Oxidative Thermal Degradation of PVC-Derived, Fiberglass, Cotton, and Jute Brattices, and Other Mine Materials

A Comparison of Toxic Gas and Liquid Concentrations and Smoke-Particle Characterization

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Donald Paul Hodel, Secretary

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius		kg	kilogram
°C/min	degree Celsius per minute		L	liter
			L/min	liter per minute
cm	centimeter		μm	micrometer
cm^2/p	square centimeter per particle		mg	milligram
cm^3/s	cubic centimeter per second		mL	milliliter
			pct	percent
ft	foot		p/cm^2	particles per square centimeter
ft^2	square foot			
g	gram		ppm	part per million
in	inch		yd^2	square yard

OXIDATIVE THERMAL DEGRADATION OF PVC-DERIVED, FIBERGLASS, COTTON, AND JUTE BRATTICES, AND OTHER MINE MINERALS

A Comparison of Toxic Gas and Liquid Concentrations and Smoke-Particle Characterization

By Maria I. De Rosa[1] and Charles D. Litton[2]

ABSTRACT

The Bureau of Mines performed experiments to determine concentrations of toxic gases and liquids, and smoke-particle diameters and diameter-concentrations evolved during degradation of PVC-derived brattice with and without nylon-woven fabrics, fiberglass, cotton, and jute brattices, and other mine materials.

The samples were exposed in a 20-L chamber at temperatures of 150° to 450° C, with a chamber airflow of 10 L/min; 27.3 cm^3/s of which was directed into a submicrometer-particle detector-analyzer.

During the degradation of PVC-derived brattice, large concentrations of hydrogen chloride (TLV, 5 ppm; STEL, 100 ppm) evolved at a temperature as low as 200° C. The minimum toxic load of 3.1 mg or 40 ppm in 50 L of dilution air, with 0.1-g weight loss, may be reached at a mine face with 314,000 L of dilution air, at the 5th min, during which less than 1 kg of brattice undergoes combustion. Fiberglass, cotton, and jute brattices, pine wood dust, and coal dust showed small concentrations of carbon monoxide evolving during early stages of combustion. Hydrogen cyanide gas evolved from the PVC-derived, nylon-reinforced brattice; at a later stage of combustion, large concentrations of carbon monoxide and dense smoke evolved from all PVC-derived brattices.

Experiments to characterize smoke particles showed that marked differences exist in particle diameter-concentrations among the materials.

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INTRODUCTION

Plastic brattices have gained wide acceptance in the mining industry, mainly because of their easy maintenance and handling, and their long life. For these reasons, plastic brattices may be preferable to other types of brattices, such as cotton and jute. Plastic brattices, as well as all other brattices, are used as temporary stoppings, emergency curtains, and to divert exhaust air from the mining face. Face brattice is approximately 100 ft long by 7 ft high, with a surface area of 78 ft^2; a plastic face brattice weighs approximately 30 kg.

There are many types of plastic brattices. Those tested in the present experiments were manufactured from polyvinyl chloride (PVC) with plasticizers; some of the brattices were reinforced with nylon-woven fabrics. However, the PVC polymer has been found to release concentrations of hydrogen chloride (HCl) at a temperature as low as 180° C (1).[3] The gas, absorbed immediately by water droplets and entrapped in respirable soot particles, is carried to the eyes, throat, and lungs (2), incapacitating miners during the initial, critical time needed for escape planning and preparation. At higher temperatures, large concentrations of carbon monoxide (CO) and carbon dioxide (CO_2) are released during combustion of the plasticizers (3). Dense smoke, also released from the combustion of the plasticizers, may render the escape efforts almost impossible. Traces of hydrogen cyanide (HCN) concentrations, released during the combustion of nylon fabric (4), may aggravate the condition.

During the experiments for the analysis of toxic gas and liquid concentrations, the Bureau of Mines exposed samples of 11 PVC-derived brattices, some of which were reinforced with nylon-woven fabrics, to oxidative thermal degradation at furnace temperatures of 250° and 450° C, with a chamber airflow of 10 L/min. For comparison, samples of fiberglass, cotton and jute brattices, pine wood dust, and coal dust were also exposed to the same test conditions. A list of the materials is presented in table 1. During the experiments for the characterization of smoke particles, samples of PVC-derived and jute brattices, coal dust and solid coal, pine wood dust, and solid pine wood were exposed to furnace temperatures ranging from 150° to 450° C; a fraction (27.3 cm^3/s) of the chamber air flow was directed into the Bureau of Mines particle detector-analyzer, to determine the mean particle diameters (dg) in centimeters or in micrometers, and the product of the particle diameter and mean particle concentration (dgno) in particles per square centimeter.

