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Primary Gas Toxicities and Smoke Particle Characteristics During Combustion of Mine Brattices

Development of a Test Parameter

By Maria I. De Rosa and Charles D. Litton

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

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T S Ary, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L/min	liter per minute
°C/min	degree Celsius per minute	min	minute
cm	centimeter	mm	millimeter
cm ² /p	square centimeter per particle	mol	mole
cm ² /(p·g)	square centimeter per particle per gram	pct	percent
ft	foot	p/cm ²	particle per square centimeter
g	gram	ppm	part per million
in	inch	ppm/g	part per million per gram
L	liter	wt pct	weight percent

PRIMARY GAS TOXICITIES AND SMOKE PARTICLE CHARACTERISTICS DURING COMBUSTION OF MINE BRATTICES

Development of a Test Parameter

By Maria I. De Rosa¹ and Charles D. Litton²

ABSTRACT

The U.S. Bureau of Mines performed experiments to determine if primary gas toxicities that evolve during the early ($\sim 300^\circ\text{C}$) and later ($\geq 400^\circ\text{C}$) combustion stages of polyvinyl chloride and chlorinated brattices could be predicted by a smoke particle characteristic, which could be used as a simple and inexpensive test parameter.

The experiments were conducted in an approximately 20-L furnace at set furnace temperatures of 250° and $1,000^\circ\text{C}$, for 14 min duration, with an airflow through the furnace of 10 L/min. The variables studied, as a function of time, were the hydrogen chloride (HCl) and carbon monoxide (CO) concentrations, sample and furnace temperatures, the sample mass weight loss, the average smoke particle diameter (d_p) and number concentration (n_o), and the product of the average smoke particle diameter and concentration ($d_p n_o$). Results show that the inverse of the smoke particle diameter-concentration ($1/d_p n_o$) correlates directly with the primary gas toxicities evolved during both stages of combustion.

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INTRODUCTION

In 1984, the U.S. Bureau of Mines, within its mission to create and maintain safety in the mines and, specifically, to assess the hazard of mine materials during fire, initiated a series of experiments to characterize smoke particles and primary gas toxicities evolved during the combustion of mine materials. It was found (1)³ that smoke particles produced by different combustibles differed in average diameter (d_p), average number concentration (n_o), and the product of average diameter and concentration ($d_p n_o$).

A correlation was established (2) between the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$), measured during the combustion of various materials, and the toxicity data obtained with similar materials and reported by Alarie (3) (animal study) and Paciorek (4) (gas analyses). In subsequent studies (5-7), simultaneous measurements were made of gas toxicities and smoke

particle characteristics, and it was found that the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$) correlated directly with the primary gas toxicities evolved during the combustion of polyvinyl chloride (PVC) and chlorinated mine conveyor belts.

In this study, the Bureau set out to correlate the smoke particle characteristic $1/d_p n_o$ with the primary gas toxicities [hydrogen chloride (HCl) and carbon monoxide (CO)] evolved during the early ($\sim 300^\circ\text{C}$) and later ($\geq 400^\circ\text{C}$) combustion stages of PVC, fiberglass, and burlap mine face brattices, wood, and coal. These correlations may allow the development of a test parameter for assessing, simply and inexpensively, the toxic hazard of these combustibles during fire, as compared with the hazard posed by wood and coal.

BACKGROUND

Natural and synthetic organic materials, when heated, release gaseous species whose toxicity and rates of release depend on the nature of the material, on the temperature, and on the ease of thermal decomposition of the material (5-7). Compared with natural materials, synthetic polymer materials release gases that are much more toxic, at an earlier time, because of resin composition and the fact that in the presence of even moderate heat, the cohesive and covalent bonds of the polymer chain break easily, resulting in the release of combustible gas molecules, which in the presence of oxygen burst into flames (8).

PVC mine brattices are manufactured from PVC resins, formed by the free radical polymerization of the vinyl chloride monomer (hydrochlorinated acetylene or ethylene reacted with chlorine), and plasticizers. The homopolymer (vinyl chloride) contains 57 wt pct Cl_2 , released slowly as HCl at 200°C and rapidly at 300°C . Dehydrochlorination of PVC is a complex elimination process, dependent on temperature and time, involving an "unzipping" operation with chlorine atoms as the chain carriers; the chain sequence is initiated by a radical produced at a structural defect rather than by direct carbon-chlorine split (9). The predominance of HCl during the early combustion stage suggests that the polyene structure, formed by dehydrochlorination of the material, is inherently unstable at these temperatures, and rearrangements and product elimination take place during the actual "zip" dehydrochlorination. This elimination produces a complex pattern of hydrocarbons, with aromatic material (benzene) predominant; as many as 70 compounds were observed during the thermal decomposition of PVC resins (mostly aromatic and unsaturated hydrocarbons) with small amounts of the vinyl chloride monomer (10). Oxygen plays a catalytic role during the

degradation by assisting the dehydrochlorination and product elimination and by increasing the number of initiation sites (11).

At 300°C , the main toxic risk from the PVC decomposition products is HCl. HCl, with a short-term exposure limit (STEL) of 25 ppm and immediately dangerous to life and health (IDLH) at 100 ppm, is both a sensory and pulmonary irritant (12). As a sensory irritant of the upper respiratory tract, experienced by breathing through the nose (as observed in laboratory animals), HCl depresses the respiratory rate. As a pulmonary irritant, experienced by breathing through the mouth (as observed in humans), HCl causes severe damage to the lower respiratory tract. Alarie (13) found that the HCl LC50 (lethal concentration at which 50 pct of animals die) for cannulated laboratory animals (simulating human breathing habits) was only 1,100 ppm, compared with 10,000 ppm for the noncannulated laboratory animals. Furthermore, PVC can produce large amounts of particulate matter, on whose particle surface HCl is absorbed and transported. The actual amount depends on the conditions of combustion (oxygen and temperature). The pulmonary damage from PVC smoke inhalation has been shown to be more severe than that from HCl alone, probably because the particulates may be drawn into and deposited deeper in the lungs, where the absorbed and/or dissolved HCl enhances the toxic effects. The HCl LC50 has been found (14) to decrease from 5,600 ppm for pure HCl gas to 1,900 ppm for PVC products. HCl may also be condensed by moist air to form corrosive hydrochloric acid mist, which together with smoke can obscure vision, thus interfering with escape and rescue. At higher temperatures ($\geq 400^\circ\text{C}$), the dehydrochlorinated residue yields large quantities of CO, producing an added toxic effect. The amount depends on the presence of additives, lubricants, heat and light stabilizers, and fire and smoke retardants in the resin. The

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

carboxyhemoglobin content of laboratory animals dead in PVC fires was found (15-16) to be 13 to 30 pct compared with the expected 85 pct for pure CO (table 1), and the CO LC50 was found to be 900 ppm compared with 4,600 ppm for pure CO.

