HEDL-TME 78-73
UC-70

DIVISION OF WASTE MANAGEMENT PROGRAMS PROGRESS REPORT

JANUARY-JUNE 1978

Hanford Engineering Development Laboratory

Compiled by:
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DIVISION OF WASTE MANAGEMENT PROGRAMS PROGRESS REPORT

January - June 1978

R. E. Lerch
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ABSTRACT

This is the tenth progress report on Division of Waste Management programs being conducted at the Hanford Engineering Development Laboratory (HEDL) for the United States Department of Energy. The report describes progress in the first half of 1978 on the following programs:

Intermediate Level Waste Solidification
Chemical Processing of Combustible Solid Waste
Application of Acid Digestion to Commercial Wastes

OTHER REPORTS - THIS SERIES

COMMERCIAL ALPHA WASTE PROGRAM QUARTERLY PROGRESS REPORT

HEDL-TME 74-50	March-June 1974	(September 1974)
HEDL-TME 74-61	July-September 1974	(November 1974)
HEDL-TME 75-41	October-December 1974	(February 1975)
HEDL-TME 75-87	January-March 1975	(October 1975)
HEDL-TME 75-102	April-June 1975	(December 1975)

NUCLEAR FUEL CYCLE AND PRODUCTION PROGRAMS PROGRESS REPORT

HEDL-TME 76-22	July-December 1975	(May 1976)

DIVISION OF WASTE MANAGEMENT, PRODUCTION AND REPROCESSING PROGRAMS PROGRESS REPORT

HEDL-TME 77-40	January-December 1976	(April 1977)
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SUMMARY

The scope of the Radioactive Acid Digestion Test Unit (RADTU) mission was changed from a strictly demonstration function to a joint R&D-production function. The RADTU will be used to process combustible transuranic contaminated defense waste from Hanford's Z-Plant. The unit was operated in a series of test runs totaling 160 hours during which approximately 500 kg of combustible waste were processed.

A separate off-gas stack was added to the RADTU enabling operation of the acid recycle equipment. This eliminated secondary liquid wastes from the process.

Additional laboratory tests were completed to determine the solubilities of thorium oxide and uranium oxide in the acid digestion system. Thorium oxide was slowly converted to thorium sulfate which is readily soluble in dilute nitric acid or water. The solubility of thorium sulfate is the concentrated sulfuric acid digestion solution was about 0.1 g/ℓ. Uranium oxide, on the other hand, was very soluble in the concentrated sulfuric acid having a solubility $\geq$440 g/ℓ.

Laboratory tests were performed to evaluate the effect of process variables on the rate of acid digestion. Of five variables evaluated, only temperature and nitric acid addition rate had significant effects on digestion rate.

I. INTRODUCTION

This is the tenth progress report issued on waste management programs at the Hanford Engineering Development Laboratory (HEDL) for the Waste Management Office of the Department of Energy (DOE). The report covers progress during the first half of 1978 on the following programs: Intermediate Level Waste Solidification, Chemical Processing of Combustible Solid Waste, and Application of Acid Digestion to Commercial Wastes.

The program on Intermediate Level Waste Solidification was started in October 1976 and has as its principle objectives 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 acceptable test procedures for soldified product forms, and verification tests of immobilized products.

The program on Chemical Processing of Combustible Solid Wastes was established to demonstrate the applicability of acid digestion for treating DOE waste materials. Overal 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 supplements the program on Chemical Processing of Combustible Solid 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 beta-gamma wastes, fixation of residues for storage, and ability to accept appropriate waste forms. The program will ensure that the developed technology will be appropriate to industrial needs.

II. INTERMEDIATE LEVEL WASTE SOLIDIFICATION (WH002)

A. PURPOSE

The purpose of the program on Intermediate Level Waste Solidification 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 acceptable test procedures for solidified product forms, and verification tests of immobilized products.

For the purposes of this 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 mRem/hr at the packaged surface, or 10 mRem/hr at three ft from the surface. The International Atomic Energy Agency (IAEA) value of 10^4 Ci/m^3 for ILW defines the upper limit. This limit 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 completion of laboratory tests to treat ILW containing iodine and on completion of a management plan for treatment of non-high-level wastes (non-HLW).

B. LABORATORY TREATMENT OF INTERMEDIATE LEVEL WASTES CONTAINING IODINE

Off-gas scrubbing with a mercuric nitrate-nitric acid solution is an attractive method for removing radioiodine from the fuel dissolution off-gas stream in fuel reprocessing plants. The resulting solution becomes an intermediate level liquid waste containing radioiodine. Composition of the scrub solution may range from 6 to 10 $\underline{M}$ HNO_3 containing 0.1 to 0.4 $\underline{M}$ $Hg(NO_3)_2$. Both mercury and iodine will potentially volatilize during calcination if this solution is added to the high level waste. Consequently, reprocessing plants using this process plan to solidify this stream separately.

Previous laboratory tests(2) have demonstrated that the solution can be successfully concentrated to form mercuric iodate slurries without significant volatilization of the iodine.

The laboratory work was completed and the results of the study are being evaluated, including tests on concentration of simulated mercuric nitrate-mercuric iodide off-gas scrubber solutions and immobilization of the residue slurry in cement.

III. CHEMICAL PROCESSING OF COMBUSTIBLE SOLID WASTES (WH003)

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 that is subsequently oxidized by nitric acid. Digestion of the waste produces a residue of inorganic sulfates or oxides that is insoluble in the acid and that can be separated as a dry residue by evaporation of the excess sulfuric acid at 350°C.

Development of the acid digestion process has progressed from laboratory and cold engineering scale tests to construction of a radioactive demonstration plant, the Radioactive Acid Digestion Test Unit (RADTU). The RADTU facility is located in the 200 West Area of the Hanford Project. Design capacity of the unit is 100 kg of waste per day. Construction of the unit was completed in June 1977 with completion of the acid fractionator addition in September 1977.

A. RADIOACTIVE ACID DIGESTION TEST UNIT

C. R. Allen

The scope of the Radioactive Acid Digestion Test Unit (RADTU) mission has been changed from a strictly demonstration function to a joint R&D-production function. The RADTU will be used to process combustible TRU defense waste from Hanford's Z-Plant. The RADTU equipment will require some modifications to increase its capacity by a factor of two to three fold (originally it was designed as a demonstration unit processing only 300 Area waste at Hanford). Laboratory and cold engineering scale experiments are underway to evaluate increased digestion capacity.

B. RADTU OPERATION

C. R. Allen, M. D. Crippen, N. J. Law and R. G. Cowan

In this reporting period, the RADTU was shutdown during February and March 1978 for installation of a separate off-gas stack which separates the RADTU fractionator off-gas from the Z-Plant effluent system. This change allows the operation of acid recycle equipment which eliminates a contaminated liquid effluent stream. The only process waste from RADTU is the digestion residue. The subsequent operation of the acid recycle equipment has been fully satisfactory and has resulted in a concentration of the combined nitric-sulfuric acid to 12 normal for recycle to the digester. The acid fractionator and associated HEPA filter system are shown in Figure 1.

