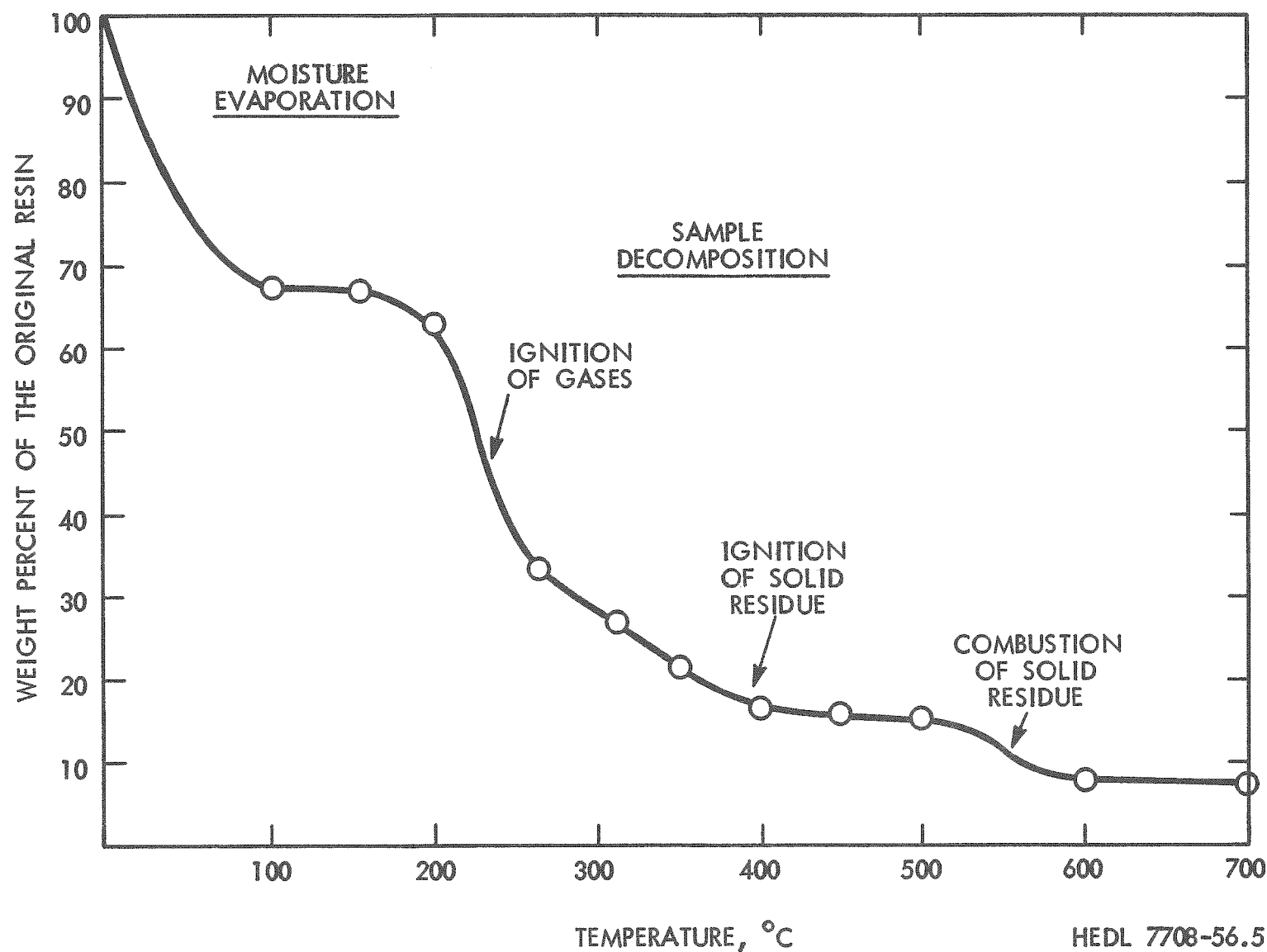


FIGURE 7. The Drying, Decomposition, and Burning Characteristics of Nitrate Form Anion Resin Exposed to Heat (Dowex SAR - 1 Hr Runs).

with the original weight. The resin used in these runs was moist and evaporation losses were observed below 100°C. Sample decomposition started at about 200°C and visual observation of sample ignition was observed at 260°C with an open flame above the sample. Most of the sample weight loss occurred between 200 and 400°C. The DSC scan (Figure 6) showed solid ignition at about 420°C. A significant weight loss occurred between 500 and 600°C, apparently due to combustion of the solid residue.

The DSC results with the nitrate form of this resin mixed with bitumen were very similar to the DSC results with the resin (nitrate form) only, as shown by comparison of the DSC scans in Figures 6 and 8 and by the data in Table 4. The data in Table 4 also show that of the three anionic forms of the resin tested (chloride, hydroxide, and nitrate) only the nitrate form of the resin produced a bitumen product having an initial exothermic reaction temperature lower than that of the bitumen itself.

C. COMPARATIVE LEACH RATE MEASUREMENTS

W. O. Greenhalgh

The current Nuclear Regulatory Commission (NRC) licensing guidelines for reactor radwaste systems requires that all radioactive wet wastes be solidified and a verification of the solidification be made.⁽⁴⁾ However, solidification is a broad term and the extent that the liquid wastes and/or radionuclides are bound within the solid varies widely. Measurement of various leach rates allows evaluation of the relative binding capability of the solid when exposed to water systems.

Leach tests were performed on several simulated waste products immobilized in cement, urea formaldehyde (UF), and bitumen. In addition, some leach tests were conducted on acid digestion process residue for comparative purposes.

There are two general types of leach tests, i.e., static and dynamic (still or moving water). A modified dynamic type of leach test was chosen for the evaluation for the following reasons:

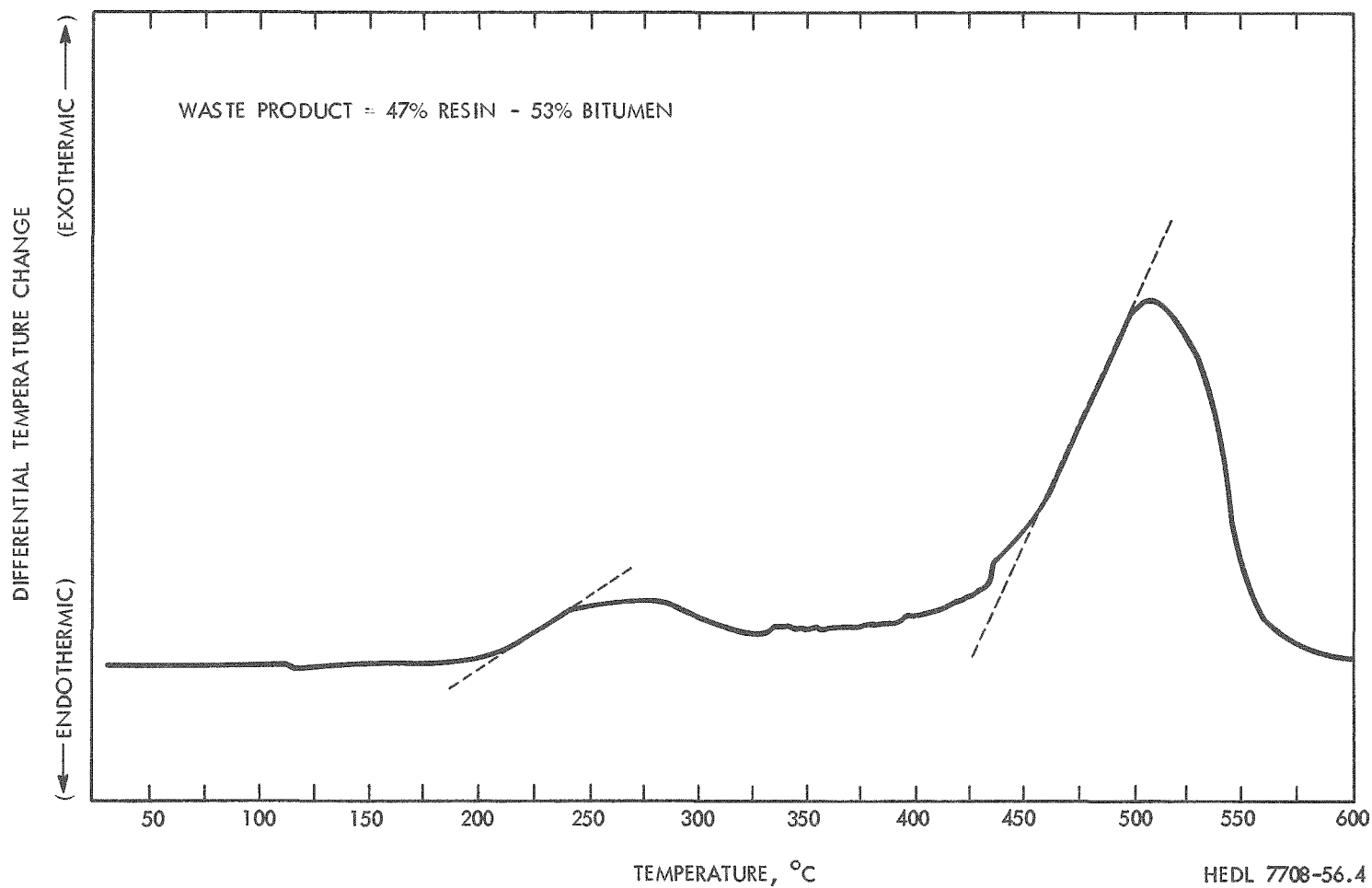


FIGURE 8. A DSC Temperature Scan of Nitrate Form Anion Resin-Bitumen Product.

- 1) It minimizes formation of surface films that may inhibit diffusion.
- 2) Analyses tend to be more consistent due to the continued water mixing.
- 3) The leach rates are used primarily for comparative purposes and not for determining an absolute value.
- 4) The dynamic leaching system may be more realistic for analysis of dispersal situations particularly in the case of hypothetical transportation accidents.

Several different leach rate procedures for solidified radwastes have been developed, but most are primarily designed for leach tests on glass. There is presently no universally accepted method, although the IAEA⁽⁵⁾ and a USA Leach Rate Testing Committee⁽⁶⁾ are seeking to establish a standard test method.

The general leach rate procedure used in this study involved placing 60 to 130 cc blocks of simulated waste solids into 250 ml of deionized-distilled water. The solids in all cases contained non-radioactive salts for leach test analyses. The solid samples and water were placed in plastic containers and agitated by placing the containers on an orbital lab shaker set at 100 rpm, as shown in Figure 9; previous leach testing using ultrasonic agitation⁽⁷⁾ is being limited to accelerated leaching studies because of ultrasonic heating effects. The aqueous leachant was sampled and replaced daily (except for weekends) for 14 days. Cement samples were allowed to cure for one week prior to the leach tests. Shapes included cylindrical pellets and truncated cones (Figure 10), and cubical forms (Figure 11). The present intent is to standardize on the cubical form whenever possible. In most cases, the same form was used in each series of tests.

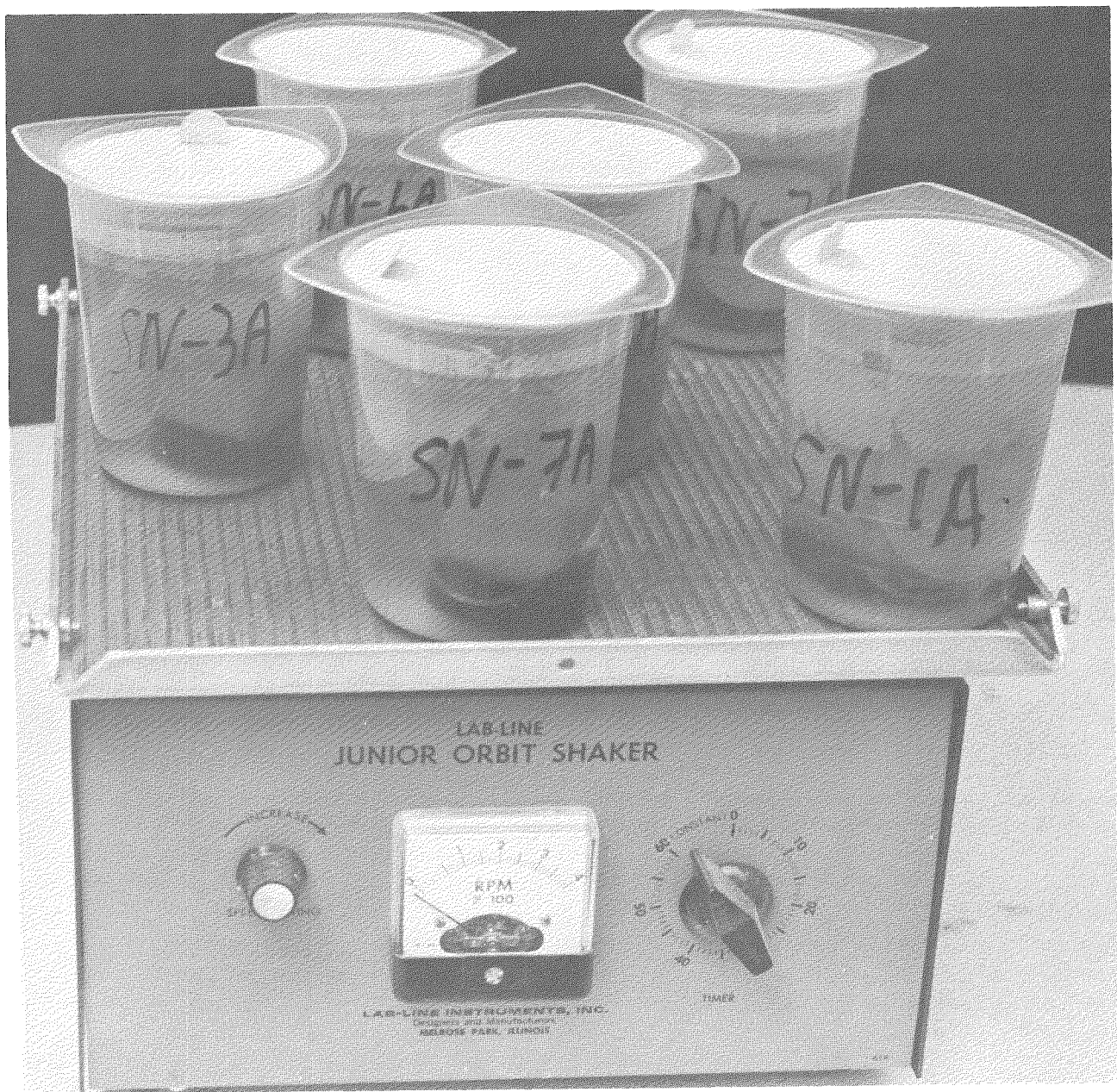


FIGURE 9. Leach Rate Testing using an Orbital Laboratory Shaker for Gentle Agitation.

