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Lehigh Portland Cement Company
Union Bridge, Maryland

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Wayne T. Sanderson and Daniel Almaguer, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Desktop publishing by Kate L. Marlow. We wish to acknowledge special assistance during the plant survey by Mr. Harvey Kirk III, Mr. James Harris, and the employees of the Lehigh Portland Cement Company.

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Health Hazard Evaluation Report HETA 96–0226
Lehigh Portland Cement Company
Union Bridge, Maryland
May 1997

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SUMMARY

On July 17, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Safety and Training Supervisor of the Lehigh Portland Cement plant in Union Bridge, Maryland, for help in evaluating an "unidentifiable bleach odor" inside one of the cement kilns. The odor was noticeable only when the kiln was shut down for maintenance. Maintenance personnel working inside the kiln reported respiratory and eye irritation. The kiln operates continuously throughout the year and no health hazard had been reported during normal operations. Therefore, the health hazard evaluation was placed on hold until the next scheduled maintenance period. NIOSH was notified on November 21, 1996, that the kiln would be shut down for repair from December 2 until December 5, 1996.

On December 3, 1996, workers entered the kiln to remove and replace 25 feet of refractory brick at the front–end of the kiln. Reported symptoms experienced by workers during previous maintenance operations suggested that they had been exposed to irritant gases or dusts. Personal breathing zone (PBZ) samples were collected for chlorine, sulfur dioxide, and respirable and total dust. Area samples were collected at three sampling locations inside the kiln for chlorine, inorganic acid, sulfur dioxide, oxides of nitrogen, ozone, respirable, total, and inhalable dusts. Respirable dust samples were further analyzed for crystalline silica, and total dust samples were further analyzed for arsenic, cadmium, copper, chromium, magnesium, nickel, and zinc content.

Chlorine was not detected on any PBZ samples and only trace concentrations of sulfur dioxide were detected while workers were working inside the kiln. None of the PBZ or area dust samples exceeded the applicable occupational exposure criteria. Quartz and cristobalite were not detected in any of the dust samples. Area sampling for chlorine and inorganic acid showed no detectable concentrations inside the kiln. Ozone was not detected at any location while workers were inside the kiln.

After work inside the kiln had been completed and all workers had exited the kiln, the conditions present during previous episodes were recreated. The electrostatic precipitator serving kiln #4 was reduced to half strength, the east precipitator unit was turned on, and the west precipitator unit and the induced draft fan were turned off. Chlorine and ozone measurements were then collected from outside the kiln. Chlorine was not detected at the front end of the kiln. However, ozone was detected at concentrations of 0.6 to 0.7 ppm on two ozone color indicator tubes (0.09 to 0.11 ppm ozone was detected using a Metrosonic pm–7700 Toxic Gas Monitor). Background readings for ozone in the plant yard were 0.02 to 0.03 ppm.

Chlorine and ozone measurements were also collected through a portal at the back end of the kiln. Chlorine was not detected. However, an ozone indicator tube was saturated after two pump strokes, indicating that ozone concentrations inside the kiln were well above 0.7 ppm. A direct reading meter reveled a concentration of 4.5 ppm. The NIOSH recommended exposure limit (REL) is 0.1 ppm as a 15-minute ceiling limit. Afterwards, the electrostatic precipitator was turned completely off and the induced draft (ID) fan was turned on. Within 10 minutes the ozone concentration detected by the direct reading meter dropped to 0.16 ppm and within one–half hour the meter readings had decreased to background levels.

Occurrences of eye and upper respiratory irritation during kiln repair activities can be causally related to ozone exposures. Ozone generated by an operating electrostatic precipitator back–drafted into the kiln when the induced draft fan was turned off. Experimental recreations of events resulted in ozone concentrations inside the kiln approaching 5 ppm, 50 times the NIOSH ceiling of 0.1 ppm. It is reasonable to assume that similar exposures were encountered during previous kiln maintenance operations. Although dust measurements did not indicate that workers performing maintenance inside the kiln were exposed to excessive concentrations of dust, crystalline silica, or metals, respirators can reduce concentrations of inhaled dust particles which may dry and irritate nasal passages and upper airways.

