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AK STEEL COKE WORKS
ASHLAND, KENTUCKY

NIOSH INVESTIGATORS
Max Kiefer, CIH
Robert Malkin, DDS

SUMMARY

On October 25, 1993, the National Institute for Occupational Safety and Health (NIOSH) received an employee request for a health hazard evaluation (HHE) at the AK Steel Company (formerly Armco Steel), Coke Department, in Ashland, Kentucky. Exposure to contaminants generated during the collecting and blending of coal tar sludge with coal prior to processing in the coke ovens was identified as the area of concern.

On January 10, 1994, NIOSH investigators conducted a site visit to review the coal tar sludge process and byproducts area, evaluate work practices, conduct environmental monitoring to assess exposure to airborne contaminants, and interview employees. Personal breathing zone (PBZ) and area air sampling was conducted to evaluate levels of coal tar pitch volatiles (CTPV), polynuclear aromatic hydrocarbons (PAHs), benzene, and naphthalene. Bulk samples of coal tar sludge were obtained. Area sound level monitoring was conducted at the coal car shaker area to assess noise levels inside and outside control booths during "shaker" operation. At that time, 19 employees were interviewed by the medical investigator.

During this site visit the sludge-coal blending process (use of a front loader and screw conveyor to mix the sludge into coal) was not in operation due to inclement weather and the process could not be fully evaluated. Therefore, a follow-up visit was conducted on June 13-15, 1994, to evaluate exposures to CTPVs, PAHs, benzene, naphthalene, and respirable coal dust. A questionnaire was administered and 1-hydroxy pyrene (1-HP), an indicator of exposure to the PAH pyrene, was measured in the urine of 18 of 22 employees working in the sludge-coal handling areas. Dermatologic interviews and examinations were made available to all participants in the urine testing and dermatologic interviews were conducted with 17 and examinations were performed on 11.

No CTPVs or PAHs were detected on any of the filters collected during the January 11, 1994, survey. However, some lower molecular weight PAHs were detected on backup sorbent tube samples. NIOSH has not established Recommended Exposure Limits (RELs) for these lower molecular weight PAHs. A concentration of 0.8 parts per million (ppm) benzene was found on an 81 minute area sample collected in the cab of a vehicle loading the coal-sludge mixture. The NIOSH REL for benzene is 0.1 ppm as an 8-hour time-weighted average and 1 ppm as a 15-minute short-term exposure limit. All coal sludge bulk samples contained numerous common PAHs associated with coal tar products, including the 5 PAHs listed in the Occupational Safety and Health Administration (OSHA) definition of CTPVs.

CTPVs were detected on filters from 7 of the 10 (70%) PBZ samples, and detectable PAHs were measured on 3 of the filters obtained during the June 14, 1994, survey. Lower molecular weight PAHs were detected on all 10 of the backup sorbent tubes from the PBZ samples. The highest

CTPV concentration (0.35 milligrams per cubic meter [mg/m^3]), and the greatest number of PAHs, were found on a PBZ sample obtained from a day-shift laborer. The NIOSH REL for CTPVs is 0.1 mg/m^3 of the benzene (or cyclohexane) extractable fraction of the sample. With the exception of one PAH (chrysene), NIOSH has not established RELs for any of the PAHs detected on the PBZ samples. NIOSH considers chrysene to be a potential human carcinogen and recommends exposure be reduced to the lowest feasible level. Naphthalene was detected on all samples (both area and PBZ) collected during the June 14 survey. The highest PBZ concentration was 3.5 mg/m^3 (NIOSH REL = 50 mg/m^3) from the laborer operating the coal-sludge blending auger. Both detectable and quantifiable levels of benzene were found on 5 of the 10 (50%) PBZ samples, and both area samples.

None of the bulk samples of coal dust (settled, respirable air, total air) had detectable silica (the analytical limit of detection was 0.75%). The highest concentration of respirable dust (0.75 mg/m^3) was on a PBZ sample from the evening-shift Coal Handler Operator. NIOSH has not established a specific REL for coal dust. Sound level monitoring showed levels of 103-108 decibels, A-weighted scale (dBA) while the shaker was in operation. Levels measured inside the outer shaker booth were 75-76 dBA, and 77-81 dBA inside the inner shaker booth. The NIOSH REL for noise is 85 dBA as an 8-hour time-weighted average.

A statistically significant increase was detected between pre-shift and post-shift urinary 1-HP levels ($p=0.004$). Although a biological exposure limit (BEL) has not been established for 1-HP, several samples exceeded the proposed BEL of 2.3 µmol/mol creatinine (based on the American Conference of Governmental Industrial Hygienists [ACGIH] TLV of 0.2 mg/m^3). From the dermatologic examination we found that four employees had potentially work-related skin conditions, although other explanations are possible. The most prevalent symptoms reported by workers on the questionnaire were itching skin, headache, and sinus problems.

Exposure to coal tar pitch volatiles (CTPVs), polynuclear aromatic hydrocarbons (PAHs), and potentially benzene, exceeded the NIOSH RELs during the processing of coal-tar sludge, indicating a health hazard exists due to exposure to these contaminants. The potential exists for skin contact with coal tar sludge, and improper use of personal protective equipment was observed during the NIOSH evaluation. The urine 1-HP levels documented excessive exposure to pyrene. Recommendations to reduce exposure are specified in the Recommendations section of this report.

KEYWORDS: SIC 3312 (Steel Works, Blast Furnaces (Including Coke Ovens), and Rolling Mills). Benzene, coal tar pitch volatiles, polynuclear aromatic hydrocarbons, coal dust, silica, 1-hydroxy pyrene, byproducts coke ovens, dermatitis.

INTRODUCTION

On October 25, 1993, NIOSH received an employee request to conduct a health hazard evaluation (HHE) at the AK Steel Coke Works (formerly Armco Steel Company) in Ashland, Kentucky. Reported health problems included respiratory, prostate, and intestinal cancer, hearing loss, headache, nausea, dizziness, and skin eruptions. The requesters were concerned that these health problems may be related to exposure to coal tar pitch volatiles (CTPVs) and other chemicals in the coke byproducts area, specifically the coal-tar sludge handling process.

On January 10, and June 13-15, 1994, NIOSH investigators conducted site visits to review the coal tar sludge handling process, evaluate facility safety and health programs, monitor worker exposure to chemicals in the coal handler areas, and conduct biological monitoring to assess exposure to pyrene, a polynuclear aromatic hydrocarbon (PAH). Work practices, including the use of personal protective equipment, were also assessed.

A letter describing preliminary findings and recommendations, and future actions was sent to AK management, union representatives, and the requester on February 18, 1994. Exposure monitoring results were sent to the same distribution on April 5, 1994.

BACKGROUND

Facility Description

The AK Coke Works facility in Ashland, Kentucky, was acquired by Armco Steel in 1981 (the company changed their name to AK Steel in 1994). Approximately 400 employees work at this facility, which can produce about 1,000,000 tons of coke annually at full capacity. Metallurgical coke is the residue remaining after the devolatilization of bituminous coal, and is used as a fuel and reductant in blast furnaces for steel making. This process entails heating coal to temperatures of 900-1100° C in the absence of oxygen to distill out tars, light oils, a gaseous byproduct referred to as coke oven gas, ammonia, water, and sulfur compounds, in order to produce a substance with a substantially higher carbon content. During this carbonization process, about 20-30% of the initial coal charge evolves as mixed gases or vapors.

Chemical (byproduct) recovery, slot-type coke ovens arranged in batteries (a series of ovens) are used at the AK facility. A wet load (charge) of approximately 28 tons of coal will yield about 20 tons of coke per cycle. A cycle will take from 16-24 hours to complete. The resulting coke is then pushed out of the oven and quenched with water. Standpipes on each oven collect the gases generated from the coal during the carbonization process. These standpipes are connected to large collecting mains, which transport the effluent to the byproducts plant, where the gases are separated and processed. The byproducts plant at the AK facility consists of an ammonia concentrator, boiler plant, exhauster building (houses the fans for the collecting mains), crude light oil recovery, sulfiban, and a pump house. Numerous tanks for storage of distilled or waste product are also present in the byproducts area. The coal handling building, consisting of large storage bins containing various grades of coal, is adjacent the byproducts plant.