Fiberglass brattice, by contrast, manufactured from an inorganic material (fiberglass >90 pct) bonded with a silicon resin containing fillers and small amounts of chlorinated additives for flame retardancy, would be expected to release small HCl quantities during the early stage of combustion, because of the low content of chlorinated additives, and low CO concentrations during the later stage of combustion, because of slow thermal decomposition.

Treated burlap brattice, manufactured from a natural (jute) fiber, is expected to release little HCl during the early stage of combustion and low CO concentrations during the later stage of combustion. Untreated burlap brattice is expected to release insignificant CO and HCl concentrations during the early stage of combustion and small CO concentrations during the later stage of combustion.

For an overall assessment of the hazard created by introducing various items into a mine, it is advantageous to have some reference point on which comparisons can be based. In the case of a coal mine such a reference is primarily coal, the most abundant material present, and wood, which is used extensively in mines as structural material.

During fire, coal releases large quantities of oxides (CO, NO, etc.), saturated hydrocarbons (methane, ethane, etc.), unsaturated hydrocarbons (ethylene, propylene, acetylene, allylene, styrene, indene, etc.), aromatic hydrocarbons (benzene, toluene, etc.), compounds of oxygen (phenol, etc.), nitrogen compounds (ammonia, etc.), and sulfur compounds (hydrogen sulfide, etc.).

Wood, composed of cellulose, lignin, hemicellulose, resins, tannin, fats, and coloring matter, yields various

combustible products derived from the degradation of all these constituents. Also, for wood, the major toxic combustion product is CO, produced in large quantities by the thermal breakdown of cellulose and lignin, and by the partial oxidation of carbon.

Table 1.-Inhalation toxicity of combustion products (16)

<i>Temperature, material, and carboxyhemoglobin content</i>	<i>Mortality¹</i>
300° C	
Polyvinyl chloride:	
25 pct CO	10 of 12
<10 pct hemoglobin . .	0 of 12
Pine wood:	
32 pct CO	0 of 18
<10 pct hemoglobin . .	0 of 12
400° C	
Polyvinyl chloride:	
45 pct CO	11 of 12
<10 pct hemoglobin . .	4 of 12
Pine wood:	
86 pct CO	12 of 12
55 pct hemoglobin . . .	1 of 12
500° C	
Polyvinyl chloride:	
70 pct CO	12 of 12
25 pct hemoglobin . . .	3 of 12
Pine wood:	
85 pct CO	12 of 12
61 pct hemoglobin . . .	8 of 12
600° C	
Polyvinyl chloride:	
76 pct CO	11 of 12
40 pct hemoglobin . . .	8 of 12
Pine wood:	
85 pct CO	8 of 12
20 pct hemoglobin . . .	0 of 12

¹Laboratory animals, 1- to 30-min exposure.

EXPERIMENTAL SYSTEM

The system (fig. 1) consists of an approximately 20-L furnace whose temperature during experiments rises automatically from ambient (fig. 2) at a rate depending on the set temperature, which can range from 100° to 1,200° C. A universal load cell, located under the furnace floor, contacts the sample cup, transmitting voltages via a bridge amplifier to a strip-chart recorder. A vacuum pump draws ambient air (10 L/min) continuously into the furnace, via an opening at the center of the furnace door, and pumps combustion air into the CO, O₂, and CO₂ gas analyzers

and into the submicrometer particle detector-analyzer (SPDA) (17). The SPDA voltages are used to compute the average smoke particle diameter (d_g), average smoke particle number concentration (n_o), and the product of the average smoke particle diameter and concentration ($d_g n_o$). A miniframe computer, via a laboratory-based real-time data acquisition system, continuously acquires, computes, and stores data of sample and furnace temperatures, airflows, gas concentrations, mass weight loss, and the SPDA voltages.

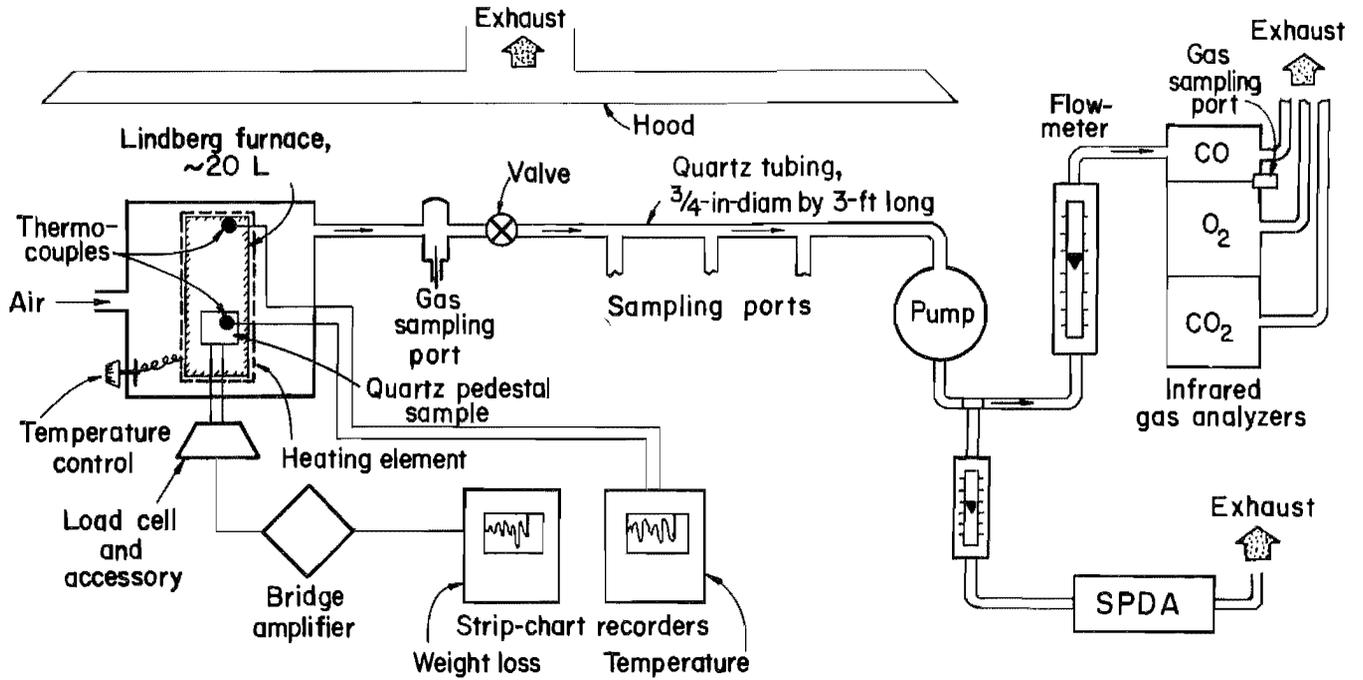


Figure 1.—Experimental system.