Keywords: SIC 3241 (Portland cement manufacturing), Portland cement, kiln maintenance, electrostatic precipitator, ozone, respiratory irritation

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INTRODUCTION

On July 17, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Safety and Training Supervisor of the Lehigh Portland Cement plant in Union Bridge, Maryland, for help in evaluating an "unidentifiable bleach odor" inside one of the cement kilns. The odor was only noticeable when the kiln was shut down for maintenance. Maintenance personnel working inside the kiln reported respiratory and eye irritation. The kiln operates continuously throughout the year and no health hazard had been reported during normal kiln operations. Therefore, the health hazard evaluation was placed on hold until the next scheduled maintenance period. NIOSH was notified on November 21, 1996, that the kiln would be shut down for repair from December 2 until December 5, 1996. This report describes the results of the survey that was conducted during this period.

The original cement plant was built at Union Bridge, Maryland, in 1910. The plant was purchased by Lehigh Portland Cement Company in December 1925, completely modernized in 1939, and again in 1957.[1] The second modernization more than tripled the size of the plant, increasing its annual production capacity to 660,000 tons. Three of the kilns built at this time are currently operating. In 1970, during a third modernization and rebuilding period, a fourth kiln was constructed, increasing the plant's production capacity to 900,000 tons per year. The chlorine–like odor and respiratory irritation have only been associated with the fourth kiln, which has a dust control system separate from the three older kilns.

BACKGROUND

Portland cement is produced by heating oxides of calcium, silicon, aluminum, and iron in various combinations, up to 2700°F in a rotating kiln to form calcium–aluminum silicates.[2] The principal raw materials used at the Union Bridge plant — limestone and shale which provide the calcium and aluminum sources — are obtained from a quarry near the plant; sand — the silicon source, and mill scale — the iron source, are purchased from other companies. No chlorine–containing compounds are used in manufacturing Portland cement.

Two methods are used for manufacturing Portland cement: (1) the dry process in which the raw materials are mixed, ground, and transported into the kiln as a dry powder; and (2) the wet process in which the raw materials are mixed, ground, and transported into the kiln as a fluid slurry. The dry process is used at the Union Bridge plant. The four rotary kilns are basically 3/4 inches thick welded–steel tubes, 11.5 feet in diameter and 400 feet in length, lined with high–temperature refractory bricks 6 to 9 inches thick. No mortars, binders, or coatings are used on the bricks. The kilns rotate on a slightly inclined axis, 80 to 90 revolutions per hour. The raw materials enter the kiln through a screw feeder at the upper end of the kiln (feed–end or back–end). The materials are heated to progressively higher temperatures until they leave the lower end of the kiln (discharge–end or front–end) as calcium–aluminum silicate clinkers. Clinkers are hard, dark, glossy nodules of Portland cement.

The clinkers are dropped from the front–end of the kilns, cooled by blowing air, and then conveyed to a storage area. The clinkers are mixed using varying amounts of gypsum (hydrated calcium sulfate) to control the rate at which the cement hardens. The mixture is then ground into a fine powder in rotating ball mills to produce the finished product, Portland cement. Portland cement is then shipped in packages or as bulk in trucks or railcars.

At the Lehigh plant, pulverized coal is the primary fuel source, and scrap tires are used as a supplemental fuel source. Pulverized coal is blown into the front end of the kilns, inducing temperatures higher than the melting point of steel. Tires are automatically dropped into the middle of the kilns, one tire per revolution. The practice of burning scrap tires was begun during the summer of 1995. At one time waste oils from refineries were also used as a supplemental fuel source, but this practice was stopped in 1994.

Dust pollution control is an important aspect of kiln operation. Induced draft (ID) fans draw the waste gases from the kilns through electrostatic precipitators to remove dust particles. The remaining gases are then vented out the stacks. The three kilns which began operation in 1957 share a common exhaust system and stack. The fourth kiln which began operation in 1970 was installed with a separate exhaust system and stack. In 1992 the height of the exhaust stacks was increased due to excessive sulfur dioxide exposures from the combustion of coal in the kilns. Since that time no further problems with excessive sulfur dioxide exposures have been reported inside the plant.