The knowledge of such variables is necessary for mine management and safety personnel to plan the escape of miners during mine fires, and to assess the hazard posed by the PVC-derived brattice as compared with that of other mine materials. Finally, the characterization of smoke particles will enable the scientist to develop parameters, such as smoke toxicity and smoke obscuration, useful in assessing, a priori, the hazard of each material during fire.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Materials investigated

Material	Description
PVC-derived brattices:[1]	
1............................	PVC clear plastic, reinforced with nylon fabric.
2............................	Do.
3............................	Do.
4............................	PVC clear plastic, not reinforced with nylon fabric.
5............................	Do.
6............................	Do.
7............................	PVC yellow plastic, reinforced with nylon fabric.
8............................	Do.
9............................	PVC yellow plastic, not reinforced with nylon fabric.
10...........................	Do.
11...........................	PVC-coated jute.
Other brattice types:	
Fiberglass..................	Fiberglass-woven fabric.
Cotton......................	Cotton-woven fabric.
Jute........................	Jute-woven fabric.
Other mine materials:	
Pine wood dust..............	Pine wood dust, untreated.
Coal dust...................	Coal dust (200 mesh), Pittsburgh seam.

[1]These types of brattice are widely manufactured and distributed in the United States.

BACKGROUND

All organic materials decompose when subjected to sufficiently high temperatures. Their degradation is accompanied by evolution of gaseous and liquid species, depending upon the nature of the material and the temperature. Polyvinyl chloride ($-CH_2CHCl-$), a halogenated polymer, contains both hydrogen and halogen atoms evolving as hydrogen halide when subjected to elevated temperatures; this reaction proceeds more rapidly when the halogen is chlorine (5).

Recent studies show that hydrogen chloride evolves during the thermal degradation of PVC-derived materials, and that the reaction is accelerated in oxidizing atmospheres (6). Water droplets absorb HCl gas in a fraction of a second to produce hydrochloric acid (7). The droplets, when entrapped in respirable-size soot particles, are carried to the eyes and to the upper and lower respiratory tract, causing eye irritation, coughing, dizziness, and confusion (8). Furthermore, peripheral vasoconstriction becomes so intense that blood pressure rises, creating a very stressful condition (9). It has been found that the release of

HCl occurs earlier than that of CO, even earlier than ignition of PVC, and that the rate of generation of HCl increases with increasing temperatures. Most of the HCl has been found to be released at temperatures between 150° and 250° C. At higher temperatures, phthalate ester plasticizers, also used in PVC-derived products, produce high concentrations of CO and CO_2, together with hydrocarbons and phthalic anhydride (10). By far, the most toxic gas evolving by thermal degradation of PVC materials is HCl, with a threshold limit value (TLV) of 5 ppm, and a short-term exposure limit (STEL) of 100 ppm. Concentrations of 15 ppm HCl cause localized irritation to the eyes and throat after short exposure; concentrations of 100 ppm are considered dangerous to life; concentrations of 1,000 ppm endanger life in a matter of seconds. In table 2, we are reporting from Tewarson (11), tentative critical values of toxic gases, visibility, and temperature beyond which one may be impaired physically and mentally in a matter of seconds. Tentative

TABLE 2. — Tentative critical values of toxic gases,
visibility, and temperature

	ppm	vol pct
HCl.....................	50- 100	0.005 - 0.010
HCN.....................	110- 135	.0110- .0135
Benzene.................	1,500- 4,000	.15 - .40
CO......................	1,500- 4,000	.15 - .40
CO_2....................	40,000- 80,000	4.0 - 8.0
O_2.....................	60,000-100,000	6.0 -10.0
Temperature[1]...........	140°	NAp
Visibility[2]...........	0.2183	NAp

NAp Not applicable.
[1]Degrees Celsius.
[2]Meters.

critical values are presented because the true values at which victims die are impossible to be measured after a fire disaster (12).

OXIDATIVE THERMAL DEGRADATION AND SUBMICROMETER-PARTICLE DETECTOR-ANALYZER SYSTEMS

The degradation system (fig. 1) consists of a combustion chamber (9 by 9 by 14 in) with heating elements embedded in its inner surfaces. The furnace temperature (100° to 1,200° C), set a priori for test purposes, allows the chamber temperature to rise automatically from ambient. The rise varies from 30°-40° C/min to 40°-50° C/min, depending on how high the furnace temperature is set. During the experiments, the chamber and sample temperatures are monitored continuously with Chromel-Alumel[4] thermocouples attached to a strip-chart recorder. A universal load cell, located under the furnace floor and contacted by the chamber quartz sample-cup pedestal, transmits the sample weight loss to another strip-chart recorder. A pump draws ambient air continuously into the chamber (10 L/min) via an opening at the center of the furnace door, and sends chamber air to the gas analyzers through a quartz tube (40 in by 1 in) inserted in the upper right rear of the furnace. A flow meter is installed between the pump outlet and the infrared gas analyzers for continuous visual flow indication. The