The RADTU was operated in a series of test runs totaling 160 hours. Recycle acid was used in most of these runs. Over 500 kg of Type B* synthetic waste was processed. The waste was reduced to a residue containing about 5% of the initial weight. In separate laboratory tests more than half the residue was immobilized into a high integrity solid form, mostly glass. Overall volume reduction of waste to glass was about 75-fold.

Several minor problems with the system were discovered, analyzed, and resolved. Early operation of the system resulted in a higher than desirable loss of sulfuric acid. A Brinks® mist eliminator was installed in the off-gas stream to minimize the loss of sulfuric acid. Air was also substituted for nitrogen in the product vessel gaslift. This increased the oxidation rate of SO_2 and NO_x and subsequently improved the recovery of nitric and sulfuric acids in the scrubber column.

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*HEDL Reference Waste B (by weight): paper-15%, rags-15%, wood-10%, latex rubber-5%, hypalon rubber-10%, neoprene-10%, PVC plastic-20%, polyethylene-15%

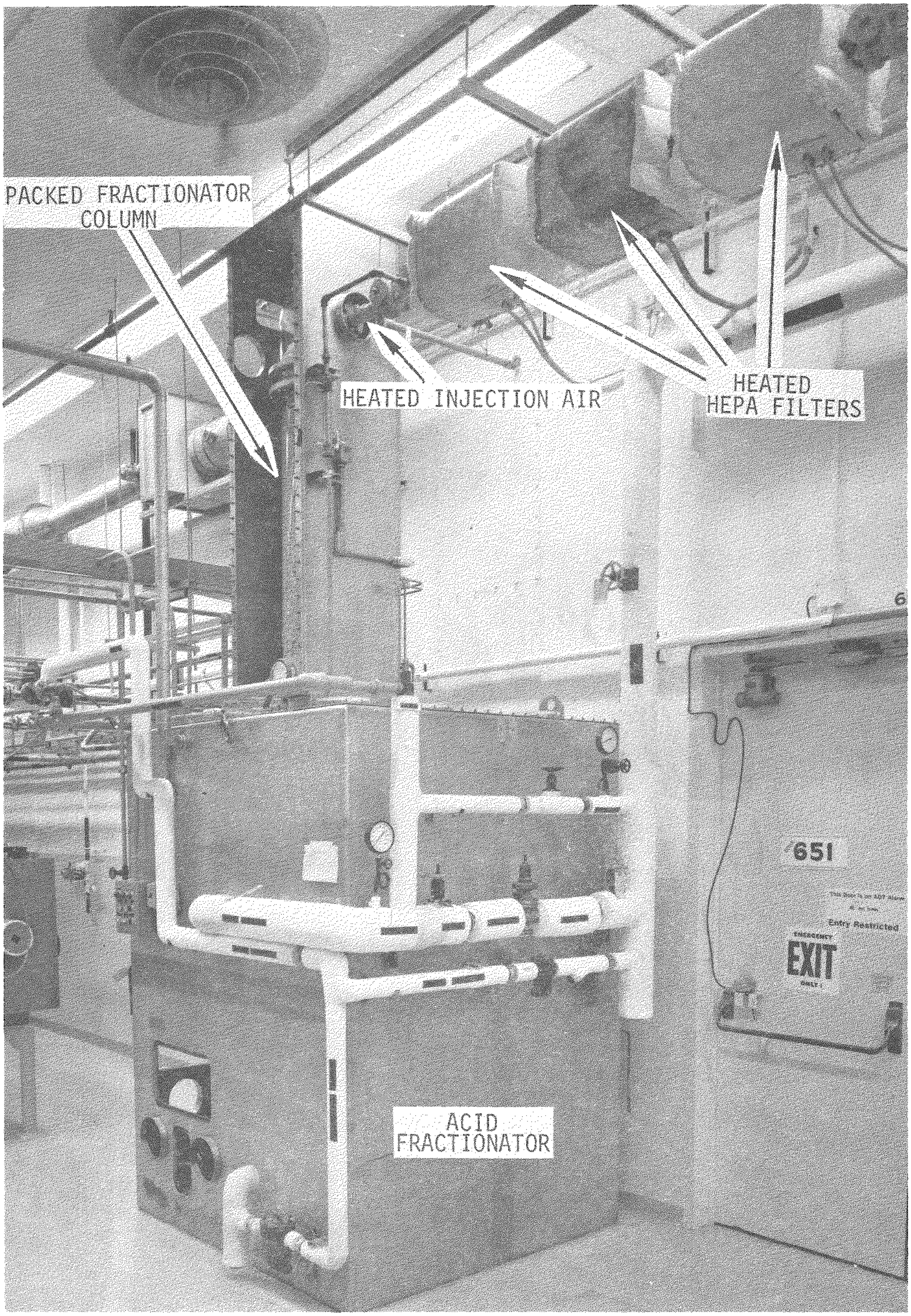


FIGURE 1. Acid Fractionator in the RADTU Facility. Neg 7803095-6cn

A minor pumping problem was caused by excessive starting torque from the pump motors. Substitution of single phase (vs three phase) motors and smaller and lighter impellers solved this problem and resulted in satisfactory performance.

Some difficulty was also encountered with a lack of uniform distribution of the waste over the surface of the digester tray. This resulted in a decreased waste digestion rate. A series of short screening runs were used to test a variety of modifications. A deflector block was used to direct the extruded waste down the tray and acid was sprayed over the waste to promote better solids-liquid contact. This resulted in improved operation.

It is planned to continue the RADTU shakedown operations through July 1978. Final modifications will then be made prior to radioactive operation.

C. MEGAS WASTE SCREENING

J. G. Bradley and R. E. Lerch

A multi energy gamma assay system (MEGAS) has been installed by HEDL on a test basis to assay non-glovebox line waste at a commercial mixed oxide fuel fabrication plant. This equipment is capable of assaying waste at the 10 nCi/g level in order to determine if the waste is either TRU or non-TRU. This work is progressing satisfactorily and is expected to be completed in August 1978. The MEGAS equipment will then be installed at Z-Plant to assay Z-Plant non-glovebox waste, thus reducing the quantities of waste requiring processing in RADTU.

IV. APPLICATION OF ACID DIGESTION TO COMMERCIAL SOLID WASTE

The primary objective of the program of Application of Acid Digestion to Commercial Wastes is to ensure that developed acid digestion technology is appropriate for nuclear industry applications. It includes the following factors: licensability, process economics, recycling of acids, shielding/ remote handling for beta-gamma wastes, fixation of residue for storage, and ability to treat commercial waste forms.

During this report period, the work has emphasized characterization of the behavior of thorium and uranium in the acid digestion system, immobilization of acid digestion residue in glass, and laboratory studies to increase the rate of digestion.