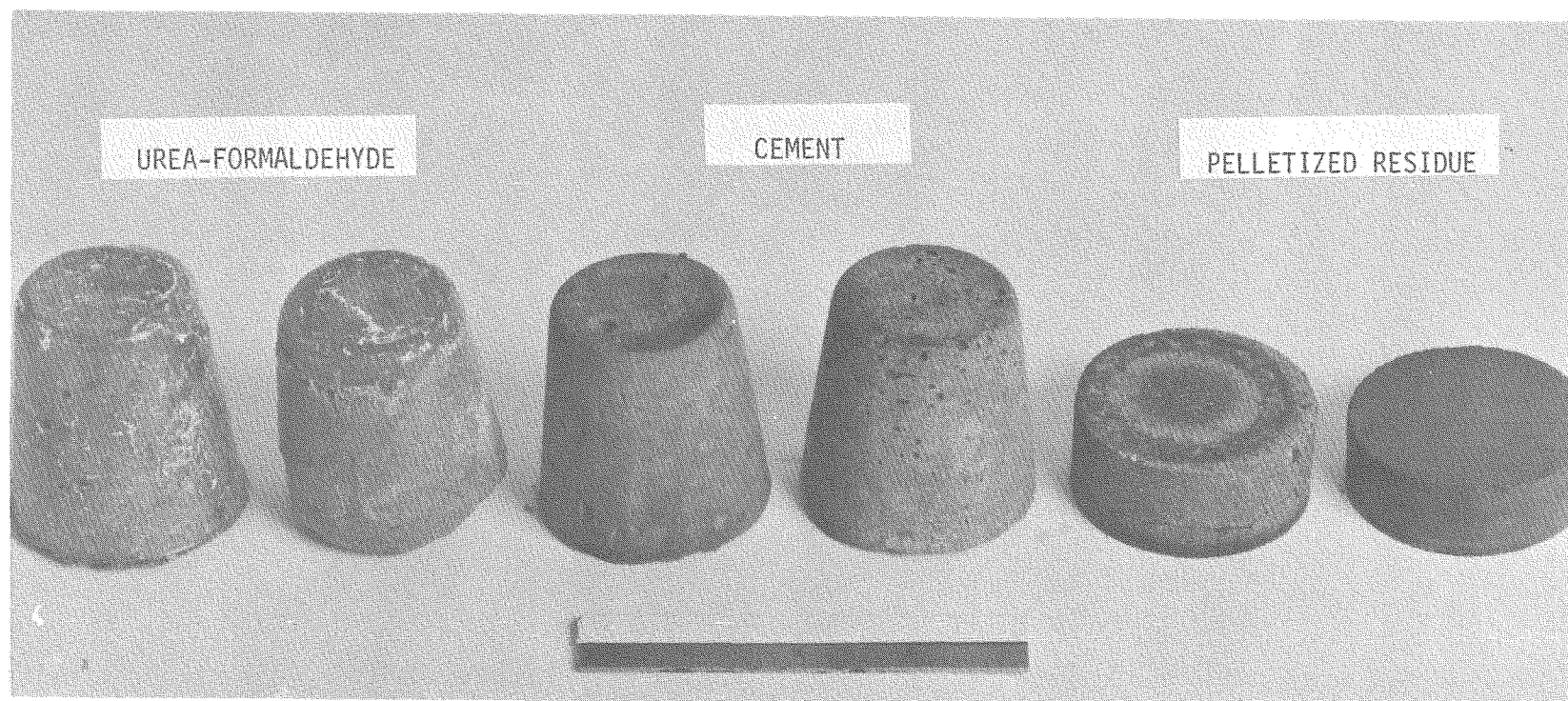


FIGURE 10. Conical Form Leach Specimens of Cement and Urea-Formaldehyde, and Pelletized ADTU Leach Specimen.

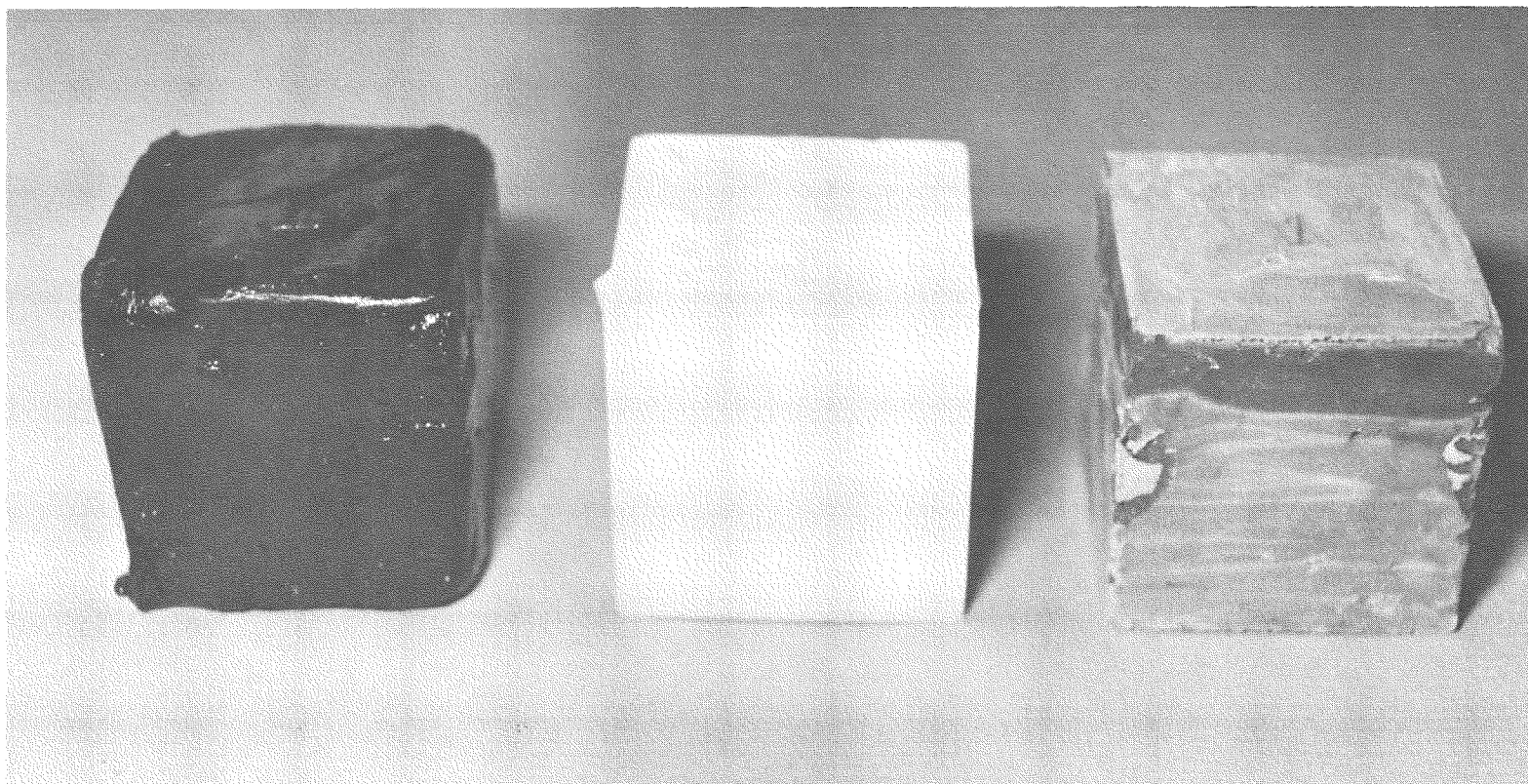


FIGURE 11. Two Inch Cube Leach Test Specimens (Bitumen, Urea-Formaldehyde, and Cement)

Neg. No. 773440-4 CN

Five series of leach measurements were made as listed briefly below:

1. Pressed pellets, urea-formaldehyde, and cement containing acid digestion residue with added uranyl nitrate were tested for uranium leach rates. Results of the tests are given in Table 6.
2. Urea-formaldehyde, bitumen, and cement containing anion exchange resin and uranyl nitrate were tested for uranium leach rates. Results of the tests are listed in Table 7.
3. Boric acid or sodium sulfate residues containing cesium chloride and strontium nitrate were immobilized in cement, bitumen, and urea-formaldehyde. These solids were tested for cesium and strontium leach rates and the results are given in Table 8.
4. Finely powered anion resin intermixed with cesium chloride and strontium nitrate was immobilized with cement, urea-formaldehyde, and bitumen. These solids were tested for cesium and strontium leach rates and the results are given in Table 9.
5. Sodium nitrate containing cesium chloride and strontium nitrate was immobilized in cement, bitumen, and urea-formaldehyde. These solids were kept sealed in their conical plastic molds, leaving only the top surface exposed. Strontium and cesium leach rates were measured and results are given in Table 11.

The results indicate that cement solids and pressed and sintered pellets exhibit the lowest leach rates for the immobilization of uranyl nitrate. Bitumen products exhibited intermediate uranium leach characteristics, and urea-formaldehyde and pressed pellets of acid digestion process residue without treatment exhibited the highest uranium leach rates.

Bitumen products exhibited the lowest leach rates for cesium and strontium. Cement exhibited intermediate cesium and strontium leach rates, except with boric acid residue solids, where a very high (poor) leach rate was

TABLE 6

LEACH TESTS ON IMMOBILIZED ADTU RESIDUE CONTAINING 10 WT% $\text{UO}_2(\text{NO}_3)_2$ ^(a)

Sample No.	Sample	ADTU Content (wt%)	Weigh, g	Volume, cm ³	Surface Area, cm ²	Cumulative Fraction Leached x (V/S), cm ^(b)	Average Leach Rate, g/cm ² -d ^(b)
UPA	Pellet pressed at 700 kg/cm ² and sintered at 900°C for 30 min.	100	104	65	97	2.68×10^{-1}	3.93×10^{-2}
UPB	Doubly pressed and sintered pellet	100	100	49	86	1.20×10^{-1}	1.83×10^{-2}
UPC	Pellet pressed and sintered with reductant ^(c) (12 day test only)	92	122	49	86	7.98×10^{-4}	1.48×10^{-4}
UUFA	Urea-formaldehyde (1 vol. U-F, 1 vol. ADTU residue, no catalyst)	40	120	100	~125	1.84×10^{-1}	1.67×10^{-2}
UUFB	Urea-formaldehyde (1 vol. U-F, 2 vol. ADTU residue, no catalyst)	67	130	100	~129	2.79×10^{-1}	2.84×10^{-2}
UCA	Type II portland cement (38 wt% water, 35 wt% cement, 25 wt% ADTU & 2 wt% sodium hydroxide)	25	182	100	~133	6.80×10^{-4}	9.8×10^{-5}
UCB	Epoxy water-proofed cement 18 wt% epoxy, 19 wt% ADTU, 29 wt% cement, 32 wt% water, & 2 wt% sodium hydroxide)	19	162	100	~133	$< 8 \times 10^{-4}$	9.7×10^{-6}

(a) ADTU residue is, in general, a mixture of metal oxides, sulfates, and clays resulting from acid digestion of combustible wastes in the acid digestion test unit discussed in section IV of this report.

(b) After 14 days leaching except as noted.

(c) Aluminum powder - 8% by weight.

TABLE 7

URANYL NITRATE LEACH RATES FROM IMMOBILIZED ANION RESIN PRODUCTS

Sample Number	Immobilizing Agent	Composition, % ^(b)			Sample Weight, g	Sample Volume, cm ³	Surface Area, cm ²	Uranium in Sample, g	Cumulative Fraction Leached x (V/S), ^(d) cm	Leach Rate, g/cm ² -day	
		Agent	Resin ^(c)	Water						First Day	Average
1	U-F ^(a)	50	50	0	137	110	130	7.34	1.33×10^{-1}	4×10^{-2}	1×10^{-2}
2	U-F	33	33	34	121	110	130	4.40	1.77×10^{-1}	1×10^{-1}	2×10^{-2}
3	Bitumen	59	51	0	109	105	125	4.40	1.80×10^{-2}	1×10^{-2}	2×10^{-3}
4	Bitumen	57	43	0	91	90	110	5.14	4.7×10^{-2}	3×10^{-2}	4×10^{-3}
5	Cement	46	46	8	189	110	130	7.34	8.0×10^{-5}	9×10^{-5}	2×10^{-5}
6	Cement	43	43	12	178	110	130	7.34	8.0×10^{-7}	6×10^{-5}	2×10^{-6}

(a) Urea-formaldehyde.

(b) Volume percent for U-F; weight percent for bitumen and cement.

(c) Dowex -1x8 Anion exchange resin; 200-400 mesh.

(d) During 14 day leach period in ambient distilled water.

TABLE 8

LEACH RATES OF CESIUM AND STRONTIUM FROM IMMOBILIZED BORIC ACID AND SODIUM SULFATE PRODUCTS

Sample No.	Immobilizing Agent	Water, Wt%	Boric Acid Content, Wt%	Sodium Sulfate Content, Wt%	Sample Characteristics			Cumulative Fraction Leached x (V/S), cm		Average Leach Rate, g/cm ² -day	
					Weight, g	Volume, cm ³	Surface Area, cm ³	Cesium	Strontium	Cesium	Strontium
11	Cement		11.1	--	114	90	20	4.5	3.8×10^{-1}	3.95×10^{-1}	3.37×10^{-2}
12	"		9.1	--	154	90	20	3.2	4.0×10^{-1}	3.91×10^{-1}	4.78×10^{-2}
13	"		7.6	--	190	90	20	2.0	2.3×10^{-1}	2.92×10^{-1}	3.34×10^{-2}
21	"		--	10.6	130	90	20	2.4	1.4×10^{-2}	2.40×10^{-1}	9.30×10^{-3}
22	"		--	7.7	189	90	20	8.1×10^{-1}	1.4×10^{-2}	1.20×10^{-1}	2.14×10^{-3}
23	"		--	6.1	217	110	23	5.2×10^{-1}	1.0×10^{-2}	8.33×10^{-2}	1.65×10^{-3}
31	"		--	12.3	105	90	20	3.3	1.5×10^{-2}	2.74×10^{-1}	7.99×10^{-4}
32	"		--	9.3	165	90	20	1.1	1.4×10^{-2}	1.44×10^{-1}	1.78×10^{-3}
33	"		--	7.5	187	90	20	5.6×10^{-1}	1.5×10^{-2}	8.24×10^{-2}	2.21×10^{-3}
AA	Bitumen		30.9	--	102	90	20	8.8×10^{-2}	5.8×10^{-2}	7.03×10^{-3}	4.64×10^{-3}
AB	"		46.0	--	75	90	20	1.8×10^{-2}	2.8×10^{-2}	1.06×10^{-3}	1.67×10^{-3}
AC	"		18.5	--	100	90	20	1.5×10^{-2}	1.9×10^{-2}	1.19×10^{-3}	1.46×10^{-3}
UF1	Urea- Formaldehyde		23.8 ^(b)	--	108	90	117	5.5×10^{-1}	9.7×10^{-2}	4.70×10^{-2}	8.33×10^{-3}
UF2	"		47.6	--	127	90	117	3.2×10^{-1}	8.5×10^{-2}	3.19×10^{-2}	8.53×10^{-3}
UF3	"		57.7	--	119	90	117	3.4×10^{-1}	1.1×10^{-1}	3.23×10^{-2}	1.00×10^{-2}
UF4	"		48.4	--	129	90	117	3.0×10^{-1}	7.4×10^{-2}	3.10×10^{-2}	7.62×10^{-3}

(a) After 14 days leaching.

(b) Plus 23.8 wt% added water.

TABLE 9

LEACH RATE OF CESIUM AND STRONTIUM FROM IMMOBILIZATION RESIN SAMPLES

Sample No.	Material Description ^(a)	Density (g/cm ³)	Cumulative Fraction Leached x (V/S), cm ^(b)		Average Leach Rate, g/cm ² -day	
			Cesium	Strontium	Cesium	Strontium
C-1	Cement ^(c)	1.83	4.67×10^{-1}	6.1×10^{-2}	3.96×10^{-2}	5.2×10^{-3}
C-2	Cement ^(c) with 14.3% Anion Resin	1.74	6.95×10^{-1}	8.6×10^{-2}	2.33×10^{-1}	2.9×10^{-2}
C-3	Cement ^(c) with 23.5% Anion Resin	1.82	6.62×10^{-1}	8.6×10^{-2}	2.48×10^{-1}	3.2×10^{-2}
UF-1	Urea-Formaldehyde (UF)	1.17	5.10×10^{-1}	4.26×10^{-2}	2.30×10^{-1}	1.9×10^{-2}
UF-2	UF with 17.9% Anion Resin	1.13	1.00	$1.36 \times 10^{-1(d)}$	4.63×10^{-1}	3.7×10^{-2}
UF-3	UF with 30.1% Anion Resin	0.96	1.00	$1.15 \times 10^{-1(d)}$	4.39×10^{-1}	3.0×10^{-2}
AS-1	Pioneer-221 Asphalt (Bitumen)	1.04	1.35×10^{-2}	9.9×10^{-4}	1.18×10^{-2}	8.6×10^{-4}
AS-2	Bitumen with 31.3% Anion Resin	1.05	2.11×10^{-2}	1.6×10^{-3}	1.69×10^{-2}	3.6×10^{-3}
AS-3	Bitumen with 46.9% Anion Resin	1.08	9.47×10^{-2}	7.1×10^{-3}	8.45×10^{-2}	6.4×10^{-3}

(a) Samples were two inch cubes; volume = 131 cm³

The resin was 200-400 mesh, Dowex-1x8 strong base anion resin.