The first occurrence of respiratory problems associated with the repair of kiln #4 was on March 19, 1993. Nine workers were replacing refractory bricks approximately 20 to 30 feet from the front end of the kiln; two were on a scaffold laying bricks in the top of the kiln, two were laying bricks in the bottom of the kiln, two were removing bricks from a conveyor and handing them to the bricklayers, two were placing bricks on the conveyor just outside the front of the kiln, and a forklift operator transported pallets of bricks to a position near the conveyor. The ID fan had been turned off at 5:00 a.m. because the night crew, who had been replacing bricks, complained of cold air drafts. The nine dayshift workers had begun replacing bricks at 7:00 a.m. By 7:20 a.m., one of the workers who was laying bricks in the bottom of the kiln reported a severe cough, headache, profuse perspiration, nausea and fatigue. The worker stated that while he was in the kiln, he noticed a chlorine, bleach–like odor. Other workers reported that they had detected a similar odor emanating from the worker's clothes. Subsequently, the symptomatic worker was taken to the hospital for evaluation. The remaining five workers who were inside the kiln also noticed the chlorine–like odor and reported coughing, headaches, sore throats, and shortness of breath, but their symptoms were not as severe. The three workers who were working outside the kiln noticed the chlorine odor but did not experience any symptoms. The ID fan was turned back on at 7:30 a.m. Soon the chlorine odor was gone and the workers were able to complete the rebricking operation.

The second occurrence of respiratory problems associated with the repair of kiln #4 was on February 11, 1996. The kiln was shut down at 4:45 a.m. when the kiln feed hopper had become clogged with wet raw materials due to a water spray problem at the back end of the kiln. At 11:30 a.m., two workers entered the back end of the kiln to loosen the clogged material using iron bars. These workers left the plant at 3:00 p.m. and did not report any odor or respiratory symptoms associated with their work. However, two replacement workers reported that they immediately detected a chlorine odor upon entering the kiln. A third worker joined the two replacement workers at 7:30 p.m. At the end of their workshift (9:00 p.m.), all three workers reported they had smelled a bleach–like odor and reported symptoms of cough, tightness in the chest, and burning eyes. Subsequently, no one entered the kiln until four, third shift workers entered at 11:30 p.m. Within a few minutes of entering the kiln all four workers reported a strong chlorine odor with subsequent symptoms of cough, chest tightness, nausea, and burning eyes and nose. It is not clear at what time the ID fan was turned off, but it was not operating at 11:30 p.m. when the four workers entered the kiln. However, when the fan was turned on, conditions became so dusty that the workers lost visibility. The workers left the kiln for 15 minutes to allow the fan to remove the odor, the fan was then turned off, the workers re–entered the kiln, and the odor and the workers' symptoms quickly returned. All the workers then exited the kiln and the unclogging operation was completed by workers standing outside the kiln.

METHODS

NIOSH was requested to monitor worker exposures when kiln #4 was shut down for scheduled maintenance. On December 3, 1996, workers entered the kiln to replace the first 25 feet of refractory brick at the front–end of kiln #4. Symptoms experienced by workers during previous maintenance operations suggested that they were exposed to irritant gases or dusts. Although the workers reported a chlorine, bleach–like odor, the raw materials for clinker production do not contain chlorine compounds and chlorine is not used in any aspect of kiln operations. However, chlorine (chlorides) measurements were collected to evaluate the possibility of chlorine being the cause of the reported respiratory symptoms. Air samples were also collected to measure concentrations of sulfur dioxide, oxides of nitrogen, ozone, and inorganic acid inside the kiln.

Sulfur dioxide and oxides of nitrogen are common by–products of coal combustion, and cause eye and upper respiratory irritation. Ozone is formed from high electrical voltage discharge in electrostatic precipitators, and has been shown to cause irritation of the eyes and mucous membranes. These gases were suspected to be present during kiln operation. Residual gas concentrations due to back–draft from the kiln exhaust system could result when the kiln was shut down for maintenance. Inorganic acids were not suspected of being present during kiln operation or maintenance, but were sampled to evaluate chlorine acid vapors as a potential cause of the workers' symptoms.

Respirable, total, and inhalable dust samples were also collected. Portland cement dust causes dermatitis and may be irritating to the eyes and nose due its alkaline, hygroscopic, and abrasive properties.[3] Portland cement has not been documented to cause pneumoconiosis, but crystalline silica (quartz and cristobalite), which causes silicosis, may be present in the raw materials used to manufacture Portland cement. Respirable dust samples, which evaluate dust exposures for the alveolar and lower airways of the lungs, were analyzed for crystalline silica to evaluate workers' potential risk for silicosis. Total dust samples were analyzed for arsenic, cadmium, copper, chromium, magnesium, nickel, and zinc content; these selected metals have been documented to affect the respiratory system (please see Evaluation Criteria Section).