A. EFFECT OF ACID DIGESTION OF THORIUM AND URANIUM OXIDES

J. A. Partridge and G. P. Bosuego

Laboratory tests on the effect of acid digestion on thorium oxide showed that the sulfuric-nitric acid system slowly converts thorium oxide to thorium sulfate. Thorium sulfate has a limited solubility in concentrated sulfuric acid but dissolves readily in water or dilute nitric acid. Uranium dioxide dissolves readily under the same conditions. The solubility of uranium in the concentrated sulfuric acid system was found to be >440 g/ℓ.

The digestion tests were conducted with thorium oxide prepared by denitration of thorium nitrate at approximately $400^{\circ}C$ followed by firing for 2 hours at either $500-515^{\circ}C$, $718-763^{\circ}C$, or $925-935^{\circ}C$. The following procedure was used: One to two grams of the oxide were placed in 200 ml of concentrated sulfuric acid in a round bottom distillation flask. The solution was maintained at $240-250^{\circ}C$ by means of a heating mantle, and concentrated nitric acid was slowly (approximately 6 ml/hour) pumped into the heated solution through a glass frit beneath the surface of the acid. Samples of the thorium solids were periodically removed for solubility tests with dilute nitric acid or water. Tests were also performed with two-gram thorium oxide pellets which had been fired at 1600°C for 4 hours. At the conclusion of each sulfuric-nitric acid treatment, the thorium solids were filtered, washed with a small amount of distilled water, and dried at 80°C in a vacuum oven. The solubility of the dried solids was then tested in water and dilute nitric acid.

Results of solubility tests on the thorium residues from the concentrated sulfuric-nitric acid treatments are shown in Table 1. With the samples of thorium oxide fired at temperatures from 500 to 930°C, the rate of conversion to thorium sulfate decreased with the increase in firing temperature, dropping from 99+% to 87% after 48-50 hours digestion. The thoria pellet which had been fired at 1600°C for 4 hours showed only slight chemical attack after 53 hours in the hot acid system. However, acid treatment of 2.1 grams of -100 mesh powder from two pulverized pellets (also fired at 1600°C) for 52 hours resulted in 3.30 grams of recovered residue (thorium sulfate) which was 99% soluble in water or dilute nitric acid.

In a test not listed in Table 1, a sample of thorium oxide fired at 930°C was treated with concentrated sulfuric acid only (no nitric acid in the system) at 240-250°C for 48 hours. The residue from that test was only 46% soluble in dilute nitric acid indicating that the presence of nitric aicd increases the rate at which thorium oxide is converted to thorium sulfate.

Analyses of the final acid solutions from the thorium oxide runs showed that thorium has a solubility in the concentrated sulfuric-nitric acid system of approximately 0.1 g Th/liter at room temperature. Results of four runs were 0.17, 0.11, 0.11, 0.11 g Th/liter, for an average value of 0.12 g Th/liter. Thorium analyses on samples from runs in which sulfuric acid only was used gave results of 0.050 and 0.046 g Th/liter, indicating that the presence of nitric acid increases the solubility of thorium in concentrated sulfuric acid. This may possibly be due to a dilution effect since the equilibrium H_2SO_4 concentration in the H_2SO_4-HNO_3 acid digester system is about 91% versus 96% for concentrated H_2SO_4 alone.

TABLE 1

SOLUBILITY OF THORIUM RESIDUE FOLLOWING TREATMENT OF ThO_2 WITH CONCENTRATED SULFURIC-NITRIC ACID AT 240°-250°C

Run No.	ThO_2 Firing Temperature (°C)	Treatment Time (Hours)	Solubility of Residue in Water or Dilute HNO_3(%)
5	500-515	15.5	100
9	500-515	50	99
6	730	35	$\sim$90-95[(a)]
		69	96.5
10	930	26	$<$50[(a)]
		48	87
12	1600 (pellet)	53	(b)
13	1600 (-100 mesh powder)	52	99

(a) Based on a visual estimate of the fraction dissolved from a residue sample taken during the course of the acid treatment run.

(b) Chemical attack was on a thin layer of the surface only.

To determine the behavior of U(IV) oxide in the concentrated sulfuric-nitric acid system, a run was made with UO_2 with the same experimental set-up as had been used with the thorium oxide runs. Initially, 30 grams of UO_2 were placed in 200 ml of concentrated sulfuric acid. Nitric acid was slowly pumped into the solution which was maintained at 240-250°C. As the UO_2 dissolved, additional increments of UO_2 were added until a total of 110 grams had been added. The final 20 grams of UO_2 had not completely dissolved at the termination of the run and it appeared that the solution was saturated with respect to uranium. The final solution, when cooled to room temperature, had a density of 2.33 g/cc and a uranium concentration of approximately 400 g/liter.

B. IMMOBILIZATION OF ACID DIGESTION RESIDUE

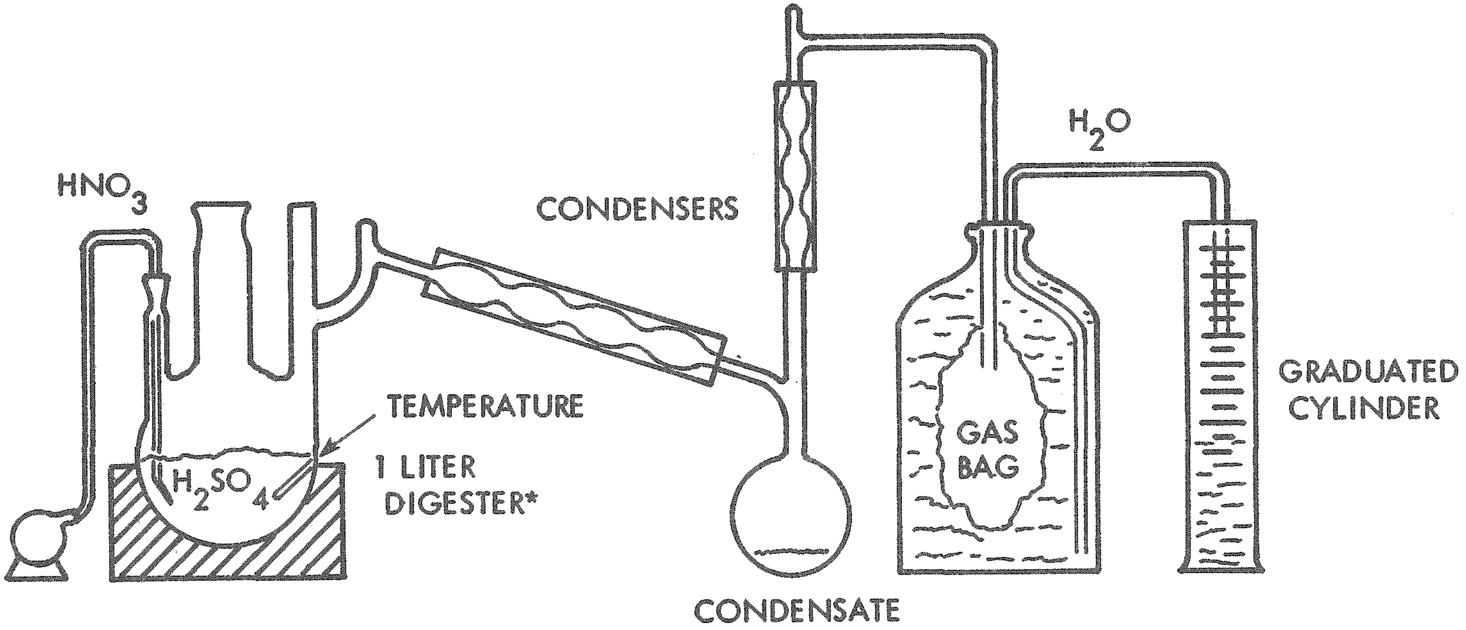
As reported previously,(2,3) immobilization of acid digestion residue in cement, urea-formaldehyde, bitumen, and glass matrices has been investigated. Immobilization of the residue in glass has been especially favorable since the immobilization process produces an additional two-fold decrease in the final volume of residue. Both direct immobilization of the residue by addition of the glass formers (sodium tetraborate and silica) to the acid slurry and a powder method which uses addition of glass formers to the dried residue have been used successfully.