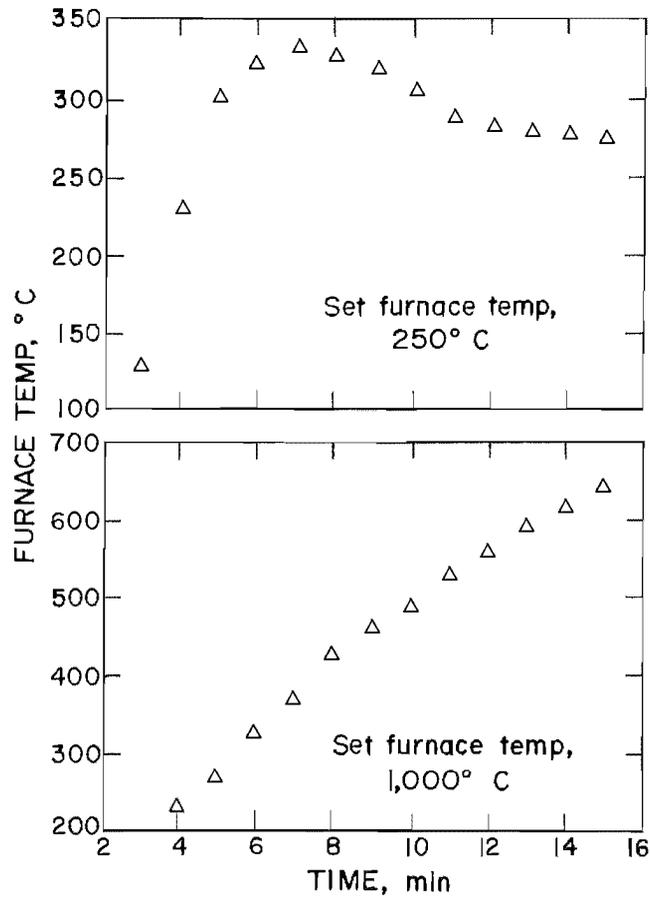


Figure 2.—Furnace temperature versus time at set furnace temperatures of 250° and 1,000° C.

EXPERIMENTAL PROCEDURE

Two sets of experiments (10 experiments in each set; each experiment repeated 3 times) were performed at set furnace temperatures of 250° C (maximum furnace temperature reached, ~300° C at the 7th minute), and 1,000° C (maximum furnace temperature reached, ~600° C at the 14th minute) for a duration of 14 min, with samples of PVC, fiberglass, and treated and untreated burlap brattices, as well as wood and coal. The experiment with fiberglass brattice was allowed to continue for 30 min (maximum temperature reached, 1,000° C). The materials are listed in table 2. A 1-g sample was placed in a 2.5-cm-diam furnace cup, and the furnace was set at the desired temperature for a 14-min duration, with a furnace airflow of 10 L/min; 1.6 L/min of this airflow was directed into the SPDA.

Syringe grab samples, stored in sealed containers, were analyzed for CO, CO₂, and O₂ by gas chromatography; HCl concentrations were determined at 250° C by short-term exposure tubes. The chlorine content of PVC and chlorinated brattice sample materials was determined by the ASTM oxygen-bomb-combustion, selective-electrode method. Other variables measured as a function of time were the sample and furnace temperatures, sample mass

weight loss, and the SPDA initial (without smoke) and experimental voltages.

Table 2.—Materials Investigated

Material	Description	Chlorine, pct
PVC brattice:		
B1	Polymer component is polyvinyl chloride.	38
B2 do	35
B3 do	30
B4 do	27
B5 do	30
B6 do	27
B7 do	31
Fiberglass brattice: B8		
	Fiberglass (>90 pct) brattice treated fire retardancy.	5
Burlap brattice:		
B9	Burlap brattice treated for fire retardancy.	7
B10	Untreated burlap brattice	0
Wood: W1 . .	Untreated pine shave wood . .	0
Coal: C1 . . .	Pittsburgh seam coal, 200 mesh; 35 pct volatile.	0

DATA REDUCTION AND ANALYSES

At 250° C set furnace temperature and 14 min duration (representing the early stage of combustion, at which most of the HCl evolves with no gross degradation of the sample), HCl and CO concentrations were measured in parts per million. The HCl and CO concentrations observed at 0.1 g of sample weight loss, adjusted to 1 g of weight loss, yielded the HCl and the CO load values (parts per million per gram). Also, the chlorine content of the material was used to calculate theoretic HCl concentrations, as follows:

Cl⁻ (18 pct) in 0.1 g sample mass weight loss in 100 L air
= 0.018 g;

moles of air
= 100 L air ÷ 22.4 L (volume of 1 mol ideal gas at 0° C and 760 mm pressure)
= 4.464 mol air;

moles of HCl as Cl⁻
= 0.018 g Cl⁻ ÷ 35.453 g (mole Cl⁻)
= 0.000508 mol Cl⁻;

moles Cl⁻ fraction in air
= 0.000508/4.464
= 0.000114 mol Cl⁻ per mole air;

Cl⁻ in parts per million
= 0.000114 × 10⁶
= 114 ppm Cl⁻;

HCl in parts per million
= 114 Cl⁻ × 36.453/35.453 (mol wt HCl ÷ mol wt Cl⁻)
= 117 ppm or 1,170 ppm/g).

The experimental load values, absolute values derived at a specific time and airflow, are important toxicological parameters, because they establish a priori the maximum concentrations of each gas expected to evolve; HCl evolves in large quantities (approaching load values) during the early (~300° C) stage of combustion, because of an early and fast dehydrochlorination process; CO evolves in large quantities (approaching load values) during a later (≥400° C) stage of combustion, because of gross degradation of the sample. Therefore, the HCl load values are predictive of the toxic hazard that PVC and chlorinated brattices pose during the early stage of combustion (CO concentrations are minimal at this stage); the CO load values are predictive of the toxic hazard that non-chlorinated materials pose during the later stage of combustion; and the combined HCl and CO load values are predictive of the toxic hazard that PVC and chlorinated brattices pose during the later stage of combustion.