Process Description

The blending of coal tar sludge with coal has been an ongoing process at the AK coke plant since 1991. Coal tar sludge, or tar decanter sludge, is the residue remaining from the coke byproducts recovery process. It is composed of small coal particles ("fines") and coal tar. The AK material safety data sheet (MSDS) for tar decanter sludge lists the chemical components as coal tar (67%) and coal (33%). The sludge is obtained on a daily basis from four hot tar drain tank decanters that discharge the sludge into steam heated sleds, which are moved by truck to the blending area. Other sources for coal tar sludge are six "cookers," which are cleaned on an annual basis, and two 0.5-million gallon tar storage tanks which are also cleaned annually. Blending occurs at the "swimming pool" area (an open concrete-lined pit used to store the sludge) and is conducted 2-3 hours per day, 3 days a week. During the colder winter months, the sludge is too viscous to work, so the process is shut down. This process consists of a front-loader operator mixing sludge with coal at a 1:10 ratio. A screw conveyor, located in this area, is used to mix and convey the sludge-laden coal into the appropriate storage pile. Trucks transport 80% of the sludge-laden coal to the shaker area; trains transport the rest. The coal is then dispensed through a grate into a collection pit with a conveyor system. The conveyor transports the sludge-laden coal to the coal handlers building, where it is delivered to bin # 6. Of the final coal blend delivered to the coke ovens, approximately 3% is the sludge-laden coal. About 23-26 employees (laborers and operators) work on a 3-shift basis in this coal-handling area. Figure 1 depicts the coal-sludge mixing process.

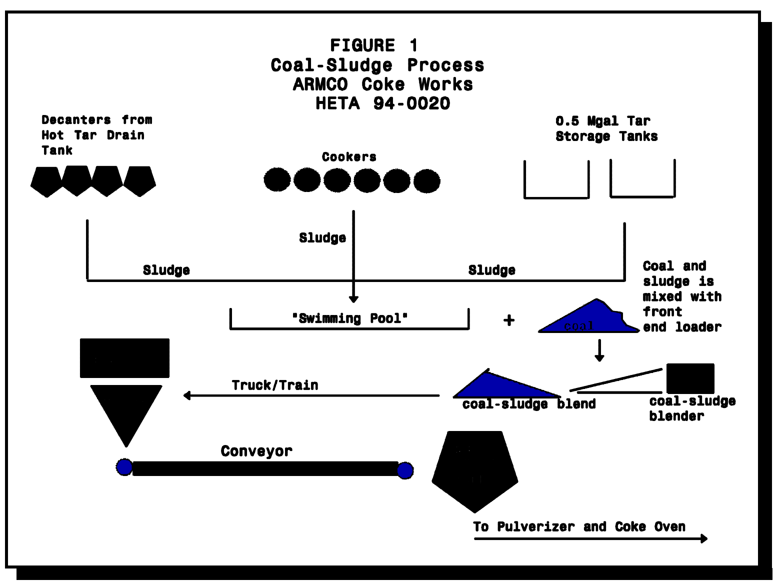

FIGURE 1
Coal-Sludge Process
ARMCO Coke Works
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Cancer Cases

Through a previous review of workers who had missed work with a diagnosis of cancer, the company was able to determine the number of coke plant workers who had contracted the disease in the last 5 years. This review determined incident cases of cancer among employees who were working at AK during the year of the survey, but missed new cases of cancer in retirees and other former workers. The employee health director identified 11 cases of cancer among the several hundred coke plant employees from 1988 to 1993 using employee absentee records. During that time period there were two cases each of kidney, bladder, colon, and prostate cancer, and one each of lung, female breast, and mouth cancer.

EVALUATION PROCEDURES

The NIOSH evaluation consisted of industrial hygiene and medical components with the following elements:

Safety and Health Program Review and Workplace Observations

- Coal tar sludge handling activities, and other work practices, were observed to assess employee use of personal protective equipment (PPE), and a general work area inspection was conducted.

- In-depth interviews were held with employees and work practices were observed for areas of the plant where workers reported more frequent and severe symptoms. The coke plant nurse was interviewed.

- AK industrial hygiene monitoring results (noise and chemical) from the evaluated area were reviewed. Additionally, the AK respiratory protection and hearing conservation program were reviewed, as well as personal protective equipment (PPE) requirements and task-specific safety procedures for handling the decanter sludge and blending the sludge with coal.

Environmental Monitoring

Processes were selected for monitoring based on an assessment of the materials handled, employee work practices, and controls utilized. Activities of concern noted by the requesters were also targeted for sampling. The sampling and analytical methodology used for this monitoring is described in Appendix A.

On January 11, 1994, personal breathing zone (PBZ) and area air sampling was conducted to evaluate exposures to coal tar pitch volatiles (CTPV), polynuclear aromatic hydrocarbons (PAHs), benzene, toluene, and naphthalene. Sampling was conducted during the loading, hauling, and dispensing of three truckloads of sludge-laden coal from the "swimming pool" storage area to the shaker area. Bulk samples of the coal tar sludge were obtained from the coal tar decanters for PAH analysis. Area sound level monitoring was conducted at the coal car shaker to assess noise levels inside and outside control booths during "shaker" operation.

On June 14, 1994, PBZ and area air sampling was conducted for CTPVs, PAHs, benzene, naphthalene, and coal dust (respirable and total). Coal handler operators and laborers at the train loading, coal hopper, coal-sludge storage pool, and coal-sludge auger/conveyor, and in the coal-handler building were monitored. The outdoor air temperature was approximately 90° F during this monitoring.

Medical

The project was predominantly focussed on 22 workers in the coal handling area and was conducted on January 10, 1994, and June 13-15, 1994. The first visit consisted of confidential interviews with employees, selected by union officials, who had expressed an interest in talking with NIOSH investigators because of their health concerns.

The return visit of June 13-15 consisted of a dermatologic exam by a NIOSH board-certified dermatologist and biologic monitoring for 1-hydroxy pyrene (1-HP) in urine. Participants in the biological monitoring were also asked to complete a questionnaire that asked about work practices, diet, and symptoms that had been frequently reported in the interviews (Table M-2). Although these symptoms are not known to be associated with exposure to coal tar, they were prevalent among employees and were included on the questionnaire to determine if PAH exposures might be associated with increased reporting. Frequency of symptoms reporting was dichotomized into symptoms that occurred at least once a month or more, or less than once a month.

Participants for 1-HP urine testing were workers in the coal-tar sludge handling areas who were working on the day and evening shifts on the days of the evaluation. All workers willing to participate were eligible for inclusion in the study. On the days of the evaluation, there were approximately 22 workers who were eligible for inclusion in the study.

Urine samples were collected from 18 of the 22 eligible workers from all work shifts. One additional sample was from a coke oven worker who was inadvertently included in the group to be tested; his sample was not included in the analysis of the data. Workers were instructed to report to the nurses' station upon arrival at work and before leaving so that pre-and post-shift urine samples could be collected from workers to determine if there was an increase in 1-HP during the course of the workday. One worker did not provide a pre-shift urine sample, and was not included in the study. The urine samples were frozen after collection and returned to Cincinnati for analysis. Analysis was performed by the method described by Tolos et al.[1a]

1-HP is the major metabolite of pyrene, a compound found in coal tar, and is formed by the liver and excreted in urine and stool.[1] Because workers in the sludge handling area had an unknown degree of skin exposure to coal tar, it was possible that air monitoring would miss a substantial portion of their exposure. The pyrene to total PAH ratio is relatively constant in the coke oven environment, and monitoring of urinary 1-HP is a viable method of assessing total PAH exposure.[2,3]

The NIOSH dermatologist conducted informal interviews with employees from throughout the coke plant who were identified by union or management officials as having potential work-related skin conditions and with all employees who participated in urine testing. In addition, examination of exposed skin surfaces was conducted for those employees reporting current skin problems.

EVALUATION CRITERIA

Environmental

General

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff use established environmental criteria for the assessment of a number of chemical and physical agents. These criteria suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It should be noted, however, that not all workers will be protected from adverse health effects if their exposures are below the applicable limit. A small percentage may experience adverse health effects due to individual susceptibility, pre-existing medical conditions, and/or hypersensitivity (allergy).

Some hazardous substances or physical agents may act in combination with other workplace exposures or the general environment to produce health effects even if the occupational exposures are controlled at the applicable limit. Due to recognition of these factors, and as new information on toxic effects of an agent becomes available, these evaluation criteria may change.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Criteria Documents and recommendations, (2) the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs), and (3) the U.S. Department of Labor Occupational Safety and Health Administration (OSHA) standards.[4-6] Often, NIOSH recommendations and ACGIH TLVs may be different than the corresponding OSHA standard. OSHA standards are required to consider the feasibility of controlling exposures in various industries where the hazardous agents are found; the NIOSH recommended exposure limits (RELs), by contrast, are based primarily on concerns relating to the prevention of occupational disease.

Coal Tar Pitch Volatiles/Polynuclear Aromatic Hydrocarbons

Coal tar and pitch is a black or brown liquid or semisolid product derived from coal. A principal source of coal tar is coke-oven plants, where crude tar is separated from coke oven condensate for refining and possibly further processing.[7] Coal tar, coal tar pitch, and creosote derived from bituminous coal may contain carcinogenic polycyclic hydrocarbon components such as benzo(a)pyrene, benzanthracene, chrysene, and phenanthrene, which belong to a class of chemicals referred to as polynuclear aromatic hydrocarbons (PAHs).[7-12] PAHs are chemicals of relatively high molecular weight that consist of two or more fused aromatic rings. Over 100 different PAH compounds have been identified.[10] Coal tar pitch volatiles (CTPVs) include PAHs that volatilize from the distillation residues of coal.