C. ACID DIGESTION RATE EXPERIMENTS

G. P. Bosuego and J. C. Simmons

A series of nonradioactive laboratory tests was performed to evaluate the digestion rate of various materials as a function of temperature, nitric acid addition rate, nitric acid addition point (above or below the surface of the sulfuric acid), agitation, and specific surface area of the waste materials. Of the five variables evaluated, only temperature and nitric acid addition rate had a significant effect on digestion rate. The other variables had lesser (and somewhat ambiguous) effects. The conditions giving maximum digestion rates were near the current conditions used in the RADTU.

The apparatus shown schematically in Figure 2 was used for the rate experiments. Five hundred milliliters of 91% sulfuric acid was placed in a one-liter digestion flask. Nitric acid (70%) was introduced through a glass tube discharging either above or below the solution. Off-gases were successively passed through two condensers to remove condensable and absorbable gases. The off-gas rate was measured by collecting the noncondensable gases (essentially only CO_2, CO, SO_2, NO, and N_2) in a submerged gasbag that displaced water to a graduated cylinder.



* FLAT BOTTOMED CASK WITH MAGNETIC STIR BAR USED FOR AGITATION TESTS

HEDL 7811-146.1

FIGURE 2. Water Displacement Apparatus Used For Off-Gas Rate Measurements.

Five representative waste materials were tested: blotter paper (58 cm^2/g), file card paper (101 cm^2/g), sections of polyethylene bottles (20 cm^2/g), polyethylene sheet (100 cm^2/g), and Hypalon rubber gasket material (3 mm thick, 5.9 cm^2/g). Each sample was added to the sulfuric acid solution as a single piece weighing one gram. Nitric acid addition and off-gas collection started simultaneously with the waste addition. The run was considered complete when the solution cleared, although in most cases gas was still being evolved slowly. Runs were made in duplicate. In several cases additional runs were made to attempt to reconcile differences between the duplicate runs. The run conditions and results are summarized in Tables 2, 3 and 4.

The reproducibility of the duplicate runs ranged from fair to good. A review of the data suggests that the previous history of the sulfuric acid may have affected the digestion rates. In several cases, the digestion rates were significantly lower with fresh than with reused sulfuric acid. This effect may be related to the presence of residual nitric or nitrosyl sulfuric acid in the used acid or to the buildup of rate accelerating materials from previously digested wastes. Where known, the source of the sulfuric acid is included in the tables.

The summarized results include the total volume of off-gas collected, the time required to collect 90% of the off-gas, the time required to clear the solution, the average off-gas rate for the collection of 90% of the off-gas, and the maximum off-gas rate. The maximum rate for the rubber and plastic samples generally occurred at or just before the time when half of the off-gas had been collected. The maximum rate for paper occurred at the start of the run and may reflect rapid expulsion of air from the digestion vessel and condensers by steam generated during the initial dehydration of the cellulose.

TABLE 2

SUMMARY OF ACID DIGESTION RATE TESTS--PAPER

Run No.	Temp. °C	Exposed Waste Area, Cm^2	H_2SO_4 Source	Stirred	HNO_3 Add Point	HNO_3 Rate, ml/min	Total Offgas, ml	Digestion Time, min		Offgas Rate, ml/min		Moles/kg waste	
								90%(a)	To Clear	Ave(b)	Max(c)	Input HNO_3	Offgas(d)
14	250	58	?(g)	Yes	Below	1.00(i)	705	1.0	1.7	646	1500	26	29
14R	"	"		"	"	1.00	840	1.0	1.7	735	2400	26	35
13	"	"	New	"	"	0.48	1000	4.7	6.3	190	1200	47	42
13R	"	"	Used	"	"	0.30	865	3.3	4.5	237	2000	21	36
2R	"	"	Used	"	"	0.11	740	6.3	9.1	105	500	16	31
2	"	"	New	"	"	0.088	1100	9.8	11.3	101	860	16	46
34	"	"	New	"	Above	1.50	980	3.1	3.0	288	1500	71	41
34R1	"	"	?	"	"	0.75	640	3.4	3.3	167	200	38	27
32R	"	"	?	"	"	0.67	950	2.5	2.7	347	2000	29	40
34R2	"	"	?	"	"	0.50	750	3.4	3.5	201	3000	28	31
32	"	"	?	"	"	0.44	1110	3.1	4.0	322	2000	28	46
12	"	"	New	"	"	0.12	545	4.5	15.0	110	1000	28	23
12R	"	"	?	"	"	0.077	580	4.7	12.2	112	2000	15	24
42	"	"	Used	No	Below	0.80	1290	1.8	1.8	650	1800	23	54
42R	"	"	?	"	"	0.80	990	1.8	2.0	500	1700	25	41
26R	"	"	Used	"	"	0.67	940	2.2	2.5	391	3000	26	39
26	"	"	Used	"	"	0.50	900	2.5	3.1	320	2400	24	38
11	"	"	Used	"	"	0.091	1020	2.8	4.8	327	2300	6.9	43
11R	"	"	Used	"	"	0.083	885	2.3	5.0	354	3000	6.5	37
28	"	"	?	"	Above	0.50	900	1.8	5.0	462	2000	39	38
28R	"	"	New	"	"	0.43	780	5.4	6.6	130	1500	44	33
30	"	101	?	Yes	Below	0.80	940	1.7	2.1	496	3000	26	39
31	"	"	Used	"	"	0.67	928	2.2	2.5	372	1300	26	39
30R	"	"	?	"	"	(0.60)	1245	1.0	1.7	1146	3000	(16)	52
31R	"	"	Used	"	"	0.33	948	2.2	2.5	390	1500	13	40
10	"	"	"	"	"	0.095	1140	3.6	8.5	284	1200	13	48
10R2	"	"	"	"	"	0.091	924	4.9	6.6	168	370	9.4	39
10R3	"	"	"	"	"	0.088	1560	8.9	11.3	158	860	16	65
10R1	"	"	"	"	"	0.081	1250	10.2	14.8	110	1700	19	52
35R	"	"	?	Yes	Above	0.86	880	2.8	2.8	285	1800	37	37
35	"	"	?	"	"	(0.75)	910	2.3	2.4	360	1540	(29)	38
33	"	"	?	"	"	0.50	939	2.5	3.0	344	1000	24	39
33R	"	"	?	"	"	0.50	990	2.8	3.0	320	1500	24	41
27R2	250	101	Used	No	Below	0.43	810	2.9	3.1	256	750	21	34
27	"	"	"	"	"	0.29	880	2.6	2.8	305	1800	13	37
27R1	"	"	"	"	"	0.29	1020	2.7	3.1	338	1700	14	43
29R	"	"	"	"	Above	0.40	940	6.3	6.8	133	1700	42	39
29	"	"	"	"	"	0.13	880	6.1	14.3	129	900	30	37
1	225	58	Used	Yes	Below	0.092	1100	8.3	12.0	120	710	17	46
1R	"	"	"	"	"	0.092	1025	8.1	12.0	115	710	17	43