(b) After 14 days leaching.

(c) Portland type II cement.

(d) The cesium was essentially leached out in 7, rather than 14 days, so the comparative values given for strontium are 7 day leach rate averages.

exhibited. Urea-formaldehyde solids generally exhibited the highest (poorest) leach rates for cesium and strontium.

In general, the leach rates decreased rapidly during the first few days of the leach tests. The cesium and strontium leach data shown in Figure 12 and Table 10 are typical of the results obtained as a function of time (these data are for sample C-2 listed in Table 9).

Figure 13 indicates that there can be a direct relationship between the extent of leaching of a solid and the percent waste residue added to the solid. The figure shows that the quantity of cesium leached from the bitumen is linearly related to the weight percent of sodium nitrate added to this set of bitumen samples. These data, together with data for urea-formaldehyde and cement samples, are given in Table 11. These tests were made under Series 5 conditions (e.g., only one end surface exposed). The Series 5 tests approximated the conditions of the recommended IAEA leach test.⁽⁵⁾ The method seemed to work well for cement and bitumen samples, since they bonded tightly to the plastic forms. However, urea-formaldehyde samples shrank away from the forms and exposed the whole surface. The resulting data were corrected for this, but it was concluded that comparative tests could best be made with all surfaces exposed to the leachant. Additional tests with different sized cubical samples are being used to test scale-up factors for extrapolation to full sized solidified blocks (e.g. 200 liter drums). The cubical shape is readily adaptable to theoretical evaluation of diffusion processes involved in the leaching process.

D. LABORATORY TREATMENT OF ILW CONTAINING VOLATILE CONTAMINANTS

J. A. Partridge, G. P. Bosuego

Mercuric nitrate - nitric acid scrub solutions are used in nuclear fuel reprocessing flowsheets for removal of iodine from dissolver off-gas streams. The resulting solutions become an intermediate level liquid waste containing radioiodine. Composition of the scrub solutions may range from 610 M HNO_3 containing 0.1 - 0.4 M $\text{Hg}(\text{NO}_3)_2$. Both mercury and iodine will potentially volatilize during evaporation of these solutions prior to waste immobilization. Consequently, reprocessing plants plan to solidify this stream separately with no volume reduction.

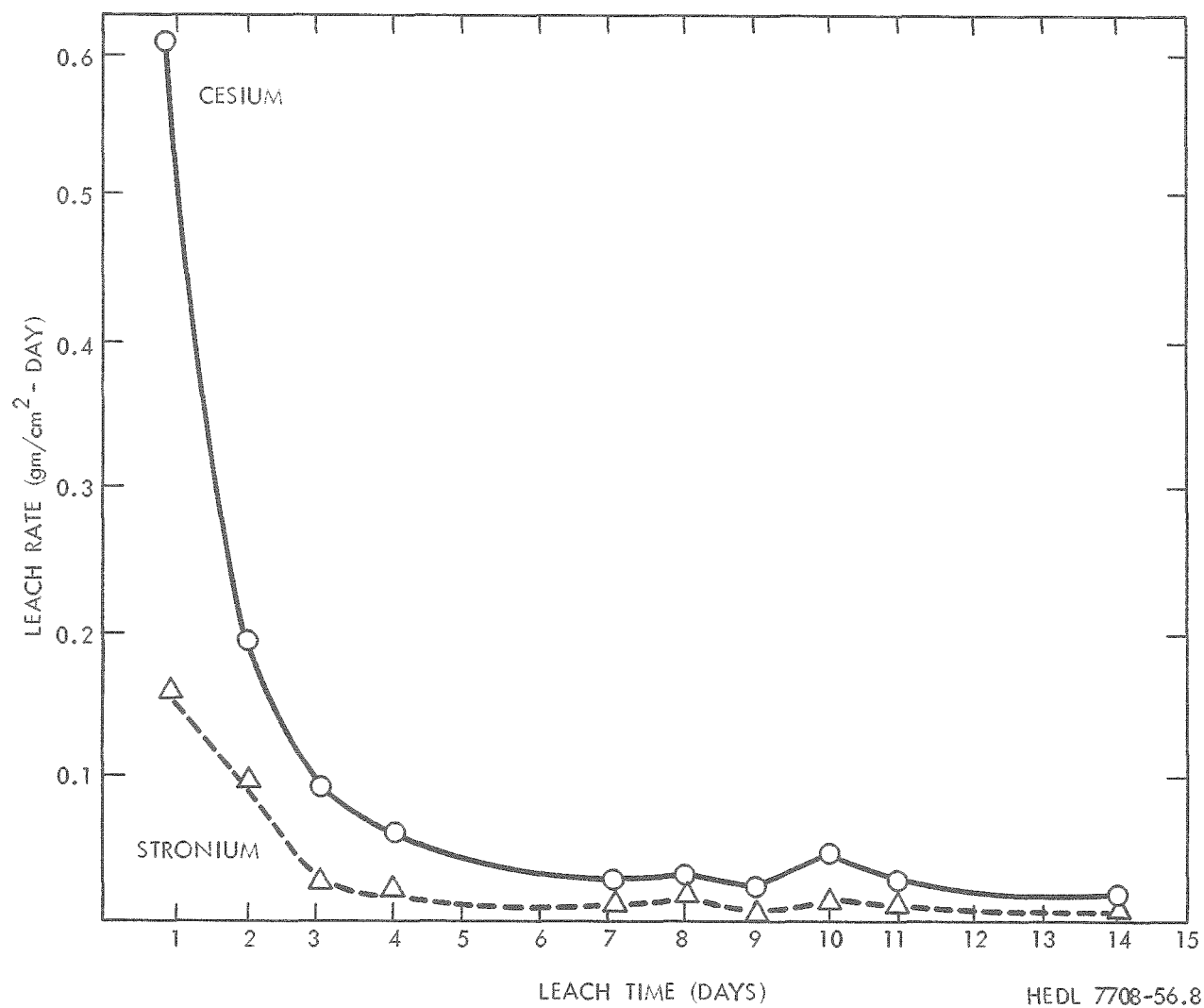


FIGURE 12. Cesium and Strontium Leach Rates in Simulated Cement-Waste Product Containing Anion Exchange Resin.

TABLE 10

CESIUM AND STRONTIUM LEACH RATES DETERMINED
IN A SIMULATED ION EXCHANGE RESIN - CEMENT WASTE SOLID^(a)

Sample Composition: 57 wt% cement, 23 wt% water, 14 wt% anion resin (Dowex 1x8; 200-400 mesh),
3 wt% cesium chloride, 3 wt% strontium nitrate.

Sample Weight: 228 g

Sample Volume: 131 cm³

Sample Surface Area: 155 cm²

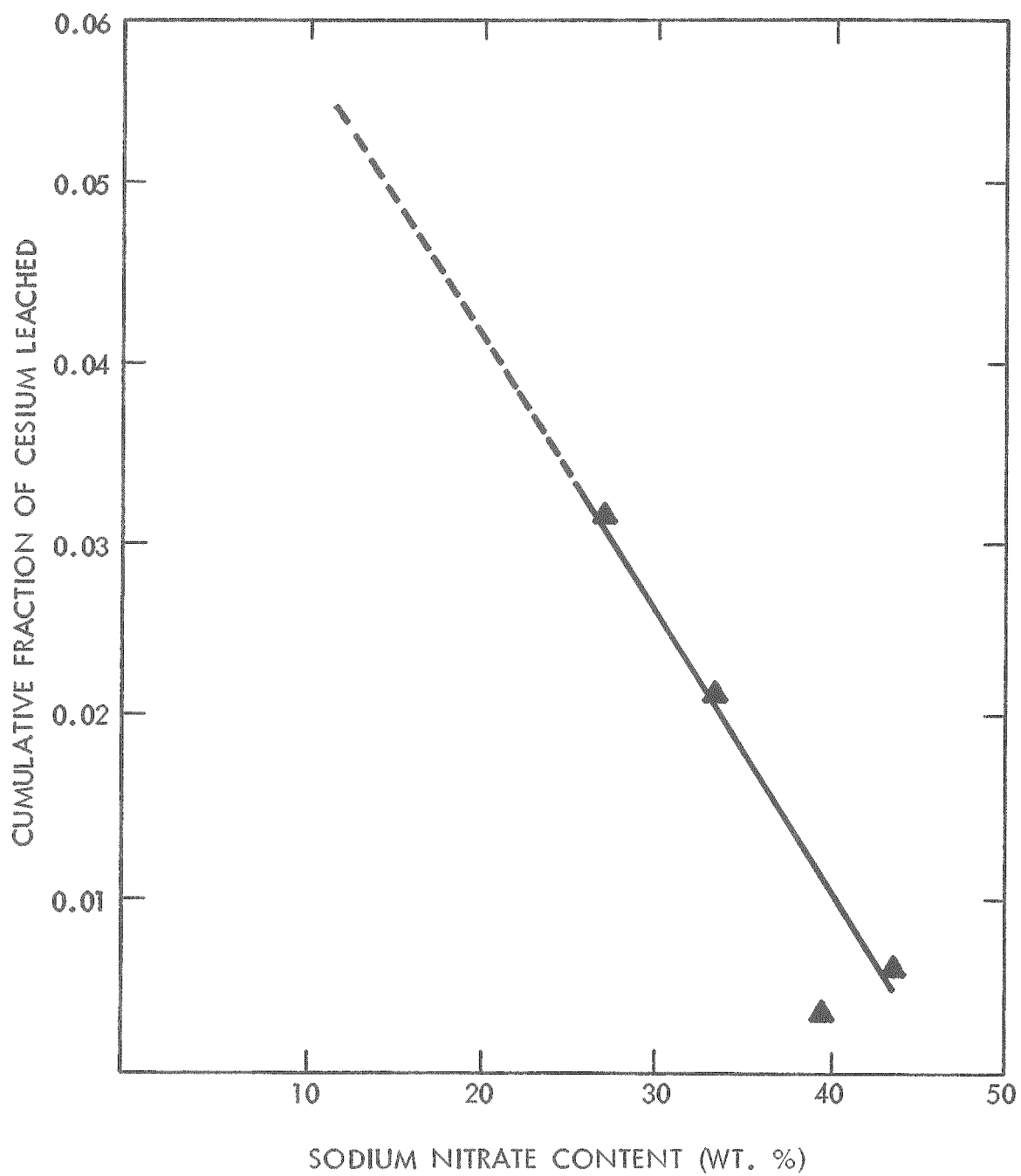
Curing Time: 7 days

Leachant: distilled water

Leachant replacement interval: daily (except weekends)

Leach Time, Days		Incremental Fraction		Cumulative Fraction		Average Leach Rate	
Incremental, t_n	Cumulative, $\sum t_n$	Leached $\times (V/S)$, cm Cesium	Strontium	Leached $\times (V/S)$, cm Cesium	Strontium	g/cm^2 -day Cesium	Strontium
1	1	3.49×10^{-1}	9.30×10^{-2}	3.49×10^{-1}	9.30×10^{-2}	6.1×10^{-1}	1.6×10^{-1}
1	2	1.10×10^{-1}	5.58×10^{-2}	4.59×10^{-1}	1.49×10^{-1}	1.9×10^{-1}	9.7×10^{-2}
1	3	4.99×10^{-2}	1.77×10^{-2}	5.09×10^{-1}	1.66×10^{-1}	8.7×10^{-2}	3.1×10^{-2}
1	4	3.47×10^{-2}	1.35×10^{-2}	5.44×10^{-1}	1.80×10^{-1}	6.0×10^{-2}	2.4×10^{-2}
3	7	4.97×10^{-2}	1.52×10^{-2}	5.93×10^{-1}	1.95×10^{-1}	2.9×10^{-2}	9.0×10^{-3}
1	8	1.86×10^{-2}	6.76×10^{-3}	6.12×10^{-1}	2.02×10^{-1}	3.2×10^{-2}	1.9×10^{-2}
1	9	1.18×10^{-2}	3.38×10^{-3}	6.24×10^{-1}	2.05×10^{-1}	2.1×10^{-2}	5.9×10^{-3}
1	10	2.54×10^{-2}	8.45×10^{-3}	6.49×10^{-1}	2.14×10^{-1}	4.4×10^{-2}	1.5×10^{-2}
1	11	1.35×10^{-2}	7.61×10^{-3}	6.63×10^{-1}	2.21×10^{-1}	2.4×10^{-2}	1.3×10^{-2}
3	14	3.13×10^{-2}	1.18×10^{-2}	6.94×10^{-1}	2.33×10^{-1}	1.8×10^{-2}	6.8×10^{-3}

(a) Sample C-2, Table 9.



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FIGURE 13. The Leaching of Cesium from Bitumen as a Function of Sodium Nitrate Content.

TABLE 11

LEACH RATES OF CESIUM AND STRONTIUM FROM IMMOBILIZED SODIUM NITRATE

Sample Number	Matrix	Water, Wt%	Sodium Nitrate, Wt%	Sample Characteristics			Cumulative Fraction Leached x (V/S), cm ^(a)		Average Leach Rate g/cm ² -day	
				Weight, g	Volume, cm ³	Surface Area, cm ²	Cesium ^(b)	Strontium ^(c)	Cesium	Strontium
UF-1	Urea-Formaldehyde	0	30.5	100	100	125	7.8×10^{-1}	5.8×10^{-2}	6.3×10^{-2}	4.41×10^{-3}
UF-2	"	23.4	23.4	105	100	125	6.1×10^{-1}	3.9×10^{-2}	4.80×10^{-2}	3.02×10^{-3}
UF-3	"	0	46.7	130	110	133	7.8×10^{-1}	4.6×10^{-2}	6.90×10^{-2}	4.10×10^{-3}
UF-4	"	31.8	31.8	120	105	129	6.4×10^{-1}	9.6×10^{-2}	3.80×10^{-2}	5.76×10^{-3}
PC-1	Cement	16.3	37.2	190	100	22	1.16	4.3×10^{-1}	1.57×10^{-1}	5.81×10^{-2}
PC-2	"	15.5	35.6	200	100	22	1.06	2.6×10^{-1}	1.51×10^{-1}	3.66×10^{-2}
PC-3	"	25.4	18.6	200	100	22	6.9×10^{-1}	2.9×10^{-1}	9.84×10^{-2}	4.14×10^{-2}
PC-4	"	24.4	17.8	210	100	22	6.9×10^{-1}	1.3×10^{-1}	1.03×10^{-1}	1.91×10^{-2}
AS-1	Bitumen	0	26.1	150	95	21	1.4×10^{-1}	9.1×10^{-2}	1.03×10^{-2}	6.76×10^{-3}
AS-2	"	0	33.3	165	95	21	1.0×10^{-1}	7.9×10^{-2}	7.58×10^{-3}	5.97×10^{-3}
AS-3	"	0	38.9	180	95	21	1.2×10^{-2}	9.3×10^{-3}	1.27×10^{-3}	9.5×10^{-4}
AS-4	"	0	43.6	195	100	22	2.3×10^{-2}	1.9×10^{-2}	2.4×10^{-3}	1.9×10^{-3}

(a) After 14 days leaching.