chamber air is monitored continuously by two analyzers: one for CO (0 to 100 ppm, and 0 to 1,000 ppm) and CO_2 (0 to 5 pct, and 0 to 25 pct), and one for O_2 (range 0 to 25 pct). Gas analysis is also performed by a gas chromatograph, with a thermal conductivity detector (TCD) and a flame ionization detector (FID), using grab samples obtained at the gas-sampling ports, and by the use of short-term HCl (0-25 ppm) and HCN (0-25 ppm) exposure tubes. Liquids, deposited at the entrance of the flow meter, during the experiments with PVC-derived brattices, are analyzed qualitatively and quantitatively for HCl by titrimetric analysis, using mercuric nitrate titrant and diphenyl carbazone indicators.
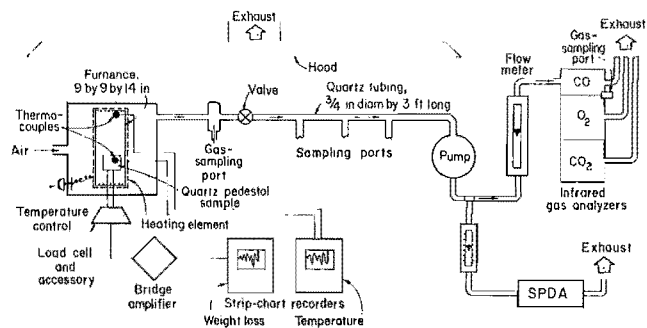
[4]Reference to specific equipment is made for identification only and does not imply endorsements by the Bureau of Mines.

FIGURE 1.—Oxidative thermal degradation and submi-crometer-particle detector-analyzer systems.

The submicrometer-particle detector-analyzer system (fig. 1) consists of a strip-chart recorder and a submicrometer-particle detector-analyzer (SPDA), through which a small quantity (27.3 cm³/s) of chamber airflow is directed. The SPDA is a prototype instrument developed by Bureau personnel; basic operating principles of the device are described elsewhere (13-14). The present version has been modified so that real-time data can be acquired for simultaneous determination of mean particle diameter and mean and particle concentration, without need for more time-consuming determination of the actual distribution of particle diameters.

EXPERIMENTAL PROCEDURE

DETERMINATION OF TOXIC GAS AND LIQUID CONCENTRATIONS

Two sets of experiments (16 experiments in each set; each experiment repeated twice) were performed at furnace temperatures of 250° and 450° C with samples of PVC-derived, fiberglass, cotton, and jute brattices, pine wood dust, and coal dust. Each 2-g sample was placed in a 1-in-diam chamber cup, and the furnace was set at the desired temperature. The airflow through the chamber was 10 L/min. Each experiment usually lasted 10 min, after which time the furnace was turned off and the charred sample was weighed. The variables measured continuously, as a function of time, were the CO, CO_2, and O_2 concentrations, weight losses, and temperatures. The gases were also analyzed chromatographically using grab samples taken at 5-min intervals, and by use of short-term HCl and HCN exposure tubes; the liquid substances, recovered at the entrance of the flow meter at the end of each experiment, were analyzed qualitatively and quantitatively for HCl by titrimetric analysis, once at each experimental temperature.

CHARACTERIZATION OF SMOKE PARTICLES

Four sets of experiments (four experiments in each set, each experiment repeated twice) were performed at furnace temperatures of 150°, 250°, 350°, and 450° C with samples of PVC-derived and jute brattices, pine wood dust and solid pine wood, and coal dust and solid coal, following the procedure outlined above, the experiments lasted 14 min. The mean particle diameter-concentration, dgno, was obtained from the ratio (r) of the experimental and initial voltage outputs (Ie/Io), according to equation 1. (See also figure 2.)

$$r = 1/K \ dgno \ (1-e^{-Kdgno}), \qquad (1)$$

where K = charging chamber constant (k=0.012), cm^2/p.

The mean particle diameter was obtained by the SPDA simultaneous current output Ic, according to equations 2 and 3.

$$dg = 0.288/(1.05 \times 10^6 \times r)$$
$$- (2.4 \times 10^4 \times \beta), \qquad (2)$$

$$\beta = e \ 3.81 \ (Ic/dgno) - 1.0, \qquad (3)$$

where β = function.
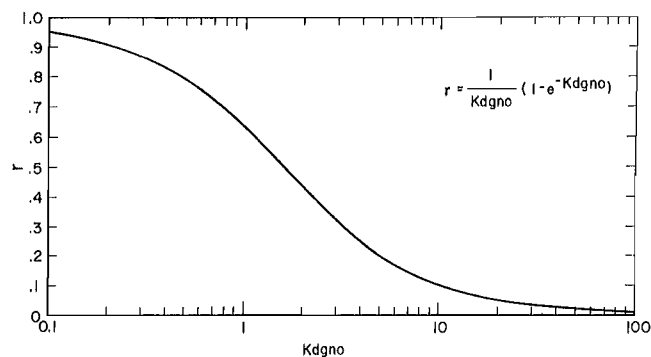
FIGURE 2.—Curve of relationship between ratio of experimental and initial voltages, and mean particle diameter-concentration.