Personal breathing zone (PBZ) samples were collected for chlorine, sulfur dioxide, and respirable and total dust by attaching sampling media to the collars of workers involved in the re–bricking operation. Area samples were collected for chlorine, inorganic acid, sulfur dioxide, oxides of nitrogen, respirable, total, and inhalable dusts at three sampling station locations inside the kiln. The area samples were collected by attaching sampling media to tri–pods positioned near the front, middle, and rear of the kiln. Table 1 summarizes all of the air sampling methods used in this evaluation.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to 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 is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),[4] (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs™),[5] and (3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).[6] In July 1992, the 11th Circuit Court of Appeals vacated the 1989 OSHA PEL Air Contaminants Standard. OSHA is currently enforcing the 1971 standards which are listed as transitional values in the current Code of Federal Regulations; however, some states operating their own OSHA approved job safety and health programs continue to enforce the 1989 limits. NIOSH encourages employers to follow the 1989 OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard and that the OSHA PELs included in this report reflect the 1971 values.

A time–weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8– to 10–hour workday. Some substances have recommended short–term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short–term. The immediately dangerous to life or health (IDLH) concentration is considered the maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection is permitted. The purpose of the IDLH is to ensure that workers can escape without injury or irreversible health effects from an IDLH exposure in the event of the failure of respiratory protection equipment.

Ozone

Ozone is a blue gas. The gas possesses a characteristic odor in concentrations of less than 2 ppm. Ozone is used as a disinfectant for air and water; for bleaching textiles, oils, and waxes; and in organic syntheses. It is also produced in welding arcs and corona discharges and by ultraviolet radiation.[7]

Ozone is an irritant of the mucous membranes and the lungs. The primary target of ozone is the respiratory tract. Symptoms range from nose and throat irritation to cough, dyspnea, and chest pain. The toxic effects of ozone can be attributed to its strong oxidative capacity. Specifically, ozone may act by initiating peroxidation of polyunsaturated fatty acid present in the cell membrane or by direct oxidation of amino acids and proteins also found in the membranes. If damage is severe, the cell dies; necrosis commonly is reported in the lungs of heavily exposed animals. In animal studies, a characteristic ozone lesion occurs at the junction of the conducting airways and the gas–exchange region of the lung following acute exposure. This anatomical site is probably affected in humans as well.[8]

The NIOSH REL is 0.1 ppm to be measured as a 15–minute ceiling concentration.[4] NIOSH has also recommended an IDLH of 10 ppm for ozone.[9] The current OSHA PEL for ozone is 0.1 ppm as an 8–hour TWA, and 0.3 ppm as a 15–minute ceiling concentration.[6] The current ACGIH TLV is also 0.1 ppm to be measured as a 15–minute ceiling concentration. However, the ACGIH has issued a notice of intended change. The proposed ACGIH TLV is based on amount of physical exertion or work load required for the job being accomplished and is to be average over an 8–hour period. The proposed TLV is 0.1 ppm for jobs requiring light physical exertion, for a moderate physical exertion the TLV is lowered to 0.08 ppm, and for a heavy physical exertion the TLV is lowered to 0.05 ppm.[5]

Chlorine

Chlorine is a greenish–yellow gas with a very pungent odor. It is slightly soluble in water, forming hydrochloric acid. Chlorine reacts with moisture in the eyes and respiratory airways to form acids. It is extremely irritating to the skin, eyes, and mucous membranes. Chlorine in high concentrations acts as an asphyxiant by causing cramps in the muscles of the trachea, swelling of the mucous membranes, nausea, vomiting, and anxiety. Acute respiratory distress including cough, blood in sputum, chest pain, dyspnea, and tracheobronchitis, pulmonary edema, and pneumonia occurs with exposure to excessive concentrations.

The NIOSH REL is 0.5 ppm to be measured as a 15–minute ceiling concentration.[4] NIOSH has also recommended an IDLH of 10 ppm for ozone.[9] The current OSHA PEL for chlorine is 1.0 ppm as a ceiling concentration.[6] The current ACGIH TLV is 0.5 ppm as an 8–hour TWA and 1.0 ppm as a 15–minute ceiling concentration.[5]

Sulfur Dioxide

Sulfur dioxide is intensely irritating to the eyes, mucous membranes, and respiratory tract. It can cause burning of the eyes and tearing, coughing, and chest tightness. Exposure may cause severe breathing difficulties. It forms sulfurous acid on contact with moist membranes.[8] Chronic exposure may result in nasopharyngitis, fatigue, altered sense of smell, and chronic bronchitis symptoms such as dyspnea on exertion, cough, and increased mucous excretion. Some individuals have become sensitized following repeated exposures. NIOSH, OSHA, and ACGIH have set a TWA exposure limit of 2 ppm (5.2 milligrams per cubic meter [mg/m^3]) for sulfur dioxide, and a 5 ppm (13 mg/m^3) short–term exposure limit.