(b) Wt% cesium chloride added to original test samples.

(c) Wt% strontium nitrate added to original samples.

Concentration of iodine-containing mercuric nitrate-nitric acid solutions by evaporation at the boiling point at atmospheric pressure is being investigated. In laboratory scale batch evaporation tests conducted in glass apparatus, 9 to 16% of the iodine was volatilized from solutions having initial compositions of 6 M HNO_3 - $0.10\text{ M Hg(NO}_3)_2$ - 0.010 M I^- and 11 M HNO_3 - 0.10 M Hg^{++} - 0.01 M I^- . The data are shown in Table 12. Iodine volatilizes as molecular iodine, which was observed both as iodine crystals in the condenser and as the characteristic iodine color in the nitric acid condensate. Most of the iodine evolution occurred during the first half of the volume reduction.

Iodine is oxidized to iodate by moderate to strong nitric acid at elevated temperature. This fact was utilized a few years ago, for example, at ORNL in studies on a method for recycling a mercuric nitrate - nitric acid scrub solution back to the iodine scrub system.⁽⁸⁾ The technique involved heating the scrub solution batch-wise to boiling under total reflux conditions to convert the mercuric iodide to mercuric iodate and thereby increase the scrubbing efficiency of a recycled scrub solution.

Boiling the simulated scrub stream under total reflux conditions prior to concentration in an effort to more completely oxidize the iodine to non-volatile iodate did not reduce the ultimate loss of iodine from the solution. For example, in the second run listed in Table 12, the solution was boiled under total reflux conditions for 8 1/2 hours, after which 16% of the iodine volatilized during a ten-fold concentration of the solution.

In the batch concentration tests listed in Table 12 a white precipitate, presumably mercuric iodate, formed in the boiling flask during each of the runs.

Work is proceeding on development of a process to reduce the volume of the mercuric nitrate - nitric acid waste solution without loss of iodine. Preliminary results are promising and indicate that volume reductions of at least 10 fold can be achieved with as little as 0.01% of the iodine being volatilized.

TABLE 12
IODINE VOLATILIZATION DURING APPROXIMATELY
TEN-FOLD CONCENTRATION OF MERCURIC NITRATE-
NITRIC ACID SOLUTIONS

Initial Composition, M			% Iodine Volatilized
[HNO ₃]	[Hg(NO ₃) ₂]	[I ⁻]	
6	0.1	0.01	13
6	0.1	0.01	16
11	0.1	0.01	9
15.3	0.1	0.01	0.01 ^(a)

(a) 6-fold concentration.

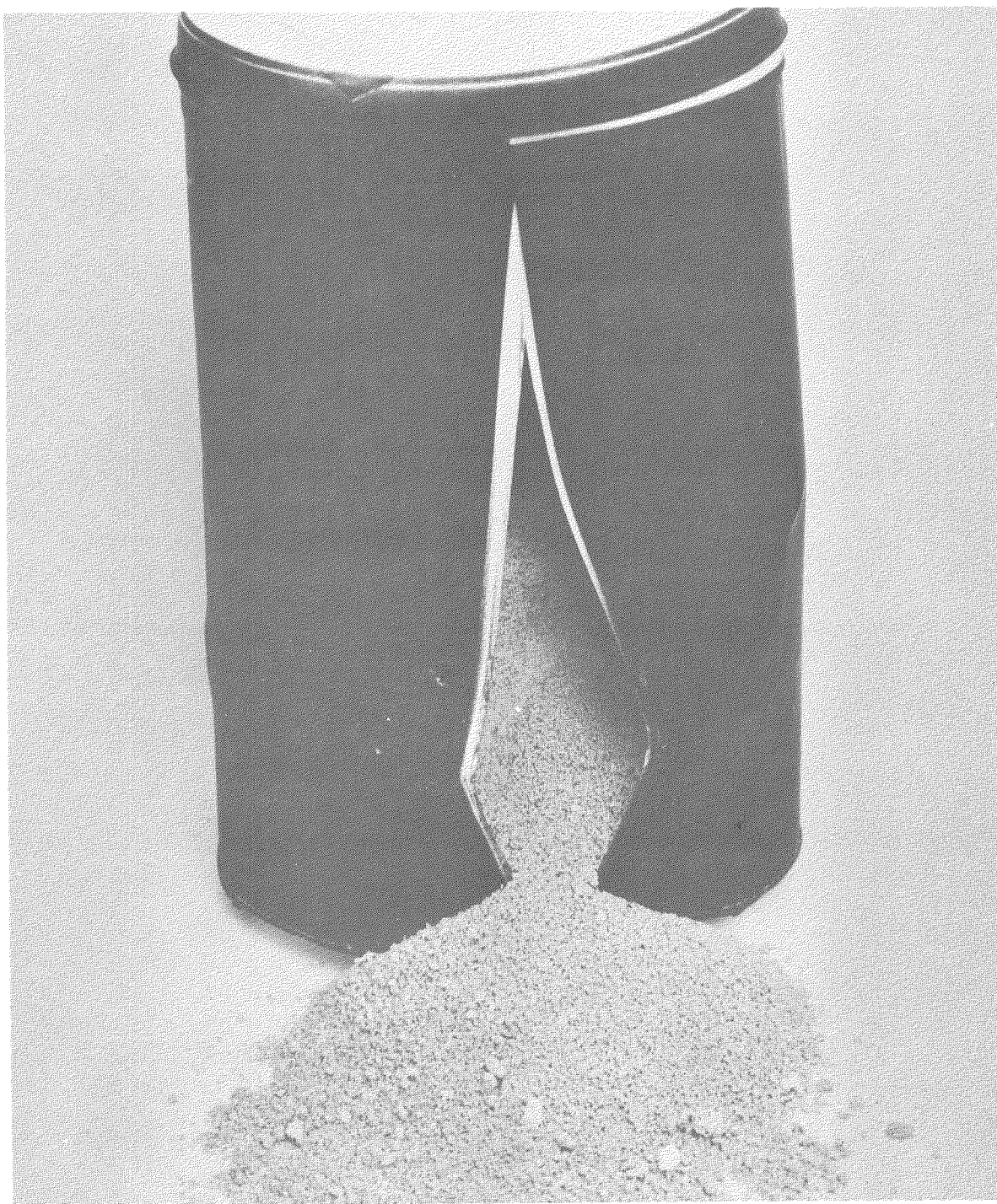
E. RESIN SWELLING IN CEMENT-RESIN IMMOBILIZATION SOLIDS

W. O. Greenhalgh, J. A. Partridge, G. P. Bosuego

A major wet waste arising from the operation of nuclear reactors is ion exchange resin. The resin in cation, anion, and mixed-bed form is used for cleaning up radionuclides from the reactor cooling water. Spent resin is discharged, dewatered, and solidified in either cement or urea-formaldehyde. Previous tests have shown that resin waste solidification efficiencies in cement have been very high (approaching 100%).⁽⁷⁾

Ion exchange resins however, exhibit some properties which might require using a lower waste loading efficiency. Ion exchange resins shrink or swell depending upon their water content, which in turn depends on the resin matrix, the ions loaded, and the temperature. Immobilization of resins changes the chemical and physical environment to which the resins are exposed, possibly causing shrinkage or swelling. Swelling can be a problem after immobilization in cement, particularly if the ratio of resin to cement is high. An example of catastrophic swelling is shown in Figures 14 and 15 wherein the cement was almost completely pulverized. Composition of the particular sample was 43 wt% wet (water had been drained from the resin) anion exchange resin (in chloride form), 38.5 wt% portland type II cement, 16.6 wt% added water, and 1.8 wt% sodium silicate solution (40° Baume) used to accelerate the setting process. This particular anion resin swells about 10% when wetted and about 20% when converted from the chloride form to the hydroxyl form. In the test, the resin was dewatered, mixed with cement and allowed to cure in air. When it was exposed to water after the cure, it swelled and produced forces exceeding the strength of both the metal container and the cement.

Resin swelling upon exposure to water was also noted in some specimens prepared for leach testing. The specimens were free standing solids while dry, but when placed into water, the solid started expanding and fragmenting.



Neg. No. 774195-4 cn

FIGURE 14. Ruptured Can and Pulverized Cement Due to Swelling of Anion Exchange Resin.

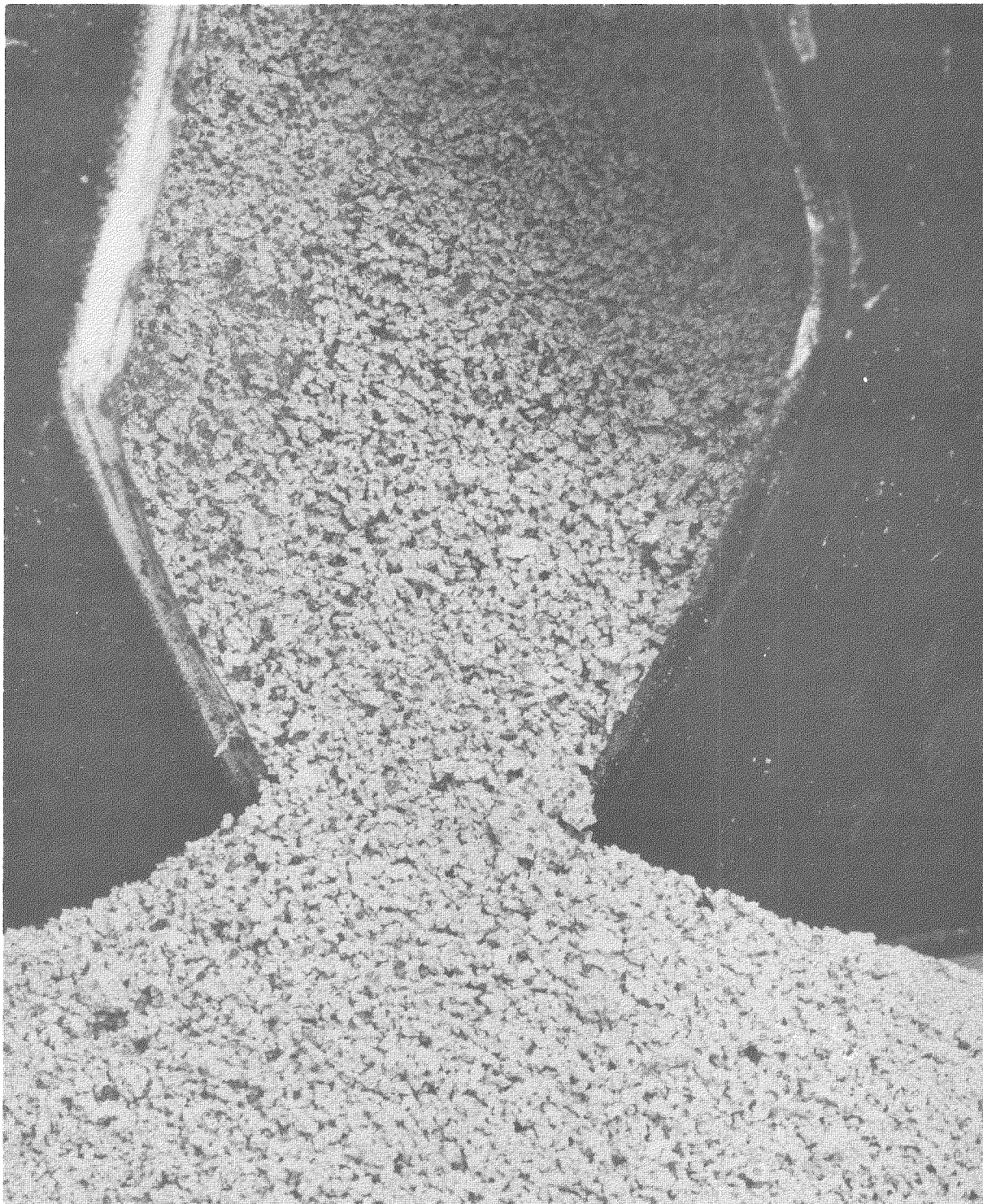


FIGURE 15. Closeup View of Ruptured Can and Pulverized Cement due to Swelling of Anion Exchange Resin.

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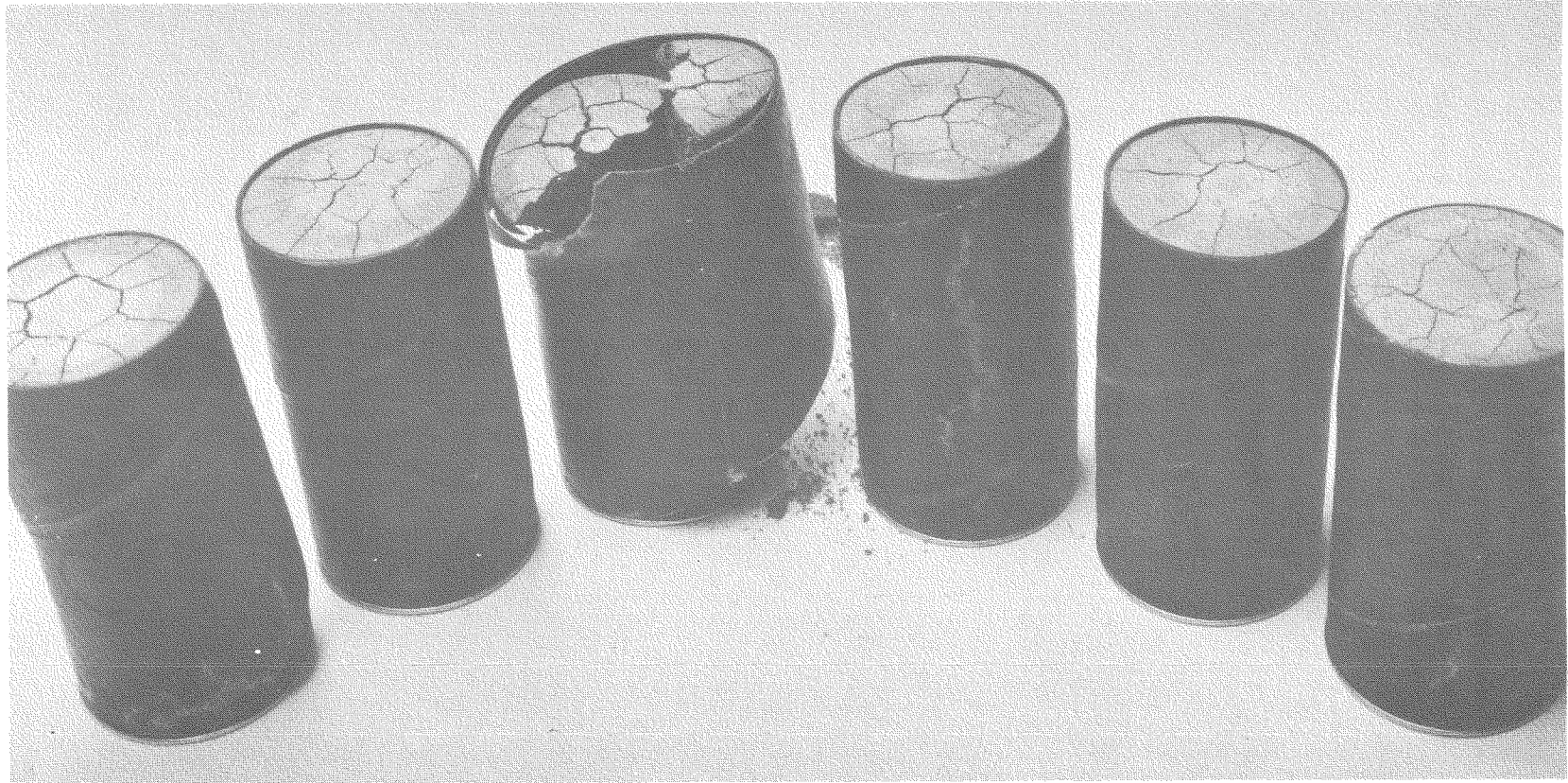
Cation resins also exhibit swelling. A series of cement specimens were prepared and, upon setting and curing, exhibited swelling as shown in Figure 16. All specimens shown exhibited some swelling as evidenced by the expanded seams in the molds.