Under the 250° C conditions, the average smoke particle diameter (d_p) was measured in micrometers, the average number concentration (n_o) in particles per cubic centimeter, and the product of the average smoke particle diameter and concentration ($d_p n_o$) in particles per square centimeter. The $d_p n_o$ is obtained from the ratio of the

SPDA experimental and initial current output (I_e/I_o) following the relationship (fig. 3):

$$I_e/I_o = 1/(K d_g n_o) (1 - \exp(-K d_g n_o)),$$

where K = charging constant ($K = 0.012 \text{ cm}^2/\text{p}$).

The $d_g n_o$ values observed during each experiment, adjusted to 1 g of sample mass weight loss, yielded the $d_g n_o$ load values (particles per square centimeter per gram). For sake of direct correlation, its inverse, $1/d_g n_o$ load (square centimeters per particle per gram) has been correlated

with the HCl load values and with the combined HCl and CO load values. (The CO load values were previously normalized to HCl values by scaling them down by a factor of 15, because CO is at least 15 times less toxic than HCl.) The $1/d_g n_o$ load values were also correlated with the combined HCl and CO load values scaled down to their STEL and IDLH values.

At 1,000° C set furnace temperature and 14 min duration, the rates of CO evolution and sample mass weight loss were observed to compare CO concentrations as predicted by the CO load values derived at 250° C and the actual concentrations evolved.

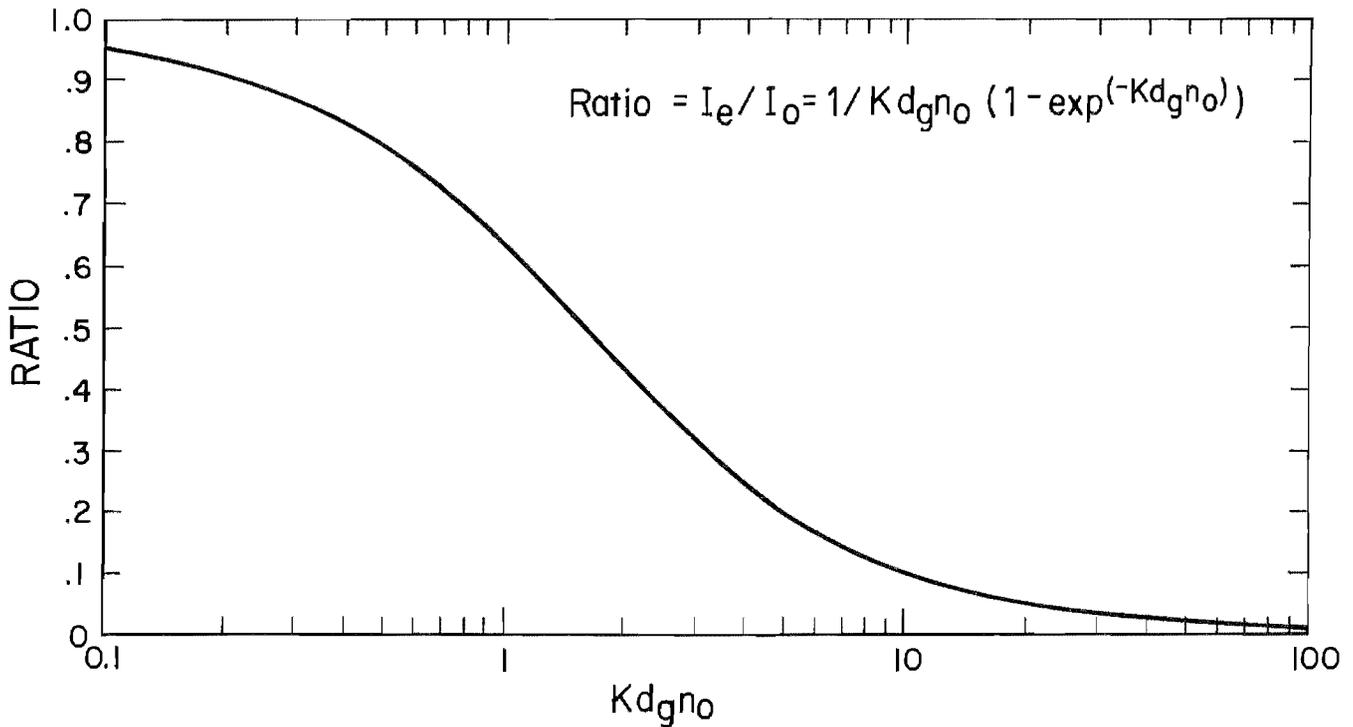


Figure 3.—SPDA current ratio (I_e/I_o) as function of smoke particle diameter-concentration product ($d_g n_o$).

RESULTS AND DISCUSSION

At 250° C, HCl was found to be the primary toxic gas for all PVC and chlorinated brattices; PVC brattices released by far the largest concentrations at the earliest time, yielding the highest HCl loads, because of the extremely high chlorine content of the material and early, large, and fast weight loss. (The amount of decomposition was ~50 pct.) These types of brattices also yielded the highest $1/d_g n_o$ values (fig. 4). By contrast, the fiberglass

and treated burlap brattices released low HCl concentrations at the latest time, yielding low HCl loads, because of a low content of chlorinated additives; in addition, the fiberglass had a low and late weight loss. (The amount of decomposition ranged between 1 pct for the fiberglass brattice and ~50 pct for the burlap brattice.) These types of brattices also yielded the lowest $1/d_g n_o$ values (fig. 4).

At this stage of combustion, low CO concentrations were released, especially by the fiberglass brattice and coal samples. (The amount of coal decomposition was 3 pct.)

At 1,000° C, CO is the primary toxic gas for all materials; the largest CO concentrations (approaching load values) were released by the PVC brattice and wood samples at the earliest time and fastest rates, because of gross degradation of the samples. (The amount of decomposition was >90 pct.) By contrast, the fiberglass brattice released extremely low CO concentrations at the latest time, because of extremely low and late weight loss. (The amount of decomposition was 2 pct.) This type of brattice never ignited, nor it ignited at temperatures above 600° C. The burlap brattices released somewhat lower CO concentrations than expected (decomposition was 80 pct), and the coal sample released large CO concentrations (much lower than load values), but only at the latest time, because of low and slow thermal decomposition (decomposition was 30 pct).

Correlations (correlation coefficient $r = 0.85$) were measured between the $1/d_g n_o$ load and the HCl load (fig. 5); between the $1/d_g n_o$ load, the combined (HCl-CO) loads, and the HCl load (fig. 6); and between the $1/d_g n_o$ load and the combined loads scaled to their STEL and IDLH values (fig. 7). Correlations were also established between the HCl load and the chlorine content of the material (fig. 8).