Particulates, Not Otherwise Classified

Often the chemical composition of the airborne particulate does not have an established occupational health exposure criterion. It has been the convention to apply a generic exposure criterion in such cases. Formerly referred to as nuisance dust, the preferred terminology for the non–specific particulate ACGIH TLV criterion is now *"particulates, not otherwise classified (n.o.c.),"* [or *"not otherwise regulated"* (n.o.r.) for the OSHA PEL]. In comments to OSHA on August 1, 1988, on their “Proposed Rule on Air Contaminants,” NIOSH questioned whether the proposed PEL for PNOR (10 mg/m^3) was adequate to protect workers from recognized health hazards.

Particulates not otherwise regulated (nuisance dusts) have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. Portland cement dusts are considered in this category. The lung tissue reaction caused by inhalation of nuisance dusts has the following characteristics: (1) the architecture of the air spaces remains intact; (2) scar tissue is not formed to a significant extent; and (3) the tissue reaction is potentially reversible.[7] Respirable particulate refers to materials that are able to reach the gas–exchange region of the lung.

The current OSHA PEL for particulates not otherwise regulated is 15 mg/m^3 for total dust and 5 mg/m^3 for the respirable portion, measured as an 8–hour TWA.[6] The ACGIH TLV for particulates not otherwise classified is 10 mg/m^3 for inhalable particulate and 3 mg/m^3 for respirable particulate.[5] These criteria were established to minimize mechanical irritation of the eyes and nasal passages, and to prevent visual interference. These are generic criteria for airborne dusts which do not produce significant organic disease or toxic effect when exposures are kept under reasonable control.[5] These criteria are not appropriate for dusts that have a biologic effect.

Silica (amorphous, quartz, cristobalite)

Amorphous silica does not have a crystalline lattice molecular configuration. Historical evaluations of amorphous silica suggest that it is of low toxicity, and it has not been reported to produce fibrotic nodules in lung tissue (characteristic of crystalline silica exposure).[8,10] The NIOSH REL for exposure to amorphous silica is a full–shift, total particulate TWA of 6 mg/m^3, providing the silica contains less than 1% crystalline forms.[9] The OSHA PEL is 80 mg/m^3 divided by the %SiO_2, as an 8–hour TWA. The ACGIH TLV for amorphous silica containing less than 1% crystalline silica is 10 mg/m^3 for inhalable particulate as an 8–hour TWA, and 3 mg/m^3 for respirable particulate as an 8–hour TWA.

Crystalline silica (quartz) and cristobalite have been associated with silicosis, a fibrotic disease of the lung caused by the deposition of fine particles of crystalline silica in the lungs. Symptoms usually develop insidiously, with cough, shortness of breath, chest pain, weakness, wheezing, and non–specific chest illnesses. Silicosis usually occurs after years of exposure, but may appear in a shorter period of time if exposure concentrations are very high. The NIOSH RELs for respirable quartz and cristobalite are 50 micrograms per cubic meter (µg/m^3), as TWAs, for up to 10 hours per day during a 40–hour work week.[4] These RELs are intended to prevent silicosis. However, evidence indicates that crystalline silica is a potential occupational carcinogen and NIOSH is currently reviewing the data on carcinogenicity.[11,12,13,14] The OSHA PELs for respirable quartz is 10 mg/m^3 divided by the value "%SiO_2+2," the PEL for cristobalite is ½ the calculated value for quartz.[9] The ACGIH TLVs for respirable quartz and cristobalite are 100 and 50 µg/m^3, as 8–hour TWAs, respectively.

Metals

Chromium (Cr) exists in a variety of chemical forms and its toxicity varies among the different forms. For example, elemental chromium is relatively non–toxic. Other chromium compounds may cause skin irritation, sensitization, and allergic dermatitis. In the hexavalent form [Cr(VI)], Cr compounds are corrosive, and possibly carcinogenic.[8] Until recently, the less water–soluble Cr(VI) forms were considered carcinogenic while the water–soluble forms were not considered carcinogenic. Recent epidemiological evidence indicates carcinogenicity among workers exposed to soluble Cr(VI) compounds. Based on this new evidence, NIOSH recommends that all Cr(VI) compounds be considered as potential carcinogens.[4] The NIOSH REL and the ACGIH TLV for chromium metal is 0.5 mg/m^3, and the OSHA PEL is 1 mg/m^3 for chromium metal.[4,5,6]