To quantify the amount and pressure of expansion, three samples were placed in a test meter (shown in Figure 17) which permitted expansion to occur in the vertical direction only. Results of the expansion tests are summarized in Table 13 for the three test specimens. While the final pressure exerted from expansion of the cement-resin samples is small compared to the compression strength of cured concrete-cement [normally about 140-280 kg/cm² (2000-4000 psi) for building concrete], the expansion occurs during setting, preventing the high resin content cement samples from achieving a good strength set.

Drums normally used for waste drum shipping containers for Hanford nuclear operations must withstand a 1.05 kg/cm² (15 psi) hydrostatic test⁽⁹⁾ while DOT 17C drums must withstand a 5-minute hydrostatic test at 1.40 kg/cm² (20 psi)⁽¹⁰⁾. Both could be exceeded for a cement-resin sample under conditions of high resin content or exposure to water after setting. Full scale tests to verify these conclusions are planned.

IV. CHEMICAL PROCESSING OF COMBUSTIBLE SOLID WASTES (KX-03-04-02)

The objective of this program is to develop and demonstrate the acid digestion process for the treatment of combustible nuclear wastes. Acid digestion is a chemical process for oxidizing combustible waste materials in concentrated acid. Waste materials are added to concentrated sulfuric acid at 250°C. The acid attacks the waste producing a char which is subsequently oxidized by nitric acid. Digestion of the waste produces a residue of inorganic sulfates or oxides which are insoluble in the acid and which can be separated as a dry residue by evaporation of the excess sulfuric acid at 350°C.



Neg. No. 2335-20N

FIGURE 16. Cement-Cation Resin Swelling Specimens (Dimensions 7.5 cm x 15 cm).

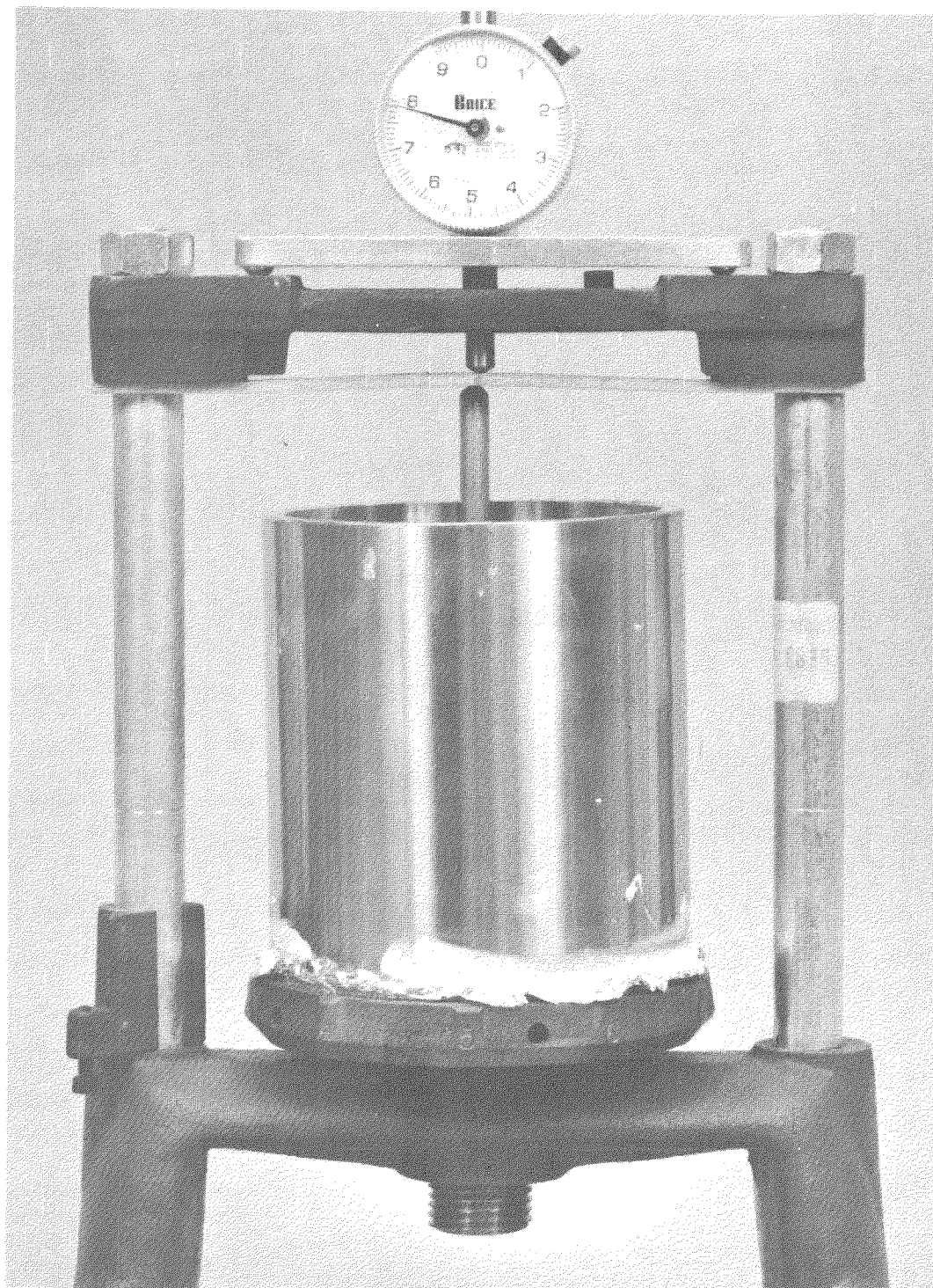


FIGURE 17. Cement Expansion Strength Measuring Device, California Type.

TABLE 13

EXPANSION OF RESIN-CEMENT TEST SAMPLES

Sample	Curing Time, days (a)	Expansion		Expansion Pressure kg/cm ²	Test Period, days
		mm	% (b)		
48 wt% anion resin (Dowex-SAR, chloride form, 40-60 mesh), dewatered (~45% moisture content)	3	1.09	1.33	0.98	8
24 wt% cement		0.41 ^(c)	0.49	1.34 ^(d)	3
28 wt% added water					
48 wt% anion resin (Dowex-SAR, chloride form, 40-60 mesh), dewatered (~45% moisture content)	0	4.27	5.17	1.90	13
24 wt% cement					
28 wt% added water					
49.6 wt% cation resin (Amberlite-200, sodium form, 40-60 mesh), dewatered (~45% moisture content)	0	2.54	3.08	2.32	13
25.2 wt% cement					
25.2 wt% added water					

(a) Time samples allowed to cure before start of measurement.

(b) Ratio of mm expansion to length of sample, times 100.

(c) Additional expansion after addition of 7-1/2 wt% water to sample.

(d) Final pressure after expansion from addition of water.

Development of the acid digestion process has progressed from laboratory scale tests to cold engineering scale tests which have been conducted in the Acid Digestion Test Unit. Primary activities during this report period have involved construction of an engineering scale unit to demonstrate the process with radioactive wastes. The unit, called the Radioactive Acid Digestion Test Unit (RADTU) is located in the 234-5Z Building, 200 West Area at Hanford.

A. RADIOACTIVE ACID DIGESTION TEST UNIT (RADTU) PROJECT (EAP-061)

C. R. Allen, R. G. Cowan, M. D. Crippen

Construction of the RADTU facility was completed in June, 1977. The 100 kg/day capacity of RADTU is adequate to handle all Hanford 300 Area transuranic wastes. The project was completed on schedule and within the estimated cost. Cold shakedown testing of the unit will begin during the next report period.

A detailed discussion of the design features of the RADTU facility was presented in the previous progress report.⁽⁷⁾ The unit was fabricated in modular units which were then moved to the 234-5Z Building for final assembly. Equipment was installed within the gloveboxes prior to shipment to the construction site to minimize labor requirements in a controlled radiation zone. Modules in various stages of construction are shown in Figures 18 through 25. Figure 18 shows the digestion module with pre-installed equipment, being unloaded at the construction site. Figure 19 shows the same module with the installed equipment in place in the process area.

Some of the features of the RADTU installation are illustrated in a series of photographs. An overall view of the process is shown in Figure 20. Figure 21 shows the feed preparation hood in which the wastes are hand sorted, shredded, and prepared for feeding to the digester. This glovebox has a nitrogen atmosphere to preclude an ignition of the waste. It has a hydrocarbon sensor to detect highly volatile combustible materials. It also contains the shredder which comminutes and mixes the waste materials.



FIGURE 18. Waste Digester Module with Equipment in Place During Unloading at RADTU Facility.

Neg. No. 773384-12

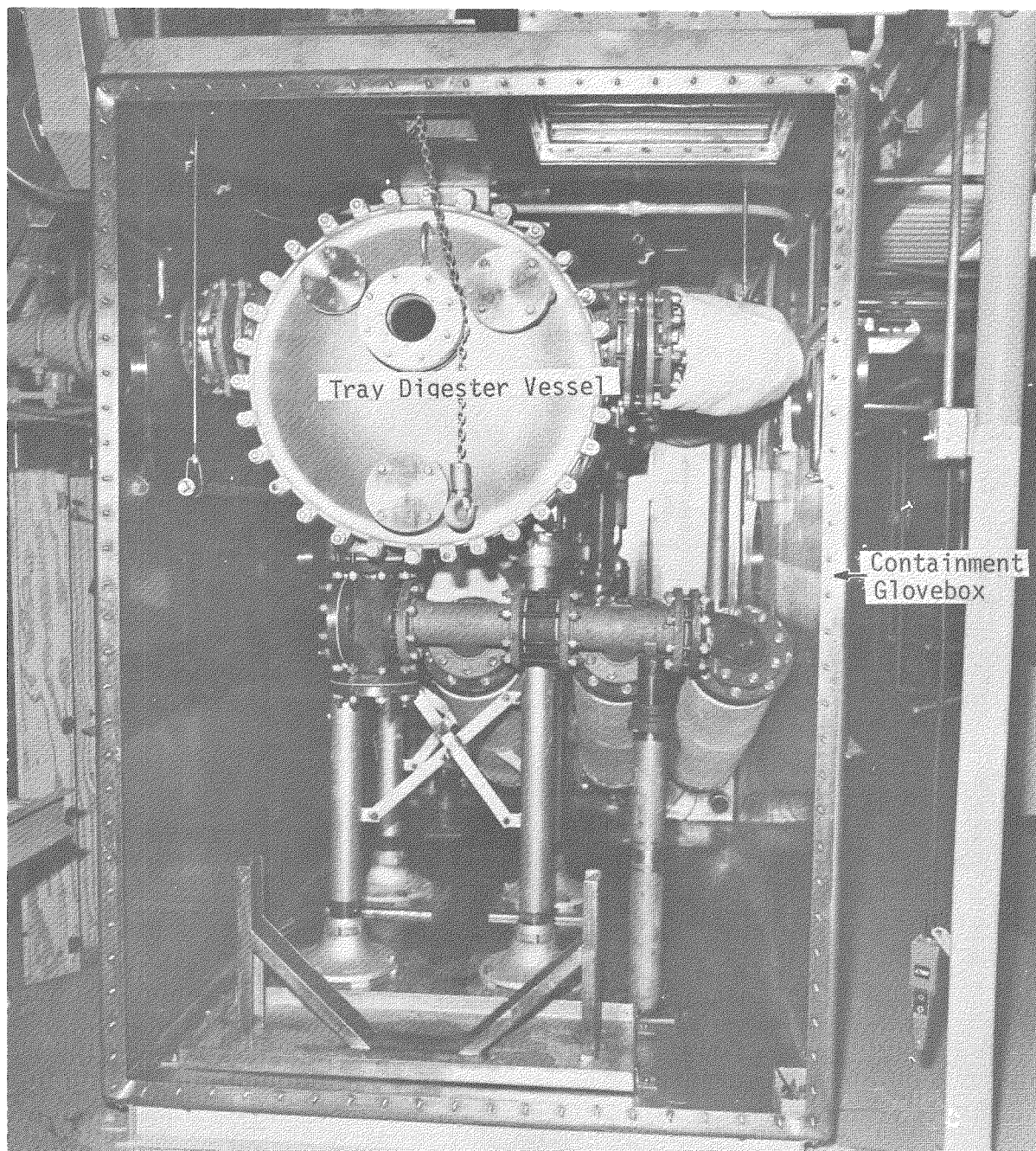


FIGURE 19. Waste Digester in Place in RADTU Facility.

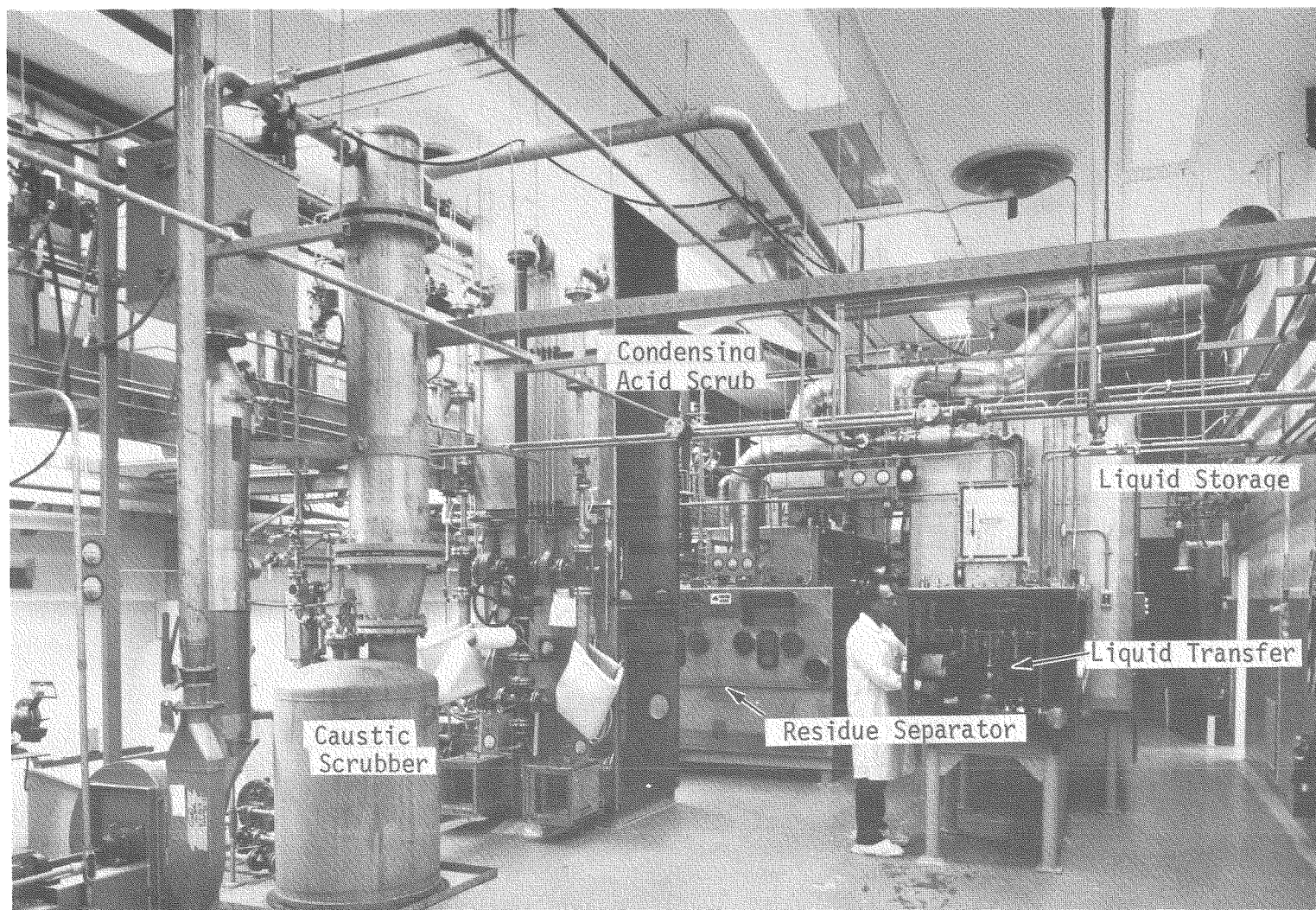


FIGURE 20. Back Portion of RADTU Facility Showing Nonradioactive Caustic Scrubber (on left), Acid Scrub Tower (in center), Residue Separation Hood, and Liquid Transfer Glovebox.

