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Spontaneous Combustion, Oxidation, and Pyrolysis of Combustible Solid Wastes Containing Transuranium Elements in Combustible and Noncombustible Containers

H. W. Godbee

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

SPONTANEOUS COMBUSTION, OXIDATION, AND PYROLYSIS OF COMBUSTIBLE SOLID WASTES CONTAINING TRANSURANIUM ELEMENTS IN COMBUSTIBLE AND NONCOMBUSTIBLE CONTAINERS

H. W. Godbee

MAY 1972

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H. W. Godbee

ABSTRACT

Solid wastes containing plutonium and other transuranium elements, frequently referred to as alpha wastes, are routinely produced during the operation of nuclear fuel production and spent fuel reprocessing plants as well as during the operation of AEC laboratories and production facilities. The transuranium contents of such wastes range from trace amounts to several grams per cubic foot. About one-half to two-thirds of the wastes, by volume, are combustible; however, reliable and efficient incinerators for reducing their volume have not as yet been developed. Therefore, it is desirable to evaluate the feasibility of storing them without pretreatment, such as incineration, in a final repository.

A series of heating tests was carried out to study the oxidation and pyrolysis of typical combustible solid wastes in small combustible and noncombustible containers at temperatures of 90 to 215°C for periods of time ranging from 10 to 205 hr. The combustible containers were plywood boxes having outside dimensions of 2 x 3 x 3 in. or 4 x 6 x 6 in. The noncombustible containers consisted of mild-steel drums with an open head, a bolt-ring closure, a hollow neoprene gasket, and a volume of 0.1 ft^3. A mixture of 75 wt % cellulosic materials and 25 wt % thermoplastic material was used to simulate alpha-contaminated combustible solid waste. In some cases, this mixture was wetted with nitric acid or sodium nitrate solution and dried before use. Each sample of the simulated waste was packed into the appropriate container to give a density of about 5 lb/ft^3 – a value that corresponds closely to the average density achieved in actual practice. It was then heated to temperature at the rate of about 15°C/hr. The buildup of pressure and the weight loss on heating were recorded. In three tests, CaO powder was added to the waste to serve as a getter for the water, carbon dioxide, and other acidic gases evolved during limited oxidation and pyrolysis.

The wastes were only slightly affected by heating up to 130°C. However, as the temperature was increased above this level, the loss in weight and the depth of brown color increased. The measured weight losses, for approximately equal heating times, ranged from

about 2 wt % at 145°C to about 4 wt % at 160°C, and to about 12 wt % at 200°C. The pressures attained in the drums varied from about 300 to 1200 in. H_2O (gage), about 200 to 1000 in. H_2O greater than expected from expansion of the original air in the drum. The pressures that developed after addition of CaO were less than those predicted from the expansion of air in the drum.

The general conclusions drawn from these tests are: (1) combustible wastes in combustible containers should not be accepted at a final repository; (2) combustible wastes in sealed noncombustible containers, such as DOT 17C and DOT 17H specification metal drums or equivalents, should be acceptable at a final repository; and (3) the quantity of gases evolved during heating of these wastes can be reduced substantially by adding a getter such as CaO.

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1. INTRODUCTION

Solid wastes containing plutonium and other transuranium elements, frequently referred to as alpha wastes, are routinely produced during the operation of nuclear fuel production and spent fuel reprocessing plants as well as during the operation of AEC laboratories and production facilities. The major AEC sites[1-3] and commercial installations[4] were recently surveyed to determine current and projected sources, amounts, and characteristics of alpha wastes and practices for their disposal. Since these wastes contain radioactive nuclides that decay very slowly, they must be contained outside the biosphere for hundreds of thousands of years.

The wastes consist of a wide assortment of solid materials generated inside glove boxes during work with transuranium elements and outside glove boxes during contamination control measures. They include items made of paper, cloth, wood, plastic, rubber, glass, ceramic, and metal, as well as salts and sludges that arise in the treatment of liquid waste streams and filters from off-gas cleanup. The transuranium-element contents of these wastes range from trace amounts to several grams per cubic foot. The significant contaminant isotopes include 87.4-year ^{238}Pu, 24,400-year ^{239}Pu, 6,600-year ^{240}Pu, 14.3-year ^{241}Pu, and 433-year ^{241}Am.

The densities of the uncompacted wastes range from about 2 to 200 lb/ft^3. About one-half to two-thirds of the wastes, by volume, are combustible and can be reduced in volume by a factor of about 50, and in weight by a factor of about 20, via incineration. About one-half to three-fourths of the wastes, by volume, are compactable and can be reduced in volume by factors of 2 to 10 via compression. The densities of the uncompacted compactable and combustible wastes vary from about 2 to 8 lb/ft^3, averaging about 5 lb/ft^3. Since the wastes are virtually free of penetrating radiation and evolve only a few hundredths of a watt per cubic foot, they do not require remote handling techniques. In favorable geographic locations, they are buried on-site; in less favorable locations, they are shipped, usually in wooden crates and steel drums, to commercial or AEC burial sites.

Since, as mentioned above, reliable, efficient incinerators for reducing the volume of the combustible wastes have not as yet been developed, it is desirable to evaluate the feasibility of storing these wastes without pretreatment (e.g., incineration) in a final repository.[5] The purpose of the laboratory work reported here was to aid in this evaluation by studying the oxidation and pyrolysis of typical combustible wastes in combustible and noncombustible containers at temperatures of about 100 to 200°C for periods of time ranging from about 10 to 200 hr.

2. SIMULATED WASTES

A preponderance of typical combustible wastes are cellulosic (viz., paper, cloth, wood, as well as many paints and plastics).[1-3] Thus, the standard waste mixture (called Type I in this report) selected to simulate combustible solid wastes consisted of a blend of 25 wt % blotter paper, 25 wt % cheesecloth, 25 wt % facial tissue, and 25 wt % polyethylene film. Each material was cut into 1-in. squares. A thermogram for the composite is given in Fig. 1; thermograms for each material making up the composite are given in Appendix A. The significant results obtained from thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of these

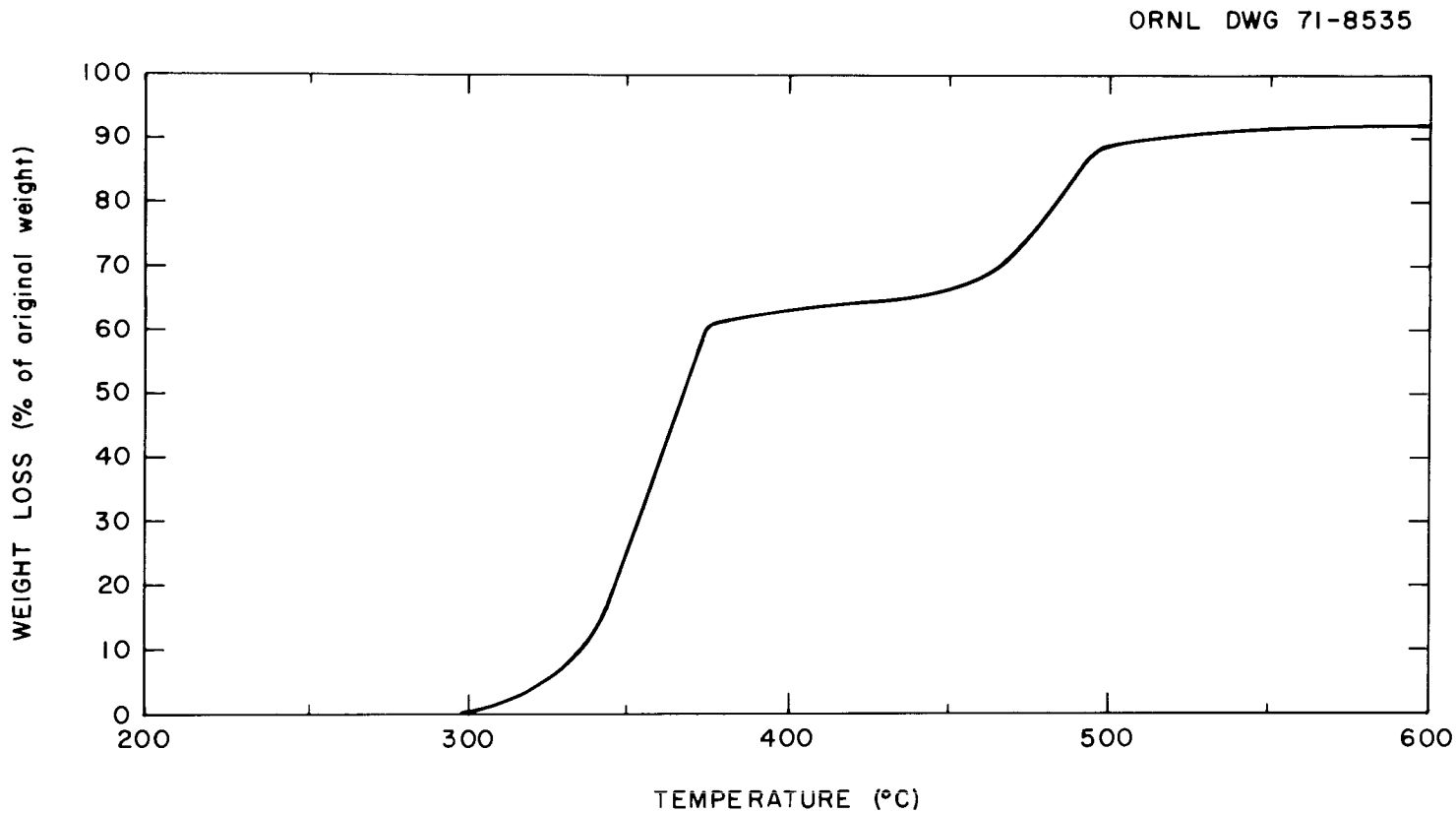


Fig. 1. Thermal Gravimetric Analysis (TGA) of Waste Composite Consisting of 25 wt % Blotter Paper, 25 wt % Cheesecloth, 25 wt % Facial Tissue, and 25 wt % Polyethylene Film. Conditions: argon flowing at 4.55 liters/hr with a heating rate of 6°C/min.

materials are summarized in Table 1. The weight losses on evacuation are close to the 6 to 8 wt % moisture range expected for cellulose when it is continuously exposed to air of normal humidity at room temperature.[6]

Two variations of the standard waste mixture were prepared to typify solid wastes containing rags and papers that had been used to wipe up acid spills and then dried, or had been used to wipe up acid spills, neutralized, and then dried. The first variation (called Type II in this report) was made by wetting one part, by weight, of the standard mixture with three parts of 2 N HNO_3 and letting the mixture air dry for several weeks with periodic stirring. The weight of the final mixture was 2.2% higher than that of the original mixture. The second variation (called Type III in this report) was made by soaking one part of the standard mixture with three parts of 2 N $NaNO_3$ solution and letting the mixture air dry for several weeks with periodic stirring. The final product contained 27.2 wt % $NaNO_3$ and 72.8 wt % standard mixture.