TABLE 3

SUMMARY OF ACID DIGESTION RATE TESTS--POLYETHYLENE

Run No.	Temp. °C	Exposed Waste Area, Cm^2	H_2SO_4 Source	Stirred	HNO_3 Add Point	HNO_3 Rate, ml/min	Total Offgas, ml	Digestion Time, min		Offgas Rate, ml/min		Moles/kg waste	
								90%(a)	To Clear	Ave(b)	Max(c)	Input HNO_3	Offgas(d)
16R1	250	20	New	Yes	Below	1.00	2400	15.7	18.0	137	165	283	100
16R2	"	"	Used	"	"	0.93	3200	10.4	12.3	276	320	180	133
16	"	"	?(g)	"	"	0.89	3200	6.2	7.8	463	920	108	133
15	"	"	Used	"	"	0.41	3300	11.9	15.5	250	410	99	138
15R	"	"	Used	"	"	0.38	3320	11.3	15.9	265	440	94	138
5	"	"	Used	"	"	0.10	4050	32.0	40.1	114	170	63	169
5R	"	"	Used	"	"	0.10	3360	16.2	37.0	186	310	60	140
45	"	"	New	"	-	0	1800	16.4	18.0(h)	99	115	0	75
45R	"	"	New	"	-	0	3340	28.2	33.3(h)	107	140	0	139
21	"	"	New	Yes	Above	1.00	2180	11.2	12.3	175	210	193	91
21R	"(f)	"	?	"	"	0.97	2720	14.0	16.0	175	190	244	113
18R	"(e)	"	?	"	"	0.73	2500	6.5	10.5	346	730	120	104
18	"	"	?	"	"	0.50	2830	10.1	15.5	251	480	122	118
41-5	"	"	New	No	Below	1.00	3320	17.1	18.9	175	280	297	138
41-2	"	"	New	"	"	0.96	3440	18.9	21.0	164	210	315	143
41-0	"	"	Used	"	"	0.92	3980	16.7	19.0	214	290	275	166
41-4	"	"	Used	"	"	0.90	2350	6.1	9.4	344	600	132	98
41-3	"	"	Used	"	"	0.85	3110	10.3	11.0	272	510	146	130
41-1	"	"	Used	"	"	0.77	2190	15.1	16.3	130	310	195	91
19	"	"	Used	"	"	0.050	4150	20.6	40.0	181	380	31	173
19R	"	"	New	"	"	0.044	3170	17.2	44.1	165	270	30	132
20	"	100	?	Yes	Below	1.11	2650	6.4	7.6	375	650	132	111
20R	"	"	?	"	"	0.92	3020	8.9	10.0	304	800	144	126
25	"	"	?	"	Above	0.096	3090	6.8	40.5	410	750	61	129
25R	"	"	Used	"	"	0.078	2720	7.9	44.0	309	600	54	113
40R	"	"	"	No	Below	1.00	2720	6.7	8.2	365	900	118	113
40	"	"	"	"	"	0.80	2630	5.8	9.4	406	640	128	110
38	225	20	?	Yes	Below	0.99	2740	22.8	25.5	108	150	396	85
38R	"	"	Used	"	"	0.89	3715	19.0	23.7	176	250	330	108
37R	"(f)	"	Used	"	"	0.61	4580	35.0	37.0	118	190	246	191
37	"	"	Used	"	"	0.52	3000	26.7	30.4	101	130	352	125
36	"	"	Used	"	"	0.12	2040	62.6	78.0	29	48	141	114
36R	"	"	New	"	"	0.10	2580	55.4	80.8	42	57	124	155

TABLE 4

SUMMARY OF ACID DIGESTION RATE TESTS--HYPALON RUBBER

Run No.	Temp. °C	Exposed Waste Area Cm^2	H_2SO_4 Source	Stirred	HNO_3 Add Point	HNO_3 Rate ml/min	Total Offgas, ml	Digestion Time. min		Offgas Rate, ml/min		Moles/kg waste	
								90%(a)	To Clear	Ave(b)	Max(c)	Input HNO_3	Offgas(d)
23	250	5.9	?(g)	Yes	Below	1.00	1790	7.9	8.5	205	250	133	75
23R	"	"	?	"	"	(0.95)	1810	8.2	8.7	200	230	(129)	75
8R	"	"	?	"	"	0.50	1515	12.0	15.3	114	200	120	63
8	"	"	?	"	"	0.41	1610	10.4	16.5	140	170	107	67
44	"	"	New	"	-	0	825	85	116(h)	8.8	78	0	34
44R	"	"	New	"	-	0	1200	62	69(h)	17.5	66	0	50
24R	"(e)	"	Used	"	Above	1.00	1815	8.3	9.0	197	260	141	76
24	"(e)	"	"	"	"	0.95	1639	8.4	9.9	175	220	148	68
17	"	"	?	"	"	0.50	1600	12.6	14.6	114	230	114	67
17R	"	"	?	:	"	0.45	1580	17.7	19.0	80	190	134	66
17R3	"	"	?	"	"	0.44	1560	15.5	17.5	91	180	122	65
22R	"	"	Used	No	Below	0.92	2300	10.4	10.8	198	260	156	96
22	"	"	"	"	"	0.79	2300	12.5	13.0	165	180	160	96
43	225	"	New	Yes	"	1.00	2580	18.6	19.7	125	220	309	108
43R	"	"	Used	"	"	1.00	2360	15.9	17.7	134	160	271	98
7	"	"	New	"	"	0.58	2500	27.1	30.0	83	100	273	104
7R	"	"	Used	"	"	0.48	1900	20.3	22.5	84	145	170	79

Notes to Tables:

(a) Time for generation of 90% of the collected offgas volume.