There are well-recognized adverse health effects associated with exposure to CTPVs and PAHs. Many PAHs, such as benzo(a)pyrene, have been shown to be carcinogenic in laboratory animals.[7-10,12] The National Toxicology Program's Seventh Annual Report on Carcinogens lists 15 PAHs that have been shown to cause lung, stomach, oral, and skin cancer in experimental animals.[12] Epidemiological studies of workers exposed to coal tar products have shown excess risks of lung, oral, and skin neoplasms.[7] Exposure to CTPVs can occur either through inhalation of volatilized products or contact with unprotected skin.

The NIOSH REL (full-shift time-weighted average) for CTPVs is 0.1 milligram per cubic meter (mg/m^3) of the benzene- (or cyclohexane-) extractable fraction of the sample, and is based on the potential risk of lung and skin cancer.[4] NIOSH also regards the presence of any PAH in CTPVs as indicative of potential carcinogenicity.[13] The OSHA PEL for CTPVs is 0.2 mg/m^3 of the benzene soluble fraction that contains one or more of the following PAHs: benzo(a)pyrene, phenanthrene, chrysene, anthracene, pyrene, acridine.[6] The ACGIH TLV for CTPVs is also 0.2 mg/m^3 for the benzene- (or cyclohexane-) soluble fraction, if that fraction contains detectable quantities of any of the following PAHs: benz(a)anthracene, benzo(a)fluoranthene, chrysene, anthracene, benzo(a)pyrene, phenanthrene, acridine, or pyrene.[8]

Benzene, Naphthalene

Benzene, also referred to as benzol, is a colorless, volatile liquid with a sweet odor similar to many aromatic hydrocarbons. The odor threshold (the level that most people can begin to smell benzene in the air) is 1.5-4.7 parts per million.[14] Benzene has numerous uses as the simplest aromatic hydrocarbon, and is produced as a by-product in the coal conversion process. Acute exposure to high concentrations causes central nervous system effects such as drowsiness, dizziness, and headache.[9,14,15] The health effect of most concern, however, is the often irreversible injury to bone marrow, which can result in anemia, leukopenia, thrombocytopenia, or pancytopenia (depression of all three cell types), which, in conjunction with bone marrow necrosis is termed aplastic anemia.[9,14] Numerous case reports and epidemiologic studies have described an association with benzene exposure and leukemia (primarily acute myelogenous leukemia), and there is sufficient evidence to consider benzene to be carcinogenic in humans.[12,14] The blood disorders associated with benzene exposure may occur without preceding symptoms.

Because of its volatility, inhalation is the major route of exposure to benzene, although skin exposure is also a concern. The route of exposure does not appear to affect the metabolic pathway of benzene.[14]

NIOSH considers benzene to be an occupational carcinogen and has established an REL of 0.1 ppm as an 8-hour TWA, and a ceiling limit (15-minute) of 1 ppm.[4] OSHA has promulgated a comprehensive standard for benzene that includes a PEL of 1 ppm as an 8-hour TWA, and a short-term exposure limit (15 minute) of 5 ppm.[16] The OSHA standard requires a number of controls and employer actions (medical surveillance, engineering controls, monitoring, respiratory protection, training) for workers exposed above the action level of 0.5 ppm.

Naphthalene is a white crystalline solid PAH with a characteristic "mothball" odor. Naphthalene is not considered to be carcinogenic, but there are other adverse health effects associated with overexposure. Naphthalene vapor is an eye irritant (may cause cataracts), a hemolytic (red blood cell destroying) agent, and a cause of headache and nausea.[(8,9)] The NIOSH REL for naphthalene is 10 ppm as a full-shift TWA, and 15 ppm as a 15-minute short-term exposure limit (15-minute).[4]

Coal Dust

Coal is a dark-brown to black solid formed from fossilized plants. It is composed of amorphous carbon and various organic and inorganic compounds. Inhalation of respirable coal dust can result in a lung disorder known as coal workers' pneumoconiosis (CWP).[(9,17,18)] Respirable dust is considered to be that portion of dust small enough to reach the deeper portions of the lungs (generally considered to be particles less than 7-10 micrometers in diameter). Coal dust may contain varying percentages of silica (up to 10%).[18] Simple CWP is diagnosed by the presence of small opacities on a chest x-ray; there may not be clinical signs or symptoms, or there may be a slight cough and blackish sputum.[9] Continued exposure can lead to progressive massive fibrosis (complicated CWP), which is associated with a reduction in lung capacity, gas exchange abnormalities, pulmonary hypertension, and death.[(9,18)] Complicated CWP is termed progressive because the disease may progress in the absence of further dust exposure.

The OSHA PEL for the respirable fraction of coal dust is 2.4 mg/m^3 if the dust contains less than 5% crystalline silica.[6] If the respirable fraction contains more than 5% crystalline silica, the PEL is determined as follows:

$$\frac{10\ \text{mg/m}^3}{\%\ \text{silica} + 2}$$

NIOSH has not established a REL for coal dust. During a 1989 project to update the OSHA PELs, NIOSH concluded that adverse health effects could occur at the proposed OSHA PEL.[4] The NIOSH REL for crystalline silica is 0.05 mg/m^3 as a full-shift TWA.[4]

Noise

Noise-induced hearing loss (NIHL) is a permanent, often insidious, sensorineural condition that will progress as exposure continues. There are many factors that affect the degree and extent of hearing loss. For instance, hearing ability will decline with age (presbycusis), and approximately 20% of the general population between age 50 and 59 experience hearing losses without any exposure to industrial noise.[19] The most important factors determining the effect of noise on hearing are: the intensity of the noise (sound pressure level), the type of noise (frequency), the duration of exposure each day, and the total work exposure (years of exposure).[(8,19)] The preferred unit for measuring sound is a logarithmic scale known as the decibel (dB). Typically, the frequency of measured sound levels are weighted to vary in intensity in a way that mimics the response of the human ear, this is referred to as the "A" scale. Thus, the weighted sound level intensities that approximate the response of the human ear are reported in dBA. In general, exposure to sound levels below 70 dBA are assumed to be safe (do not produce permanent hearing loss), while any exposure of the unprotected ear to sound levels greater than 115 dBA is considered acutely hazardous.[19] The effect on hearing of noise levels between 70 and 115 dBA will vary depending on the duration and intensity of exposure.

OSHA has established a hearing conservation standard (29 CFR 1910.95) that specifies an 8-hour PEL of 90 dBA.[20] The standard also requires the establishment of a hearing conservation program for all employees exposed to greater than 85 dBA as an 8-hour TWA. A hearing conservation program includes employee training, audiometric examinations, monitoring, hearing protection, and recordkeeping. These noise regulations use an "exchange rate" of 5 dB when calculating the PEL. That is, for every 5 dB increase above 90 dBA, the allowable exposure time is reduced by one-half. The upper limit (not to be exceeded) for impulse or impact noise is 140 dB. NIOSH recommends an exposure limit of 85 dBA as an 8-hour TWA, 5 dB less than the OSHA PEL.[21]

RESULTS AND DISCUSSION

Environmental

Air Sampling - January 11, 1994

The results of the air and bulk sampling are shown in Tables IH-1 and IH-2 respectively. As shown in Table IH-1, some of the lower molecular weight PAHs (acenaphthylene, acenaphthene, fluorene) were detected on the XAD-2 sorbent tubes. NIOSH has not established RELs for the detected PAHs. Benzene was detected on two of the three samples; the highest concentration (0.8 parts per million [ppm]) was found on an 81 minute area sample collected in the cab of the vehicle loading the coal/sludge mixture into a dump truck. The NIOSH REL for benzene is 0.1 ppm as an 8-hour time-weighted average (TWA) and 1 ppm as a 15-minute short-term exposure limit.

All of the coal sludge bulk samples contained numerous common PAHs associated with coal tar products (IH-2). The identified compounds included the 5 PAHs listed in the Occupational Safety and Health Administration (OSHA) definition of CTPVs.[6]

Air Sampling - June 14, 1994

The air sampling results from the June 14 monitoring are shown in Tables IH-3. CTPVs were detected on the filters from 7 of the 10 (70%) PBZ samples collected, and detectable PAHs were measured on 3 of these filters. Lower molecular weight PAHs were detected on all 10 of the backup sorbent tubes from the PBZ samples. The three filter samples with detectable PAHs were obtained from a day-shift Coal Handler Operator working at the hopper/shaker area where coal is dispensed from trucks or train cars, an evening-shift Coal Handler Operator working in the Coal-Handler Building and Lower End, and a day-shift Laborer working in the coal handler area. The highest CTPV concentration (0.35 mg/m^3), and the greatest number of detectable PAHs were found on a 429 minute PBZ sample obtained from the day-shift Laborer. This worker spent the majority of the work-shift in the #1 hole - a confined area containing the conveyor used to transport coal from the shaker area to the coal-handler building.