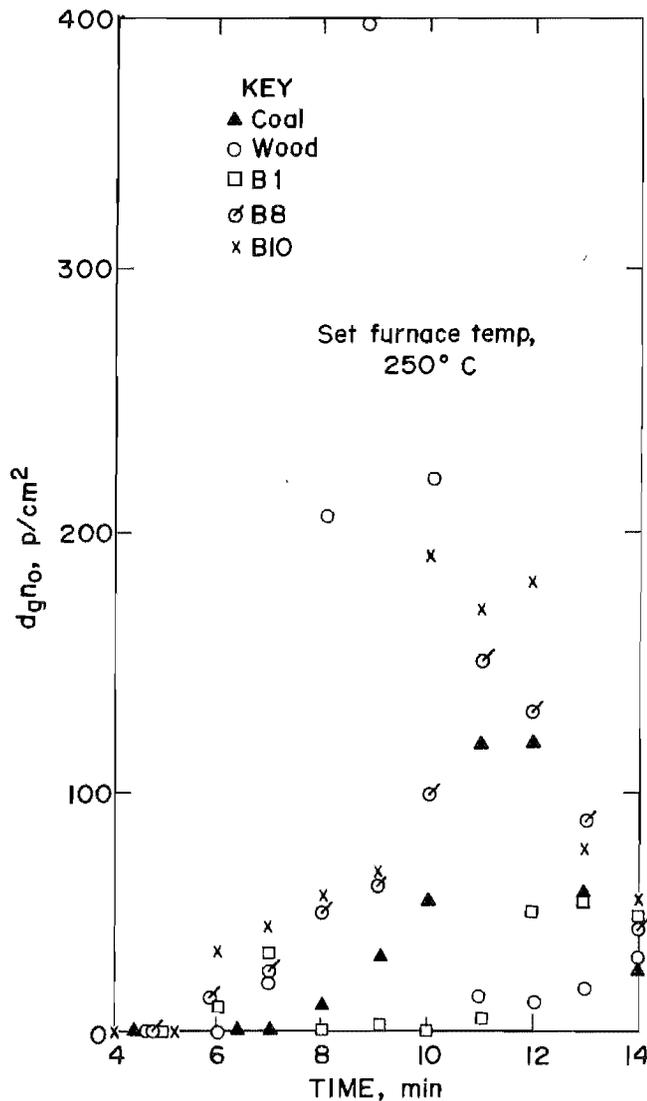


Figure 4.—Smoke particle-concentration product ($d_g n_o$) versus time at 250° C.

1. At 250° C, the PVC brattice samples released initial HCl and CO concentrations of 150 and 114 ppm at the ninth minute (90 L of air) with 0.1 g of sample weight loss (tables 3-5, fig. 9). Given the same furnace temperature and burning rates, the quantity of brattice needed to yield the same HCl and CO toxicity in a mine environment may be computed according to the ratio:

$$0.1 \text{ g} : 90 \text{ L of air} = X : 140,000 \text{ L of mine face air} \\ = 1,400 \text{ g or } 1.4 \text{ kg.}$$

At 1,000° C, the samples released maximum CO concentrations of 1,700 ppm, with maximum total weight loss of 60 pct (table 4, fig. 9).

2. At 250° C, the fiberglass brattice sample (whose loads are of theoretical derivation, because the sample weight loss was minimal even at temperatures of 1,000° C) released initial HCl and CO concentrations of <2 and 16 ppm at the ninth minute with 0.01 g of weight loss

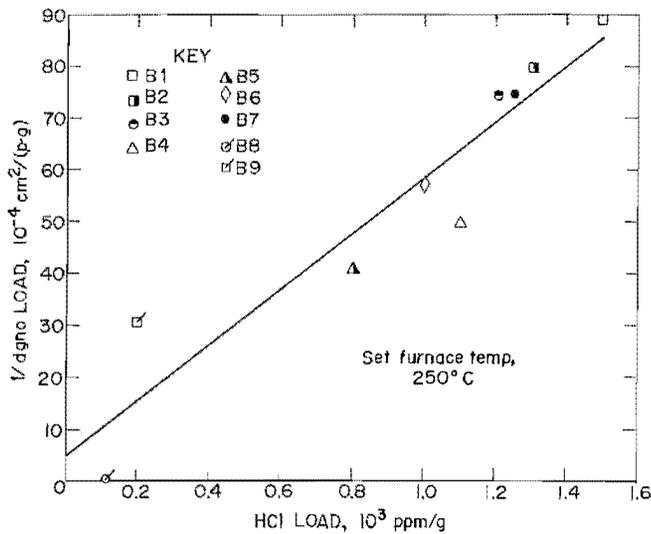


Figure 5.—Inverse of smoke particle diameter-concentration product ($1/d_g n_0$) load versus HCl load at 250°C .

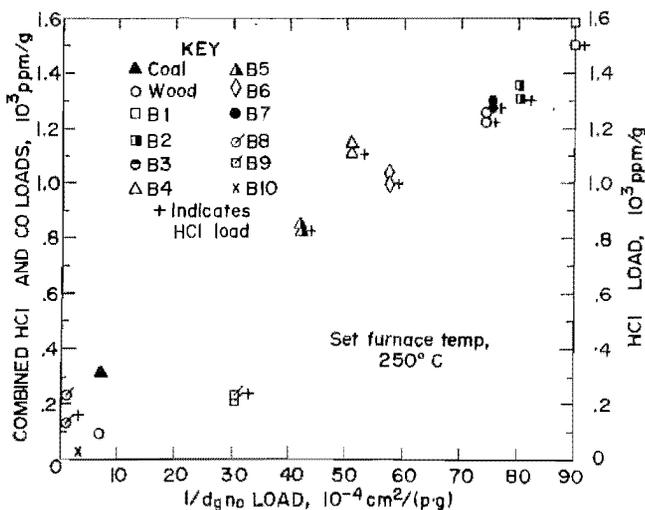


Figure 6.—Inverse of smoke particle diameter-concentration product ($1/d_g n_0$) load versus combined loads and versus HCl load at 250°C .

(total weight loss, 1 pct) (tables 3-5, fig. 9). At $1,000^\circ\text{C}$, the sample released maximum CO concentrations of 170 ppm with a total weight loss of 2 pct (table 4, fig. 9).