Inhalation of **copper** fume has resulted in irritation of the upper respiratory tract, metallic taste in the mouth, and nausea.[8] Exposure has been associated with the development of metal fume fever.[4] The NIOSH REL, the ACGIH TLV, and the OSHA PEL for copper dust is 1 mg/m^3 as a TWA.[4,5,6]

Magnesium can cause eye and nasal irritation. Exposure has been associated with the development of metal fume fever.[4] NIOSH did not agree with OSHAs proposed rule for magnesium and did not adopt an REL for this substance, the ACGIH TLV and the OSHA PEL is 10 mg/m^3 as an 8–hour TWA.[4,5,6]

Zinc has been associated with shortness of breath, minor lung function changes, and metal fume fever.[4] The NIOSH REL for zinc oxide fume and zinc oxide as total dust is 5 mg/m^3, the ACGIH recommends a TLV of 5 mg/m^3 for zinc oxide fume and 10 mg/m^3 for zinc dust, and the OSHA PEL is 5 mg/m^3 for zinc oxide fume, 10 mg/m^3 as total dust and 5 mg/m^3 as respirable dust.[4,5,6]

RESULTS

On December 2, 1996, at 7:00 p.m., kiln #4 was shut down for removal and replacement of refractory bricks from the first 25 feet of the lower end of the kiln. Kilns #1, #2, and #3 continued to operate during this maintenance operation. On December 3, at 7:00 a.m., the kiln was cool enough for workers to begin removing a coating of hard fused rock material and old refractory bricks from the interior of the kiln. By that evening, the removal portion of the operation had been completed. Repair crews then worked around the clock to complete the rebricking operation by midnight on December 4. By 2:00 a.m. on December 5, the scheduled maintenance had been completed and all workers had exited the kiln. Dust and gas samples were then placed in the middle and at the back end of the kiln. Then kiln conditions under which workers had experienced respiratory symptoms on February 11, 1996, were re–created (i.e., the ID fan was turned off and the electrostatic precipitator was operated at half capacity). During this experiment workers were not allowed inside the kiln.

The results of PBZ air samples collected from workers performing the removal and rebricking tasks are presented in Table 2. Dust exposures were somewhat higher while workers were removing coating and bricks from the kiln; however, none of the PBZ dust measurements exceeded current exposure criteria. Chlorine was not detected on the PBZ air samples and only trace quantities of sulfur dioxide were detected.

The results of the dust measurements collected at area sampling stations inside the kiln are presented in Table 3. None of these area dust samples exceeded current exposure criteria. The average total and inhalable dust measurements were similar, but the respirable samples were approximately 80% to 90% lower than the total dust measurements indicating that most of the inhaled airborne dust would be deposited in the nose, throat, and upper airways, rather than the alveoli and lower airways. The inconsistencies between the total and inhalable dust concentrations reported may be due to sampler variabilities.

Quartz and cristobalite were not detected in any of the PBZ or area respirable dust samples. However, quartz was detected in three bulk dust samples collected at the front end of the kiln, at the middle of the kiln, and at the back end of the kiln in concentrations of 2.3%, 3.5%, and 2.6%, respectively. Cristobalite was not detected in any of these samples. Concentrations of cadmium, chromium, copper, magnesium, nickel, and zinc found in the PBZ total dust samples, area total dust samples, and bulk dust samples are presented in Table 4. Arsenic was not detected in any of these samples. Only one area air sample collected at the back end of the kiln contained detectable quantities of cadmium and nickel. None of the concentrations detected in the air samples exceeded current exposure criteria. Magnesium was the only metal detected in the bulk samples in more than trace quantities. Hexavalent chromium, which has been reported to cause allergic dermatitis due to sensitization of the skin, was detected in bulk samples collected at the front, the middle, and the back of the kiln in concentrations of 16, 12, and 49 μg/gm, respectively.

Chlorine was not detected inside the kiln using either the silver membrane filters or the direct–reading color indicator tubes. Also, inorganic acids were not detected inside the kiln.

A trace quantity of sulfur dioxide was detected in one area sample, collected at the back end of the kiln between 3:52 a.m. and 8:15 a.m., on December 5 (17.98 $\mu g/m^3$ = 0.007 ppm). Ozone was not detectable using either the direct–reading color indicator tubes or the Metrosonic Toxic Gas Monitor direct–reading monitor at any location while workers were inside the kiln. Due to analytical laboratory error the results of the oxides of nitrogen samples could not be accurately determined.