(b) Based on the time required to collect 90% of the total offgas volume.

(c) Maximum sustained offgas rate (≥ 10% of the offgas collected at this rate).

(d) Based on the collected offgas volume at 24 liters/mole.

(e) Temperature slightly high during the run.

(f) Temperature slightly low during the run.

(g) Source of H_2SO_4 not identified.

(h) Incomplete digestion; solution failed to clear but no waste fragments visible.

(i) One ml/min = 1.9 g-mole HNO_3/hr per liter of H_2SO_4.

The final two columns of Tables 2, 3 and 4 concern the stoichiometry of the reactions. The overall reactions involve oxidation by both H_2SO_4 and HNO_3, yielding CO_2, CO, SO_2, NO_2, NO, N_2, H_2O, and (for Hypalon) HCl. With the laboratory set up, excess NO_2 should effectively be consumed either in oxidizing SO_2 to SO_3 or in reacting with NO and water to form HNO_2 and HNO_3. Vaporized HNO_3 should also react with SO_2 to form SO_3, which would be absorbed in the condensers as H_2SO_4. Thus, the predominent species collected in the gasbag would be CO_2, CO, SO_2, NO, and N_2. Significant amounts of SO_2 would be collected only in runs where insufficient HNO_3 is added to the system to react with both the waste and with the SO_2. Previously determined stoichiometry for the digestion reactions indicated that 90% or more of the carbon is evolved as CO_2 and that the NO to N_2 ratio in the nitric acid reaction products is typically about 3.(4) Using these values, the off-gas quantities shown in Table 5 should be obtained at complete digestion, assuming the waste materials are composed of pure monomers.

TABLE 5

CALCULATED QUANTITIES OF OFF-GASES FROM DIGESTION OF PURE WASTE MONOMERS

Moles of HNO_3	Moles Off-Gas per kg Waste[a]		
per kg Waste	Cellulose	Polyethylene	Hypalon Rubber[b]
0	107	278	190
10	97	267	177
25	80	250	161
50	65	222	134
100	65	168	109
150	65	158	109
200	65	158	109
Range:[c]			
No HNO_3	150-111	273-285	186-195
Excess HNO_3	51-86	112-214	78-147

(a) Products are assumed to be CO_2, CO (CO/CO_2 = 1/9), SO_2, NO, and N_2 (NO/N_2 = 3).

(b) Hypalon monomer is assumed to be $(CH_2)_{90}(CHCl)_{15}CHSO_3Cl$; FW = 2102.1.

(c) Products are CO_2 and SO_2 or NO for upper limit; CO_2, CO (CO/CO_2 = 0.2) and SO_2 or N_2 for lower limit.

Comparison of the theoretical quantities of off-gas in Table 5 with the measured quantities in Tables 2, 3 and 4 indicates that the reactions were apparently incomplete at the time the solutions cleared and the runs ended. Previous laboratory tests made with a similar apparatus indicated that 20-25 percent of the waste is converted to soluble organic materials that digest relatively slowly.(5) In these earlier tests, 36 grams of mixed waste materials were fed to the digester over a four-hour period together with 70% nitric acid at about 0.7 ml/minute. Total organic carbon in the digester acid was analyzed at the end of this time and periodically for two to three hours following the last waste addition while holding the temperature and nitric acid flow constant. The organic carbon content peaked at about 10 to 14 g/liter and decreased at the rate of about 0.024 g/minute at 230°C and 0.043 g/minute at 250°C. The peak organic carbon content corresponded to about 24% of the carbon introduced to the digester in the waste materials. The soluble organic carbon compounds have not been identified, but two likely candidates are oxalic acid and benzene hexacarboxylic (mellitic) acid.

The various relationships between digestion rate and the most important variables determined in this study are shown graphically in Figures 3 through 8. The illustrated runs all were made with wastes of low specific area in the stirred digester with nitric acid added below the surface of the solution.

Figure 3 shows the relative digestion rates of paper, polyethylene, and Hypalon rubber at 250°C with nitric acid added at one ml/min. Note that paper reacts much faster and produces less off-gas than either polyethylene or Hypalon. Digestion to the free carbon endpoint (clear solution) was complete for all three materials.

The effect of nitric acid addition rate on the digestion rates of Hypalon and polyethylene is shown in Figures 4 and 5, respectively. Note that digestion of Hypalon and polyethylene was incomplete when nitric acid was omitted. Nitric acid strongly assists in the carbonization of the waste and is essential in removing the free carbon within a practical time.

Finally, the relationships between digestion temperature and digestion rates are shown in Figures 6 through 8 for Hypalon, paper, and polyethylene, respectively. Digestion of the free carbon was complete for all six runs shown in these three figures.

Although there are some ambiguities in the data, the test runs indicate that the following conditions would produce the maximum digestion rate:

High temperature (above 225°C).
Nitric acid addition rates greater than 1 g-mole/hour per liter of H_2SO_4.
Nitric acid addition below the surface of the sulfuric acid.
Supplementary agitation, if necessary.
High specific areas of waste materials.

In general, RADTU currently uses processing conditions which favor high digestion rates. It uses about 50 g-moles of nitric acid per kg of waste added at the rate of about 1.7 g-moles HNO_3/hour per liter of H_2SO_4. Efforts will be made to optimize all of the variables within the RADTU system.