With the exception of one PAH (chrysene), NIOSH has not established RELs for any of the PAHs detected on the PBZ samples. Both NIOSH and the ACGIH consider chrysene to be a potential human carcinogen.[4,8] NIOSH recommends controlling exposure to chrysene to the lowest feasible limit.[4]

No CTPVs or PAHs were detected on the filters from two area samples collected at the coal-sludge storage pool and auger operator booth. Similarly, no CTPVs or PAHs were detected on the PBZ samples from the laborer operating the coal-sludge blending auger or the front-end loader operator in this area. Detectable PAHs were, however, found on the backup sorbent tubes. A noticeable tar-like odor was present, however, in this area. The dispersement effect characteristic of outdoor activities may serve to reduce the potential for exposure. A steady breeze was present in this area during the monitoring.

During the monitoring at the coal-sludge blending area, only two hours of mixing activity took place. This was considered typical by AK for this process. After completion of this task, the Laborer and Loader Operator leave the blending area and are assigned other duties. Additionally, no coal-sludge blend was dispensed into the hopper on the day-shift, and only one truck-load of the coal-sludge blend was dispensed at the hopper during the evening-shift. AK personnel indicated that the blend was typically dispensed on the evening-shift because there were less personnel on duty (no laborers) who may be affected by the odor.

Naphthalene was detected on all samples (both area and PBZ) collected during the June 14 survey. The highest PBZ concentration detected was 3.5 mg/m^3 (NIOSH REL = 50 mg/m^3) from the laborer operating the coal-sludge blending auger. The highest area concentration detected was 4.6 mg/m^3 from a sample collected at the auger operator booth. Both detectable and quantifiable levels of benzene were found on 5 of the 10 (50%) PBZ samples collected, and on both area samples. The highest concentrations detected were from 150-minute samples collected at the sludge storage area: 0.4 ppm from the laborer operating the auger screw conveyor, and 0.17 ppm from the Loader operator. This correlates with the 0.43 ppm benzene found on an area sample collected at the auger operator booth. The NIOSH REL for benzene is 0.1 ppm as an 8-hour TWA.

All bulk samples of coal dust (settled, respirable air, total air) had less than detectable levels of silica (the analytical limit of detection was 0.75%). The results of the personal air monitoring for respirable coal dust are depicted in Table IH-4. The highest concentration of respirable dust (0.75 mg/m^3) found was from a 390 minute PBZ sample taken from the evening-shift Coal Handler Operator working in the Coal-Handler Building and Lower End.

Personal Protective Equipment (PPE)/Respiratory Protection

During the site visits, NIOSH investigators observed personnel using PPE (gloves, respirators, hearing protectors) improperly. We also noted improperly maintained or stored PPE in several areas. Examples included:

- Inconsistent and sporadic adherence to the use of hearing protectors in the coal handler and shaker area.

- A supplied air escape respirator, located in the coal handlers' control room, that was covered with coal dust. A half-mask air purifying respirator, also in this room, was found hanging from the door handle by the strap, not properly cleaned and stored in a sealed container (e.g., plastic bag). Numerous disposable dust masks were found in various areas of the coal handlers breakroom.

- A worker unloading the decanter sludge sleds did not follow the polyvinyl chloride (PVC) glove requirement in the AK Job Safety Analysis Training Guide (JSAT) specified for that task.

Informal interviews with employees revealed that some workers were concerned with delays in access to PPE. AK distributes PPE to employees from a stockroom during the day-shift, and the foreman has access to this stockroom during the off-shifts. Some workers, however, stated that delays occur because the needed equipment is not always available, or that their foreman does not provide it in a timely fashion after it is requested.

Based on discussions with workers, task descriptions, and inspection of work areas, additional protective clothing may be necessary for some tasks. Specifically, disposable Tyvek® suits should be used for cleanup and maintenance in the coal handler building.

The facility has a written respiratory protection program designed to meet the requirements of OSHA regulations (29 CFR 1910.134 [respiratory protection], 1910.1028 [benzene], 1910.1029 [coke oven emissions]), and provides annual quantitative fit-testing and training to workers. This training, however, does not include proper use of disposable dust masks, which are provided to employees upon request. Management prohibits facial-hair on personnel who are required to wear respirators. However, the policy is apparently difficult to enforce as there is considerable mobility of workers from one area to another within the coke plant. During a walk-through inspection of the coke oven battery area, we observed a worker with a beard in a respirator-required area, and he was not wearing a respirator.

The company offers medical exams twice a year for workers employed for over 30 days a year in areas that are classified as OSHA-regulated (where the coke oven emission standard applies), and once a year to all other workers.

Procedural/Housekeeping

AK has developed formal written procedures for specific routine tasks (Job Safety Analysis Training Guides or JSAT) that specify the steps of the task, and the procedures for conducting the task in a safe manner. These procedures are reviewed by Safety Department Personnel. For more complex activities, AK has developed detailed written procedures (Total Job Analysis or TJA). This is a good mechanism for ensuring that safety and health precautions are incorporated into routine tasks.

Coal handlers are required to vacate the coal handler building when sludge-containing coal is being dispensed into the coal bin or is on the conveyor. However, workers do not consistently comply with this policy. Additionally, AK safety and health representatives attempted to collect surveillance data concerning skin disorders (rashes) after the sludge-coal mixing process was implemented. According to AK safety and health personnel, however, this data collection attempt has not been successful, possibly because workers are reluctant to report problems to management.

Housekeeping needed improvement in the coal handler area. Considerable build-up of coal dust and residue was observed in the coal handler conveyor area at the top of the bins. Similarly, the coal handler breakroom, where food and beverage consumption occurs, was dirty and also had considerable coal dust buildup.

There are several areas in the Lower End where flammable liquids or gases may be present. Warning signs have been posted in some areas, and no smoking signs have been posted as well.

During the NIOSH site visit, however, AK employees were observed smoking within 10-15 feet of these warning signs.

Company Industrial Hygiene Monitoring

AK safety and industrial hygiene personnel conduct both compliance-mandated and investigative environmental air monitoring. A limited review of company air monitoring data revealed that results are communicated via memo to supervisors, who are asked to inform employees. However, on the reports reviewed, there was little descriptive information about the tasks monitored (e.g., specific tasks sampled, sampling duration). Task-specific monitoring results for specific maintenance and janitorial activities, such as cleaning sludge from the tar cookers and sweeping up in the coal handler area were not available.

As reported in a July 19, 1990, company memo, monitoring results from May 16, 1990, for one worker in the coal handling area revealed a time-weighted average concentration of 2.95 milligrams per cubic meter (mg/m^3) for respirable dust. No other descriptive information was provided. The memo compared the result to an OSHA permissible exposure limit (PEL) of 5 mg/m^3 and concluded that there was no overexposure. The OSHA and Kentucky Labor Cabinet PEL, however, for the respirable fraction of coal dust (containing less than 5% crystalline silica) is 2.4 mg/m^3

A continuous carbon monoxide (CO) monitor has been installed in the Exhauster Building in the byproducts department. However, this monitor was not functioning properly, apparently because of hydrogen gas interference. High concentrations (greater than 100 parts per million) have been recorded, but no action was being taken because the readings were attributed to hydrogen interference. There are no external visible alarms other than the LED on the monitor, and there are no audible alarms to notify workers of high CO concentrations. Plant management has not implemented a protocol for responding to monitor alarms.

Machine Guarding/Noise

The screw conveyor used for blending the coal-sludge mixture at the "swimming pool" area is inadequately guarded. Additional shielding is necessary to reduce the potential for an operator to fall into the conveyor mechanism.

There is inadequate signage at the shaker area warning personnel of high noise levels during the shaker operation. The shaker is used intermittently, with no readily apparent advance warning.

Area sound level monitoring during the shaker operation showed levels of 103-108 decibels, A-weighted scale (dBA), as measured with a calibrated Quest Type II sound level meter operating in the slow response mode. These levels were measured approximately 10 feet from the shaker while the shaker was in operation. Levels measured inside the outer shaker booth during shaker operation were 75-76 dBA, and 77-81 dBA inside the inner shaker booth. These measurements indicate that insulation on both the inner and outer shaker booth is attenuating noise generated by the shaker to an acceptable level.

Medical

Employee Interviews

The NIOSH medical investigator interviewed 17 employees at the plant and two employees by telephone. The job duties and number of employees interviewed included: coal handlers (10), laborers (3), coke oven (3), and one exhaust operator, one swingman, and one welder. Many employees, particularly laborers, work in various areas throughout the plant on any given day.