After all workers had exited the kiln, sampling equipment for total dust, inhalable dust, respirable dust, and metals, was placed inside between 3:30 and 4:00 a.m. on December 5, and at 4:01 a.m. the ID fan was turned off. The electrostatic precipitator serving kiln #4 was reduced to half strength, with the east precipitator unit turned on and the west precipitator unit turned off. Between 4:30 and 5:00 a.m., workers who were working on the kiln floor near the front of kiln #4 reported a faint odor resembling the odor they had smelled when workers experienced respiratory symptoms on February 11, 1996; the odor was described as a chlorine or bleach–like. The odor was distinctive, but intermittent. At 6:45 a.m. the NIOSH investigator began taking chlorine measurements using direct–reading color indicator tubes and ozone measurements using direct–reading color indicator tubes and the Metrosonic Toxic Gas Monitor direct–reading meter near the front and back ends of kiln #4. Chlorine was not detected on two color indicator tubes collected at the front of the kiln. However, a reading of 0.6 to 0.7 ppm ozone was detected on two ozone color indicator tubes and a reading of 0.09 to 0.11 ppm ozone was detected using the Metrosonic monitor at the front end of the kiln. Background readings collected with the Metrosonic monitor in the plant yard yielded 0.02 to 0.03 ppm.

At 7:15 a.m., investigators collected chlorine and ozone measurements through a portal at the back end of the kiln. Chlorine was not detected using a color indicator tube, but two pump strokes on an ozone indicator tube saturated the tube. (The ozone color indicator tube is calibrated to detect ozone concentrations between 0.05 and 0.7 ppm with $\pm$25% accuracy using ten strokes of a hand–held air pump.) This measurement indicated that the ozone concentrations inside the kiln were well above 0.7 ppm. The Metrosonic direct– reading meter detected a concentration of 4.5 ppm, and the reading remained stable for several minutes. The hands and sleeves of the investigator who took the measurements through the portal had a strong, pungent chlorine or bleach–like odor. Several workers stated that the odor on the investigator's hands and clothing was identical to the odor they had smelled during the two previous respiratory irritation episodes.

At 7:40 a.m., the electrostatic precipitator was turned off and the ID fan was turned on. By 7:50 a.m. the ozone concentration detected using the Metrosonic direct–reading meter had dropped to between 0.16 to 0.17 ppm. Within one half–hour after the ID fan was turned on and the precipitator was turned off, the Metrosonic meter readings had decreased to background levels. A summary of the ozone measurements is presented in Table 5.

DISCUSSION

The measurements collected during the kiln repair operations at the Lehigh Portland cement plant between December 3 and December 5, 1996, support the conclusion that the previous occurrences of eye and upper respiratory irritation were caused by exposure to ozone and not chlorine compounds. The source of the ozone was the electrostatic precipitator. When the ID kiln exhaust fan had been turned off while the precipitator continued to operate, ozone back–drafted from the precipitator into the kiln area. Measurements indicated that the ozone concentrations may have approached 5 ppm, well above existing exposure criteria.

Sulfur dioxide was only detected in trace concentrations and was unlikely to have contributed to the irritation outbreaks. Airborne dust levels and quartz and metals concentrations did not indicate that workers were at increased risk for pneumoconiosis (silicosis) or other significant pulmonary effects. However, while working inside the kiln the wearing of personal respirators can reduce concentrations of inhaled dust particles which may dry and irritate nasal passages and upper airways. The irritation outbreaks were not temporally associated with the burning of used tires or waste oils, so combustion products from these materials probably did not cause the irritation symptoms. Chlorine was not detected at any of the sample locations and is not used in the production of Portland cement. The distinctive chlorine–like odor and the irritation symptoms experienced by workers on previous occasions was clearly caused by ozone from the electrostatic precipitators.

CONCLUSIONS

The chlorine–like odor and respiratory and eye irritation symptoms that workers experienced when repairing kiln #4, were caused by ozone. Ozone back–drafted into the kiln from the electrostatic precipitator when the precipitator was operating and the induced draft (ID) fan was turned off. The ozone concentrations inside the kiln during previous maintenance operations may have approached 5 ppm, 50 times the NIOSH ceiling REL. Ozone is a potent irritant to the eyes and all mucous membranes.[15] Symptoms following acute exposure to ozone include coughing, chest tightness, burning eyes, headache, and severe fatigue. Pulmonary edema may occur, sometimes several hours after exposure has ceased.