3. EXPERIMENTAL APPARATUS

The experimental apparatus consisted basically of wooden and metal containers for the waste, an oven to maintain the temperature level, a metal block to ensure uniform temperatures in the metal containers, temperature controllers and recorders, and pressure monitors.

The combustible containers were 1/8-in.-thick plywood boxes having outside dimensions of 2 x 3 x 3 in. or 4 x 6 x 6 in. The as-fabricated boxes were modified by the addition of an electrical terminal in the center of each end, so that a Nichrome resistance wire (to simulate a spark or source of ignition) could be embedded in the waste, and by the addition of three thermocouple wells extending into the center of the box at approximately the top, middle, and bottom planes. The noncombustible containers consisted of drums with an open head, a bolt-ring closure, and a hollow neoprene gasket. They were fabricated of 0.024-in.-thick mild-steel and had an outside diameter of 5 in., a height of 9 in., and a volume

Table 1. Summary of Results[a] Obtained from Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of Materials Used in Simulated Alpha Waste

Sample	Weight Loss on Evacuation[b] (%)	Total Weight Loss (%)	Rapid Weight Loss Range (°C)	Significant Weight Loss Range (TGA) (°C)	DTA[c] Response Range (°C)	Temperature of Maximum DTA Response (°C)	Melting or Softening Range (°C)	Temperature of Constant Weight Loss (°C)
Blotter paper	6.7	91.7	338-375	240-375	282-386	364	-	487
Cheesecloth	9.0	96.2	343-375	232-375	285-389	361	-	509
Facial tissue	6.6	90.1	321-363	226-363	304-375	351	-	499
Polyethylene	0.0	101.3	449-492	245-492	241-501	478	91-132	498
Composite[d]	5.6	92.1	333-496	269-376	295-384	356	102-126	506

[a]Conditions: argon flowing at 4.55 liters/hr with a heating rate of 6°C/min.

[b]Evacuated to 20 μm Hg and backfilled with argon.

[c]Aluminum oxide reference material.

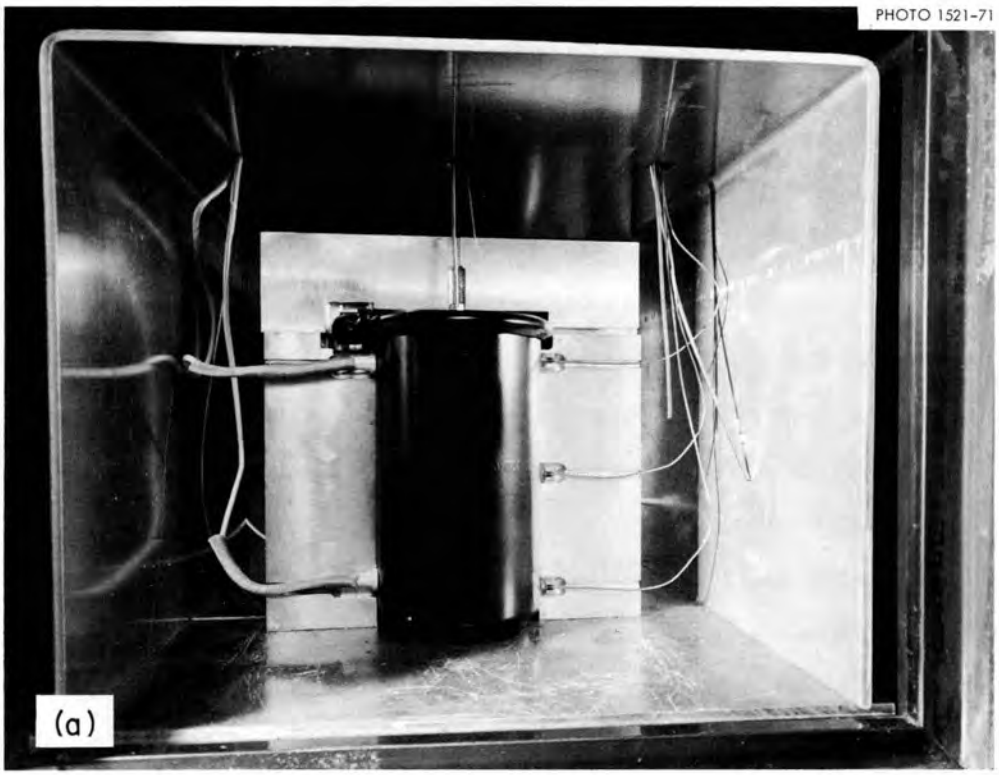
[d]Composite composed of 25 wt % blotter paper, 25 wt % cheesecloth, 25 wt % facial tissue, and 25 wt % polyethylene.

of 0.1 ft^3. The as-received drums were modified by the addition of (1) two electrically insulated terminals on one side so that a resistance wire could be embedded in the waste; (2) three thermocouple wells extending into the center of the drum at approximately the top, middle, and bottom; (3) a 0.5-in.-thick machined lid; and (4) a pressure tap on the lid (Fig. 2). The massive metal block encasing each drum to minimize temperature fluctuations was made of aluminum. It was 12 in. high, 12 in. in diameter, and machined out in the center to accommodate the drum. Figure 3 shows the drum positioned in the rear half of the block and surrounded by the block. The 4-kVA controlled-temperature oven (Fig. 3) used to maintain a chosen temperature level was 19 in. wide, 18 in. deep, 15 in. high, and lined with 1/4-in. aluminum plate to permit even distribution of the temperature at the walls. One heating element (1 kVA) was embedded uniformly in the bottom, while a second element (3kVA) was embedded uniformly in the top and sides of the oven. The temperatures of the elements were controlled by off-on pyrometer-type temperature control instruments with proportional and reset action. All temperatures were measured with Chromel-Alumel thermocouples. The thermocouples distributed throughout the wooden box and the metal drum, attached to the top and bottom of the drum, and distributed throughout the oven were swaged assemblies of either 30 or 22 AWG wire with magnesia insulation and with 1/16- or 1/8-in.-OD sheathing tubes of 310 stainless steel. The emfs of the thermocouples were recorded on self-balancing variable range potentiometers with chart speeds of 1 in./hr. Three pressure monitoring devices were attached to each drum: a pneumatic pressure transmitter with the range set for 0 to 1400 in. H_2O (gage), a differential pressure (DP) cell with the range set for 0 to 800 in. H_2O (gage), and a DP cell with the range set for 0 to -100 in. H_2O (gage). The pressure signals were fed to pneumatic recorders with chart speeds of 3/4 in./hr. No pressure monitoring devices were attached to the boxes since they were not gas-tight.

(a)

(b)

Fig. 2. Photographs of the (a) Assembled and (b) Disassembled 0.1-ft^3 Drum Showing Electrically Insulated Terminals, Thermocouple Entry Ports, and Lids with Pressure Tap, Bolt Ring, and Gasket.



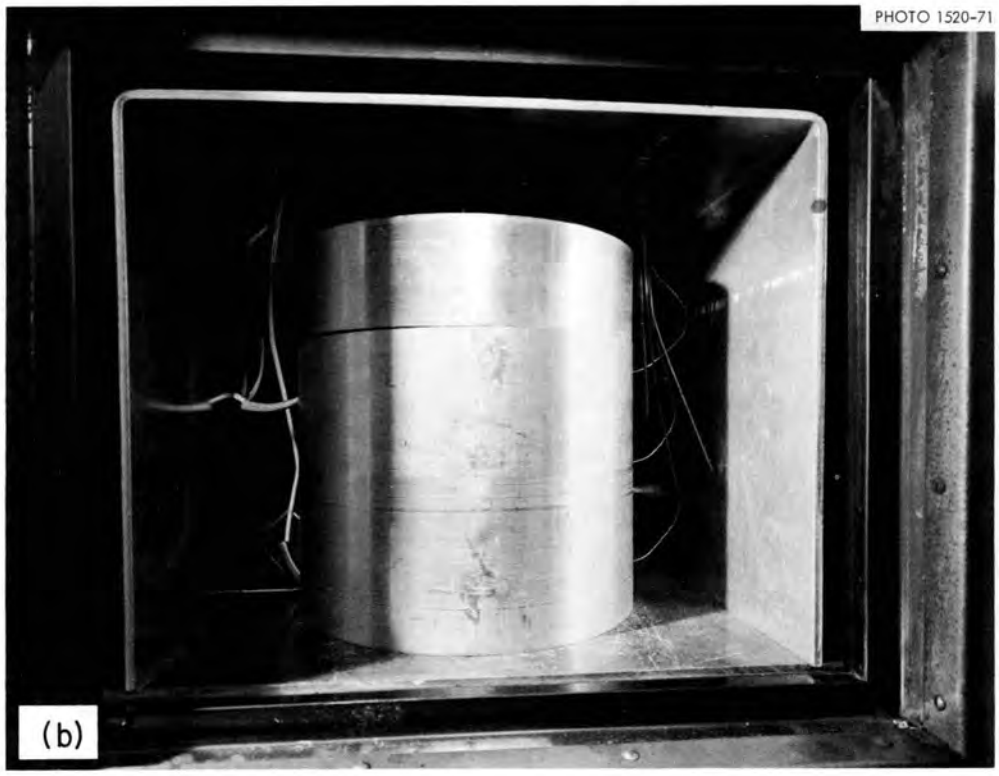


Fig. 3. Photographs Showing (a) the Assembled Drum in the Rear Half of the Aluminum Block, and (b) the Drum Surrounded by the Block in the Oven.

