

Exposure to Coal Tar Pitch Volatiles at Coke Ovens

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Personnel of the Pennsylvania Division of Occupational Health began surveying for exposure to coal tar pitch volatiles at coke ovens in 1966. A routine of sampling procedure and method of analysis has been developed, and ten coke oven installations have been surveyed. Approximately 320 samples were collected with filters mounted in plastic holders attached to the workers' shirt collars, and an integrated sample of 3 to 6 hours was obtained. Samples were also collected at various fixed locations. The results of these surveys have been compiled to determine exposure levels of specific jobs and work situations. The report indicates that all exposures are in excess of the threshold limit value.

Introduction

Workers on coke ovens are thought to have a higher incidence of lung cancer than the general population. This is alleged to be caused by exposure to polynuclear aromatic hydrocarbon compounds, including coal tar pitch volatiles (CTPV), which are generated during the coking process.¹⁻⁴ The American Conference of Governmental Industrial Hygienists has established a threshold limit value for coal tar pitch volatiles (benzene-soluble fraction of total particulate) of 0.2 mg/m³ of air, for an 8-hour daily exposure.⁵

Pennsylvania is a center of the steel industry and has eleven by-product coking facilities with 30% of the nation's coking capacity.⁶ In 1966, personnel of Pennsylvania Department of Health began working on methods to survey and to analyze for CTPV. The sampling and analytical methods and the initial findings have been published.⁷ This report details the findings of surveys at ten of the by-product coking facilities in this state.

Description of Operations

Coke is a product of the destructive distillation of bituminous coal; it finds its major application in the production of steel. It is manufactured either by the beehive or by-product (retort) process. The beehive process is no longer used substantially in Pennsylvania and was not considered in this survey.

A typical (by-product) coke oven is 10 to 15 feet high, 35 to 45 feet long, and approximately 18 inches wide. A hundred, or fewer ovens are generally assembled into a battery, and several batteries are combined into a coking facility. Each oven receives a charge of 10 to 18 tons of coal. Heat is applied to the walls of the ovens, and the volatiles are generated and conducted through pipework into a by-product recovery plant to be processed into xylene, toluene, etc. After a coking time of 16 to 20 hours, the coke is pushed through the oven into a quench car, emitting dense clouds which are principally dust. It is during the charging operation that workers are exposed to polynuclear aromatic hydrocarbons. Lesser sources of such exposure are the numerous cracks and leaks in the oven doors, charging ports, and standpipes.

The following eleven job classifications (in-

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cluding a miscellaneous category) are required in the operation of coke ovens and were studied in our surveys:

Larry car operator: Fills the coal hoppers on the larry car by manipulating levers on a platform outside the car; drives the car into position above the charging ports; discharges coal into these ports by manipulating levers inside the cab; and adjusts the standpipe(s) by means of a long rod. These duties involve exposure both inside and out of the larry car cab, and at times, during charging, the operator is exposed for short periods to heavy concentrations of coal dust as well as effluent gases.

Lidman: Opens the charging ports and repositions the lids after charging; seals ports with coal or sealing compound; and is responsible for general maintenance of the top of the battery. His major exposure is related to the charging operation.

Tar chaser (spray tender): Loosens tar accumulations in the collecting main by means of a rod with a spoon-type end; while doing this, may be exposed to high concentrations of polynuclear aromatic hydrocarbons.

Pusher machine operator: Directs the leveling bar into the oven to level the deposited coal; removes the oven doors and activates the pushing ram through the oven to push out the coke. At some facilities there may be a separate pusher side door machine. These two jobs (where separate operators were involved) have been combined for the purposes of this report.

Coke side machine operator (doorman): Removes the coke side oven door and positions the coke guide so that hot coke is pushed through the guides into the quench car.

Benchman: Cleans the oven door and jambs and inspects for damage; douses and removes fallen hot coke and, at some facilities, patches cracks in the door seal.

Quench car operator: Drives the quench car (hot car, locomotive) with its load of hot coke to the quenching tower and deposits the quenched coke onto a wharf.

Luterman: Applies luting compound (a sealant) to the doors. Seven of the ten coking facilities have "self-sealing" doors, and this job

is found only at those plants that have oven doors designed to be luted.

Heater: Checks the temperature of each oven with a pyrometer, regulates gas reversals, and maintains records. This job involves varying periods of exposure at different locations with a significant amount of time in the control area.