RESULTS AND DISCUSSION

The results are summarized in tables 3 through 6, and in figures 3 through 10.

DETERMINATION OF TOXIC GAS AND LIQUID CONCENTRATIONS

Furnace Temperature of 250° C

1. The PVC-derived brattices released large quantities of HCl. HCl concentrations larger than 25 ppm were detected after the 5th min for all PVC-derived brattices. The brattices reinforced with nylon fabrics released also traces of HCN of approximately 5 ppm. The HCl, reacting immediately with water vapor, was then visible as an oily liquid along the quartz tube and at the entrance of the

flow meter as the experiment progressed. A fraction of the liquid (0.14 mL), deposited during the experiment using brattice 4, was analyzed titrimetrically for
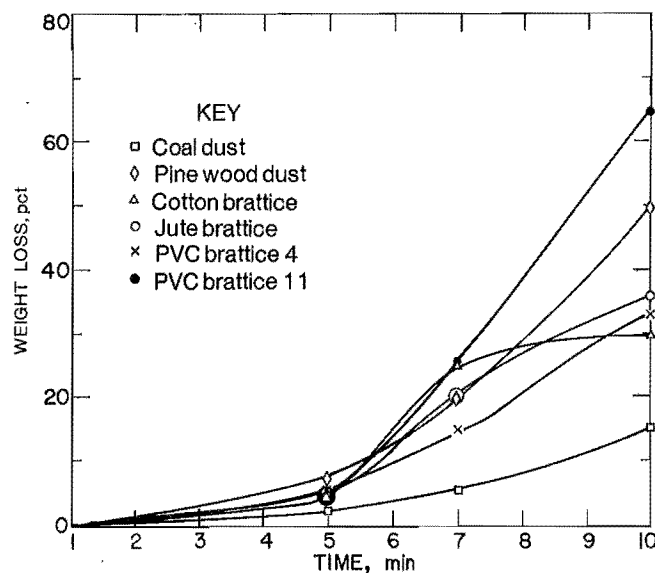
FIGURE 4.—Weight loss versus time during oxidative thermal degradation of brattices and other mine materials at 250° C.