3. At 250°C , the treated burlap brattice sample released initial HCl and CO concentrations of 20 and 35 ppm at the ninth minute with 0.1 g of weight loss (total weight loss, 60 pct) (tables 3-5, fig. 9). At $1,000^\circ\text{C}$, the sample released maximum CO concentrations of 264 ppm, with a total weight loss of 96 pct (table 4, fig. 9). The untreated burlap brattice sample released initial CO concentrations of 45 ppm at the ninth minute with 0.1 g

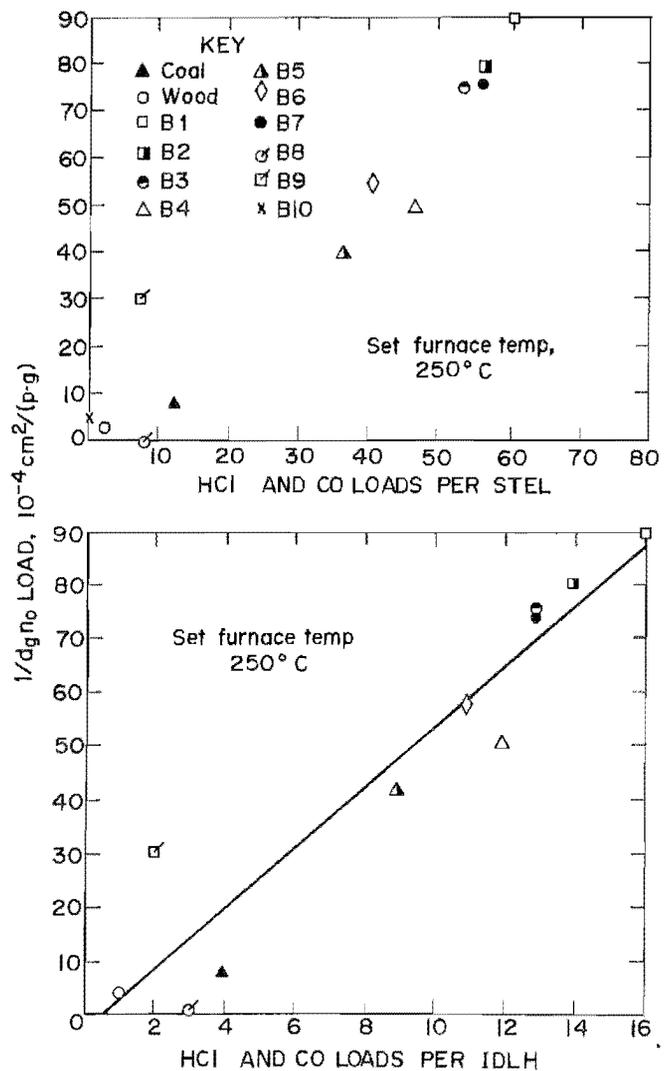


Figure 7.—Inverse of smoke particle diameter-concentration product ($1/d_g n_0$) load versus combined loads per STEL and per IDLH at 250°C .

of weight loss (total weight loss, 56 pct) (tables 3-5 and fig. 9). At $1,000^\circ\text{C}$, the sample released maximum CO concentrations of 300 ppm, with a total weight loss of 96 pct (table 4, fig. 9).

4. At 250°C , the wood sample released initial CO concentrations of 135 ppm at the ninth minute with 0.1 g of weight loss (total weight loss, 86 pct) (tables 3-5, fig. 9). At $1,000^\circ\text{C}$, the sample released maximum CO concentrations of 1,060 ppm, with a total weight loss of 96 pct (table 4, fig. 9).

5. At 250° C, the coal sample released initial CO concentrations of 47 ppm at the ninth minute with 0.01 g of weight loss (total weight loss, 3 pct) (tables 3-5, fig. 9). At 1,000° C, the sample released maximum CO concentrations of 1,420 ppm, with a total weight loss of 30 pct (table 4, figure 9).

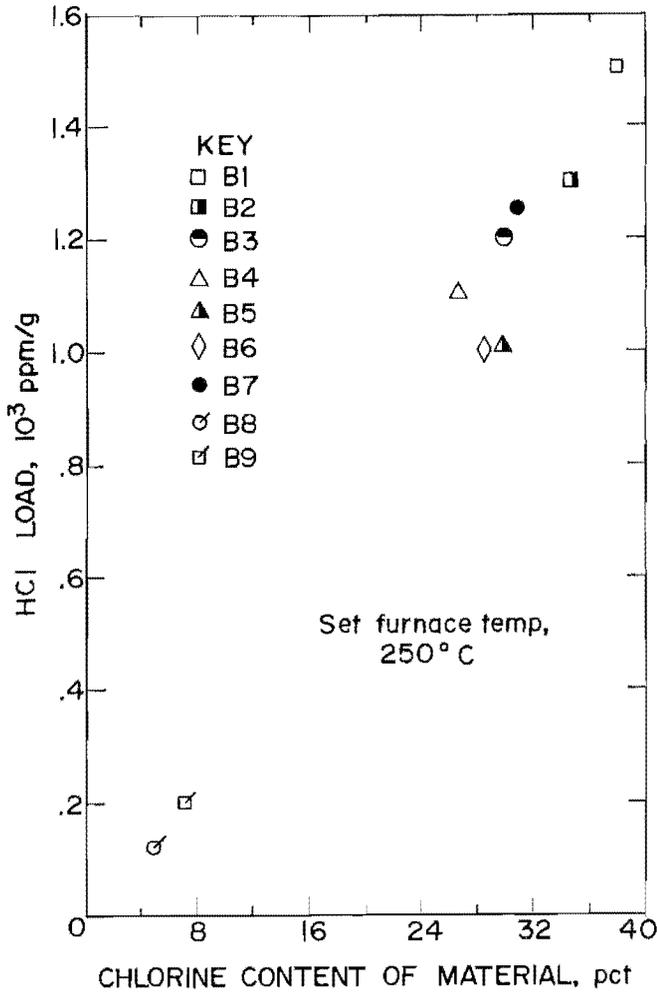


Figure 8.—HCl load versus chlorine content of material at 250° C.

