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Note

CELLULOSE THERMALLY DECOMPOSES AT 70°C

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Low-temperature thermal degradation of organic materials has the potential for generating various gases. A large percentage (20—25%) of the retrievably-stored wastes that are contaminated with transuranic (TRU) radionuclides are organic materials [1]. During geologic storage, gases generated from such materials potentially could breach a repository and decrease containment integrity. This has previously been an area where insufficient data existed for risk assessment analyses [2]. Since November 1977, a research program has been in progress at the Los Alamos National Scientific Laboratory to study decomposition of materials under anticipated geologic storage conditions. The study of low-temperature thermal degradation has constituted a large segment of this program.

Temperatures selected for this work represent those that might occur in the Waste Isolation Pilot Plant (WIPP) proposed for southeastern New Mexico. A temperature of about 20°C would be expected in the WIPP during its operating phase. If heat-generating wastes were emplaced at 75 or 150 kw acre^{-1}, the expected temperatures would peak at 40 or 70°C, respectively, 200 years after repository sealing, and then slowly decline.

The thermal degradation studies in this program consisted of two phases: (1) determination of threshold decomposition temperatures for a broad range of common materials found in plutonium laboratories; and (2) long-term, surveillance experiments with selected matrices at the previously mentioned temperatures (20, 40, and 70°C).

EXPERIMENTAL

Materials from each of three general categories (cellulosics, plastics, and rubbers) were subjected to thermogravimetric analyses using aerobic (air) and anaerobic (nitrogen) atmospheres to determine threshold decomposition temperatures. The temperature at which a sample began to lose weight (exclusive of sorbed water) was taken as the threshold decomposition temperature. Previous experiments [3] showed that oxygen was rapidly consumed to produce a relatively anaerobic atmosphere over organic TRU wastes. Consequently, the majority of the threshold decomposition experiments were performed in a nitrogen atmosphere.

To perform these studies, a Mettler II thermobalance was used. Because this particular instrument was designed for high-temperature work (>1000°C) it was modified to operate at lower temperatures. After modification was completed, the instrument operated well at temperatures as low as 40 and 70°C. The experimental parameters used for the threshold decomposition studies were: instrument, Mettler TA-II thermobalance using the low power tap on the transformer and a custom-fabricated molybdenum crucible cover; gas flow rate, 10–20 cm^3 min^{-1}; temperatures, 20 → 500°C; heating rate, 10°C min^{-1}; and sample size, 60–80 mg.

For the surveillance experiments, test materials were sealed in stainless steel cylinders to allow evolved gases to accumulate for long periods of time. Stainless steel was required because many of the materials were plutonium contaminated [4]. In these experiments, thermal degradation was monitored by pressure increases caused by gas evolution. It was easier to measure a small quantity of gas by its pressure than by its mass equivalent. Typically, 50 g of a material were sealed in a Hoke 300 cm^3 cylinder. The cylinders were then placed in laboratory ovens at 40, 70, or 100°C. The 100°C temperature was included as an overtest temperature to obtain rate data more quickly. Some of the cylinders were stored at ambient laboratory temperature (19–23°C).

Additional experiments determined whether thermal degradation would be accelerated by potential catalysts that the wastes might contact in the WIPP. For threshold decomposition studies, four potential catalysts were selected: sodium chloride, powdered iron, powdered iron oxide, and powdered ferrous chloride. These potential catalysts were applied to the surfaces of the test materials. The loadings ranged from 2 to 38 wt.% in accordance with the textures of the materials. For the surveillance experiments, the number of catalysts was reduced to two (sodium chloride and ferrous chloride) because a literature search indicated only these two might increase gas evolution or lower decomposition temperatures of the test materials. The loadings for these experiments were about 2 wt.%.

RESULTS AND DISCUSSION

Threshold decomposition temperatures measured in air for various cellulosic, plastic, and rubber materials are presented in Table 1. Pylox (polyvinyl chloride) gloves had the lowest threshold decomposition temperature, 150°C. All of the cellulosics evolved about 2–3 wt.% water when heated through the 40–110°C range. This water was determined to be in or on the materials, not chemically bound, by desiccation experiments. No other category of materials evolved water below 110°C. However, Hansen [5] proposed a reaction mechanism for the thermal oxidation of hydrocarbon polymers that produces water. A typical thermogram for one of the materials (bitumen) is given in Fig. 1.