Miscellaneous category: Includes wharfmen, who control the gates which direct the quenched coke onto a conveyor; spellmen, who substitute for regular operators during breaks; patchers; and repairmen.

Among these work positions, the larry car operator, lidman, and tar chaser work on top of the battery; the luterman, benchman, and door machine operator work on the sides of the battery. The pusher machine and quench car run on tracks parallel to and a few yards from the battery.

Sampling Procedure

Breathing-zone samples were collected by means of battery-operated personal-type portable air pumps. Prewashed silver membrane filters having an 0.8-micron pore size were mounted with cellulose backup pads in plastic holders and attached to the shirt collars of the workers. Only the small plastic plug was removed during sampling because of the possibility of the filters' being burned by hot cinders and to minimize tampering and accidental damage.

The workers were fitted with the sampling apparatus at the start of the work shift. Samples were collected on a continuous basis so that integrated samples, reflecting periods of peak exposure as well as rest breaks, were obtained. Each sample was collected for as long a period as possible—that is, until the pump's battery became exhausted or until the filter became so clogged that the resistance was too great for the pump to overcome.

Each sampling apparatus was checked periodically and the flowmeter reading recorded. Airflow calibrations were maintained for each sampling apparatus. Average sampling rates varied from 2.0 to 2.8 liters/min. Total air volumes ranged from 103 to 1220 liters. Sixty

TABLE I
Exposure to Benzene-Soluble Fraction of
Coke Oven Particulates According to Job Title

Job Title	Number of Samples	Average ^a	Median ^a	Range ^a	Percent <TLV ^b
Coke side benchman	18	1.08	0.77	0.09- 2.14	5.6
Door machine operator	25	2.11	1.70	0.04- 6.51	4.0
Heater	39	1.07	0.82	N.D.- 2.98	10.3
Larry car operator	39	3.05	2.73	0.28- 8.78	0.0
Lidman	61	3.22	2.30	0.42- 17.89	0.0
Laterman	18	2.57	2.30	0.25- 4.82	0.0
Miscellaneous	18	0.93	0.95	0.18- 2.16	5.6
Pusher machine operator	23	0.39	0.33	N.D.- 0.93	30.4
Pusher side benchman	28	2.03	1.17	N.D.-14.59	10.7
Quench car operator	23	0.94	0.43	N.D.- 7.20	26.1
Tar chaser	27	3.14	2.37	0.04-14.70	7.4
Total	319	2.08	1.42	N.D.- 17.89	7.8

^aMilligrams per cubic meter of air.

^bTLV = 0.2 mg/m³ of air, based on exposure for an 8-hour work day.

N.D.—none detected.

percent of the samples had air volumes greater than 500 liters.

We were concerned that an internal bias might have developed from clogged samples—that is, that samples with a low total volume were those that had been subjected to short periods of extremely high concentrations, and that these samples made our results an amalgam consisting of normal and abnormal exposures.

Statistical evaluation indicated that samples of low total air volume had concentrations of par-

and coal tar pitch volatiles as randomly distributed as those with greater air volumes.

We interpret this to signify that our concern was unjustified. We infer, from our survey experience, that the moisture content of the air has a great effect on the clogging of the filters;

that is, we experienced a high incidence of clog-

in samples collected on the coke wharf. The air at this location is not particularly dusty,

but it is very moist.

General air samples were taken to determine relative concentrations at various locations in the coking facilities. These samples were collected using the filter-backup pad arrangement described previously. Electrically powered pumps having flow rates of 15 to 30 liters/min were used to collect samples where electric power was available. The mean total air volume was 774 liters.

The samples were analyzed by a standardized benzene extraction method.^{7,8} Each sample required eighteen gravimetric determinations (made with an analytical balance accurate to 0.01 mg) and 3 hours of refluxing in a Soxhlet extractor.⁷ Total particulate concentrations were also calculated.

Results

Three hundred and nineteen samples were collected in the workers' breathing zones. The results of analysis are indicated in Table I. Exposures at all job classifications were greater than the threshold limit value.

It should be stated that our laboratory personnel noticed staining on many of the backup pads in the later surveys. We theorize that improper seating caused leakage around the edges. A lack of history about this staining makes it impossible to determine if (as we believe) this was the case in the earlier surveys, and no attempt was made to adjust our results.