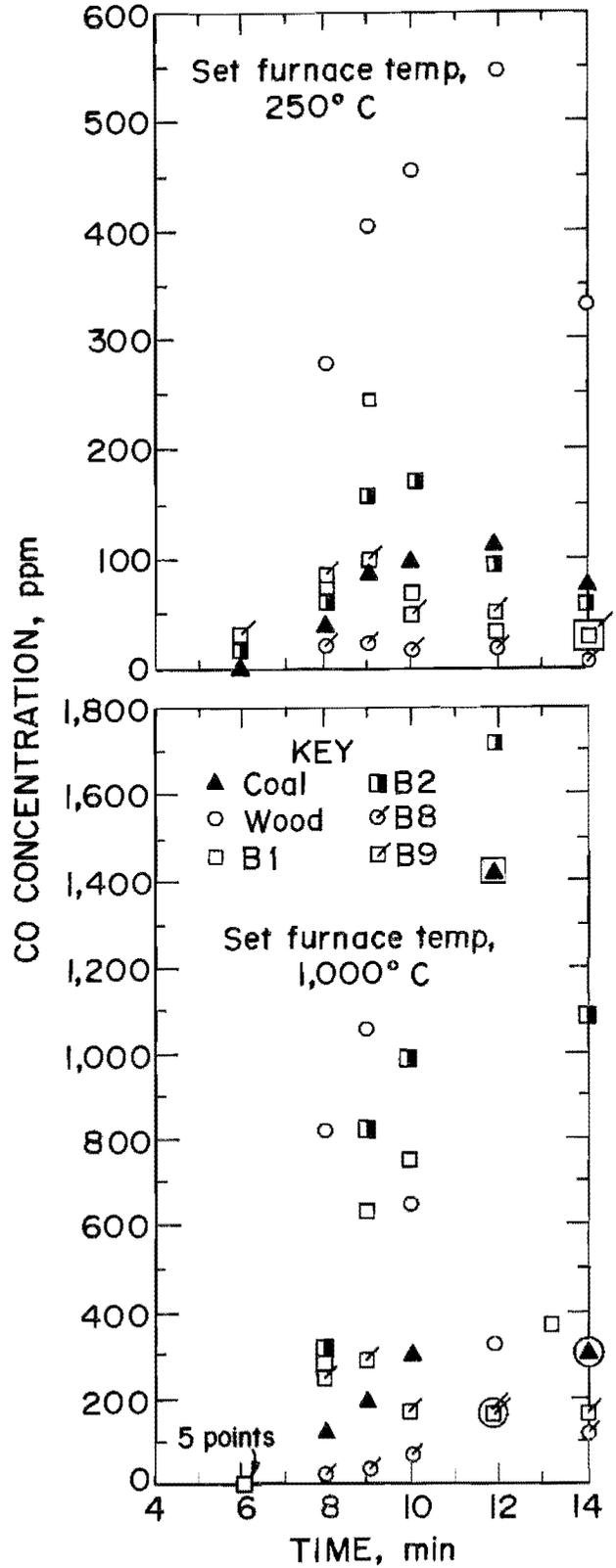


Figure 9.—CO concentrations versus time at 250° and 1,000° C.

Table 3.—Oxidative thermal degradation data at 250° C;¹ furnace airflow 10 L/min

Material investigated ²	HCl, ppm	WL, g	CO, ppm	Load			
				³ HCl, ppm/g	³ CO, ppm/g	⁴ HCl and CO, ppm/g	⁵ 1/d _{g,n_o} , cm ² /(p·g)
PVC brattice:							
B1, 38 pct Cl ₂	150	0.1	114	1,500	1,140	1,576	0.009
B2, 35 pct Cl ₂	130	.1	73	1,300	730	1,348	.008
B3, 30 pct Cl ₂	120	.1	75	1,200	750	1,250	.0074
B4, 27 pct Cl ₂	110	.1	75	1,100	750	1,150	.005
B5, 30 pct Cl ₂	80	.1	94	800	940	874	.0041
B6, 27 pct Cl ₂	100	.1	76	1,000	760	1,050	.0057
B7, 31 pct Cl ₂	125	.1	85	1,250	850	1,306	.0075
Fiberglass brattice:							
B8, 5 pct Cl ₂	<2	⁶ .01	16	⁷ 120	⁷ 1,600	227	.00005
Burlap brattice:							
B9, 7 pct Cl ₂	20	.1	35	200	350	223	.0007
B10	0	.1	45	0	450	30	.0003
Wood: W1	0	.1	135	0	1,355	90	.0004
Coal: C1	0	⁶ .01	47	0	4,700	313	.001

WL¹ Weight loss.

¹9th minute.

²1-g sample.

³Derived from concentration observed at 0.1 g of sample weight loss, at a specific time and airflow, adjusted to 1 g of weight loss.

⁴Combined HCl and CO loads. Each CO load value has been normalized to HCl values by scaling it down by a factor of 15, because CO is at least 15 times less dangerous than HCl.

⁵Inverse of d_{g,n_o} value. Each d_{g,n_o} value derives from total d_{g,n_o} values adjusted to 1 g of sample weight loss.

⁶Maximum weight loss observed.

⁷Theoretic concentrations only; sample underwent very little decomposition ((2 pct) at 1,000° C set furnace temperature), and no further decomposition at higher temperatures was observed.

Table 4.—Comparison of oxidative thermal degradation data; furnace airflow 10 L/min

Material investigated ¹	250° C						1,000° C						
	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, °C	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, °C	
PVC brattice:													
B1	12	6	20.9	550	0.56	264	13	6	20.7	1,700	0.96	268	
	66	8	20.9	800			322	8	20.7	2,400			366
	224	9	20.8	730			320	9	20.6	2,600			410
	88	10	20.8	810			314	10	20.5	2,800			450
	36	12	20.8	710			298	12	20.5	3,000			524
	20	14	21	610			283	14	20.5	3,600			588
B2	12	6	20.9	700	.62	264	10	6	20.8	620	.96	266	
	73	8	20.8	770			320	8	20.7	910			365
	154	9	20.8	860			325	9	20.6	1,240			409
	163	10	20.8	850			314	10	20.6	1,330			449
	84	12	20.8	780			295	12	20.5	1,800			529
	50	14	20.8	760			280	14	20.5	2,300			589
B3	11	6	20.8	610	.53	260	12	6	20.8	460	.96	277	
	154	8	20.8	720			320	8	20.7	800			328
	172	9	20.8	920			325	9	20.7	1,010			375
	140	10	20.8	770			315	10	20.6	1,100			419
	62	12	20.8	750			295	12	20.6	1,340			536
	140	14	20.8	640			290	14	20.7	1,500			600
B4	12	6	20.8	540	.44	260	10	6	20.8	480	.96	228	
	28	8	20.8	500			320	8	20.7	900			354
	135	9	20.8	590			318	9	20.7	1,100			382
	166	10	20.7	630			313	10	20.6	1,200			401
	107	12	20.8	530			290	12	20.6	1,400			501
	25	14	20.8	510			280	14	20.7	1,600			570
B5	20	6	20.9	710	.49	264	12	6	20.8	1,700	.96	269	
	45	8	20.9	700			320	8	20.8	2,300			369
	94	9	20.8	800			325	9	20.7	2,500			413
	103	10	20.8	830			314	10	20.7				455
	50	12	20.9	820			295	12	20.7	2,650			530
	21	14	20.5	840			290	14	20.7	3,200			594

See explanation notes at end of table.