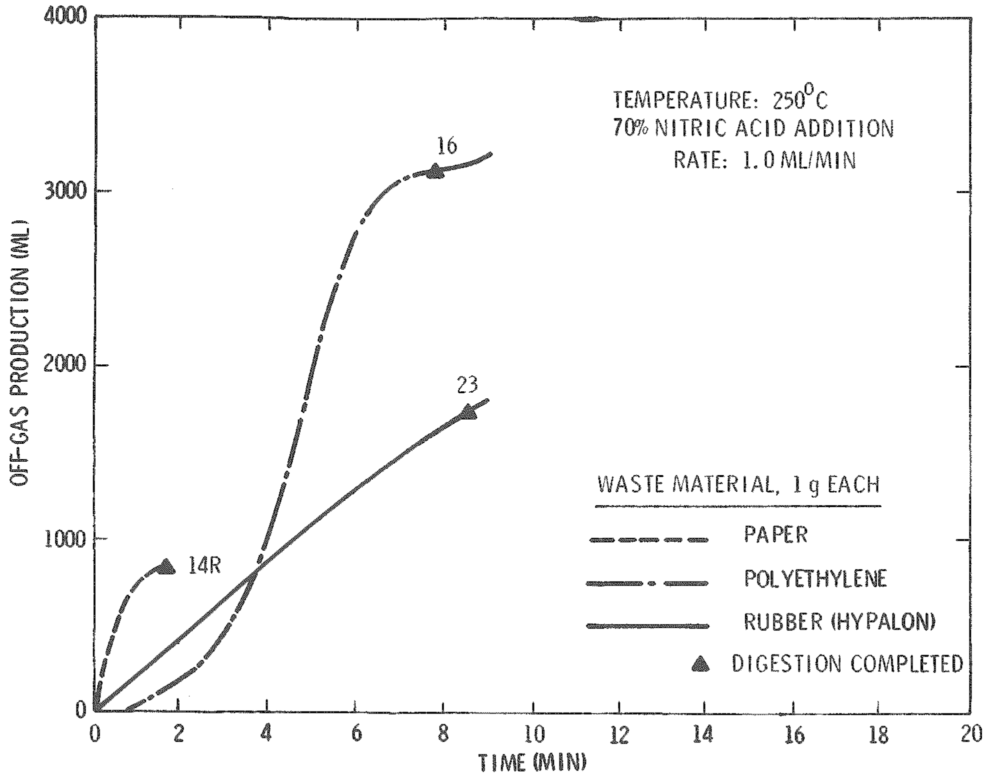


FIGURE 3. Relative Digestion Rates of Paper, Polyethylene, and Hypalon Rubber. HEDL 7811-146.5

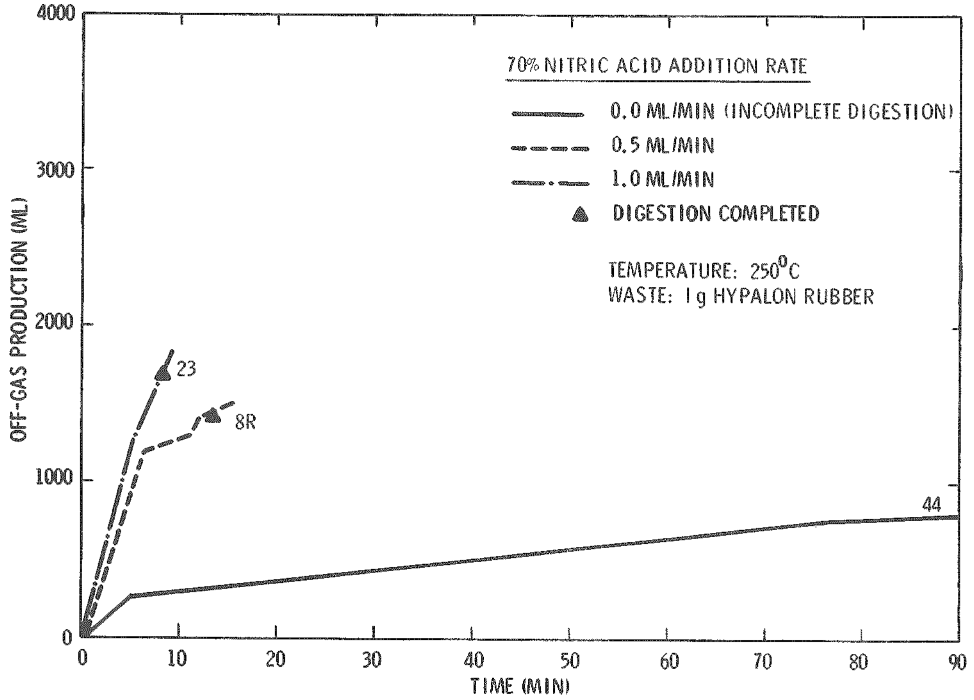


FIGURE 4. Effect of Nitric Acid Addition Rate on Digestion of Hypalon Rubber. HEDL 7811-146.3

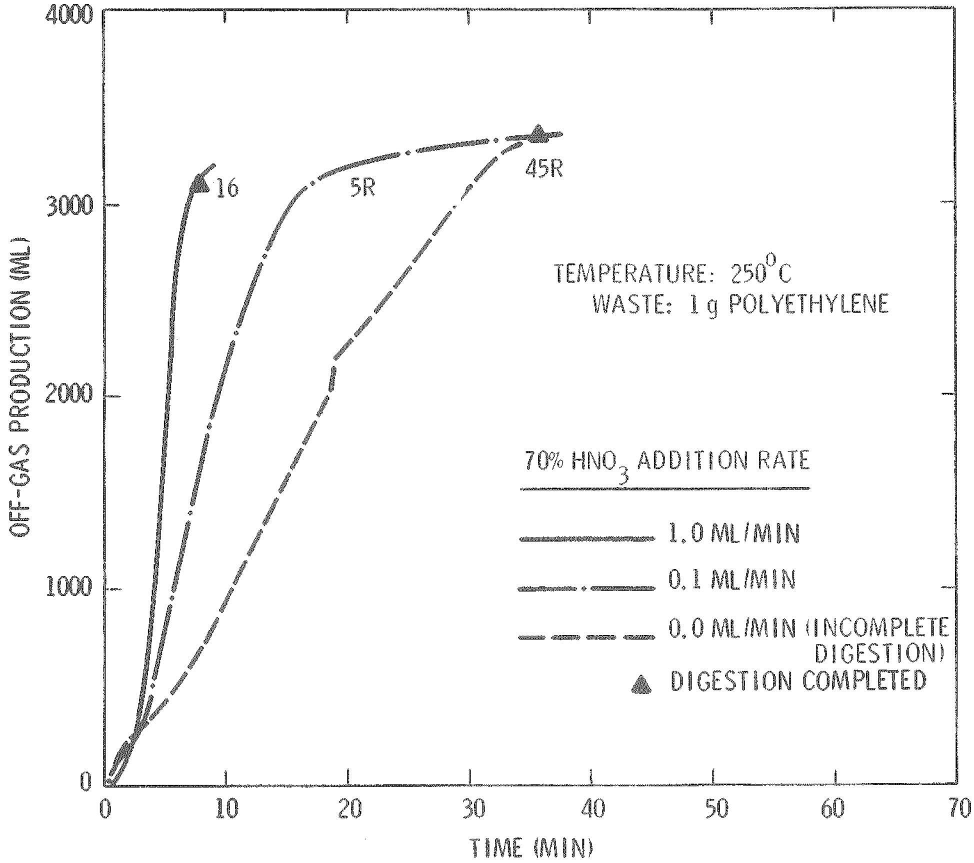


FIGURE 5. Effect of Nitric Acid Addition Rate on Digestion of Polyethylene. HEDL 7811-146.7