Figure 1 depicts the relative magnitude of exposures for those job classifications which are located in specific areas. The figure indicates that the magnitude of exposure is inversely proportional to the distance from the ovens. For example, the larry car operator, the lidman, and the tar chaser work directly on the ovens and have much greater exposure levels than the

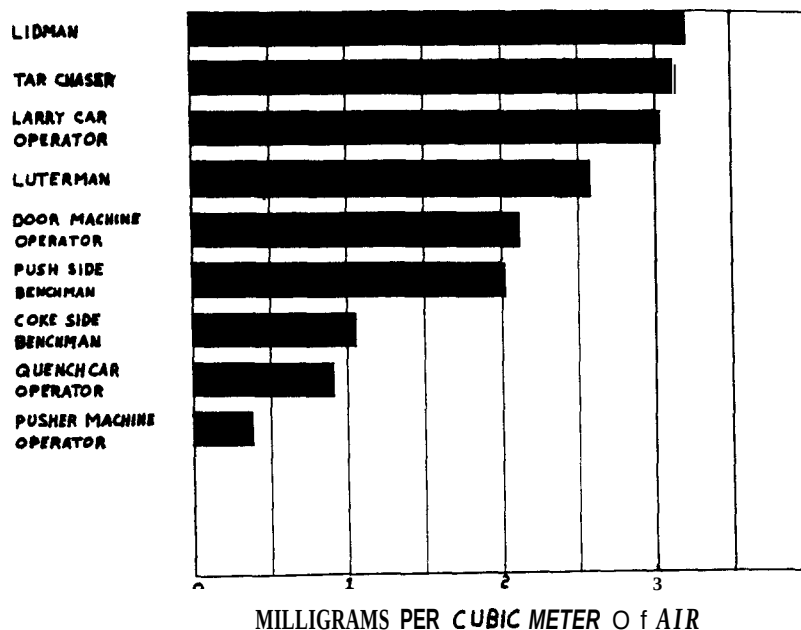


Figure 1. Comparison of exposure versus job title.

quench car operator and the pusher machine operator, who are several yards from the oven doors.

Table II lists exposure levels according to company. The average of exposures at all companies is greater than the threshold limit value. The differences among companies are influenced by the number of samples collected at each job classification, and interpretation of the results is also complicated by the fact that some jobs do not exist at some companies. Because of these factors, comparison of average exposures between companies is difficult.

Table III lists the variation in the average (mean) of exposures among job classifications and among companies. We realize that some of the averages are based on a small number of samples, but the trends are clear. The pusher machine operator and the quench-car operator have relatively low exposure (except in one instance), which is to be expected because of their relative distance from the coke ovens. The coke side benchman and the pusher side benchman have roughly the same duties and their exposures per company are comparable, except in one instance. This table also indicates that

some of the differences among companies may be more apparent than real. For example, the high overall mean for company E is explained by the unusually high exposure rates found for the tar chaser. Company A, with the smallest overall mean, has uniformly low exposure rates, and company H, with the greatest overall mean, has uniformly high exposure rates. However, if the tar chaser's exposure at company E is excluded, the χ^2 test indicates no significant differences in exposures among companies at a 95% confidence level.

Table IV lists the results of sampling in locations where workers are apt to congregate and indicate that exposures may be found in any location on or near a coke oven.

Because of the interest in respirable sampling, an attempt was made to correlate the amounts of coke oven particulates in samples collected as described with those collected using a 10-mm nylon cyclone elutriator.⁹ The results of the twenty-four paired samples are listed in Table V. The correlation coefficient is 0.30, indicating, in these samples, a very slight degree of correlation.

The presence of BaP (3,4-benzpyrene) was

TABLE II

Exposure to Benzene-Soluble Fraction of
Coke Oven Particulates According to Company

Plant	Number of Samples	Average CTPV ^a	Range ^a	<TLV ^b
A	22	1.02	0.09- 3.45	2
B	24	1.68	0.03- 9.04	2
C	24	2.16	N.D.- 8.78	4
D	28	1.55	N.D.- 6.21	2
E	17	3.30	0.24- 14.70	0
F	40	1.98	N.D.- 6.89	4
G	40	1.95	0.06- 9.24	2
H	34	3.24	0.08-17.89	3
I	44	1.94	N.D.-14.59	5
J	46	2.02	0.17- 7.20	1
Total	319	2.08	N.D.-17.89	25
				319 = 7.8%

^aMilligrams per cubic meter of air.^bTLV = 0.2 mg/m³ of air, based on exposure for an 8-hour work day.
N.D. - none detected.

investigated by fluorescence spectroscopy. Seventy-five percent of 212 samples fluoresced at 403 mμ upon activation at 373 mp. This concurs with the activation-fluorescence characteristics of BaP.