4. EXPERIMENTAL PROCEDURE

Each sample of simulated waste to be heated was weighed and placed in the desired container (see Sect. 3). In tests with combustible containers, lids were fitted onto the filled plywood boxes and these boxes were, in turn, placed in the oven. In some instances, the boxes were fully exposed to air; in others, they were enveloped with a layer of crushed salt about 3 in. deep, held in place by a wire mesh frame. The larger boxes were tested separately, while the smaller ones were used in a 3 x 3 x 3 array. In tests with noncombustible containers, a gasket, a lid, and a bolt ring were placed on each drum, and the bolt was tightened until the ends of the ring were 9/16 in. apart. In some cases, the gasket was coated with a silicone rubber adhesive before use. The filled drum was weighed and placed in the rear half of the aluminum block in the oven (Fig. 3). The various thermocouples, electrical leads, and, in the case of drums, the pressure readout line were connected to the container. The drums were leak checked at room temperature by pressurizing them to about 1400 in. H_2O (gage) with compressed air and requiring that this pressure remain essentially constant for approximately 2 hr. Drums that leaked under these conditions were sealed by continued tightening of the bolt ring. The front half of the aluminum block was positioned, and the temperature of the system was increased to the desired level. By using a 1-kVA power input to the oven, the system reached essentially steady-state temperature in about 4 hr at the 90°C level and in about 11 hr at the 200°C level; this is equivalent to a heating rate of about 15°C/hr. When the boxes reached a selected temperature level, the resistance wire was energized. The drums were held at temperature for a preset period of time or until the gasket was obviously breached. At the end of the heating period, each system was allowed to cool to room temperature. The cooled drum plus contents was weighed; then the waste residue was removed from the drum and weighed. The residue from the combustible containers were not weighed; only qualitative observations of their appearances were made.

5. RESULTS AND DISCUSSION

Ten heating tests were made in the wooden boxes using the standard waste mixture (Type I waste): three using a 4 x 6 x 6 in. box open to air; four using a 4 x 6 x 6 in. box enveloped by crushed salt; and three using a 3 x 3 x 3 array of 2 x 3 x 3 in. boxes enveloped by crushed salt. Sixteen heating tests were made in the metal drums: ten using the standard mixture (Type I waste); one using the standard mixture wetted with nitric acid (Type II waste); two using the standard mixture mixed with sodium nitrate (Type III waste); and three using the standard mixture with the addition of a getter (CaO). The standard waste mixture was studied at nine temperatures, while the two variations were studied at only one or two selected temperatures.

Heating per se failed to produce a flame in any of the tests with simulated combustible alpha waste in small wooden boxes. In each case, the waste simply gave off fumes and gray smoke when the resistance wire was energized and held at red heat. Only a charred black residue (from the waste and the box) was left when the wire remained on for 1 to 2 hr. However, the fumes and gray smoke could be ignited with an open flame. In those tests in which the boxes were covered with salt, the flame was more difficult to establish.

The results of heating simulated combustible alpha wastes between 90 and 215°C in small steel drums are summarized in Table 2. Representative pressure-time and temperature-time curves for wastes heated to temperatures of 125°C and 200°C, respectively, are shown in Fig. 4 (Table 2, run 4) and Fig. 5 (Table 2, run 11). The pressure-time results for the other runs are plotted in Figs. 7(a)-7(d) in Appendix B, and the remaining temperature-time results are plotted in Figs. 8(a)-8(d) in Appendix C. These data are the basis for the following discussion and analysis.

The wastes were only slightly affected by heating up to 130°C (Table 2, runs 1-5), as indicated by little or no weight loss and by no obvious or only slight color change. However, as the temperature was increased above this level, the weight loss and depth of brown color increased (Table 2, runs 6-13). In a broad sense, these

Table 2. Results from the Heating of Combustible Solid Waste in Noncombustible Containers[a]

Run	Waste Type[b] and Mass (g)	Lid and Gasket Type[c]	Time (hr) To Reach Maximum Temperature	Time (hr) At Maximum Temperature	Temperature Max. (°C)	Maximum Observed Pressure [in. H_2O (absolute)]	Weight Loss (g)	Weight Loss (%)	Comments and Observations
1	I (228)	A	4	45	90	678	0.0	0.0	No obvious change in solids.
2	I (228)	D	7	162	120	867	0.1	0.04	Solids are tan. Incipient melting of plastic.
3	II (233)	A	7	89	125	740	0.6	0.3	Solids are brown. Incipient melting of plastic.
4	III (313)	B	7	111	125	680	0.2	0.06	Solids are tan. Incipient melting of plastic.
5	I (228)	A	9	134	130	778	0.0	0.0	Solids are tan. Incipient melting of plastic.
6	I (228)	C	9	135	145	1074	4.9	2.1	Solids are light brown. Melting of plastic.
7	III (313)	C	10	58	150	1061	5.1	1.6	Solids are brown. Melting of plastic.
8	I (228)	C	10	110	160	1264	8.0	3.5	Solids are brown. Plastic melted.
9	I (228)	B	10	10	185	>1200[d]	12.7	5.6	Solids are light brown. Plastic melted.
10	I (228)	D	11	10	195	1635	13.7	6.0	Solids are brown. Plastic melted.
11	I (228)	B	11	105	200	1592	26.7	11.7	Solids are dark brown. Plastic melted.
12	I (228)	B	11	55	205	>1200[d]	14.4	6.3	Solids are dark brown. Plastic melted.
13	I (228)	B	11	52	205	1532	13.2	5.8	Solids are dark brown. Plastic melted.
14	IV (285)	D	11	39	210	567 (651)[e]	0.5	0.2	Solids are light brown. Plastic melted.
15	V (342)	D	11	205	215	617 (657)[e]	0.9	0.3	Solids are brown. Plastic melted. Vacuum (-100 in. H_2O) on cool-down.
16	VI (456)	D	11	205	215	567 (657)[e]	0.8	0.2	Solids are brown. Plastic melted.

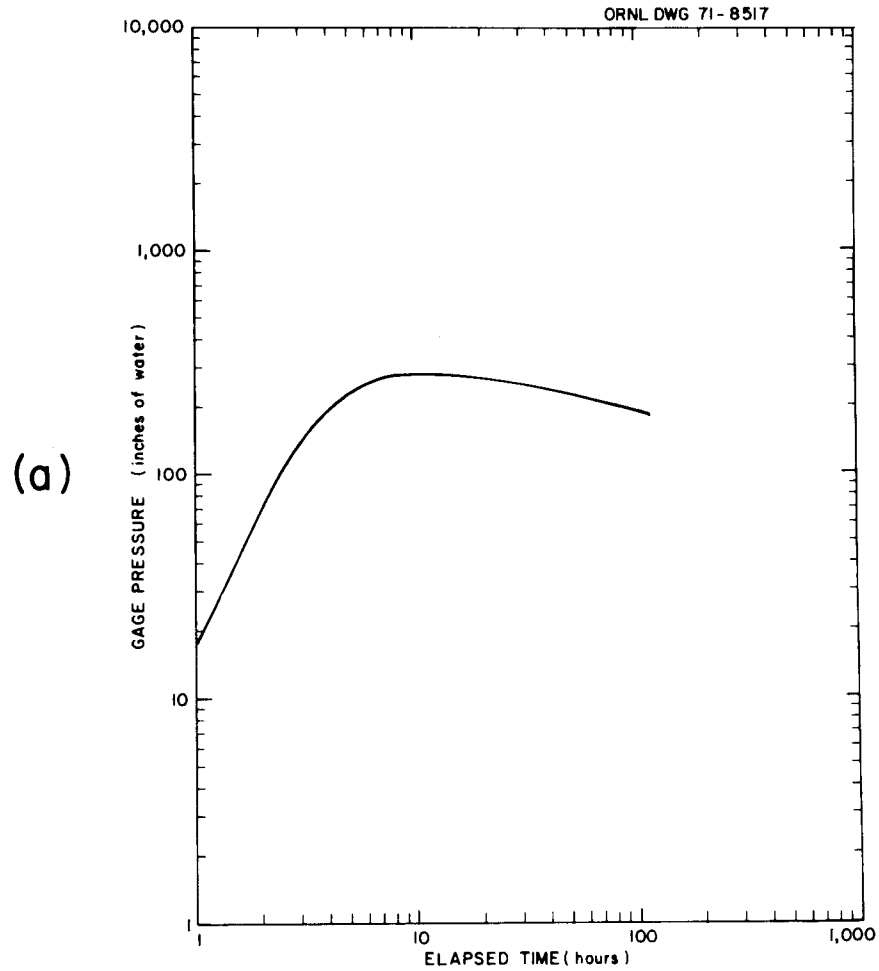
[a]Container was a mild-steel drum with lid, rubber gasket, bolt-ring closure, and a volume of 0.1 ft^3.

[b]
I. Standard waste (Type I) was composed of 25 wt % blotter paper, 25 wt % cheesecloth, 25 wt % facial tissue, and 25 wt % polyethylene film, each cut into 1-in. squares.
II. Waste Type II was prepared by wetting one part standard waste with three parts (by weight) of 2 N HNO_3 and letting the mixture air dry for several weeks with periodic stirring. The weight of the final mixture was 2.2% higher than that of the standard waste.
III. Waste Type III was prepared by soaking one part standard waste with three parts (by weight) of 2 N $NaNO_3$ solution and letting the mixture air dry for several weeks with periodic stirring. The final mixture contained 27.2 wt % $NaNO_3$ and 72.8 wt % standard waste.
IV. Waste Type IV was prepared by mixing four parts of standard waste with one part (by weight) of bone-dry CaO.
V. Waste Type V was prepared by mixing two parts standard waste with one part CaO.
VI. Waste Type VI was prepared by mixing one part standard waste with one part CaO.

[c]
A. Original lid and gasket.
B. Original lid and gasket plus silicone-rubber sealant (glue).
C. Machined lid and original gasket.
D. Machined lid and original gasket plus silicone-rubber sealant (glue).