FIGURE 3.—Chamber temperature versus time at 250° and 450° C.
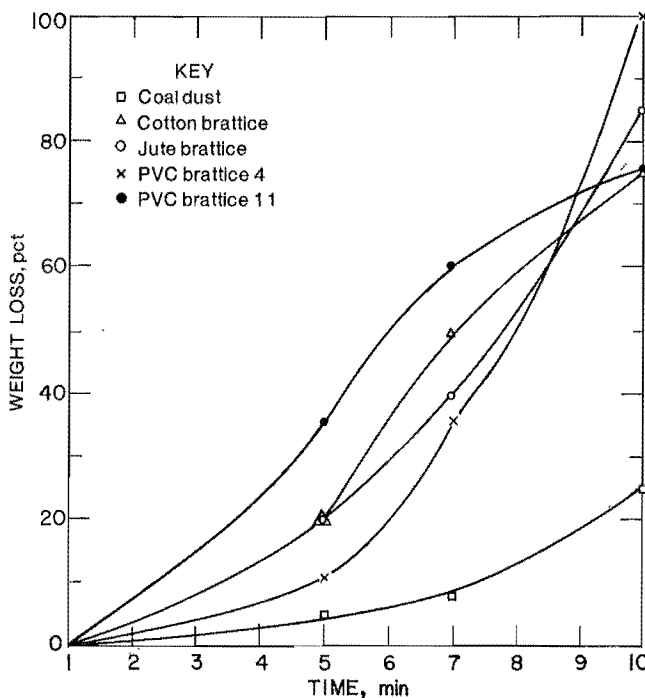
FIGURE 5.—Weight loss versus time during oxidative thermal degradation of brattices and other mine materials at 450° C.
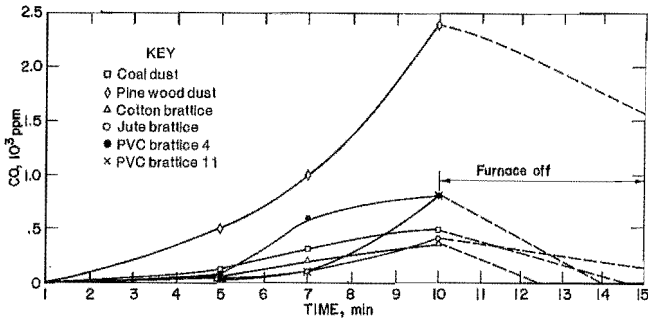
FIGURE 6.—Carbon monoxide concentrations versus time during oxidative thermal degradation of brattices and other mine materials at 250° C.
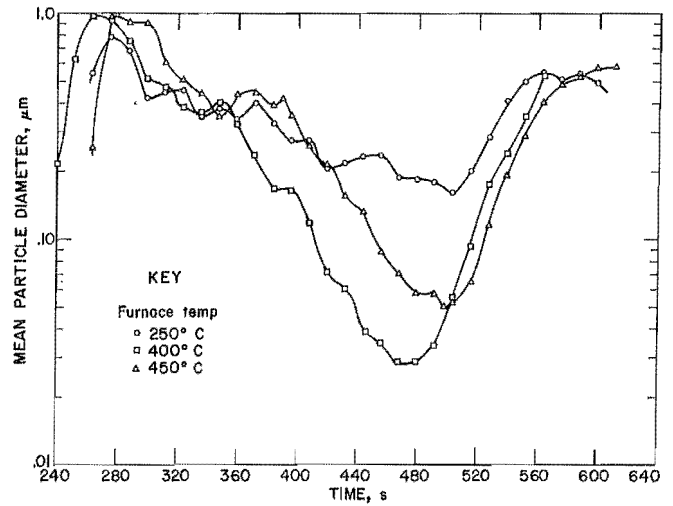
FIGURE 8.—Mean particle diameter versus time during oxidative thermal degradation of jute brattice at various furnace temperatures.
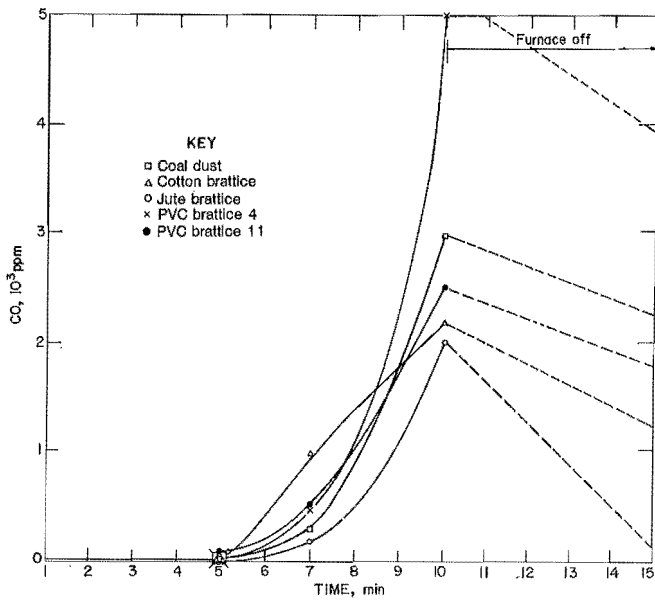
FIGURE 7.—Carbon monoxide concentrations versus time during oxidative thermal degradation of brattices and other mine materials at 450° C.

HCl and found to contain 3.1 mg HCl in water or 40 ppm in 50 L of dilution air, if the gas evolved at the 5th min, during the combustion of 0.1 g of brattice. The same toxic load may be reached at a mine face (100 by 16 by 17 ft) with 314,000 L of dilution air if less than 1 kg (<3 ft^2) of a brattice undergoes combustion (ratio of 0.1 g weight loss to 50 L dilution air = X to 314,000 L dilution air), and if no further dilution occurs. However, a toxic load of 300 mg HCl/g of weight loss, or 380 ppm/0.1 g of weight loss in 50 L of dilution air, has
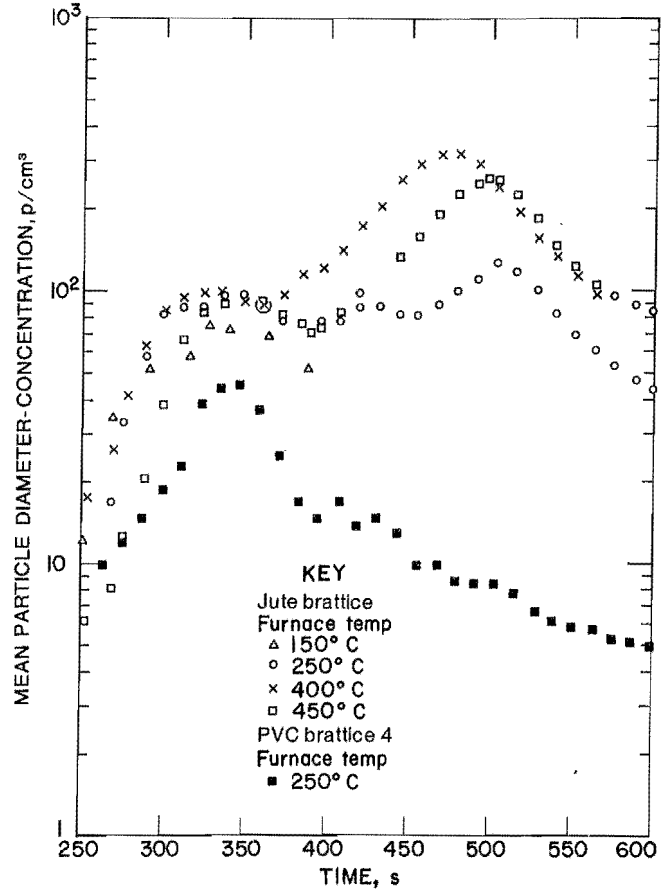
FIGURE 9.—Mean particle diameter-concentration versus time during oxidative thermal degradation of jute brattice and PVC-derived brattice at various furnace temperatures.