An attempt was made to investigate the relationship between CTPV and total particulate. This was done with the hope of establishing some estimate of the CTPV concentration in a sample. A fairly strong linear relationship was found to exist between CTPV and total particulate, with a correlation coefficient of +0.72.

It was observed that several workers were wearing respirators while standing in dust clouds. The Pennsylvania Division of Occupational Health has recommended the use of respirators during intermittent periods of high exposure, as an interim measure. Obviously, engineering and operational changes will be necessary to control the exposure of workers, particularly topside. The industry is engaged in an extensive program directed to these objectives. Ultimately the answer may lie in automation of these jobs, in operational or process changes such as a continuous coking process, or in elimination, through some process of making steel without coke. These alternatives are also under study by the industry.

The lack of adequate maintenance is apparent in many plants. Leakage at the oven doors is widespread and difficult to control in the older ovens. Strict attention to maintenance and repair of oven doors and jambs can minimize this source of exposure.

The nation's steel manufacturers and the American Iron and Steel Institute (AISI) are working together to develop measures to control exposures to polynuclear aromatic hydrocarbon. One interim approach is directed to the design of a new respirator with a battery-driven pump to pull air through an English-wool filter into a facepiece.

To control emissions during charging, dust collection equipment on the larry car has been used in Europe and has gained some popularity in this country. This equipment presents some safety hazards (explosions), and stack tests on the earlier installations have not been too encouraging.

The AISI proposes to control emissions during the charging operation by using the ovens themselves as exhaust ventilators. By redesigning the standpipes, adjusting the steam aspiration, and controlling the sequence of charging into the oven (only one lid removed at a time), it is believed possible to increase the

suction enough to significantly reduce emissions. Redesign of the larry car's hoppers and sequential charging will eliminate emission through the hoppers and blockage of the draft through the oven due to uneven filling. Also, the larry car cab will be enclosed and the operator will be supplied with filtered air. Magnetic lid lifters will reduce the lidman's exposure.

If these proposals prove to be workable, a significant step toward controlling exposures and air pollution will be accomplished.

It must be emphasized that these suggested changes are expensive and complicated; they would require constant maintenance and are several years in the future. Until they prove to be effective, reasonable supervision and enforcement of operating practices, maintenance, and personal protective programs must be maintained.

Summary

Evaluation of 319 breathing zone and 31 general air samples indicates that exposure to CTPV for all job classifications in all coking facilities is greater than the threshold limit value of 0.2 mg/m^3 of air, based on an 8-hour daily exposure. Exposure tends to be proportional to proximity to the coke ovens—the nearer the worker to the oven, the greater his exposure.

Simultaneous samples were taken by means of a cyclone elutriator in 24 cases, and these samples were compared to regular samples. Very slight correlation was found.

The presence of BaP was tentatively identified in 75% of 212 samples.

The relationship between volatiles and total particulate was analyzed statistically. Correlation coefficients of 0.7 to 0.9+ (depending on job and/or site) were determined. More work is necessary on this aspect.

Industry's proposals for the reduction of exposures were reviewed. It is technically feasible and hygienically desirable to eliminate the job of luting coke oven doors.

Conclusion

At the time the study was initiated, a litera-

TABLE III
Comparison of Exposures among Jobs and among Companies^a

Company	Coke Side Bench-man	Door Machine	Heater	Larry Car Operator	Lidman	Luterman	Miscellaneous	Pusher Machine Operator	Pusher Side Bench-man	Quench Car Operator	Tar Chaser	Mean
A	0.76	0.76	1.12	2.73	2.06		0.74	0.56	0.87	0.19		1.02
B	1.58	2.64	0.61	1.64	3.14			0.43	1.42	0.35		1.68
C		2.00	0.65	8.33	2.02	3.53	0.24	0.15		0.83		2.16
D	0.73	0.84	1.40	2.73	2.06			0.30	0.61	N.D.	1.18	1.55
E		0.85	0.61	2.76	3.34	2.62	1.35			0.76	11.59	3.30
F	0.76	0.74	1.38	4.30	3.78			0.52	0.70	0.34	3.32	1.98
G		3.43	1.41	1.11	1.95	2.18	0.57	0.37		0.25	3.31	1.95
H		3.91	1.11	4.97	6.27			0.22	1.24	0.77	1.62	3.24
I	1.09	1.18	0.78	2.62	1.88		2.15	0.53	4.44	0.27	2.34	1.94
J	2.35	3.11	1.05	2.50	3.23		1.06	0.31	2.09	2.67	1.81	2.02
Mean	1.08	2.11	1.07	3.05	3.22	2.57	0.93	0.39	2.03	0.94	3.14	2.08