[d]Differential pressure cell in line at the time had an upper limit of 800 in. H_2O (gage).

[e]Calculated assuming air is a perfect gas; i.e., $P = 400(T/297)$.



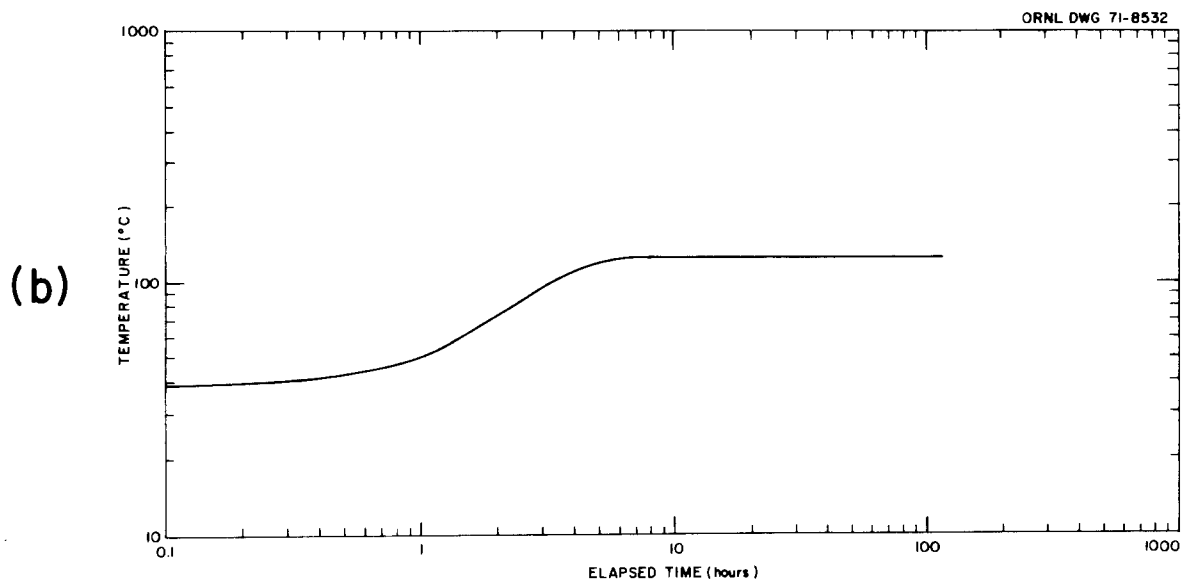
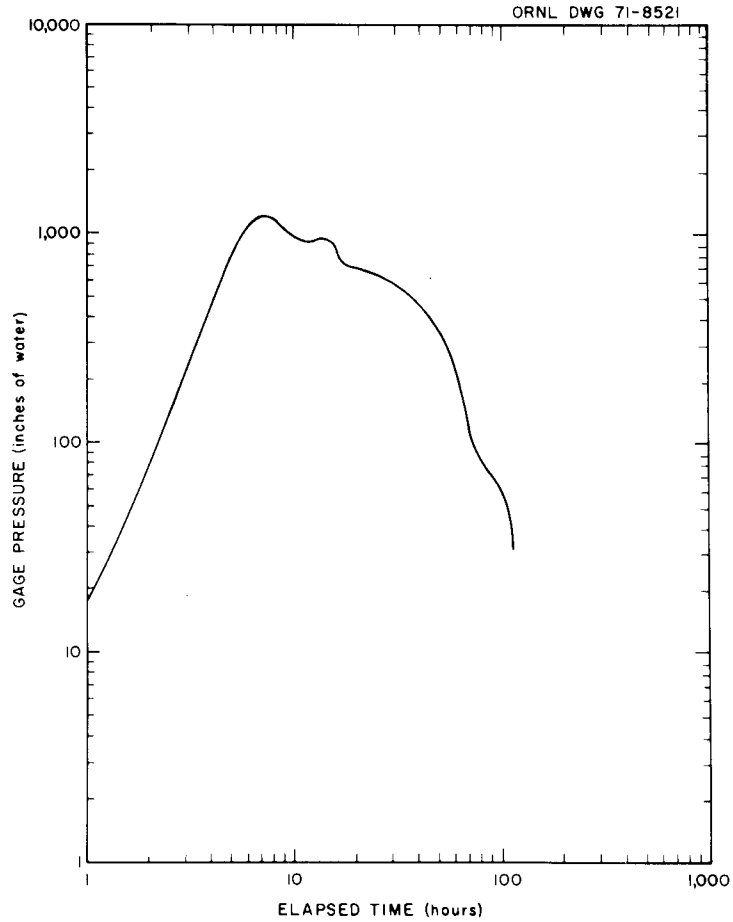


Fig. 4. Pressure-Time and Temperature-Time Results for Run 4 (see Table 2).

(a)



(b)

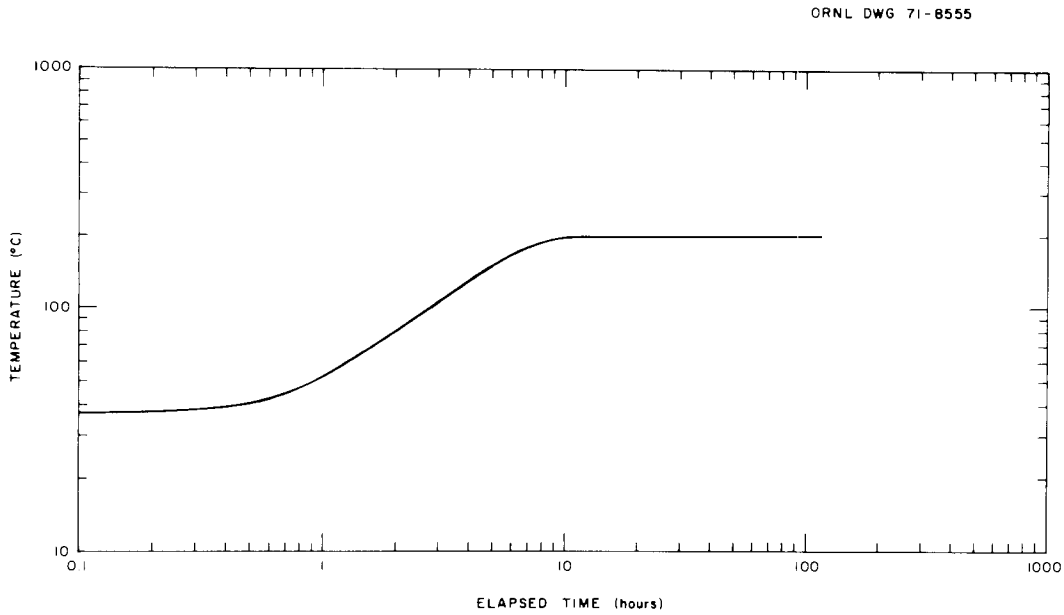


Fig. 5. Pressure-Time and Temperature-Time Results for Run 11 (see Table 2).

observations are in accord with those reported by others[7] concerning the effect of heat on cellulose, namely, " . . ., cellulose can be heated at temperatures up to 140°C, and if the duration of treatment is kept below 4 hrs with a low initial moisture content, very little change will occur. Above 140°C cellulose undergoes both chemical and physical modifications . . ." The weight losses measured, for approximately equal heating times, ranged from about 2 wt % at 145°C (Table 2, run 6) to about 4 wt % at 160°C (Table 2, run 8), and to about 12 wt % at 200°C (Table 2, run 11). Generally, the results show increasing weight loss with increasing temperature and time at temperature. No real difference was discerned in the behavior of Types I, II, and III wastes at the temperatures and times studied. In several of the runs, the resistance wire embedded in the waste in the drums was energized and held at a red heat for several minutes. The only noticeable effect was increased charring of the waste in the vicinity of the wire.

Gaseous products from the destructive distillation of cellulose in vacuum are reported[8] to be carbon dioxide, carbon monoxide, water vapor or steam, and small amounts of hydrocarbons such as methane and ethane. Gases such as those above from pyrolysis, water vapor or steam and carbon dioxide from oxidation (limited oxidation because of the limited amount of oxygen in the drum), and water vapor or steam from adsorbed water are expected to be evolved during the heating of combustible alpha wastes in sealed containers. Comparisons between the maximum pressure observed in each run, the pressure expected from expansion of the original air in the drum at the maximum temperature of the run (oxidation and pyrolysis occur to such a slight extent that the net number of moles of gas in the drum should not be affected appreciably), and the vapor pressure of saturated steam at each maximum temperature were made (Table 3). In runs 1-13, the maximum pressure observed was greater than that predicted for expansion of air in the drum, and the difference between the maximum pressure and the expanded air pressure was less than the vapor pressure of saturated steam at that temperature. The weight of water that must be vaporized to give this pressure difference was calculated using the perfect gas law (Table 3). The volume of the gas space in the filled drum, for application in gas

Table 3. Comparison of Maximum Pressures Observed During Heating of Simulated Combustible Alpha Wastes with Pressures Expected from Expansion of Air in the Drum and of Saturated Steam

Run	Waste Type[a]	Temperature, Max. (°C)	Pressure [in. H_2O (absolute)] Maximum Observed	Due to Expansion of Original Air[b]	Difference Between Max. Pressure and Expanded Air	Saturated Steam[c]	Grams[d] of Water Vapor or Steam Required in Vapor Space of Drum to Give Pressure Difference (Max. Observed - Expanded Air)
1	I	90	678	489	189	282	0.74
2	I	120	867	529	338	805	1.22
3	II	125	740	536	204	941	0.73
4	III	125	680	536	144	941	0.52
5	I	130	778	543	235	1090	0.83
6	I	145	1074	563	511	1670	1.74
7	III	150	1061	570	491	1920	1.65
8	I	160	1264	583	681	2500	2.23
9	I	185	>1200	617	>583	4560	>1.81
10	I	195	1635	630	1005	5690	3.06
11	I	200	1592	637	955	6360	2.88
12	I	205	>1200	644	>556	6940	>1.66
13	I	205	1532	644	888	6940	2.65

[a] I. Standard waste (Type I) was composed of 25 wt % blotter paper, 25 wt % cheesecloth, 25 wt % facial tissue, and 25 wt % polyethylene film, each cut into 1-in. squares.
II. Waste Type II was prepared by wetting one part standard waste with three parts (by weight) of 2 N HNO_3 and letting the mixture air dry for several weeks with periodic stirring. The weight of the final mixture was 2.2% higher than that of the standard waste.
III. Waste Type III was prepared by soaking one part standard waste with three parts (by weight) of 2 N $NaNO_3$ solution and letting the mixture air dry for several weeks with periodic stirring. The final mixture contained 27.2 wt % $NaNO_3$ and 72.8 wt % standard waste.