Two or more employees reported the following symptoms during the interviews: rash or skin irritation (7 employees), headache (5 employees), burning skin (5 employees), dizziness (3 employees), burning or sore throat (2 employees), and blood in the stool or urine (2 employees). Nine employees mentioned that their symptoms were aggravated with exposure to coal tar and coal tar sludge. Three employees mentioned that exposure to coal tar fume in an area known as the #1 hole was particularly intense, especially in summer. The "hole" is an underground area surrounding the conveyor belt that transports coal, including coal that has been mixed with coal tar or sludge, to the storage hoppers. It is open only at one end and is accessible by a stairway. There is no forced ventilation. Workers reported that coal tar emissions concentrate in this area, particularly in the summer months.

Dermatologic evaluation

Seventeen employees participated in the dermatologic evaluations. Of these, 11 employees had skin complaints and underwent a skin examination. Two individuals had normal skin exams. Among the other nine there was one case each of the following: hand dermatitis, actinic keratoses, papular erythema (possible insect bite), seborrheic keratosis, sebaceous hyperplasia, telangiectasias, folliculitis, nonspecific erythema, and psoriasis.

Skin effects of pyrene exposure

Exposure to PAHs, such as in coal tar products, can result in a wide variety of dermatologic manifestations. These include changes in the physical appearance of the skin, such as erythema (redness), edema (thickening), and hyperpigmentation (darkening), as well as symptoms of pruritus (tar itch). Body hairs and oil glands of the skin can be affected. Folliculitis (inflammation around body hairs) and comedones (blackheads) are common sequelae. Tar-exposed skin can be more susceptible to damage from ultraviolet radiation (UVR) found in sunlight. A variety of skin growths are associated with UVR and tar. These include keratotic papillomas (tar warts), keratoacanthomas, actinic keratoses (potentially pre-skin cancers), basal cell carcinomas, and squamous cell carcinomas. In most settings radiation from the sun is the primary cause of occupationally induced skin cancers. However, coal tar products might be additive or synergistic to UVR and function as initiators or promoters for skin cancers.

Descriptions of potentially work-related dermatologic diagnoses

1. Hand dermatitis is a relatively common skin disorder with a rather extensive list of potential causes. This includes multiple chemicals found at home and in the workplace, extensive wet work, and possible genetic factors. In the individual examined no distinct etiology was apparent.

2. Nonspecific erythema may be an early sign of either allergic or irritant contact dermatitis. Once again the list of etiologic agents is extensive and possibly work-related but none was apparent in the individual.

3. Actinic damage and the formation of actinic keratoses are a direct result of ultraviolet radiation damage from sun exposure. This can occur recreationally or in the outdoor work setting. Tar products may play a role in their formation.

4. Folliculitis can result from a variety of factors. These include irritative effects from solvents or polycyclic hydrocarbons.

In this investigation four individuals had one of the above skin conditions that were potentially work-related or work-aggravated, although there may be non-occupational explanations for these conditions.

1-hydroxypyrene in urine and questionnaire results

Eighteen of the twenty-two workers in the sludge-handling area participated in this part of the study. Job classifications of the workers included: (1) coal handler operators (6 workers), (2) coal handler or pump maintenance (5 workers), (3) laborers (2 workers), (4) other (5 workers including one welder, crane operator, repairman, foreman, and loader operator). Additionally, one coke oven worker participated but was not included in the analysis. All workers were males, with a mean age of 41 and nine smoked cigarettes.

Pre-shift urinary 1-HP concentrations ranged from 0.16 to 2.96 µmol/mol creatinine (mean 1.04) and post-shift levels ranged from 0.24 to 4.85 (mean 1.8). Using a paired t-test, this difference was statistically significant ($p=0.004$). Levels of 1-HP by job title are given in Table M-1. The highest post-shift 1-HP levels were found in the laborers (3.7 µmol/mol creatinine). Workers who smoked had higher pre-shift 1-HP levels (1.2 µmol/mol creatinine) than non- smokers

(0.9 µmol/mol creatinine) although the post-shift 1-HP levels were identical (1.8 µmol/mol creatinine). The one coke oven worker who was sampled had a post-shift 1-HP concentration of 3.3 µmol/mol creatinine.

Workers reported that respirators were worn "always" by seven of the workers and "sometimes" by another seven workers. However, nine of those 14 (64%) reported on the questionnaire that they were able to smell chemicals while wearing the respirator. However, workers who smelled chemicals while wearing a respirator had neither a higher pre-shift 1-HP level (p=0.92) nor a higher post-shift 1-HP levels (p=0.94) on the day of the survey when compared to workers who did not smell chemicals. NIOSH investigators did not observe any workers wearing respirators in the coal handling area during our site visit.

Smoking was not found to be related to 1-HP levels. The nine workers who smoked cigarettes had a statistically insignificant increased pre-shift levels of 1-HP (mean 1.2 µmol/mol creatinine for the smokers as compared to a mean of 0.73 µmol/mol creatinine for the nonsmokers, p=0.21). Post-shift levels of 1-HP were virtually identical in both groups (mean 1.77 µmol/mol creatinine for the smokers and 1.65 µmol/mol creatinine for the non-smokers, p=0.87).

The questionnaire asked workers about symptoms that were reported during the interviews. The mean 1-HP urine concentration of those with a symptom at least once a month and without the symptom are presented in Table M-2. The most prevalent symptoms reported on the questionnaire that occurred more than once a month were sinus problems, itchy skin, and headaches. There was no statistically significant difference between post-shift 1-HP levels and reported symptoms, with the exception of headache. However, workers who reported a symptom at least once a month tended toward higher post-shift 1-HP levels than those not reporting a symptom. This was the case for every symptom except rashes.

Discussion

PAHs may enter the body through different routes, namely, the skin, respiratory system, and gastro-intestinal tract.[22] The uptake of PAH through the skin is very relevant in terms of the internal dose, and the dermal absorption is reported to be 50-90% of the total PAH uptake among some occupationally exposed workers.[23] Thus, air monitoring alone may underestimate the total exposure of a workers at AK Steel. The use of 1-HP as a biological marker for exposure would reflect total exposure. Other advantages of the use of 1-HP as a marker of exposure are that sample contamination is not likely since 1-HP is a metabolite formed in the body, and has a low limit of detection (1.37 nmol/liter).[(23-24)]

Jongeneelen et al. suggested a biologic exposure limit (BEL) of 2.3 µmol/mol creatinine, based on the ACGIH TLV of 0.2 mg/m^3 for CTPVs.[3] However, the NIOSH REL (full- shift time-weighted average) for CTPVs is 0.1 mg/m^3 of the benzene (or cyclohexane) extractable fraction of the sample and is based on the potential risk of lung and skin cancer. The NIOSH REL would probably correspond with a lower urinary 1-HP concentration. In Jongeneelen's study, the average pre-work 1-HP in urine was 0.91 µmol/mol creatinine.[3] Another study determined that the upper limit of the normal (without occupational exposure) value was 1.31 µmol/mol creatinine.[25] In this study, seven workers had a post-shift 1-HP above the proposed biological exposure limit (BEL) of 2.3 µmol/mol creatinine and 2 workers had a pre-shift level above that amount.

The effect of smoking on urinary 1-HP excretion among workers exposed to CTPVs is controversial. Jongeneelen, et al. found that smoking resulted in a greater increase in urinary 1-HP in coke oven workers than non-exposed (to coke oven emissions) controls.[2] Using thiocyanate excretion as a marker for cigarette smoking, Buchet et al. found that smoking can explain only 2.3% of the variance in urinary 1-HP excretion among coke oven workers.[26] Treatment for psoriasis with a coal-tar based ointment can result in increased 1-HP excretion; one study found urinary levels of 1-HP of 547 µmol/mol creatinine in coal tar treated psoriasis patients as opposed to 0.14 µmol/mol creatinine in untreated patients.[27] In this study, a greater difference between pre- and post-shift 1-HP concentrations was found in smokers (0.9 µmol/mol creatinine) than in non-smokers (0.6 µmol/mol creatinine). Besides the contribution of cigarette smoke to pyrene exposure, it is possible that contamination of the cigarette with coal tar from worker's hands might occur, possibly resulting in both ingestion and inhalation.

The use of the drug Cimetidine (Tagamet), may affect pyrene metabolism and result in lower levels of 1-HP. In this study two workers reported the use of Tagamet, but their 1-HP levels were among the highest in the study (post-shift 1-HP of 3.8 and 2.4 µmol/mol creatinine). It is possible that use of Tagamet was sporadic and did not affect pyrene metabolism, or their 1-HP levels may have been more elevated had they not been using Tagamet.