Table 4.-Comparison of oxidative thermal degradation data; furnace airflow 10 L/min--Continued

Material investigated ¹	250° C						1,000° C					
	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, °C	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, °C
PVC brattice--con.												
B6	15	6	20.8	640	.49	265	12	6	20.8	1,500	.96	270
	71	8	20.8	740		315	102	8	20.7	1,800		370
	202	9	20.8	810		320	182	9	20.7	2,000		420
	140	10	20.8	810		314	424	10	20.7	2,500		460
	71	12	20.8	680		295	600	12	20.7	3,000		540
	24	14	20.8	620		290	312	14	20.6	3,500		600
B7	10	6	20.9	660	0.54	270	8	6	20.8	460	0.96	276
	55	8	20.8	740		320	107	8	20.8	550		373
	84	9	20.8	770		325	305	9	20.8	710		416
	101	10	20.8	770		314	424	10	20.7	790		457
	60	12	20.5	3,000		295	664	12	20.7	900		532
	55	14	20.4	4,000		290	356	14	20.7	1,130		596
Fiberglass brattice:												
B8	8	6	20.9	540	.01	269	10	6	20.8	660	.02	264
	14	8	20.9	600		320	33	8	20.8	700		363
	16	9	20.8	560		325	42	9	20.8	710		407
	13	10	20.8	580		314	72	10	20.8	740		447
	11	12	20.9	570		295	167	12	20.7	740		522
	8	14	20.9	560		290	125	14	20.7	740		588
Burlap brattice:												
B9	33	6	20.8	690	.59	268	13	6	20.9	630	.96	274
	75	8	20.8	990		318	264	8	20.8	1,270		370
	91	9	20.8	1,120		320	227	9	20.7	1,290		411
	64	10	20.8	1,020		315	171	10	20.75	1,110		451
	45	12	20.8	800		295	168	12	20.7	1,450		523
	14	14	20.8	680		290	174	14	20.65	2,110		588
B10	20	6	20.9	560	.56	265	14	6	20.85	640	.96	268
	105	8	20.9	900		319	285	8	20.6	3,600		366
	104	9	20.9	850		313	253	9	20.5	4,600		410
	76	10	20.9	830		305	296	10	20.8	1,700		450
	30	12	20.9	620		290	120	12	20.7	1,300		524
	21	14	20.85	540		285	186	14	20.75	2,300		588
Wood: W1 ..												
	7	6	20.85	550	.86	260	7	6	20.8	71	.96	271
	277	8	20.8	1,227		320	833	8	20.5	3,800		372
	405	9	20.8	1,450		322	1,060	9	20.7	1,900		418
	457	10	20.7	1,390		295	63	10	20.7	1,800		459
	548	12	20.7	1,720		290	33	12	20.7	1,800		534
	328	14	20.7	1,890		285	327	14	20.7	3,000		599
Coal: C1 ...												
	10	6	20.9	890	.03	260	193	6	20.75	1,700	.30	260
	47	8	20.8	880		320	123	8	20.7	2,400		361
	79	9	20.8	980		318	200	9	20.7	2,600		405
	92	10	20.8	940		305	289	10	20.55	2,800		447
	104	12	20.8	900		295	1,420	12	20.5	3,000		526
	74	14	20.8	950		290	313	14	20.55	3,600		591

WL Weight loss,
¹1-g sample.

Table 5.--Toxic load data at 250° C; furnace airflow 10 L/min

Material investigated ¹	² HCl		² CO		² HCl and CO	
	STEL	IDLH	STEL	IDLH	STEL	IDLH
PVC brattice:						
B1	60	15	3	1.0	63	16
B2	52	13	2	.5	54	14
B3	48	12	2	.5	50	13
B4	44	11	2	.5	46	12
B5	32	8	2.5	.65	35	9
B6	40	10	2	.5	42	11
B7	50	12.5	2.3	.6	52.3	13
Fiberglass brattice: B8	5	1	4	1	9	2.5
Burlap brattice:						
B9	8	2	1	.2	9	2.2
B10	0	0	1	.2	1	.2
Wood: W1	0	0	3	1	3	1
Coal: C1	0	0	12	4	12	4

IDLH Immediately dangerous to life and health (HCl, 100 ppm; CO, 1,500 ppm).

STEL Short-term exposure limit (HCl, 25 ppm; CO, 400 ppm).

¹1-g sample.

²Load or loads per STEL and IDLH.

CONCLUSIONS

According to these findings, the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$) load correlates directly with the HCl and CO toxic loads. HCl is the primary toxic gas during the early (~300° C) stage of combustion for all PVC and chlorinated brattices; CO is the primary toxic gas during a later ($\geq 400^\circ$ C) stage of combustion for all materials tested.

The PVC brattices released by far the largest HCl concentrations at the earliest time, yielding the highest HCl load, because of the extremely high chlorine content of the material and early and fast weight loss. By contrast, all the chlorinated brattices released the smallest HCl concentrations, because of the low content of chlorinated additives; in addition, the fiberglass had extremely low and late weight loss. At this stage CO does not pose a risk for all materials. An optimum content of chlorinated additives could be derived experimentally and required for these last types of brattices, which would impart fire-resistant properties and at the same time yield the lowest possible HCl concentrations during the early, critical stage of combustion.

At a later stage of combustion ($\geq 400^\circ$ C), the largest CO concentrations were released at the earliest time by all PVC brattice samples, followed by the wood sample, because of gross decomposition of the samples. By

contrast, the fiberglass brattice sample, followed by the burlap brattice samples, released much lower CO concentrations, because of the extremely low weight loss of the fiberglass brattice and/or the nature of the fiber. Of interest is the fact that the fiberglass brattice never underwent ignition, even at temperatures higher than 600° C. The coal sample released large CO concentrations, but only at the latest time, because of small and late weight loss.

It is evident that the PVC brattices are extremely dangerous under fire conditions, because of their high chlorine content and ease of thermal decomposition, which allows the release of large HCl concentrations during the earliest stage of combustion when miners must plan and prepare for escape. The burlap brattices, and especially the fiberglass brattice, burn less easily, yielding less toxic concentrations during the early and later stages of combustion, allowing some time to plan for escape or even to contain the fire.

The excellent correlations of the smoke particle characteristic $1/d_p n_o$ load with the HCl and the combined HCl and CO loads suggest its use as a test parameter for assessing simply and inexpensively the toxic hazard that these types of combustibles pose during fire.

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