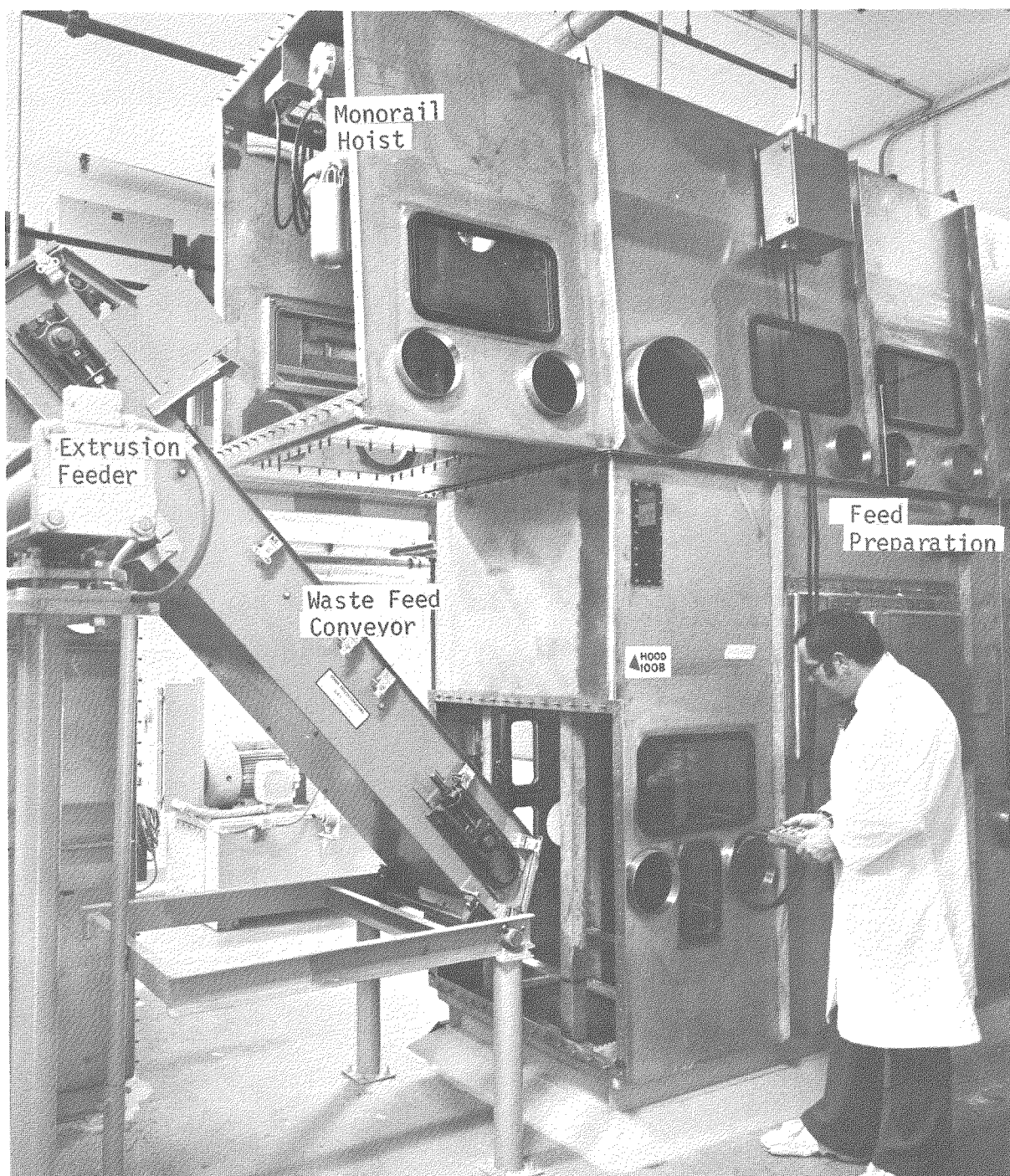


FIGURE 21. Front Side of Waste Preparation Hood Showing Waste Feed Conveyor and Extrusion Feeder.

77C192-1

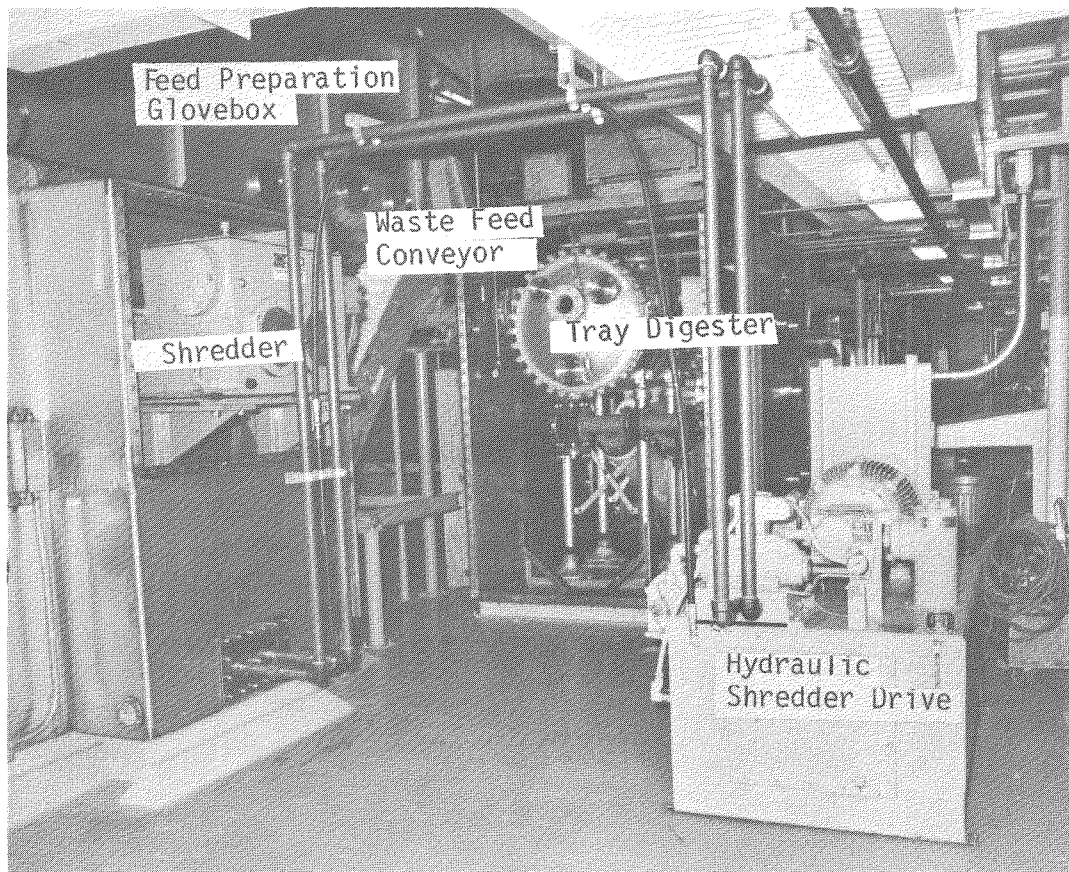
The waste shredder is a heavy duty machine which has been tested in the non-radioactive acid digestion system during the past year. Its heavy duty nature means that the machine is not taxed during the shredding of the combustible materials and occasional tramp metal which may be in the waste. Under these conditions, it is expected that the equipment will require minimal maintenance.

The shredded waste material is passed into a flighted conveyor which can also be seen in Figure 21. The flighted conveyor delivers an increment of waste into the opening of the extrusion feed assembly which is also shown in the same figure. The extrusion feed system delivers an increment of waste to the digester. This arrangement controls the mass of material which can be introduced into the digester at any one time. The combination of shredder, conveyor and extruder provides a safeguard against the inadvertent introduction of a large mass of highly reactive chemicals into the system.

The main digester vessel is shown in Figures 19 and 22. One of the significant features of this module is that it has no moving parts. The acid is recirculated by means of a gas lift. Provision has been made for ready inspection of the internal components and removal of the tray.

The off-gas treatment for the RADTU system is illustrated in Figures 23 and 24. The first unit is a packed column which operates as a condensing acid scrubber. Air is introduced into the off-gases as they enter the scrubber to facilitate the oxidation of the oxides of nitrogen and sulfur to nitric and sulfuric acids. The absorbed nitric and sulfuric acids are concentrated and reused in the digester. The second scrubber tower, shown in Figure 23, will function as a final acid recovery scrubber for NO_x . The scrubber is constructed of stainless steel. For operational simplicity, the only items of equipment with moving parts, the recirculation pump for each scrubber, have been placed in a separate glovebox which has been provided with ready access for maintenance.

The final glovebox in the process system is shown in Figure 25. The interior of this glovebox is shown in Figure 26. The glovebox contains most



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FIGURE 22. Front Portion of RADTU with Waste Preparation Hood (on Left), Digester Module (in Center), and Hydraulic Drive for Shredder (on Right).

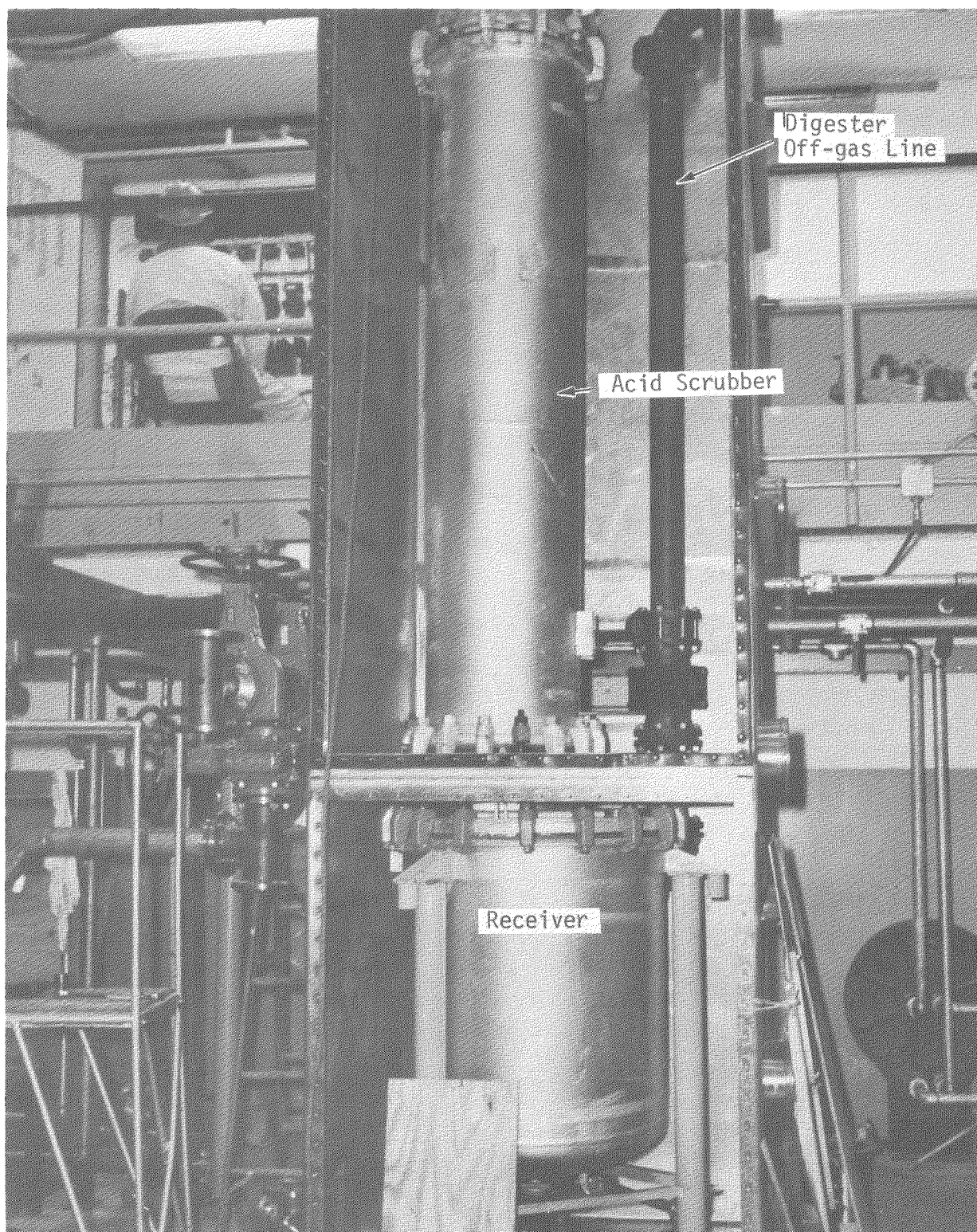


FIGURE 23. Acid Scrubber and Hood During Field Assembly.

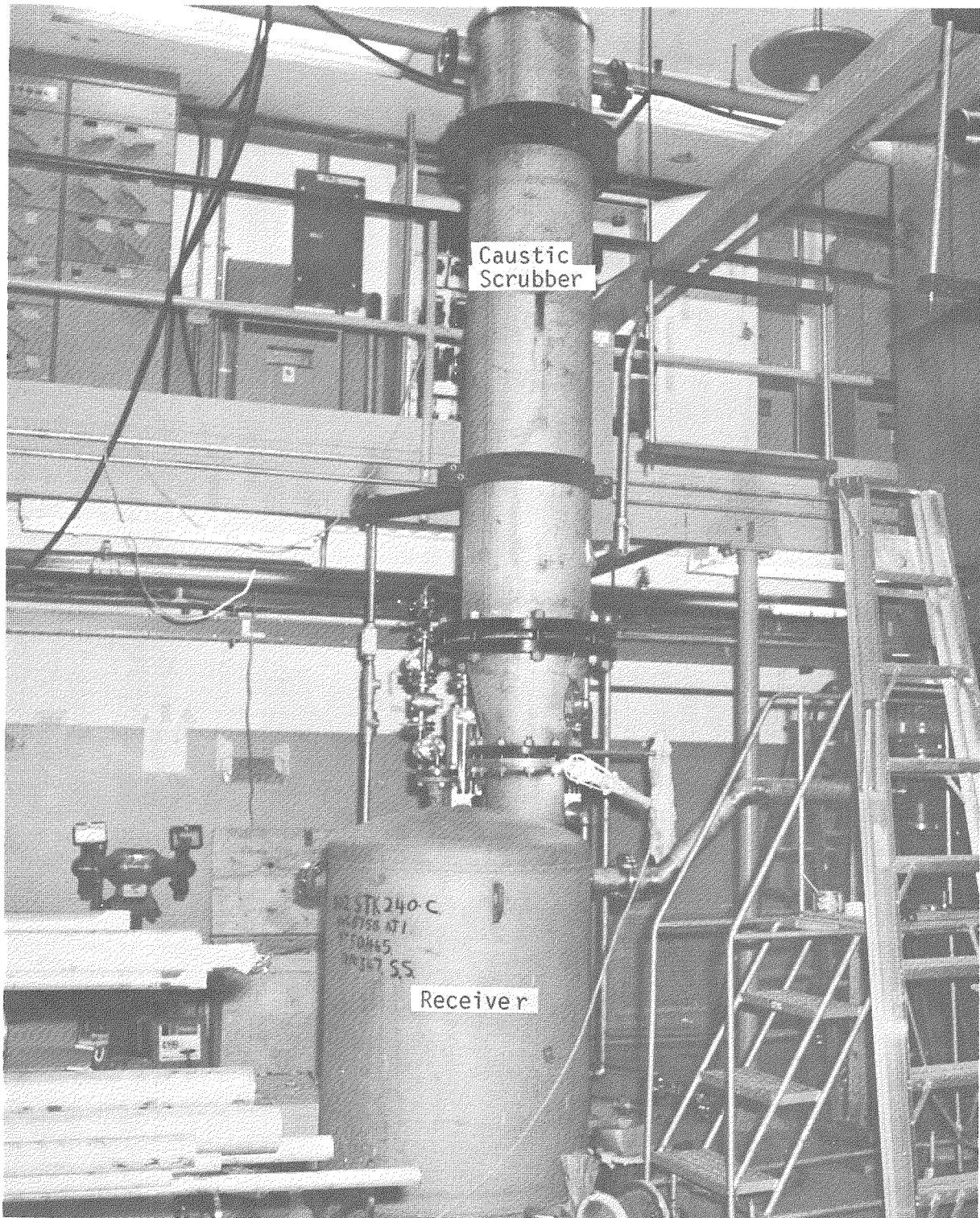


FIGURE 24. Caustic Scrubber During Assembly in RADTU Facility.