The finding of a 1-HP level of 3.3 µmol/mol creatinine in one coke oven worker who participated in the study suggests that CTPV exposure was potentially above the OSHA PEL. The OSHA coke oven standard established regulated areas in which workers must wear properly fitted respirators designed to lower exposures to below the OSHA standard. This 1-HP urine sample result indicates the respirator, or respirator program, is not sufficiently protective. Skin contact with CTPVs is also a possibility, although inhalation is considered the primary route of exposure in the coke oven area.

Studies of other coke oven workers exposed to pyrene have yielded results similar to what was found in this study. Jongeneelen found, in non-smokers, a pre-shift mean 1-HP level of 0.77 µmol/mol creatinine and a post-shift mean level of 1.78 µmol/mol creatinine.[2] However, the workers in that study had higher airborne exposures to PAHs than those at AK Steel. Coke oven workers in the Jongeneelen study had average airborne exposure to PAHs ranging form 6.9 to 17.0 µg/m^3 and airborne mean pyrene exposure of 0.6 to 2.0 µg/m^3. In our study, only a trace of pyrene was detected on one personal sample at a level of approximately 1 µg/m^3. This is probably because these workers were not exposed to coke oven gases but were predominantly exposed to coal tar sludge. When the sludge is cool, as it was when handled by the workers we studied, the vapor pressure of pyrene is low enough to preclude a large airborne exposure. The results of this study demonstrate the absorption of pyrene without measurable pyrene in personal air samples. For these workers, substantial exposure through the skin was observed based on both work practice assessments and biological measurement of a pyrene metabolite.

Two cases each of kidney and bladder cancer were reported from a company review of plant health records. Identification of cases through employee absentee records is not definitive and no statement can be made as to whether this finding represents either an excess of cancer or whether these individual cases are due to workplace exposures. Bladder, lung, and kidney cancer have been linked to chemical exposures of coke oven workers in another study.[28] Redmond et al. found a relative risk for kidney cancer of 7.5 in coke oven workers.[29] A study of aluminum workers exposed to CTPVs reported an excess of cancer of the lung, stomach, esophagus, and bladder.[30] Because a link between coke oven emissions and cancer has already been epidem-iologically established in large-scale studies, we did not think it would be informative to conduct another study at a single plant. Therefore, the focus of this HHE was on assessment of exposure and recommendations for control.

CONCLUSIONS

An industrial hygiene and medical evaluation was conducted to assess worker exposure to contaminants during the processing of coal tar sludge and coal in the byproducts area of the AK Coke Works facility in Ashland, Kentucky. Exposure to CTPVs, and PAHs, and potentially to benzene, exceeded the NIOSH RELs for the activities monitored, indicating that a health hazard exists due to exposure to these contaminants.

Airborne exposure to CTPVs containing PAHs were highest in the areas where the coal-sludge blend was dispensed onto the conveyor (hopper-shaker area) for transport to the coal-handler building. The potential also exists for skin contact with coal tar sludge, and improper use of personal protective equipment was observed during the NIOSH evaluation.

There was a statistically significant increase in urinary 1-HP concentration during the work shift, indicating exposure was occurring on the job. Several results exceeded 2.3 µmol/mol creatinine, calculated to correspond to the ACGIH TLV of 0.2 mg/m^3. Skin contact appears to be the likely route of exposure, as only one air sample detected pyrene, and pyrene was present in all bulk samples. Eleven of the seventeen employees interviewed had skin complaints, and four had potentially work-related skin conditions. Besides skin problems, the most prevalent symptoms reported by workers on the questionnaire were headaches and sinus problems.

RECOMMENDATIONS

1. The preferred method for reducing exposure to CTPVs and PAHs during the processing of coal-tar sludge is to eliminate the practice of blending the sludge with coal, and instead disposing of the sludge in an approved manner that conforms with all appropriate environmental regulations. If this is not possible, engineering controls such as enclosure, direct piping, and forced local exhaust ventilation at the #1 hole should be investigated and implemented if feasible. Respirators should be used only for those situations where engineering and administrative controls would not reduce employee exposures to acceptable

2. The JSAT system is a good mechanism to develop task-specific safety requirements. Management should expand this mechanism to include many non-routine tasks that involve handling or contact with potentially hazardous materials (e.g., cleaning sludge from the tar cooker, janitorial sweeping in the coal handler building). Total Job Analysis (TJA) is also a good mechanism for defining safety requirements for more complex tasks. Supervisor and management enforcement of these requirements is necessary to ensure that they are effective. The monthly safety meetings held by each department could be used to review selected JSATs.

3. Ensure PPE requirements (respirators, gloves, hearing protectors, etc.) are followed by all employees. Supervisor enforcement and worker awareness of mandatory PPE requirements should be enhanced. Workers handling the coal-tar sludge and coal-sludge blend should use protective equipment such as elbow length gloves and respirators to reduce the potential for both skin and inhalation exposure to CTPVs. These workers should be informed of the potential hazards associated with handling coal-tar sludge and the coal-sludge blend, and of the precautions necessary to reduce exposure.

4. Task-specific industrial hygiene evaluations, including monitoring, should target non-routine activities such as those noted in Recommendation #2.

5. Review air sampling data from the survey conducted on May 16, 1990, and identify the specific task monitored that resulted in the 2.95 mg/m^3 time-weighted average exposure to respirable coal dust. Management should reevaluate this activity, implement controls, and provide respiratory protection as an interim control measure.

6. Include training on the proper use of dust masks in the Facility Respiratory Protection Program. Specific tasks where it is acceptable to use these masks should be defined based on objective data (air sampling results). Employees should be informed when it is acceptable to use this type of respirator. The NIOSH document: *Respirator Decision Logic* is one source of information that can be used to help make this determination (previously sent). Consider implementing a plant-wide policy to ensure that employees who use

respirators have no hair in the facepiece seal area. Ensure that respirators and other PPE are properly cleaned, maintained, and stored. Routine workplace inspections should be conducted (e.g., by the safety committee or department employees) to ensure that PPE is in acceptable condition.

7. Housekeeping in the coal handlers building and coal handlers breakroom should be improved. Assign responsibility to ensure that these areas are routinely cleaned.

8. Review the system for providing worker access to PPE, especially during off-shift work hours. PPE must be readily accessible to all employees.

9. To protect against occupational exposure to high noise levels, management should: (1) place signs in the shaker area notifying workers of high noise levels and requiring the use of hearing protection when the shaker is in operation, (2) install a warning mechanism (e.g., lights) to notify personnel before shaker operation starts, and (3) conduct additional sound level monitoring to ensure all high noise areas are identified and properly posted.

10. Resolve the interference issue with the CO monitor in the Exhauster Building. If a CO monitor is necessary in this area, then a unit that functions properly, with appropriate audible and visible alarms, should be installed. A response protocol and training to ensure that workers take appropriate safeguards in the event of an alarm is necessary. If a monitor is not necessary, based on an objective review of the risk of high CO levels, the device should be removed.

11. Workers should be encouraged to report any occupational health problems to the employee health department, and plant management should utilize those reports to identify and correct potentially hazardous job duties. All employees with potentially work-related skin conditions should be encouraged to seek help from the plant nurse or physician; there should be a mechanism for dermatologic consultation if indicated. Plant management should develop a system of surveillance for occupational skin rashes to identify practices or procedures that can result in dermatitis. Consider starting an employee skin care program to include the dissemination of information on skin care in the workplace and the offering of annual skin exams by a dermatologist or other qualified physician. Personal hygiene in the workplace should be stressed. Replacement of soiled clothing and availability of washing facilities will limit the exposure of the skin to potentially harmful chemicals.

12. Review all activities requiring workers to access the area known as the #1 hole. This area may be classified as a confined space (either permit required or non-permit required) as defined by the Occupational Safety and Health Administration (OSHA) standard 1910.146 (or the Kentucky Labor Cabinet equivalent). Procedures should be developed to ensure

personnel entering this area are not exposed to hazardous levels of air contaminants, physical and mechanical hazards (heat stress, moving machinery), and that only authorized, trained personnel enter this area.

13. Review the facility smoking policy and ensure smoking is prohibited in areas where flammable materials or explosive concentrations of flammable gas may be present, and that this policy is strictly enforced.

14. Employees should be given information on protection from sunlight. Employees exposed to CTPVs who work outdoors should be offered sunscreens (sun protection factor of at least 15) and encouraged to wear long-sleeve clothing and headgear with brims and ear covers.