TABLE 3. – Oxidative thermal degradation data at 250° C

(Chamber airflow, 10 L/min)

Material (2-g samples)	Maximum CO, ppm			Maximum CO$_2$, ppm 10th min	Maximum HCl, ppm 7th min	Maximum HCN, ppm 7th min	Temperature, °C		Weight loss, g			Maximum weight loss, pct
	10th min	7th min	5th min				Chamber 7th min	Sample 7th min	10th min	7th min	5th min	
PVC-derived brattices:												
1...........................	650	250	50	1,000	>25	≤5	325	320	0.6	0.2	0.1	30
2...........................	700	300	60	1,000	>25	≤5	320	320	.4	.2	.1	20
3...........................	800	300	60	1,000	>25	≤5	320	320	.7	.2	.1	35
4...........................	800	300	40	1,500	[1]>25	0	310	320	.5	.2	.1	25
5...........................	810	200	40	1,500	>25	0	310	320	.6	.2	.1	30
6...........................	800	250	40	1,500	>25	0	310	320	.8	.2	.1	40
7...........................	1,000	300	60	800	>25	≤5	310	320	1.0	.3	.2	50
8...........................	600	300	70	4,000	>25	≤5	310	320	.6	.2	.1	30
9...........................	800	200	50	3,500	>25	0	320	320	.6	.3	.2	30
10...........................	800	200	80	1,500	>25	0	315	310	.6	.2	.1	40
11...........................	1,000	400	100	1,000	>25	0	315	310	1.2	.2	.1	60
Other brattice types:												
Fiberglass.............	200	100	50	1,000	≤5	0	315	310	.12	.02	.01	6
Cotton................	380	200	50	2,000	0	0	315	310	.6	.5	.1	30
Jute..................	400	100	50	1,700	0	0	300	310	.7	.5	.1	35
Other mine materials:												
Pine wood dust........	2,400	300	50	5,000	0	0	315	310	1.0	1.0	.20	50
Coal dust.............	600	300	50	2,000	0	≤5	310	310	.3	.1	.05	15

[1]A small quantity (0.14 mL) of the liquid recovered during this experiment was analyzed titrimetrically and found to contain 3.1 mg HCl or 40 ppm in 50 L of dilution air.

TABLE 4. - Oxidative thermal degradation data at 450° C

(Chamber airflow, 10 L/min)

Material (2-g samples)	Maximum CO, ppm			Maximum CO$_2$, ppm 10th min	Maximum HCl, ppm 7th min	Maximum HCN, ppm 7th min	Temperature, °C		Weight loss, g			Maximum weight loss, pct
	10th min	7th min	5th min				Chamber 7th min	Sample 7th min	10th min	7th min	5th min	
PVC-derived brattices:												
1......................	5,400	400	50	4,000	>25	⩽5	490	490	1.9	0.8	0.7	95
2......................	5,000	600	50	4,000	>25	⩽5	490	490	1.6	.5	.2	80
3......................	4,500	500	15	4,500	>25	⩽5	500	490	1.5	.5	.1	75
4......................	5,200	400	15	4,500	[1]>25	0	490	490	1.7	.5	.2	85
5......................	5,000	400	10	5,000	>25	0	495	490	2.0	1.0	.5	100
6......................	4,600	600	15	5,000	>25	0	490	490	2.0	1.0	.1	100
7......................	4,800	600	50	5,000	>25	⩽5	500	490	1.8	.8	.1	100
8......................	6,100	600	35	6,500	>25	⩽5	500	490	1.8	1.0	.4	90
9......................	4,500	400	20	5,500	>25	0	500	490	2.0	.5	.1	100
10.....................	5,000	300	20	8,000	>25	0	500	490	2.0	.3	.1	100
11.....................	2,200	500	30	5,500	>25	0	500	490	1.5	.4	.2	75
Other brattice types:												
Fiberglass............	500	300	50	1,000	⩽5	0	495	490	.15	.1	.01	7
Cotton................	2,200	600	50	8,000	0	0	490	495	1.5	1.0	.4	95
Jute..................	1,000	200	20	2,000	0	0	495	490	1.7	.8	.4	85
Other mine materials:												
Pine wood dust........	3,500	500	50	1,000	0	0	490	495	1.8	.8	.2	90
Coal dust.............	3,000	300	10	2,000	0	⩽5	495	490	.5	.15	.1	25

[1]A small quantity (0.14 mL) of the liquid recovered during this experiment was analyzed titrimetrically and found to contain 3.1 mg HCl or 40 ppm in 50 L of dilution air.