Because several of the materials in each category (cellulosics, plastics, and rubbers) have similar characteristics and threshold decomposition temperatures in air, only a few representative materials from each category were chosen to represent the entire category for additional studies. These

TABLE 1

Threshold decomposition temperatures in air

Material	Temp. (°C)
Cellulosics [a]	
Scott utility wipes	185
Kleenex tissues	185
Diaper paper (PE-backed)	190—195
Cloth (cotton twill)	185
T-shirt (cotton)	185—190
Cheesecloth	205
Wood	175
Fiberboard	185—190
Plastics	
Pylox gloves (PVC)	150
Tygon tubing (PVC)	175
Polyethylene	210
Polypropylene	195—200
Lucite [poly(methyl methacrylate)]	170—175
Teflon [poly(fluoroethylene)]	430—435
Rubbers	
Hypalon	165
Neoprene	175—180
Durasol/neosol	180
Latex	195
Bitumen [b]	275

[a] Water loss observed at 40—110°C.

[b] Not a rubber material.

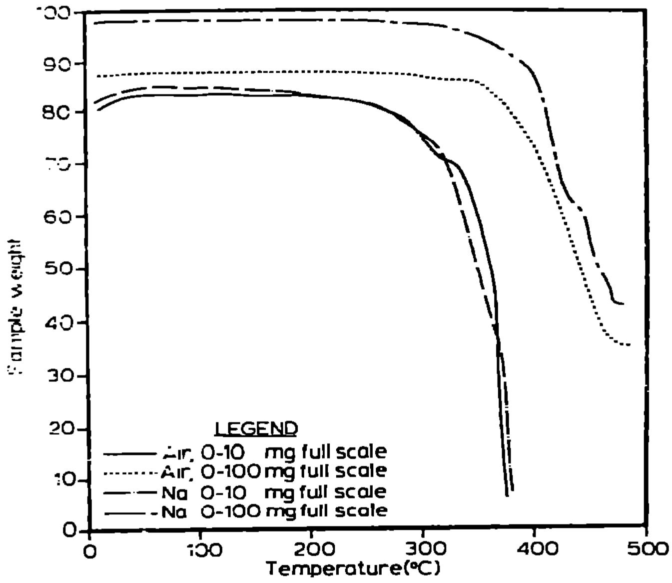

Fig. 1. Thermograms of bitumen.

materials and their measured threshold decomposition temperatures in nitrogen are given in Table 2. Anaerobic decomposition of cellulose (paper) starts at approximately the same temperature as it does in air. Unless the degradation mechanisms are considered, this may seem surprising. Schwenker and Beck [6] conducted pyrolysis—gas chromatographic experiments to investigate degradation mechanisms of cellulose in different atmospheres. They concluded that the thermal degradation mechanism of cellulose was nonoxidative, and hence, independent of the atmosphere. Consequently, the threshold decomposition temperatures under aerobic and anaerobic conditions should be about equal. For polymethyl methacrylate (plexiglas or Lucite) and Hypalon, the anaerobic decompositions start at slightly lower temperatures than they do in air. Catalyzed threshold decompositions also are presented in Table 2. No significant lowerings were observed for any of the materials with any of the potential catalysts.

Even though the observed threshold decomposition temperatures are significantly higher than the maximum anticipated repository temperature, it is possible that the materials could decompose very slowly during the very long storage times and accumulate appreciable quantities of gases. In fact, Murphy [7] states that cellulose should decompose even at room temperature at a very slow, but finite rate. The reason that a weight change is not observed on the thermobalance at low temperatures may be kinetic, i.e., the weight loss may be so small and may occur so slowly that it cannot be observed instrumentally. Consequently, the surveillance experiments were performed to increase the sensitivity of observation.

Gas generation rates for the thermal decomposition of cellulose are presented in Table 3. For some of the tests, decomposition may occur by two mechanisms: (1) thermal degradation; and (2) radiolytic degradation. Radiolytic degradation of cellulose is discussed elsewhere [8]. From the data presented in Table 3, it is apparent that the gas generation rates are so low that truly quantitative statements cannot be made on the rates of thermal decomposition at or below 100°C.

However, gas analysis data show that thermal decomposition is occurring. Although thermal degradation at temperatures as low as 100°C has been postulated, to my knowledge, this is the first time that thermal degradation of cellulose has been demonstrated to occur at 100°C. Mass spectrometric

TABLE 2

Threshold decomposition temperatures in nitrogen

Material	None	NaCl	Fe_2O_3	$FeCl_2$	Fe powder
Utility wipes	185	180	185	170—195	195
Cotton	185	195	200	170—195	205
Lucite	150	155	170	185	160
Polyethylene	320	290	295	330	335
Hypalon	160	175	160	155	160
Bitumen	290				

TABLE 3

Decomposition of cellulosics (paper)