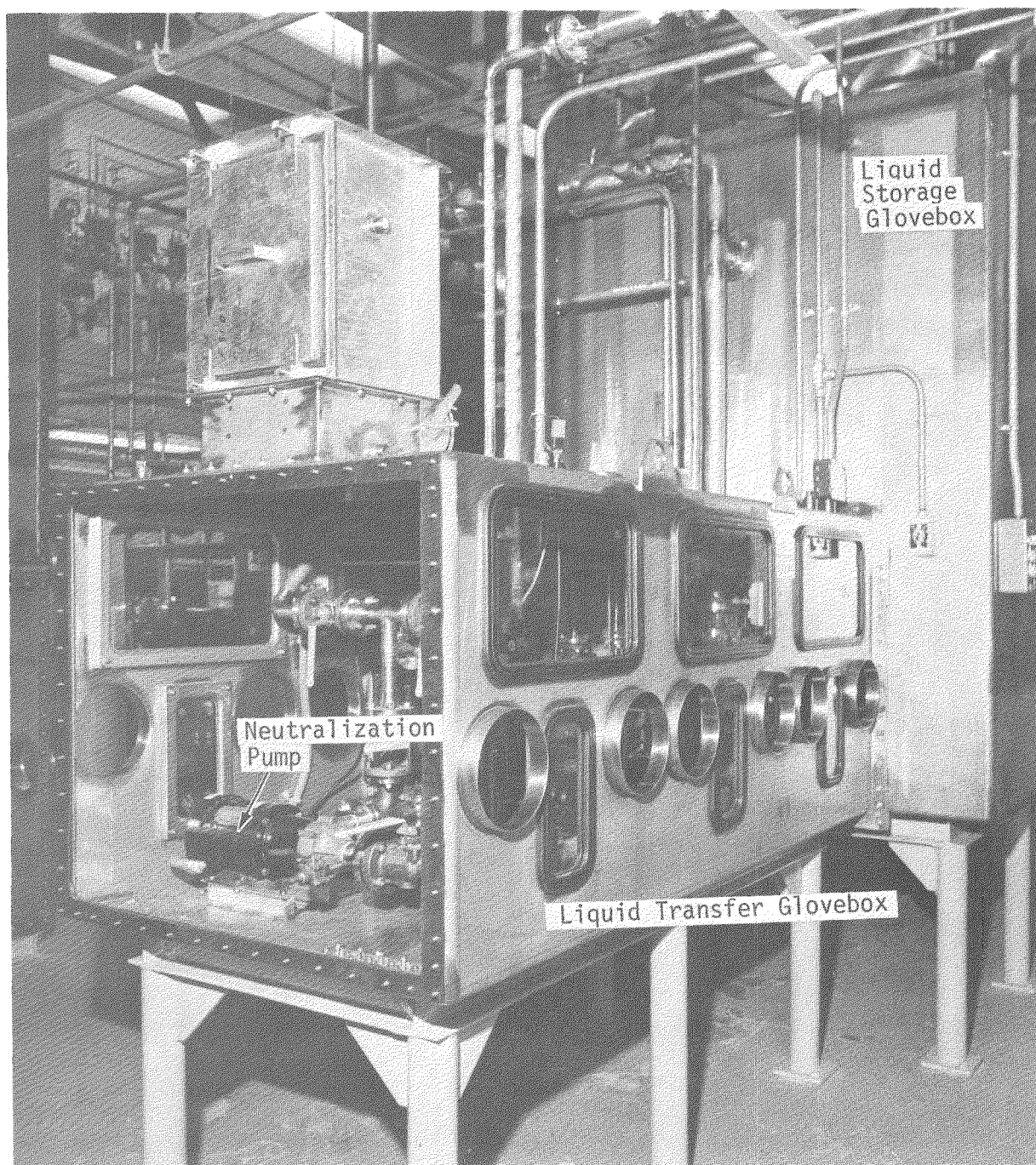


FIGURE 25. Liquid Transfer Glovebox Containing Radioactive Solution Pumps in Place in RADTU Facility.

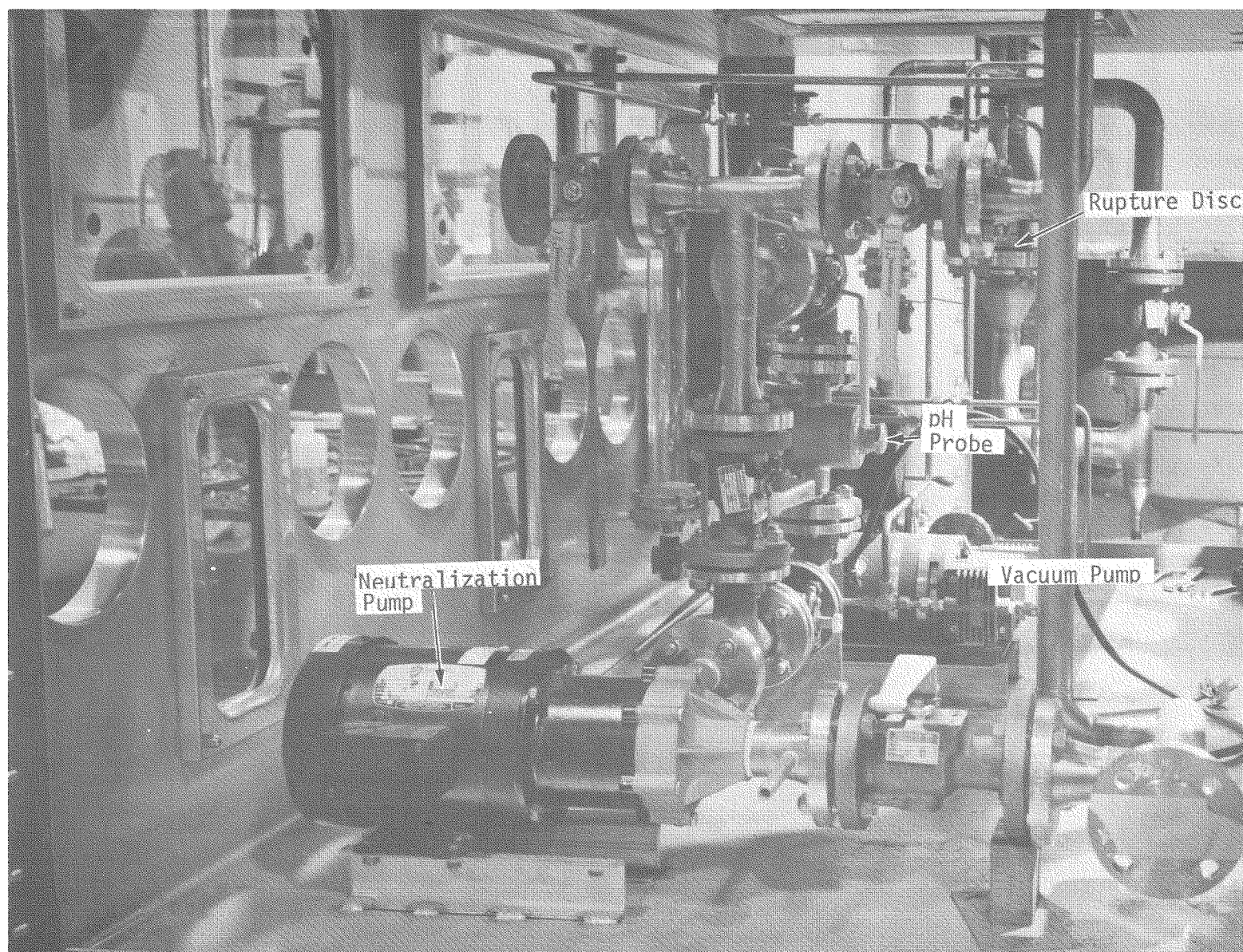


FIGURE 26. Closeup of Liquid Transfer Glovebox Showing Solution Transfer Pumps.

of the process equipment which will have a higher maintenance requirement, e.g., vacuum pump, pH probes, and valves. The glovebox is designed so that the equipment is readily accessible for maintenance or replacement. There are no flanges, screwed joints, or connections in acid lines or contaminated liquid lines which are not contained within a glovebox. All lines carrying contaminated or corrosive materials have been fabricated from certified materials under strict quality assurance criteria.

The process is controlled from an instrument control room (Figure 27) located on the floor above the RADTU processing equipment. This room provides a view of the processing area and access to a mezzanine which immediately borders major items of process equipment.

B. ACTIVITIES RELATED TO RADTU

R. G. Cowan, J. R. Divine, C. R. Allen

The activities which were performed in support of RADTU during this period included the design of an acid recycle unit for installation in RADTU, the completion of the Safety Analysis Report (SAR) for RADTU, and completion of various items of documentation required for the project.

1. Acid Recycle

The detailed design of an acid recycle addition to RADTU was completed in May and a design review was held in mid-June. Essential features of the acid recycle module include: (1) a glass-lined steel fractionator vessel with a steam heated jacket, (2) a glass fractionating column filled with ceramic packing, (3) a scrubbing tower to remove NO_x and recycle it back to the fractionator, (4) heated HEPA filters for the off-gas stream, and (5) continuous monitoring of the off-gases for both radionuclides and NO_x . Consistent with RADTU design, the acid recycle equipment is designed for simplicity and minimum maintenance.



FIGURE 27. Process Control Instrument Panel in RADTU Facility.

Neg. No. 77C972-100

Orders have been placed for the equipment items involving long lead times; this includes the fractionator vessel and module containment. Construction activities will begin in July with completion scheduled by October, 1977.

2. RADTU Safety Analysis Report (SAR)

The SAR for RADTU was completed and issued in June 1977. The primary purpose of the Safety Analysis Report is to document the safety analyses which have been performed and to demonstrate that:

- All potential major hazards have been identified for the Radioactive Acid Digestion Test Unit (RADTU).
- Safety features commensurate with the hazards have been provided.
- Credible failures of the safety features in this system would have acceptable results.

The kinds of accidents considered in the SAR include process failures, equipment failures, failure to follow procedures, failure of engineered safety features, and the effects of natural forces on both nuclear and industrial safety. To ensure that all accident conditions and consequences were adequately considered, the safety program began with a series of risk management meetings in which a list of conceivable accidents for the acid digestion process in general and the RADTU, in particular, were generated.

After the conceivable accidents were defined, they were grouped into common areas. The areas of interest were investigated first in the laboratory. Tests were then performed by an independent hazards analysis laboratory at extreme process conditions which might result from equipment failures or operating errors⁽⁷⁾. Operating procedures were tested in the Acid Digestion Test Unit (ADTU) at HEDL and the system's operability, flexibility and operating characteristics were determined.

In addition, a detailed "worst case" cause and effect scenario was developed for each potential accident. Then the credibility (probability) of each accident was analyzed using literature data, laboratory data, and data obtained from the ADTU and the independent hazard analysis laboratory. For those accidents deemed serious and credible, the consequences of the accident in terms of dose from exposure to radioactive materials was determined. From these numbers, a risk* of various accidents was calculated, Table 14. The risks given in Table 14 may be compared to individual exposure limits given in ERDAM-0524 "Standards for Radiation Protection". The limits are 5×10^{-1} rem/yr, whole body, and 3.0 rem/yr bone. They are considerably larger than the risks associated with the RADTU.

Consideration of the risk analyses, process safety studies, and engineered safety features results in the determination that the risk of injury from the RADTU to operating personnel is very small. With its remote location, the risk to the public from mechanical injury is zero and the risk

TABLE 14

SUMMARY OF RISKS* DUE TO POTENTIAL ACCIDENTS AT RADTU

<u>Item</u>	Whole Body Risk ^(a)	Bone Risk
	<u>rem/yr</u>	<u>(rem/yr)</u>
Earthquake	9.2×10^{-5}	5.2×10^{-3}
Fire	1.7×10^{-9}	9.6×10^{-8}
Transportation Accident	2.3×10^{-10}	1.3×10^{-8}
Breach of Glovebox	2.4×10^{-10}	1.3×10^{-8}
Criticality	5.4×10^{-12}	1.5×10^{-11}
Gas Explosion	8.6×10^{-13}	4.8×10^{-11}

(a) Maximum off-site individual at 4 km distance.

*Risk is defined as the product of a dose and the probability of the occurrence of the dose.

from radiation exposure is negligible. On the other hand, there are considerable potential benefits associated with the treatment of combustible transuranic wastes to provide volume reduction, removal of transuranic contaminants, and stabilization and fixation of the residue.

3. RADTU Documentation

The development, design, construction and operation of a process facility requires a comprehensive study and documentation program. This is to ensure the public that no important phases have been omitted and also to demonstrate that all safety criteria have been met, that safe operating conditions can be maintained.

The various reports and documents required for RADTU and their current status are shown in Table 15. The SAR has been issued as summarized above. HEDL review of the operating procedures and the training procedures is underway and preparation of a status report on acid digestion has been started.

A training manual to be used for instructing new operators for RADTU is in final preparation. The training will consist of classroom and applied studies conducted by the RADTU design and development staff and by other HEDL staff with expertise in safety and other areas. Understanding of the course material will be determined by periodic exams. Elements of the proposed training course include the following:

- General Safety
- A Review of Chemistry and Mathematics
- Handling Procedures for Acids and Bases
- Procedures for Handling Glass and Glass-lined Steel
- Equipment Operations
- Radiation and Nuclear Safety
- RADTU Design
- Operating Parameter and Non-Standard Operations and Responses
- RADTU and Building Emergency Procedures

TABLE 15

DOCUMENT STATUS

	<u>Started</u>	<u>HEDL Review in Progress</u>	<u>Final Review in Progress</u>	<u>Published</u>
Safety Analysis Report	X	X	X	X
Operating Procedures	X	X	X	
Emergency Procedures	X	X	X	
Training Procedures	X	X		
Status Report	X	X		

V. APPLICATION OF ACID DIGESTION TO COMMERCIAL SOLID WASTE (KX-03-02-04)

The primary objective of the program on Application of Acid Digestion to Commercial Wastes is support of development of acid digestion technology. It will ensure that acid digestion is developed to meet the requirements for processing commercial, nuclear fuel cycle combustible wastes: including licensability, process economics, recycling of acids, shielding/remote handling for β - γ wastes, fixation of residue for storage, and ability to accept appropriate waste forms. The program will also ensure that the developed technology is appropriate for industrial application.