[b] Calculated by assuming that air is a perfect gas; i.e., $P = 400\ (T/297)$.

[c] From R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick (Eds.), Chemical Engineers' Handbook, 4th ed., p. 3-192, McGraw-Hill, New York, 1963.

[d] Calculated by taking the pore-free densities of cellulose, polyethylene, and sodium nitrate to be 1.4, 0.9, and 2.26 g/cc, respectively, and by assuming that the perfect gas law holds for water vapor or steam; i.e., $W = 1.42(P/T)$ for Types I and II wastes and $W = 1.40(P/T)$ for Type III waste, where W is weight of water vapor or steam in grams, P is absolute pressure difference in in. H_2O, and T is temperature in degrees Kelvin.

law calculations, was determined using the measured volume of the drum, the weight of materials added to the drum, and the published densities of cellulose, polyethylene, and sodium nitrate. Assuming that the loss of weight on evacuation (Table 1) is due to loss of adsorbed water, the water added to the drum with each 228-g batch of standard waste mixture is calculated to be 12.8 g. This amount of water is from 4 to 25 times that (Table 3) needed to explain the difference between the observed maximum pressure and the pressure expected from gas expansion.

Runs 1 and 5 were judged to be the only runs in which the drums (i.e., the gaskets) did not leak, as evidenced by no weight losses (Table 2) and monotonic pressure-time traces obtained during heating [Fig. 7(a) in Appendix B]. Although the gaskets held pressures of 1400 in. H_2O (gage) during cold (ambient temperature) testing, it is not unreasonable to expect that they would leak after many hours of exposure to high (90-215°C) temperatures. The 17C and 17H specification metal drums most commonly used as waste containers have leakage test requirements of about 400 in. H_2O (gage)[9] and 200 in. H_2O (gage),[10] respectively, at ambient temperatures with no time requirements. The results of runs 1-16 (Table 2 and Figs. 4, 5, 7, and 8) showed that pressures as high as 200 to 400 in. H_2O (gage) are not reached in the drums until the temperatures are between 90 and 115°C. These temperatures are well beyond those normally encountered in handling and shipping alpha wastes.

Three runs (Table 2, runs 14-16) were made in which a basic inorganic getter (CaO) was added to the drums to prevent buildup of pressure as a result of the presence of gases – primarily water and carbon dioxide, but also other acidic gases – evolved during the thermal degradation and limited oxidation of solid combustible waste. In these runs, which were carried out at about 200°C, bone-dry CaO was mixed with the waste [Table 2, Figs. 7(d) and 8(d)] in increasing amounts to give CaO-to-waste-weight ratios of 1/4, 1/2, and 1. The weight losses in these runs were only 0.2 to 0.3%, whereas the losses in comparable runs at about 200°C without a getter were about 6 to 12%. Further, the maximum pressures observed in the runs in which CaO was added were less than the pressure rises expected from expansion of the original air (Table 2); they are about one-half the pressure test requirement for DOT 17C

specification metal drums and about equal to the requirement for DOT 17H drums.

6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been reached from these studies on heating simulated combustible alpha wastes in wooden boxes and metal drums:

1. Combustible wastes packaged in combustible containers such as wooden crates should not be acceptable at a final repository. In the event that pyrolysis or limited combustion occurs, such containers will not ensure against the entrance of air to the waste or prevent the release of smoke and fumes and, possibly, entrained alpha nuclides.

2. Combustible wastes packaged in sealed noncombustible containers such as DOT 17C and DOT 17H specification metal drums or equivalents should be acceptable at a final repository. These containers when properly sealed can hold the gases that are evolved during handling and shipping. If released, these gases could possibly entrain alpha nuclides.

3. The quantities of gases evolved during heating of these wastes can be reduced by adding getters, such as alkaline-earth oxides, that form stable compounds with the principal gases formed during slow and limited oxidation as well as pyrolysis of the waste solids.

The results of this investigation suggest some interesting areas for further work with combustible solid wastes in sealed drums. These areas include: (1) heating the filled drums at much higher rates to simulate exposure to a very high heat flux (e.g., in a fire); (2) studying waste mixtures that contain additional representative solid combustibles such as rubber and polyvinyl chloride (some of the waste systems should be studied in pressure vessels so that interpretation of their behavior on heating will not be complicated by leaks); and (3) evaluating ways of sealing steel drums so that they do not leak during handling and shipping.

7. ACKNOWLEDGMENTS

Appreciation is expressed to J. P. Nichols for his helpful advice during the course of the studies and to R. C. Lovelace for his valuable aid in carrying out the tests and collating the results.

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10. Ibid., Section 178.118-13.

9. APPENDIX A: TGA OF COMPONENTS IN SIMULATED SOLID WASTE

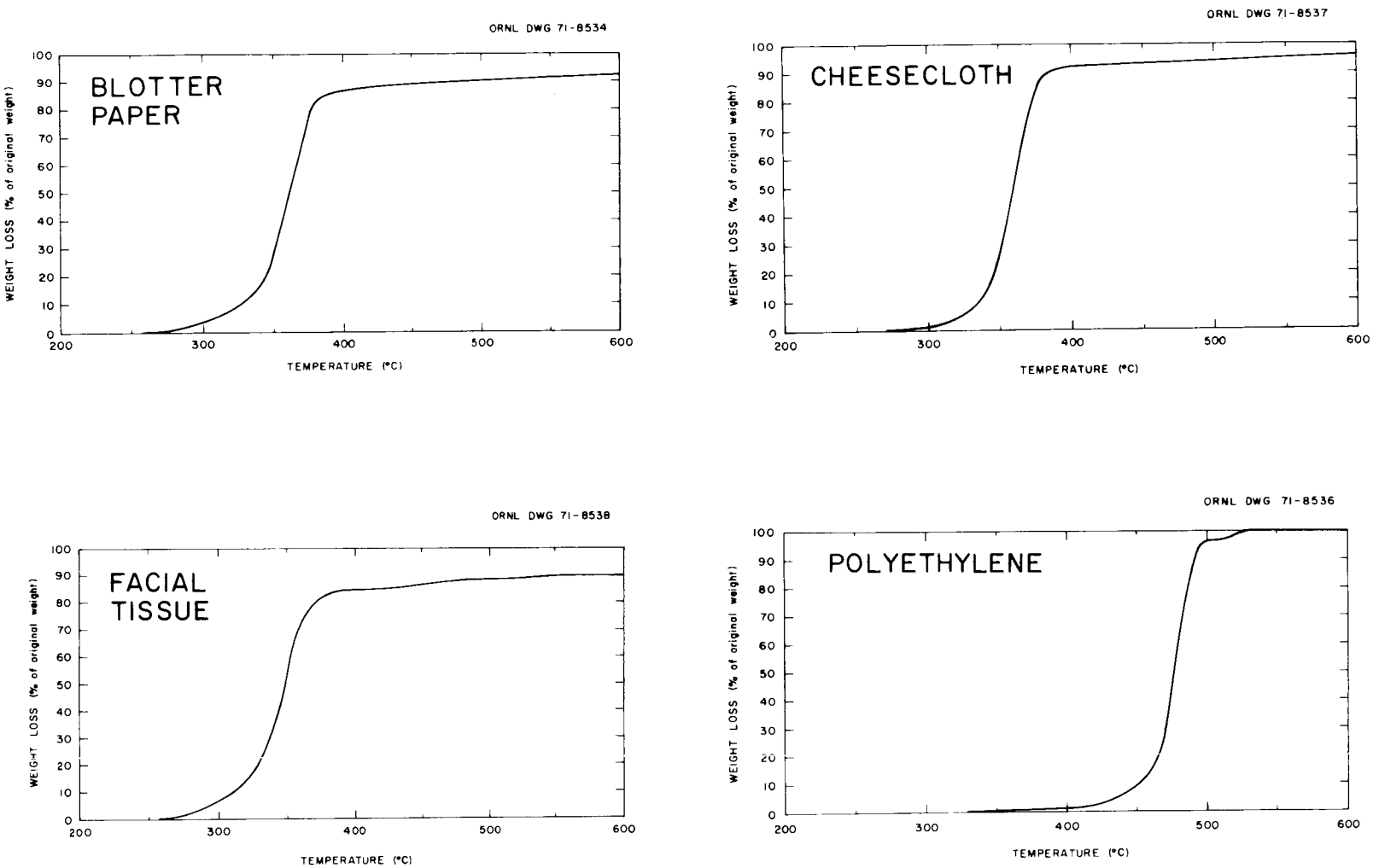


Fig. 6. Thermal Gravimetric Analysis (TGA) of Materials Comprising Waste Composite (Type I). Conditions: argon flowing at 4.55 liters/hr with a heating rate of 6°C/min.