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AUTHORSHIP AND ACKNOWLEDGMENTS

Evaluation Conducted and Report Prepared By:	Max Kiefer, MS, CIH Regional Industrial Hygienist NIOSH Atlanta Regional Office
	Robert Malkin, DDS Supervisory Epidemiologist Medical Section, NIOSH, HETAB
	Greg Kinnes Industrial Hygienist Industrial Hygiene Section, NIOSH, HETAB
	John Decker Regional Industrial Hygienist NIOSH Atlanta Regional Office
	Boris Lushniak, MD Medical Officer Medical Section, NIOSH, HETAB
	Mustafa Ragab Visiting Scientist Medical Section, NIOSH, HETAB
Originating Office:	NIOSH Hazard Evaluations and Technical Assistance Branch Division of Surveillance, Hazard Evaluations, and Field Studies NIOSH Cincinnati, Ohio
Laboratory and Technical Support	William P. Tolos Division of Biomedical and Behavioral Sciences Applied Biology Branch NIOSH Cincinnati, Ohio

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1. AK Steel Company Coke Department: Ashland Works
2. HHE Requestor
3. Department of Labor/OSHA Region IV
4. Kentucky Labor Cabinet/Occupational Safety and Health Program

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table IH-1
Personal and Area Air Monitoring Results
AK Coke Department: Ashland, Kentucky
HETA 94-0020, January 11, 1994

Sample Description	Sample Time (min)	Contaminants	Concentration (mg/m^3)
Area sample in cab of vehicle loading coal/sludge mixture into a dump truck	09:54-11:15 (81)	CTPVs (Filter)	ND
		PAHs (Filter)	ND
		PAHs (XAD-2)	
		Acenaphthylene	0.026
		Acenaphthene	0.02
		Fluorene	(0.012)
		Naphthalene (XAD-2)	0.53
		Naphthalene (Charcoal Tube)	0.71
		Benzene (Charcoal Tube)	0.8 [0.25 ppm]
Personal sample from truck driver moving sludge/coal mixture to dumping area	09:55-11:10 (75)	CTPVs (Filter)	ND
		PAHs (Filter)	ND
		PAHs (XAD-2)	
		Acenaphthene	(0.008)
		Fluorene	(0.001)
		Naphthalene (XAD-2)	0.074
		Naphthalene (Charcoal Tube)	ND
		Benzene (Charcoal Tube)	(0.19)
Area sample at coal mixing area where the coal/sludge mixture is dumped.	10:07-11:12 (65)	CTPVs (Filter)	ND
		PAHs (Filter)	ND
		PAHs (XAD-2)	ND
		Naphthalene (XAD-2)	0.03
		Naphthalene (Charcoal Tube)	ND
		Benzene (Charcoal Tube)	ND

mg/m^3 = milligrams of contaminant per cubic meter of air
ppm = parts of gas or vapor per million parts air
ND = none detected
CTPVs = coal tar pitch volatiles
PAHs = polynuclear aromatic hydrocarbons
() = values in parentheses indicate the concentration was between the analytical level of detection (LOD) and the level of quantification (LOQ).

NIOSH Recommended Exposure Limits (RELs) for the contaminants sampled are as follows:

CTPVs = 0.1 mg/m^3 time-weighted average (TWA - lowest detectable limit). NIOSH considers CTPVs to be a potential occupational carcinogen if any PAHs is detected in the CTPV
PAHs = RELs have not been established for the PAHs detected in the samples
Naphthalene = 50 mg/m^3 as a full-shift TWA, 75 mg/m^3 as a 15-minute short-term exposure limit (STEL)
Benzene = 0.32 mg/m^3 (0.1 ppm) as an 8-hour TWA, 3.2 mg/m^3 (1.0 ppm) as a ceiling limit. NIOSH considers benzene to be a potential occupational carcinogen.

Table IH-2
Bulk Sampling Results: Coal Tar Sludge
Common PAHs, Confirmed by Retention Time Standards and Mass Spectra
AK Coke Department: Ashland, Kentucky
HETA 94-0020, January 11, 1994

Analyte	Concentration Detected (mg/gm)			
	#1 BH Decanter	#2 BH Decanter	#1 Decanter	"Swimming Pool"
Naphthalene	30	24	36	17
Acenaphthylene	8.2	9.3	10	2.7
Acenaphthene	0.37	0.14	0.11	0.23
Fluorene	6.9	3.0	1.8	4.5
Phenanthrene*	46	27	13	24
Anthracene*	11	5.5	2.5	5.9
Fluoranthene	34	18	8.3	16
Pyrene*	36	14	6.3	17
Benzo(a)anthracene	9.7	2.4	1.2	5.1
Chrysene*	12	2.5	1.2	5.3
Benzo(b)fluoranthene	4.2	0.66	0.35	2.5
Benzo(k)fluoranthene	9.3	1.0	0.48	5.0
Benzo(a)pyrene*	10	0.62	0.30	5.8
Indeno(1,2,3-cd)pyrene	ND	0.15	0.07	2.3
Dibenzo(a,h)anthracene	ND	ND	ND	ND
Benzo(g,h,i)perylene	3.8	0.18	0.08	2.4

* = Listed PAHs in OSHAs Coal Tar Pitch Volatile Definition
mg/gm = milligrams analyte per gram sample

Table IH-3
Personal and Area Air Monitoring Results
AK Coke Department: Ashland, Kentucky
HETA 94-0020, June 14, 1994

Sample Description	**Sample Time (min)**	**Contaminants**	**Concentration (mg/m^3)**
Personal Sample: Coal Handler Operator - moving and unloading at the train loading area.	05:52-12:03 (372)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	0.14 ND 0.008 0.027 ND ND
Personal Sample: Coal Handler Operator working at the coal hopper area	05:54-11:31 (337)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	0.13 ND 0.01 0.03 ND ND
Personal Sample: Loader operator at the coal-sludge storage pool	06:22-08:51 (151)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthylene Acenaphthene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	ND ND (0.004) (0.004) 0.44 ND 0.55 [0.17ppm]
Personal Sample: Laborer operating the auger screw conveyor at the coal-sludge storage pool	06:26-08:52 (147)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthylene Acenaphthene Fluorene Phenanthrene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	ND ND 0.05 (0.006) (0.006) (0.006) 3.46 3.23 1.32 [0.4 ppm]
Personal Sample: Coal handler Laborer, works at hopper where the coal/sludge mixture is dumped.	07:12-13:00 (288) [note: Pump had to be restarted - time is total pump operation time]	CTPVs (Filter) PAHs (Filter) Naphthalene Acenaphthene Fluorene Fluoranthene PAHs (XAD-2) Acenaphthene Phenanthrene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	0.31 (0.001) (0.001) (0.002) (0.002) 0.05 0.004 0.27 ND 0.19 [0.06ppm]

Table IH-3 (Continued)
Personal and Area Air Monitoring Results
AK Coke Department: Ashland, Kentucky
HETA 94-0020, June 14, 1994

Sample Description	**Sample Time (min)**	**Contaminants**	**Concentration (mg/m^3)**
Personal Sample: Laborer in the coal handler area	07:40-14:46 (429)	CTPVs (Filter)	0.35
		PAHs (Filter)	
		Naphthalene	0.005
		Acenaphthylene	(0.001)
		Fluorene	(0.001)
		Phenanthrene	(0.003)
		Anthracene	(0.001)
		Fluoranthene	(0.001)
		Pyrene	(0.001)
		Benzo(a)anthracene	(0.001)
		Chrysene	(0.001)
		PAHs (XAD-2)	
		Acenaphthylene	(0.001)
		Acenaphthene	0.05
		Phenanthrene	(0.001)
		Naphthalene (XAD-2)	0.21
Area Sample: Operator booth at coal-sludge storage pool during screw-conveyor operation and coal sludge blending	06:52-09:15 (143)	CTPVs (Filter)	ND
		PAHs (Filter)	ND
		PAHs (XAD-2)	
		Acenaphthene	0.01
		Fluorene	(0.01)
		Acenaphthylene	0.06
		Phenanthrene	(0.006)
		Naphthalene (XAD-2)	4.58
		Naphthalene (Charcoal Tube)	2.89
		Benzene (Charcoal Tube)	1.37 [0.43ppm]
Area Sample: Operator booth at coal-sludge pool, after conveyor operation and blending ceased.	09:19-14:54 (335)	CTPVs (Filter)	ND
		PAHs (Filter)	ND
		PAHs (XAD-2)	
		Acenaphthylene	0.02
		Acenaphthene	(0.004)
		Fluorene	0.007
		Phenanthrene	0.01
		Naphthalene (XAD-2)	0.51
		Naphthalene (Charcoal Tube)	0.44
		Benzene (Charcoal Tube)	(0.04)(.01ppm)
Personal Sample: lower end train engine operator	13:21-19:12 (351)	CTPVs (Filter)	0.06
		PAHs (Filter)	ND
		PAHs (XAD-2)	
		Acenaphthylene	(0.001)
		Acenaphthene	(0.002)
		Naphthalene (XAD-2)	0.03
		Naphthalene (Charcoal Tube)	ND
		Benzene (Charcoal Tube)	(0.03)(.01 ppm)

Table IH-3 (Continued)
Personal and Area Air Monitoring Results
AK Coke Department: Ashland, Kentucky
HETA 94-0020, June 14, 1994

Sample Description	Sample Time (min)	Contaminants	Concentration (mg/m^3)
Personal sample: Coal Handler Operator in the coal-handler building and lower end	13:25-19:48 (390)	CTPVs (Filter) PAHs (Filter) Benzo(ghi)perylene PAHs (XAD-2) Acenaphthene Naphthalene (XAD-2)	0.34 (0.001) 0.026 0.16
Personal Sample: Coal Handler Operator at the hopper	14:13-19:13 (300)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthene Naphthalene (XAD-2) Naphthalene (Charcoal Tube) Benzene (Charcoal Tube)	0.50 ND 0.01 0.03 ND (0.03)(.01 ppm)
Personal Sample: Laborer at the coal handler area.	14:48-15:41 (53)	CTPVs (Filter) PAHs (Filter) PAHs (XAD-2) Acenaphthene Naphthalene (XAD-2)	ND ND 0.08 0.40

mg/m^3 = milligrams of contaminant per cubic meter of air
ppm = parts of gas or vapor per million parts air
ND = none detected
CTPVs = coal tar pitch volatiles
PAHs = polynuclear aromatic hydrocarbons
() = values in parentheses indicate the concentration was between the analytical level of detection (LOD) and the level of quantification (LOQ).