Work on this program began in the last quarter of CY-76. Initial efforts were concentrated on application of acid recycle to acid digestion and on safety studies to meet licenseability requirements. These items are discussed in more detail in the following sections.

A. OFF-GAS CLEANUP AND RECYCLE ACID STUDIES

R. G. Cowan

To meet environmental standards, the acid digestion process off-gas must be cleaned and the amount of secondary waste resulting from operation of the process must be minimized. Studies were completed to demonstrate

acceptable off-gas cleanup and to develop complete acid recycle for the process. The major effort in this reporting period was directed toward engineering scale demonstration of the acid recycle flowsheet developed from previous laboratory data.⁽⁷⁾

A new acid fractionation unit, shown in Figures 28 and 29, was tested in the Acid Digestion Test Unit (ADTU). Figure 30 shows the flowsheet for the off-gas stream and the acid recovery system. The tests confirmed the validity of the zero liquid effluent flowsheet proposed for RADTU. A comparison of engineering test data with predicted flowsheet values is shown in Table 16.

TABLE 16

ADTU ACID RECYCLE SYSTEM PERFORMANCE

	<u>Chemical Component</u>	<u>Run 86 Data</u>	<u>Predicted Value</u>
Off-gas Scrubber Discharge	H ⁺	6.3 <u>N</u>	6.5 <u>N</u>
	HNO ₃	18%*	20%
	H ₂ SO ₄	12%	9%
	HCl	0.3%	1%
Recycle Acid	H ⁺	13.8 <u>N</u>	14 <u>N</u>
	HNO ₃	33.5%	37%
	H ₂ SO ₄	24.2%	20%
	HCl	63 ppm	Trace
Cl ⁻ Off-gas (Fractionator)	H ⁺	1.0 <u>N</u>	1.4 <u>N</u>
	NO ₃ ⁻	5%	4%

*Percentages are in weight percent.

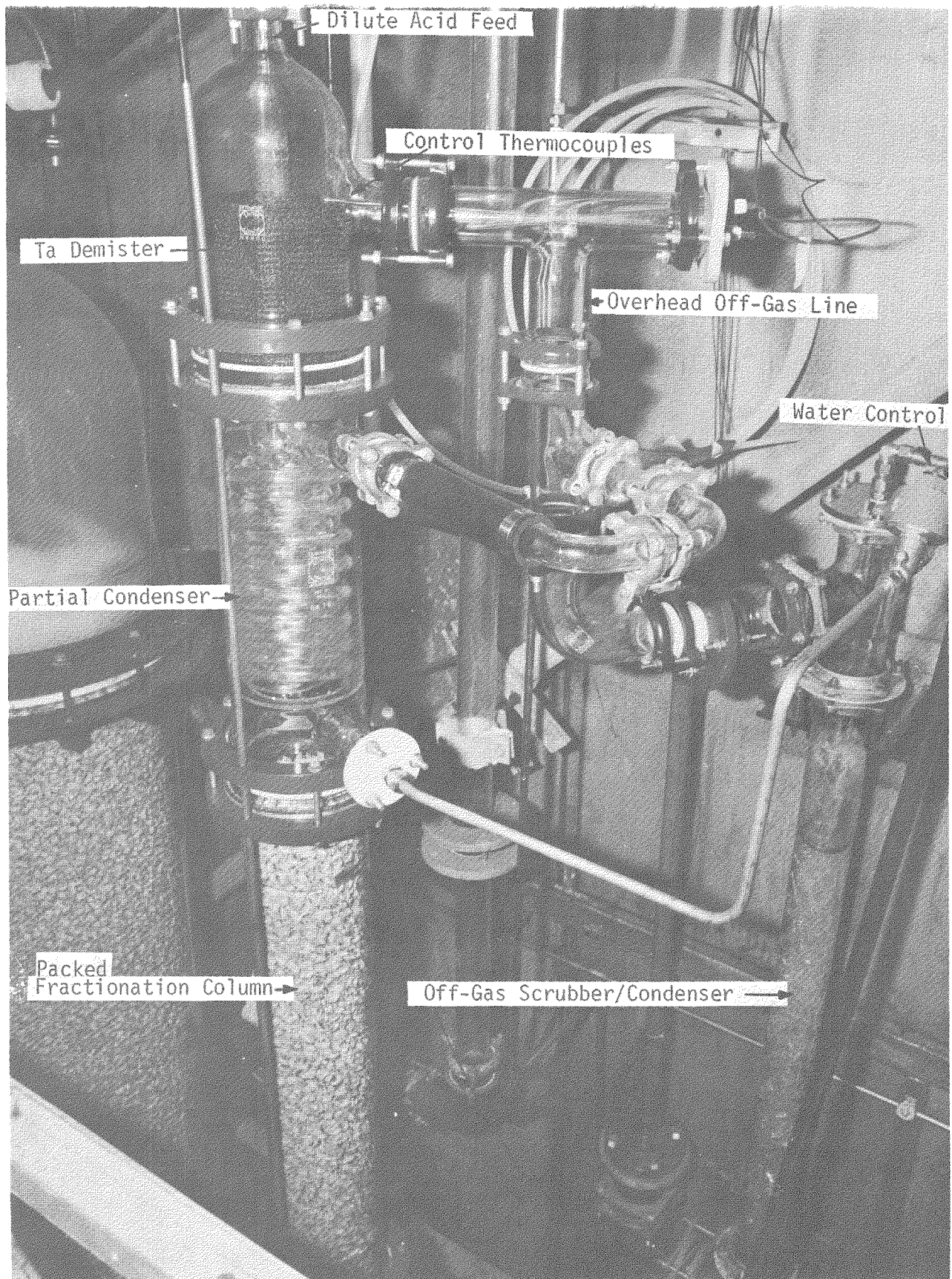


FIGURE 28. Recycle Acid Reboiler.

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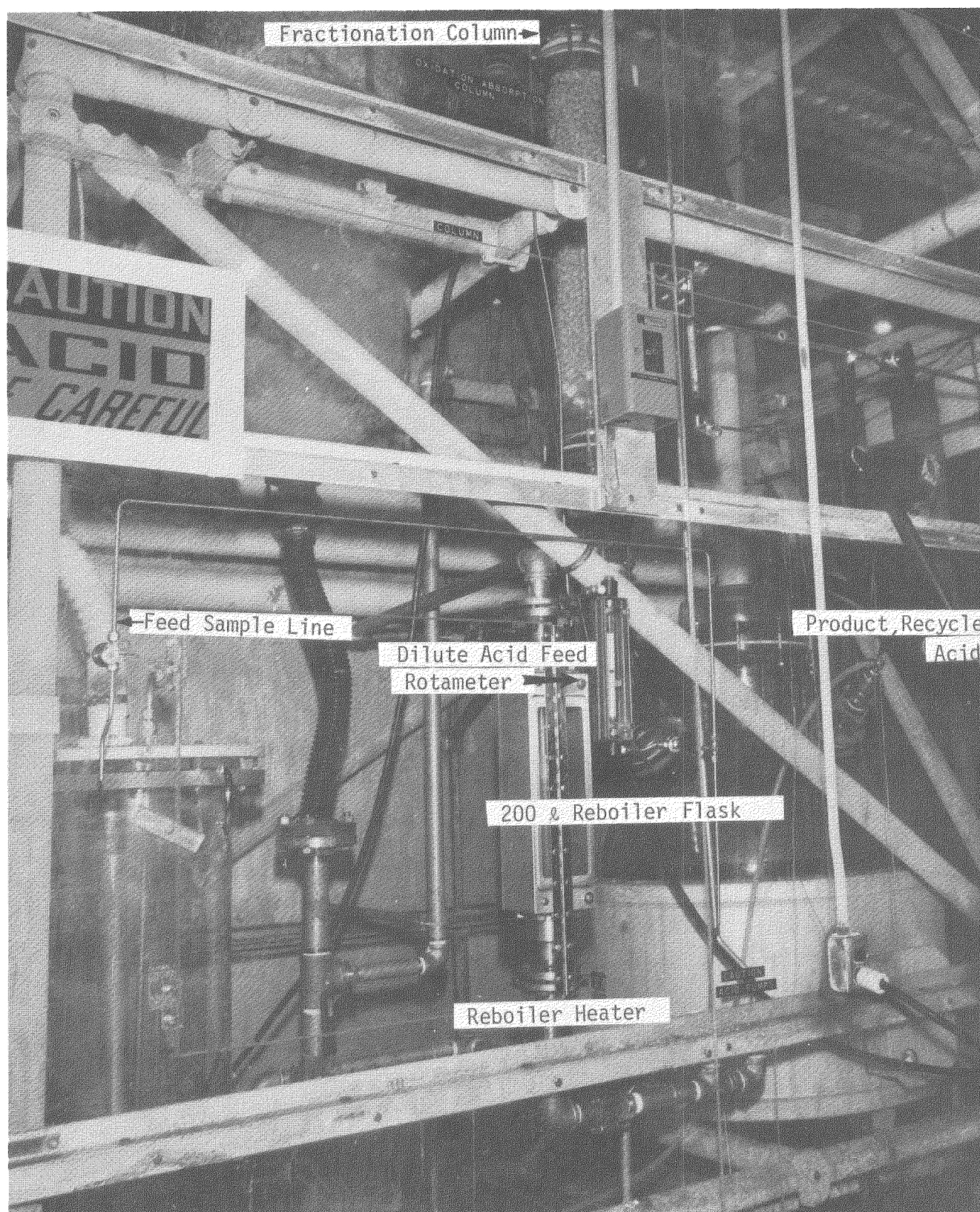
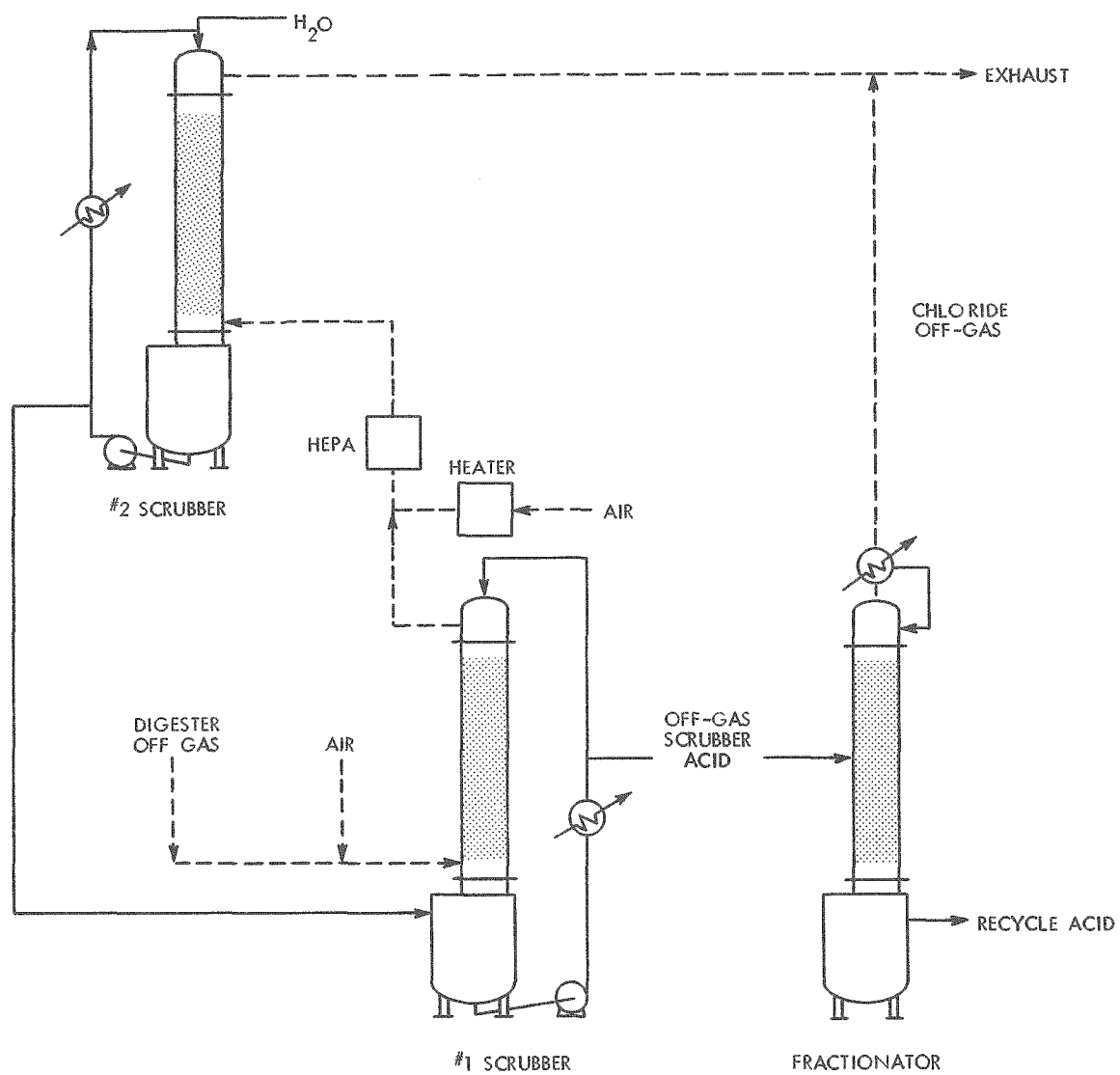


FIGURE 29. Recycle Acid Fractionator.

Neg. No. 773483-4CN



HEDL 7708-56.9

FIGURE 30. Equipment Arrangement For Off-gas Cleanup and Acid Recycle Studies in ADTU.

The off-gas from the digester is somewhat higher in sulfuric acid than was predicted but the total acid strength is almost exactly as predicted. The fractionator overhead is slightly higher in nitrate and lower in chloride. The recycle acid from the fractionator is higher in sulfuric and lower in nitric acids than predicted; however, these variations will not significantly affect RADTU operation. The acid fractionator performed well, verifying the acid recycle concept.

B. SAFETY STUDIES

C. R. Allen

Safety tests which evaluated acid digestion safety and potential hazards during postulated process upset conditions were completed by the Hazards Research Corporation, Denville, NJ. These tests were performed under flow conditions in a reactor simulating acid digestion. The reactor was a dynamic model of the digester gas flow system. The digester mockup consisted of a horizontal glass tube 1.5 m long and 7.6 cm in diameter. The lower half of the tube contained hot H_2SO_4 at 250°C . Nitric acid and volatile organics were introduced in various proportions including those which were detonatable in bomb tests. Gaseous H_2O and N_2 were also added over varying concentration ranges to study the effect of diluents. The fuel was added continuously and also in rapid increments so that the effect of an excessive charge of volatile liquid to RADTU could be simulated. A hot wire was used to ignite the mixtures if autoignition did not occur.

Results of the tests showed that except for the most extreme conditions, pressure excursions did not occur in the flow system even for mixtures which detonated in bomb tests. In order to get a pressure excursion, it was necessary to use 100 percent HNO_3 with no diluent and to introduce the fuel (methanol) in excess quantities (three-fold greater than stoichiometric). Under these conditions, with the simulated RADTU flow system, the mixture deflagrated and a total pressure rise of 0.84 kg/cm^2 (12 lb/in^2) occurred before the system was manually shut down.

The results of these tests show that a RADTU pressure excursion would be highly unlikely, since it required both 100 percent HNO_3 as an oxidant plus large quantities of volatile liquid fuel. The RADTU oxidant, 57 percent HNO_3 , always contains diluent water while the entry of large quantities of volatile liquid fuel is controlled by hand sorting, the shredding operation and controlled waste feed rates. A volatile hydrocarbon sensor is used as an additional safeguard. Furthermore, if a pressure excursion were to begin, the automatic controls on fuel and oxidant respond rapidly enough to terminate the reaction with only a small pressure pulse. As an added safety measure, the digester system has been designed to contain a full scale vapor phase detonation.

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