10. APPENDIX B: PRESSURE-TIME RESULTS OBTAINED BY HEATING WASTES IN STEEL DRUMS

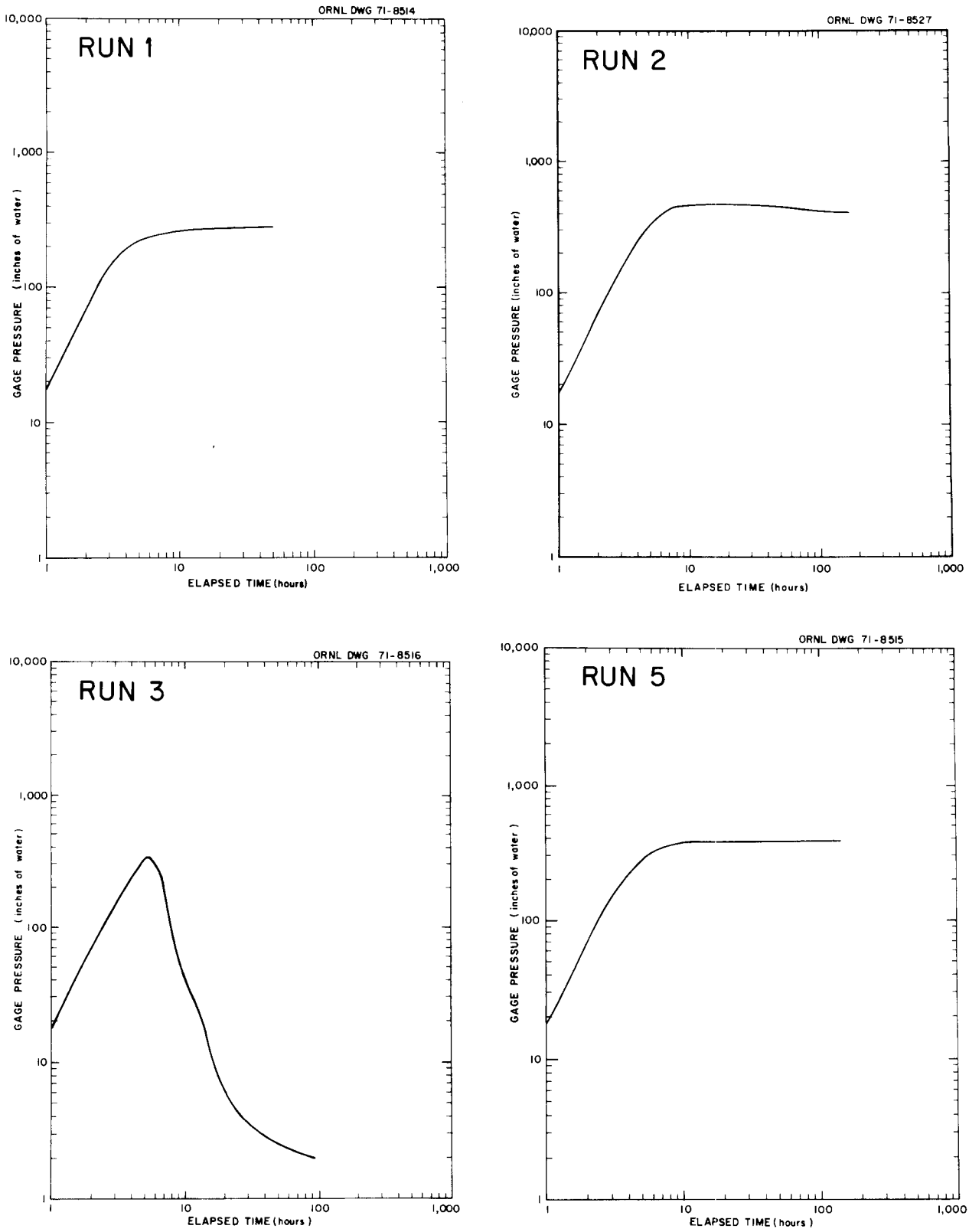


Fig. 7(a). Pressure-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

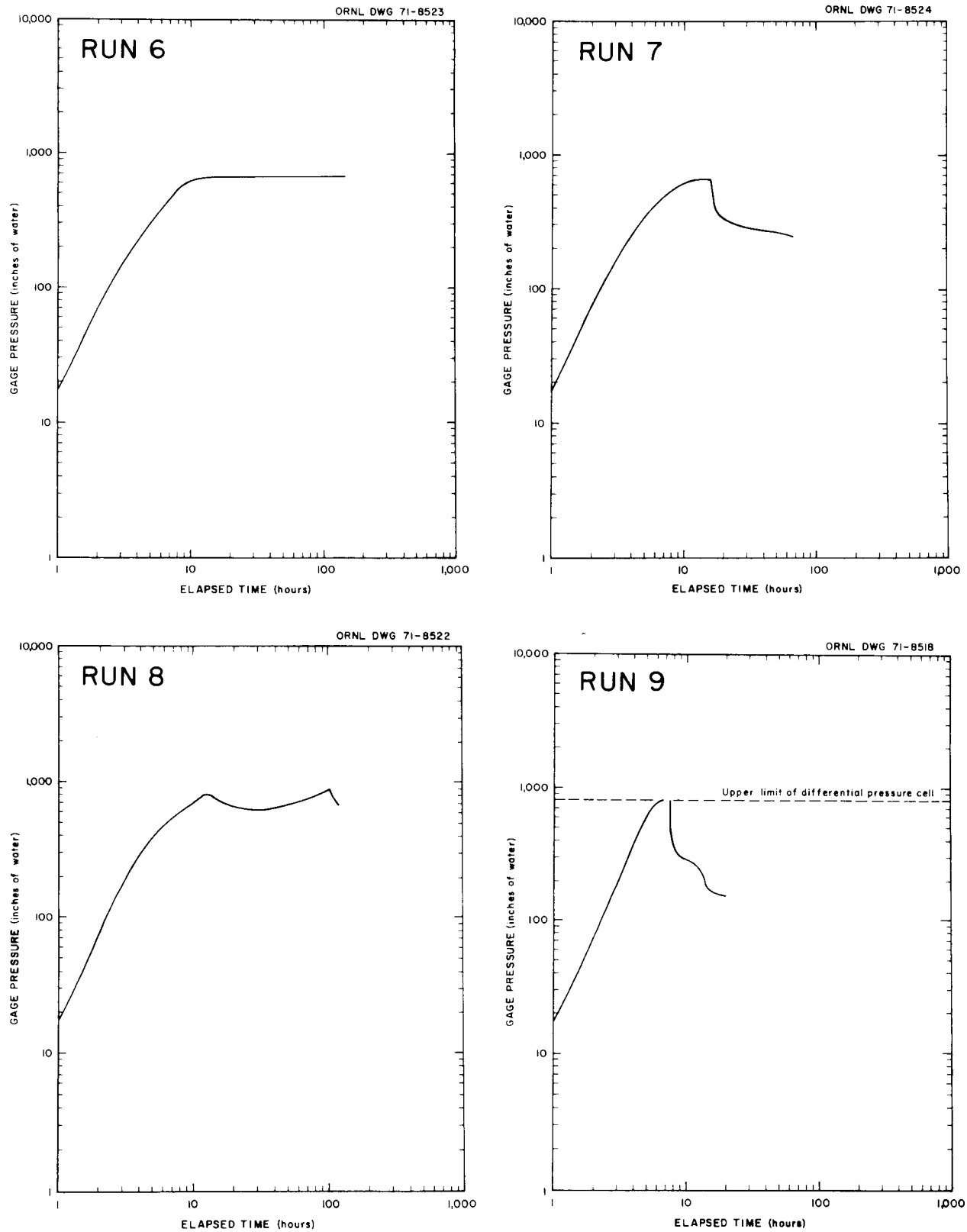


Fig. 7(b). Pressure-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

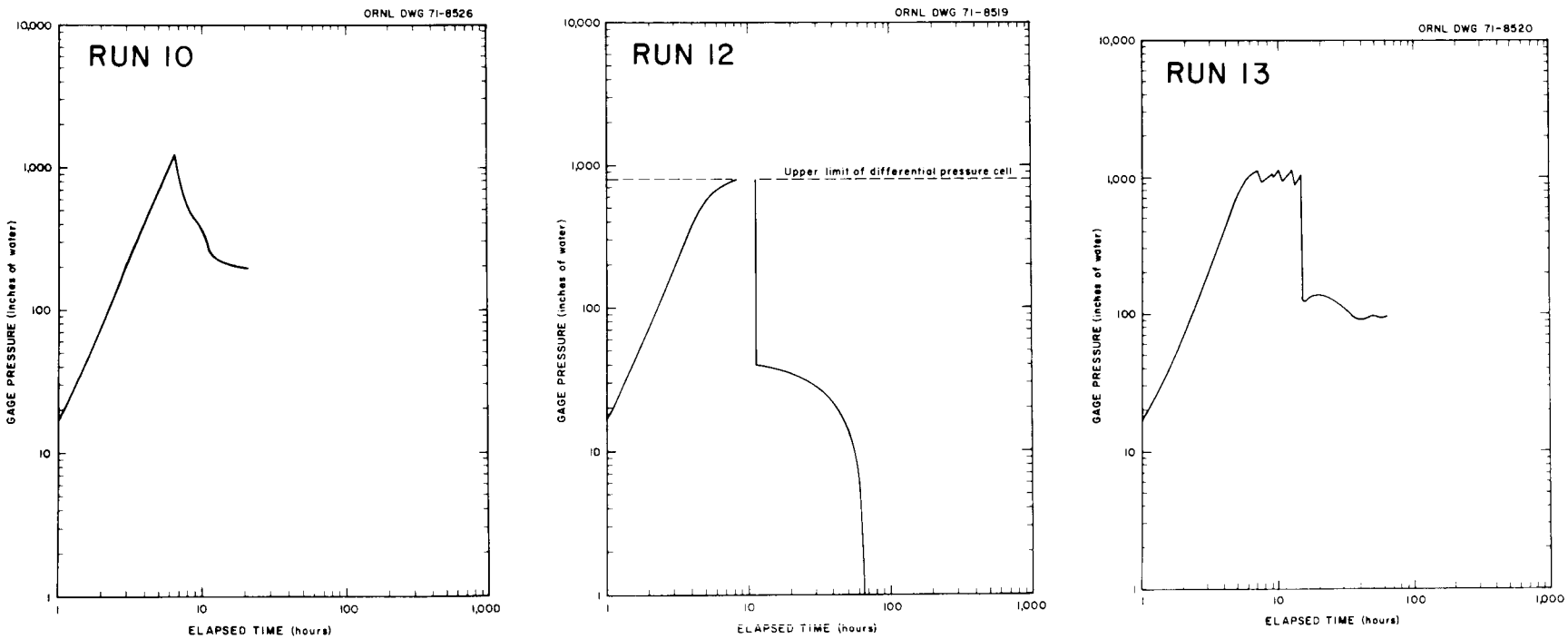


Fig. 7(c). Pressure-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