^aValues in milligrams per cubic meter of air.
N.D.—none detected.

TABLE IV

Concentrations of Coke Oven Particulates (Benzene-Soluble Fraction)
in Selected Locations

Location	Number of Samples	Average ^a	Median ^a	Range ^a	%<TLV ^b
Reversing room	15	0.30	0.30	N.D. - 0.80	46.1
Foreman's office	5	0.10	0.09	0.04 - 0.16	100.0
Wash room/line-up room	7	0.56	0.54	N.D. - 1.66	28.6
Vending machine area	3	0.20	0.04	N.D. - 0.56	66.1
Total	30	0.21	0.16	N.D. - 1.66	53.3

^aMilligrams per cubic meter of air.^bTLV = 0.2 mg/m³ of air, based on exposure for an 8-hour work day.
N.D. none detected.

TABLE V

Comparison of Coke Oven Particulates (Benzene-Soluble Fraction)
Collected Using a Cyclone Prefilter versus Samples without Prefilter

Job Title	With Prefilter	Without Prefilter
Larry car operator	2.73	2.98
	1.66	5.66
	0.42	3.33
	0.17	2.20
	1.32	1.00
Lidman	0.31	1.67
	1.13	0.35
	1.10	3.75
	1.30	1.66
	1.59	2.79
	2.46	1.44
Coke side benchman	0.77	1.52
	0.13	0.52
	1.66	1.35
Pusher side benchman	0.48	0.62
	0.15	1.98
Heaters	1.52	2.17
	0.92	1.36
	1.29	1.05
	N.D.	0.71
Tar chaser	1.06	1.18
Pusher side machine operator	0.54	0.30
Door machine operator	0.98	0.84
Ouench car operator	0.22	N.D.

ture search revealed a dearth of information available about CTPV and coke ovens. It was learned that several steel companies had conducted surveys and that the AISI had begun to formulate proposals with regard to evaluation and control of coke oven emissions. It is suggested that, in view of the time, money, and effort that will have to be spent to combat this problem, a group should be formed to coordinate efforts. We believe that the combined

interest of industry, labor, and government is needed to improve the conditions for the coke oven worker.

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Approved Respirators Listed

Respiratory protective devices currently approved for use in hazardous mine atmospheres are listed in a report by the Bureau of Mines, U. S. Department of the Interior. The devices are approved jointly by the Secretaries of the Interior and of Health, Education, and Welfare. The list covers devices approved for use in oxygen-deficient atmospheres, and in the presence of specific gases, vapors, dusts, mists, and fumes. An appendix to the report provides names and addresses for the manufacturers of the listed devices. Tables in the publication list devices jointly approved for use in mines, without further testing, until March 30, 1974. Each table gives pertinent data on one type of respirator, including the Bureau "Schedule" or requirements under which it was tested and approved. Tables for respirator types are: Self-contained breathing apparatus; gas masks; supplied-air respirators; dust, fume and mist respirators; and chemical cartridge respirators.

Under newly established rules the Bureau of Mines will continue to promulgate requirements for mine respirators; the National Institute for Occupational Safety and Health will test them; and those that pass will be approved jointly by the Secretaries of Interior and of HEW. Also, the Bureau will publish lists of devices approved for use in mines, while NIOSH will list those approved for use in other hazardous industrial atmospheres. The testing of respirators, according to schedule requirements, has been a function of the Bureau of Mines for many years and is now in the process of being transferred to NIOSH.

Respirators Approved by the Bureau of Mines as of May 24, 1972, Information Circular 8559, by E. J. Kloos and R. H. Schutz, is a revision of a previous list. A free copy of the new list can be obtained from the Publications Distribution Section, Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213. Requests should note both the title and number of the report.