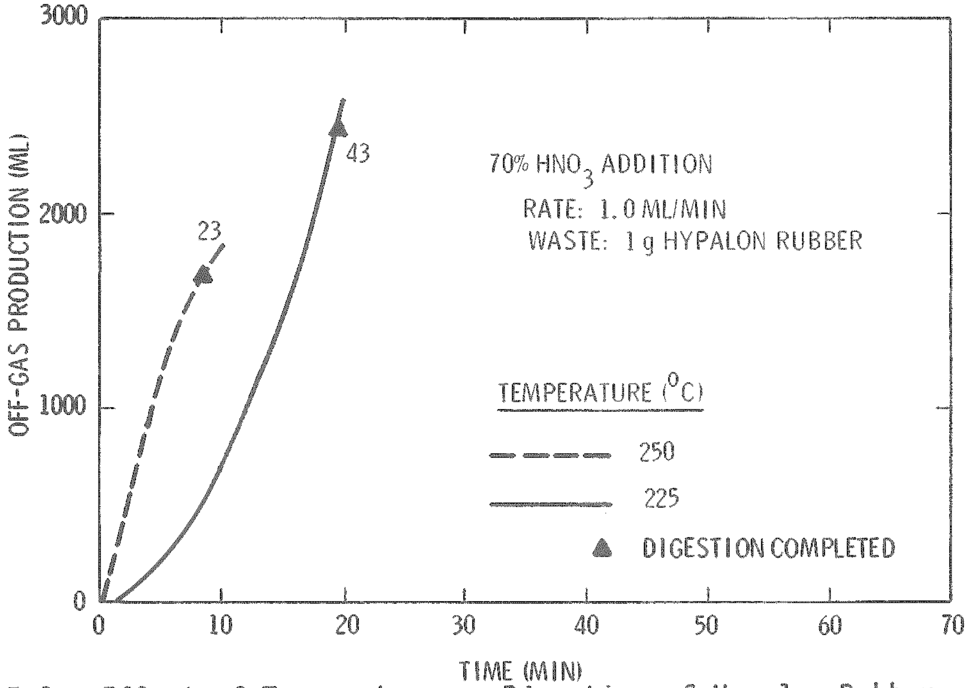


FIGURE 6. Effect of Temperature on Digestion of Hypalon Rubber. HEDL 7811-146.6

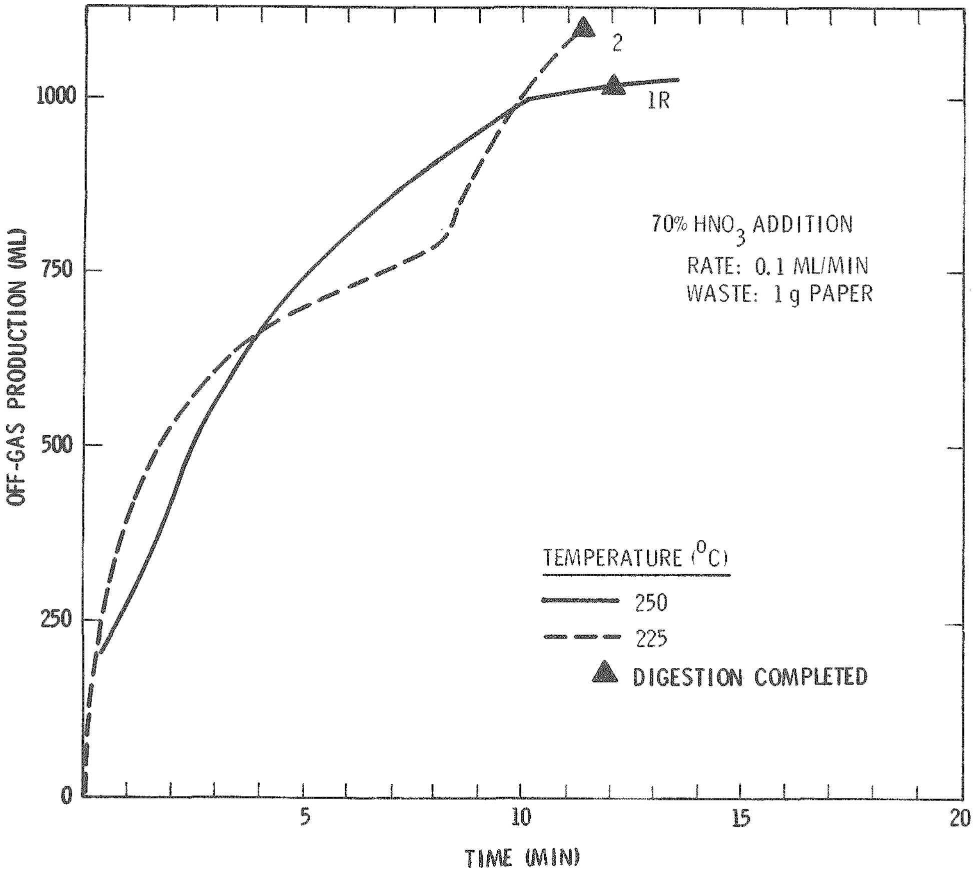


FIGURE 7. Effect of Temperature on Digestion of Paper. HEDL 7811-146.4

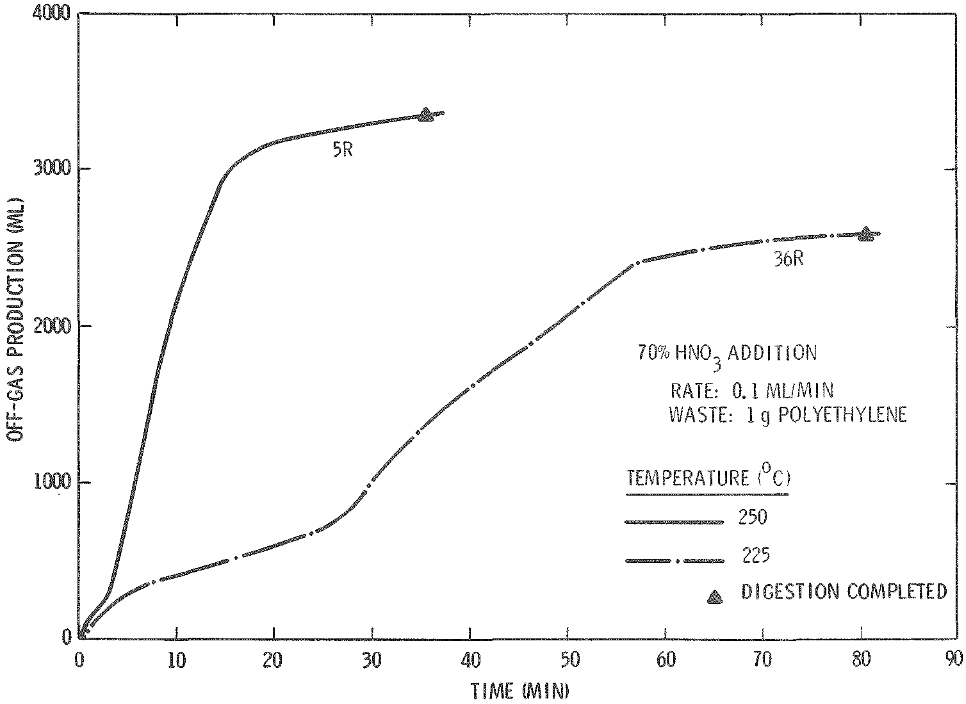


FIGURE 8. Effect of Temperature on Digestion of Polyethylene. HEDL 7811-146.2

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