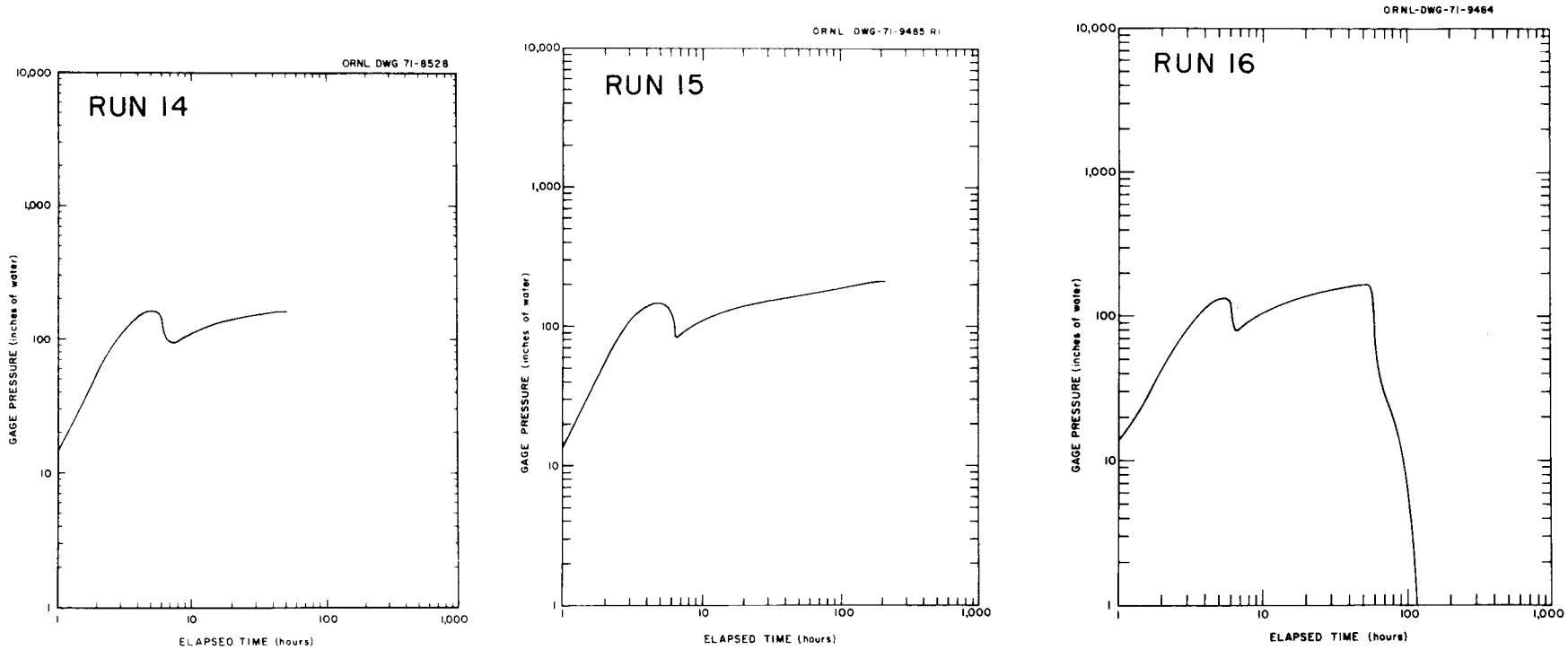


Fig. 7(d). Pressure-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

11. APPENDIX C: TEMPERATURE-TIME RESULTS OBTAINED BY HEATING WASTES IN STEEL DRUMS

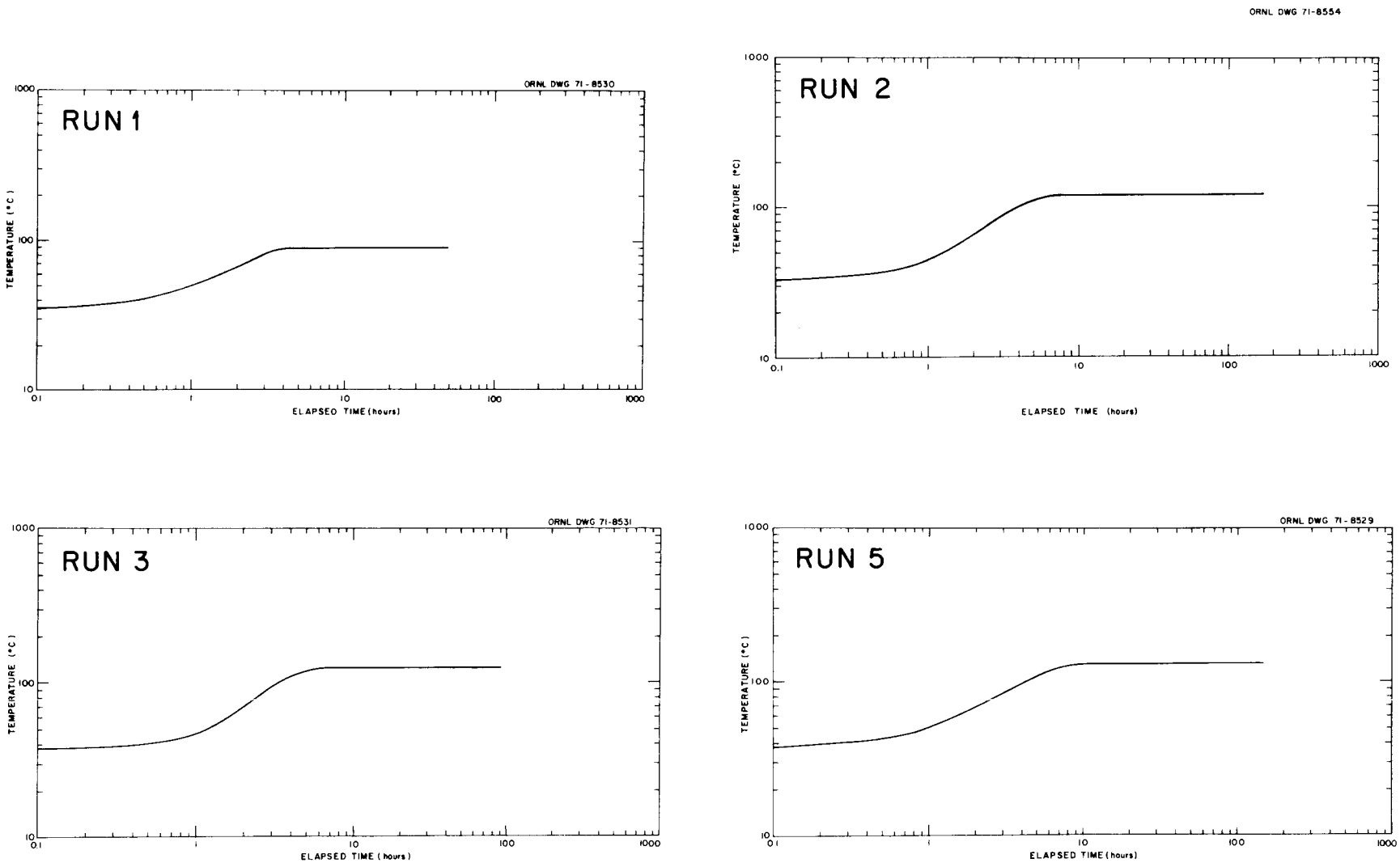
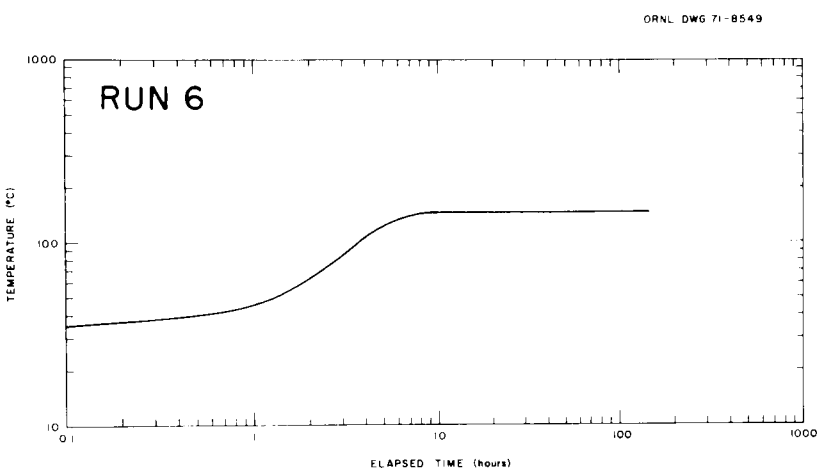
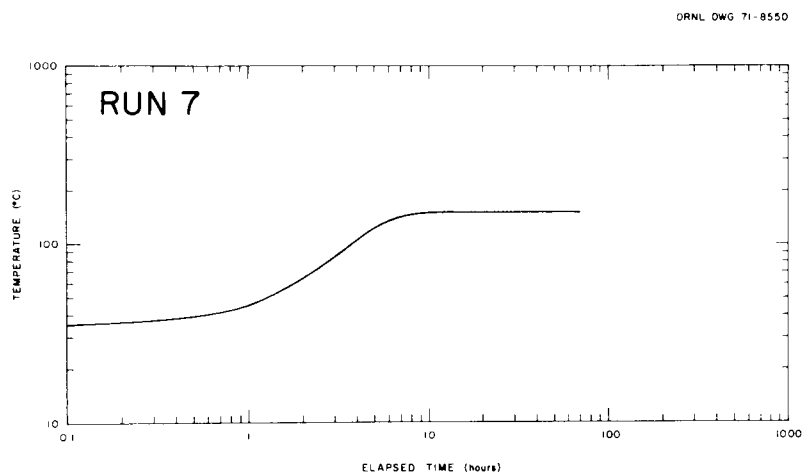
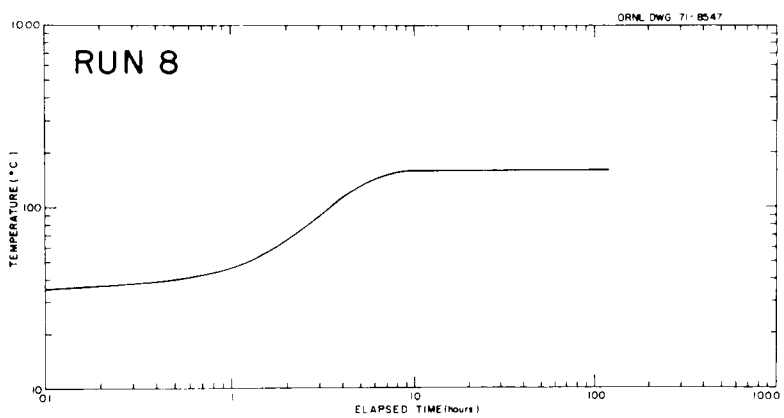


Fig. 8(a). Temperature-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.