TABLE 5. – Hydrocarbon concentrations during oxidative thermal
degradation at 250° and 450° C, parts per million

(Chamber airflow, 10 L/min; time, 10th min)

Material (2-g samples)	At furnace temperature of—										
	250° C			450° C							
	CH_4	C_2H_6	C_2H_4	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	C_5H_{12}
PVC-derived brattices:											
1.............................	20	3	25	475	25	295	40	12	110	40	0
2.............................	25	5	30	535	25	325	45	10	65	85	0
3.............................	5	0	15	405	25	280	30	10	60	20	0
4.............................	5	0	10	330	30	200	20	15	105	5	0
5.............................	10	0	10	400	15	175	40	7	85	3	0
6.............................	5	0	15	420	30	255	35	6	50	0	0
7.............................	0	0	0	490	45	360	35	15	120	5	0
8.............................	25	0	15	550	30	310	45	12	95	4	0
9.............................	10	0	0	360	30	185	40	20	115	12	5
10.............................	5	0	0	495	15	270	40	8	110	0	0
11.............................	10	0	0	160	20	80	15	6	20	0	0
Other brattice types:											
Fiberglass.................	0	0	0	50	6	8	0	2	0	0	0
Cotton.....................	0	0	0	100	7	45	3	2	30	0	0
Jute.......................	0	0	0	90	6	7	0	2	0	0	0
Other mine materials:											
Pine wood dust..............	90	0	25								
Coal dust...................	15	27	10	535	60	100	0	12	25	40	0

TABLE 6. – Oxygen concentration during
oxidative thermal degradation at
250° and 450° C, percent

(Chamber airflow, 10 L/min; 10th min)

Material (2-g samples)	250° C	450° C
PVC-derived brattices:		
1.....................	20.80	19.8
2.....................	20.65	19.8
3.....................	20.70	19.9
4.....................	20.50	20.0
5.....................	20.70	19.8
6.....................	20.80	20.1
7.....................	20.70	19.9
8.....................	20.55	19.7
9.....................	20.60	20.0
10.....................	20.70	19.8
11.....................	20.80	19.9
Other brattice types:		
Fiberglass.............	20.80	19.9
Cotton.................	20.80	19.8
Jute...................	21.00	20.6
Other mine materials:		
Pine wood dust........	20.25	19.8
Coal dust.............	20.60	20.0

been reported (15); this toxic load may be reached in 314,000 L of dilution air if less than 1 kg of brattice burns. Dense smoke filled the chamber during each experiment. For PVC-derived samples, the maximum weight loss of 50 pct and the maximum CO concentration of 800 ppm were reached at the 10th min; differences observed among the PVC-derived brattices were insignificant.

2. The fiberglass brattice underwent a 6-pct weight loss and yielded a CO value of 200 ppm at the 10th min, 75 pct lower than that observed for PVC-derived brattice. However, traces of HCl were observed.

3. The cotton brattice underwent a 30-pct weight loss, and jute brattice had a 35-pct weight loss; both yielded a maximum CO concentration of 40 ppm at the 10th min, 50 pct lower than that observed for PVC-derived brattice.

4. The pine wood dust samples produced CO concentrations of 2,400 ppm at the 10th min, and an 80-pct weight loss.

5. The coal dust sample had a 15-pct weight loss and yielded a CO value of 600
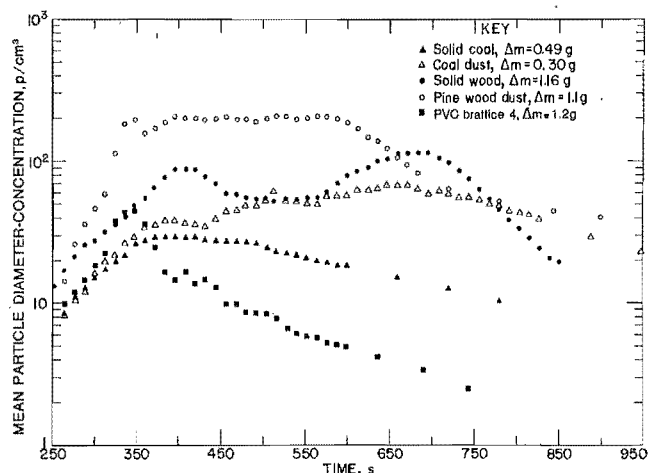
FIGURE 10.—Mean particle diameter-concentration versus time during oxidative thermal degradation of PVC-derived brattice and other mine materials at 250° C.

ppm at the 10th min, 25 pct lower than the level observed for PVC-derived brattice. Traces of HCN were detected at the 10th min. During the experiments with all types of samples, the maximum chamber temperature of 330° C was reached at the 7th min.