Dose rate	Temperature (°C)							
	20		40		70		100	
	Elapsed time (days)	Gas rate [a] (moles/d-g)	Elapsed time (days)	Gas rate [a] (moles/d-g)	Elapsed time (days)	Gas rate [a] (moles/d-g)	Elapsed time (days)	Gas rate [a] (moles/d-g)
4×10^5 nCi/g	733	0.05	676	0	255	0.5	43	2.0
					352	0.4	127	2.8
					450	0.3	233	1.6
					699	0.3	309	1.6
							402	1.5
							653	2.0
4×10^4 nCi/g	641	0	636	0	200	0.3	61	1.3
					297	0.1	177	1.6
					395	0.1	293	1.3
					644	0.1	386	1.2
							637	1.3
No Pu	[b]	[b]	665	>0	241	0.07	[b]	[b]
					338	0.05		
					436	0.08		
					685	0.08		

[a] Gas generation rates must be multiplied by 10^{-6}, for example, 0.05×10^{-6} moles/(d-g).

[b] No experiment in progress.

analyses show that the evolved gas is 90—95 mole % CO_2 and 5—10 mole % H_2. Water may also be produced, but cannot be determined by our mass spectrometer. After 519 days exposure at 100°C, one experiment with a very low level of plutonium contamination was terminated. The gases which escaped from the test cylinder when a valve was removed had a char-like odor. Sectioning of the valve revealed tarry degradation deposits that had condensed from the gases evolved from the cellulose. The carbon to hydrogen ratio of the condensation products was 1.7 : 1. This residue was not volatile at 200°C so a mass spectrum could not be obtained. Also, cellulose has been observed (by gas evolution) to decompose at 70°C and possibly at 40°C. No experimental evidence yet obtained verifies thermal degradation at 20°C. Two other series of similar experiments with polyethylene or a composite (35% cellulose, 23% polyethylene, 12% polyvinyl chloride, 15% neoprene, and 15% Hypalon) exhibit thermal degradation at 100 or 70°C. Gas generation is just barely observable for them.

Several surveillance experiments were performed using either sodium chloride or ferrous chloride as potential catalysts on polyethylene or cellulosics. Based on observable, but very small, increases in gas pressure the following tentative statements are made:

(1) sodium chloride may catalyze decomposition of polyethylene at 40°C;

(2) sodium chloride may slightly catalyze decomposition of cellulosics (paper) at 40°C;

(3) ferrous chloride catalyzes decomposition of paper at 40°C; and

(4) some very slight decomposition of paper (thermal or bacterial) appears to occur in the absence of plutonium or catalysts at 40°C.

The experiments in this series were terminated when a laboratory oven malfunctioned and cooled off. All the test cylinders depressurized, probably due to condensation of the gaseous decomposition products on the cylinder walls. The cylinders failed to repressurize after repair of the oven.

Sandia National Laboratory has concluded from these data that gas generation from thermal degradation of organic TRU wastes does not present a hazard for the WIPP [9].

SUMMARY

Thermal decomposition was not observed by thermogravimetry to occur for any of the materials studied at temperatures lower than 150°C. Other, more sensitive, experiments prove that thermal decomposition occurs for cellulose at temperatures as low as 70°C, and indicate that a slight amount of decomposition may occur at 40°C. Some materials may slightly catalyze thermal decomposition at 40°C.

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NOTE ADDED IN PROOF

Upon the conclusion of this research program, all of the thermal experiments were terminated. The test cylinders were disassembled and their contents removed for inspection. Figure 2 shows degradation of cellulosics, while Fig. 3 shows degradation of composites. The most severely degraded materials were cellulosics and polyvinyl chloride. Polyethylene had to be scraped off the walls of the 100°C test cylinder because it had melted onto them.