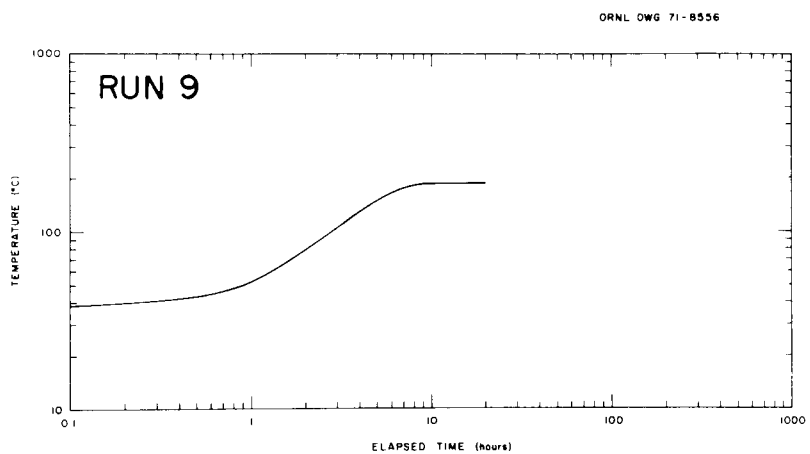


Fig. 8(b). Temperature-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

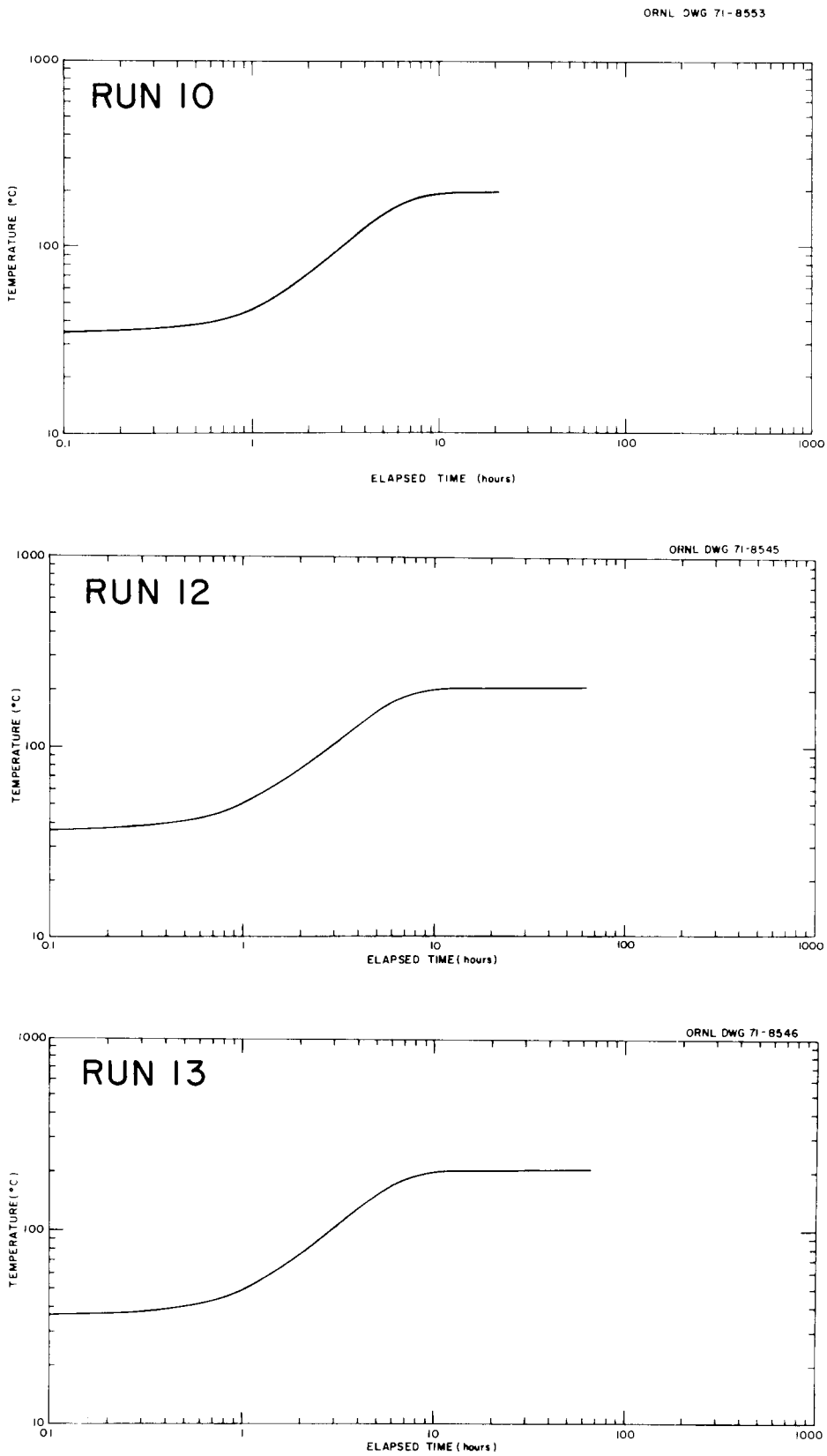


Fig. 8(c). Temperature-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

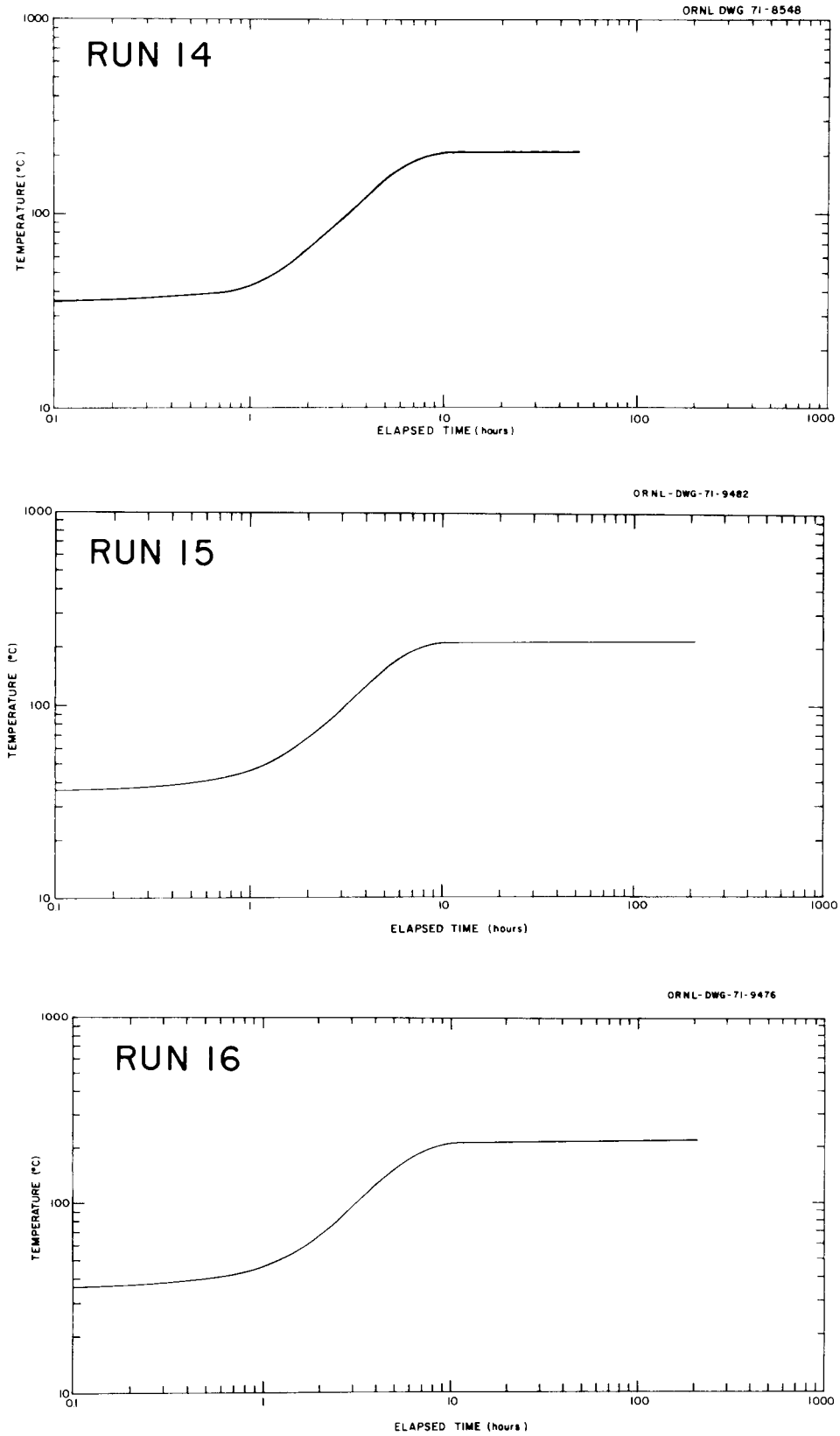


Fig. 8(d). Temperature-Time Results Obtained by Heating Combustible Solid Wastes in Steel Drums.

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