NIOSH Recommended Exposure Limits (RELs) for the contaminants sampled are as follows:

CTPVs = 0.1 mg/m^3 time-weighted average (TWA - lowest detectable limit). NIOSH considers CTPVs to be a potential occupational carcinogen if any PAHs is detected in the CTPV
PAHs = With the exception of chrysene, RELs have not been established for the PAHs detected in the samples. NIOSH recommends controlling exposure to chrysene to the lowest feasible limit (LFL).
Naphthalene = 50 mg/m^3 as a full-shift TWA, 75 mg/m^3 as a 15-minute short-term exposure limit (STEL)
Benzene = 0.32 mg/m^3 (0.1 ppm) as an 8-hour TWA, 3.2 mg/m^3 (1.0 ppm) as a ceiling limit. NIOSH considers benzene to be a potential occupational carcinogen.

Table IH-4
Personal Air Monitoring Results: Respirable Coal Dust
AK Coke Department: Ashland, Kentucky
HETA 94-0020, June 14, 1994

Sample Description	Sample Time (min)	Respirable Dust Concentration (mg/m^3)
Personal sample: Coal Handler Operator in the coal-handler building and lower end	13:25-19:48 (390)	0.75
Personal Sample: Coal Crusherman in the coal-handler building	06:45-12:42 (357)	0.08

mg/m^3 = milligrams of contaminant per cubic meter of air
The OSHA Permissible Exposure Limit for the respirable fraction of coal dust that contains less than 5% crystalline silica is 2.0 mg/m^3. NIOSH has not established an REL for coal dust.

All bulk samples (settled coal dust, respirable air, total air) showed the coal dust to contain less than 0.75% (the limit of detection) silica.

Table M-1 1-HP Level by Job Title HETA 94-0020 June 13-15, 1994 AK Steel Coke Works, Ashland, Kentucky			
job title	**number**	**mean pre-shift** (μmol/mol creatinine)	**mean post-shift** (μmol/mol creatinine)*
laborer	2	1.6	3.7
coal handler operator	6	0.4	0.6
coal handler maintenance	5	1.4	2.4
other	5	1	1.6

* difference between job titles statistically significant p=0.03

Table M-2 1-HP Levels for Workers Reporting Symptoms Once a Month or More At Work AK Steel Coke Works, Ashland, Kentucky June 13-15,1994.				
Symptom	percent reporting symptom once a month or more at work n=19	Post-shift 1-HP level (μmol/mol creatinine)		p value
		Symptom present once a month or more at work	Symptom present less than once a month at work	
dizziness	26	2.6	1.5	0.16
nausea	16	3.3	1.5	0.06
burning skin	37	2	1.7	0.68
sinus problems	58	2	1.6	0.55
headache	42	2.6	1.3	0.05
itching skin	47	2	1.6	0.58
rash	26	1.4	2	0.45
irritated eyes	37	2.1	1.6	0.49

Sampling and Analytical Methodology

The environmental monitoring was conducted utilizing established analytical protocols (NIOSH analytical methods).[1] Personal samples were obtained with calibrated air sampling pumps attached to selected workers and connected, via tubing, to sample collection media placed in the employees' breathing zone. Monitoring was conducted throughout the duration of the task. After sample collection, the pumps were post-calibrated and the samples submitted to the NIOSH contract laboratory (Data Chem, Salt Lake City, Utah) for analysis. Field blanks were submitted with the samples. Specific sampling and analytical methods used during this survey were as follows:

Coal Tar Pitch Volatiles (CTPVs)/Polynuclear Aromatic Hydrocarbons (PAHs)

Sampling for CTPVs and PAHs was conducted using Gilian HFS 513A air sampling pumps. The monitoring was conducted using flow rates of approximately 1 liter per minute (l/m). The samples were collected by first drawing air through a 2 micrometer (µm) pore size, 37 millimeter (mm) teflon (Zefluor®) filter, followed by a washed XAD-2 (Supelco ORBO® 43) sorbent tube. After sample collection, the filters were transferred with forceps to a scintillation vial, and the sorbent tube was capped. The vial and the sorbent tube were then wrapped in aluminum foil, placed in an insulated container with a bagged refrigerant, and shipped to the laboratory for analysis. The filters were then extracted with benzene and analyzed for CTPVs and PAHs according to NIOSH method 5023 (CTPVs) and 5515 (PAHs). The limit of detection (LOD) for the CTPV analysis was 0.05 milligrams (mg) per sample. The LOD and limit of quantification (LOQ), in micrograms (µg) per sample, for the PAH analysis were as follows:

Analyte	LOD (µg/sample)	LOQ (µg/sample)
Naphthalene	0.5	1.5
Acenaphthylene	0.5	1.5
Acenaphthene	0.5	1.5
Fluorene	0.5	1.5
Phenanthrene	0.5	1.5
Anthracene	0.5	1.5
Fluoranthene	0.5	1.5
Pyrene	0.5	1.5
Benzo(a)anthracene	0.5	1.5
Chrysene	0.5	1.5
Benzo(b)fluoranthene	0.5	1.5
Benzo(k)fluoranthene	0.5	1.5
Benzo(e)pyrene	0.5	1.5
Benzo(a)pyrene	0.5	1.5
Indeno(123-cd)pyrene	0.5	1.5
Dibenz(ah)anthracene	1	3.0
Benzo(ghi)perylene	0.5	1.5

Benzene, Toluene, Naphthalene

Integrated air samples were obtained using standard charcoal tubes (100 milligrams front section/50 milligrams backup) as the collection medium. The samples were collected using constant-volume SKC model 223 low-flow sampling pumps. Flow rates of approximately 100 cc/min were used to collect the samples. The pumps are equipped with a pump stroke counter and the number of strokes necessary to pull a known volume of air was determined. This information was used to calculate a cc's air per pump stroke "K" factor. The pump stroke count was recorded before and after sampling and the difference used to calculate the total volume of air sampled. After sample collection, the tubes were capped and shipped to the laboratory analysis. The tubes were desorbed with carbon disulfide and analyzed according to NIOSH 1501. The LODs for the contaminants sampled were: toluene (0.01 mg/sample), benzene (0.001 mg/sample), naphthalene (0.001 mg/sample).

Bulk Samples

The bulk samples were collected in 120 milliliter amber collection jars and sent, under separate sample shipment, to the laboratory for analysis. A portion of each sample was then sonicated in benzene until complete dissolution, and then analyzed by gas chromatography/mass spectroscopy (GC/MS). Compounds were identified by their mass spectra and retention time characteristics, and quantified by determining relative response factors obtained from standards, and comparison of these values to the detected values.

Respirable Coal Dust/Crystalline Silica

Personal air sampling for respirable coal dust was conducted using Gilian HFS 513 air sampling pumps. A flow rate of 1.7 liters per minute (lpm) was used to draw sample air through an MSA cyclone and a tared, 37 millimeter, 5 micron pore size, polyvinyl chloride filter. The cyclone removes the non-respirable fraction of particulate so the filter will collect only that portion of the dust (<10 micrometers) that penetrates to the deeper areas of the lung. Sampling was conducted for the duration of the coal handler employee's workshift. A bulk sample of settled coal dust, as well as a high-volume respirable and total dust air sample, taken from the work area, was submitted to the analytical laboratory to determine the percent and type of silica present, and identify potential analytical interferents. Analysis was conducted according to NIOSH 7500 and 0500.

Noise Monitoring

Area sound level measurements were obtained with a calibrated hand-held Quest Type II sound level meter. The meter was operated in the slow-response mode, A-weighted scale.

Reference

1. NIOSH [1984]. NIOSH manual of analytical methods, 3rd rev. ed. Vol.1/2 (supplements 1985, 1987, 1989). Eller, RM, ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.