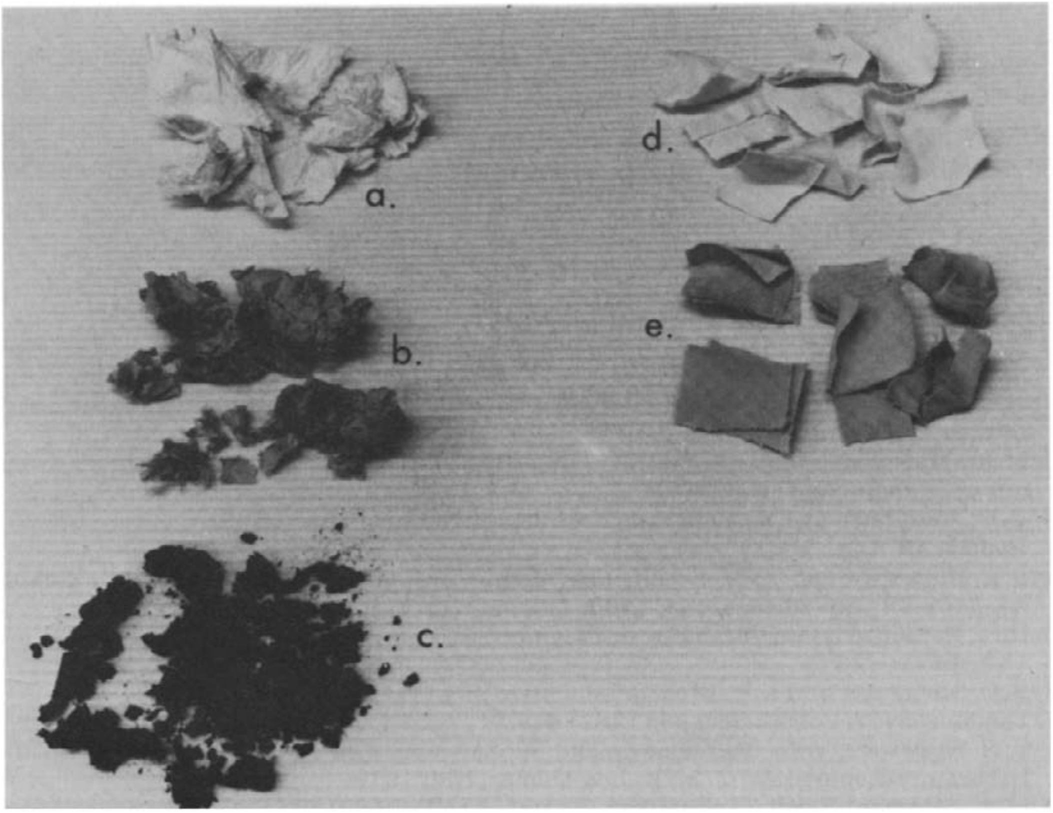

Fig. 2. Thermal degradation of cellulosics. (a) Paper after 24 months exposure at 40°C; (b) paper after 24 months exposure at 70°C; (c) paper after 7 months exposure at 100°C; (d) cotton cloth after 22 months exposure at 40°C; (e) cotton cloth after 22 months exposure at 70°C.

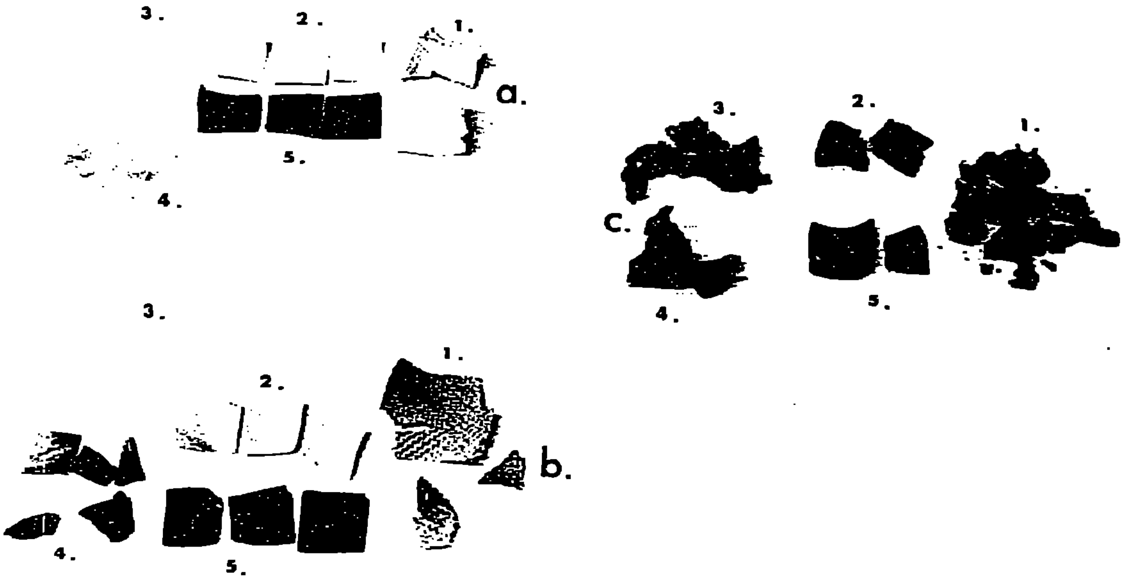

Fig. 3. Thermal degradation of composites after 22 months exposure at (a) 40°C; (b) 70°C; and (c) 100°C. (1) Paper; (2) Hypalon; (3) polyethylene; (4) polyvinyl chloride; (5) neoprene.

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