Furnace Temperature of 450° C

1. The PVC-derived brattices yielded large quantities of the same oily liquid observed under the previous experimental temperature. A fraction of the liquid derived from an experiment using sample 4 was analyzed qualitatively for HCl by titrimetric method, and found to contain 3.1 mg HCl in water. Long soot filaments were observed in the chamber after each experiment. At the 10th min, the maximum weight loss of 95 pct and the maximum CO concentration of 5,000 ppm were observed; differences among the PVC-derived brattice samples were insignificant.

2. The fiberglass brattice had a 7-pct weight loss and yielded a CO value of 500 ppm at the 10th min, 90 pct lower than that observed for PVC-derived brattice. However, we did observe HCl concentrations of approximately 5 ppm after the 10th min.

3. The cotton and jute brattices displayed a large weight loss (85–95 pct), however, the maximum CO value of

2,000 ppm was 60 pct lower than that observed for PVC-derived brattice. Of critical importance, furthermore, is the fact that the CO concentration observed at the 5th min is of nominal value (50 ppm); this fact and the absence of HCl and other toxic gases may allow time for miners to escape or even to contain the combustion at its onset.

4. The pine wood dust sample produced CO concentrations of 3,500 ppm and a 90-pct weight loss at the 10th min.

5. Similarly, the coal dust sample yielded a maximum CO value of 3,000 ppm, 40 pct lower than that observed for PVC-derived brattice, coinciding with only 25-pct weight loss at the 10th min.

Large quantities of hydrocarbons, such as methane and benzene, evolved only during the degradation of PVC-derived brattice. The maximum chamber temperature (500° C) was reached at the 10th min during the experiments with all types of samples.

CHARACTERIZATION OF SMOKE PARTICLES AT FURNACE TEMPERATURES OF 150°, 250°, 350°, AND 450° C

A typical set of data is shown in figures 8 through 10. In figure 8, the mean particle diameter is plotted as a function of time for jute brattice exposed to each furnace temperature. In figure 9, the mean particle diameter-concentration, dgno, is plotted as a function of time for the same experiments, and for PVC-derived brattice exposed to one temperature only. In general, the reaction tends to increase as the temperature ranges from 150° to 250° C. At 450° C, the reaction appears to have slowed, probably because of dissipation of more volatile matter during the early stages of thermal degradation. Most of the material tested behaved in a similar manner, with differences occurring in both mean diameter and concentration as the tests proceeded. By far, the most interesting results were obtained for the product dgno for different samples subjected to identical test conditions. Figure 10 illustrates the relative values obtained for the samples exposed to temperatures of 250° C. The PVC-derived

brattice tends to have low dgno value; this phenomenon may be due to the fact that the majority of particles, being in the liquid state, are not characterized by the SPDA, or that the particles are being trapped by the oily substances deposited along the ventilation system prior to reaching the SPDA. In contrast, the wood has considerably higher values; similar data have been obtained for rubber (not shown here). For this material, much higher dgno values were obtained, indicating higher tendency to produce smoke.

CONCLUSIONS

On the basis of our findings, PVC-derived brattice is extremely dangerous under fire conditions, especially in confined mine environments with distant exits. Large concentrations of hydrogen chloride (TLV, 5 ppm; STEL, 100 ppm) evolve from the thermal degradation of the brattice at temperatures as low as 200° C. The minimum toxic load of 3.1 mg or 40 ppm in 50 L dilution air, measured in the present experiments, may be reached at a mine face with 314,000 L of dilution air, at the 5th min, during which less than 1 kg of brattice undergoes combustion. The HCl gas, absorbed immediately by water drop-lets and entrapped in respirable soot par ticles, is carried to the eyes, throat, and lungs. This incapacitates the miners during the critical time needed to contain the combustion at its onset or plan and prepare for escape. Traces of HCN, also evolved from the combustion of brattice reinforced with nylon fabrics, increases the toxic load. Dense smoke reduces visibility dramatically and slows the rate of escape, increasing the miner's risk of being trapped in a toxic environment with a depleted air supply. The usage of other types of brattices (cotton or jute) does not resolve the problem; however, these brattices seem to be less hazardous during fire, especially during its earliest stage, allowing some time to plan for escape or even to contain the combustion. Fiberglass brattices would be preferable because of lower burning rate and, therefore, lower yields of CO concentrations; however, the yields of HCl, as small as they may be, render the brattice potentially dangerous. In the future, before combustible materials are brought into deep mines—especially if they are in large quantities—should undergo more stringent testing to determine their thermal stability and toxicity. The differences in particle diameter-concentrations observed among mine materials may be predictive of hazard parameters.

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