Chlorine was not detected inside the kiln. Concentrations of sulfur dioxide detected inside the kiln were well below established criteria and would not cause eye and respiratory irritation. Dust measurements did not indicate that workers performing maintenance inside the kiln were exposed to excessive concentrations of dust, crystalline silica, or metals.

RECOMMENDATIONS

Before workers enter the kiln, the electrostatic precipitator should be turned off and the ID fan should continue to operate. If the ID fan has to be turned off, the precipitator should remain off and the fan should be run for several minutes to remove residual ozone before workers enter the kiln. While workers are inside the kiln, the ozone levels should be periodically monitored.

Workers should be warned of the symptoms of excessive exposure to ozone. If they begin to experience these symptoms, they should exit the area (kiln) and report their symptoms to their supervisor and plant health and safety staff.

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Table 1 (Page 1 of 2)
Summary of Sampling and Analytical Methods
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Analytical Limit of Detection (LOD) per Sample
Chlorine	1.0	PTFE prefilter (25 mm diameter, 0.5 µm pore size) followed by silver membrane filter (25 mm diameter, 0.45 µm pore size)	NIOSH Method No. 6011	1 µg
	0.02	Dräger™ color indicator tube	Color reaction with solid sorbent material	0.1 ppm
Sulfur Dioxide	1.0	Cellulose ester membrane filter (37 mm diameter, 0.8 µm pore size) followed by a sodium carbonate–treated cellulose ester filter	NIOSH Method No. 6004	0.5 µg
Oxides of Nitrogen	0.025	Two triethanolamine–treated molecular sieve sorbent tubes with oxidizer tube placed in between	NIOSH Method No. 6014	1 µg
Ozone	NA	Metrosonic pm–7000 toxic gas monitor	Electrochemical sensor	0.02 ppm
	Hand–held bellows pump	Dräger™ color indicator tube	Color reaction with solid sorbent material	0.05 ppm
Inorganic Acid	0.5	Silica gel in a sorbent tube	NIOSH Method No. 7903, Acids, inorganic	3 µg

Table 1 (Page 2 of 2)
Summary of Sampling and Analytical Methods
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Analytical Limit of Detection (LOD) per Sample
Respirable Particulate and Crystalline Silica	1.7	Tared PVC filter (37 mm diameter, 0.8 µm pore size)	NIOSH Method No. 0500, Gravimetric analysis NIOSH Method No. 7500, Quartz and cristobalite analysis	10 µg gravimetric 10 µg quartz 20 µg cristobalite
Total Particulate and Metals (As, Cd, Cu, Cr, Mg, Ni, Zn)	2.0	Tared PVC filter (37 mm diameter, 0.8 µm pore size)	NIOSH Method No. 0500, Gravimetric analysis NIOSH Method No. 7300, Trace metal analysis	10 µg gravimetric 3 µg arsenic 0.008 µg cadmium 0.5 µg chromium 0.08 µg copper 0.5 µg magnesium 0.5 µg nickel 0.5 µg zinc
Inhalable Particulate	1.0	Tared PVC filters in an IOM cassette	Filters were pre–weighed and post–sampling weighed on a Mettler A–20 balance. The difference between the initial and final weights yielded total weight.	20 µg

Table 2
Personal–breathing–zone Air Samples Collected
During Maintenance on Kiln #4
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Type of Sample	Time Sample Collected	Concentration mg/m^3
December 3, 1996 – Workers Removing Coating and Old Bricks from First 25 feet of Kiln #4		
Total Dust	11:04 a.m. – 6:36 p.m.	3.75
Respirable Dust	11:04 a.m. – 6:36 p.m.	0.41
Chlorine	10:56 a.m. – 6:38 p.m.	ND
Sulfur Dioxide	10:56 a.m. – 6:38 p.m.	Trace
December 4, 1996 – Workers Rebricking First 25 feet of Kiln #4		
Total Dust	7:32 a.m. – 3:45 p.m.	1.24
Respirable Dust	7:32 a.m. – 3:45 p.m.	0.13
Chlorine	7:41 a.m. – 4:50 p.m.	ND
Sulfur Dioxide	7:41 a.m. – 4:50 p.m.	Trace

Abbreviations:
ND – nondetectable
Trace – quantity detected is between the analytical limit of detection and the analytical limit of quantitation

Table 3
Area Air Samples for Dust Collected at Locations Inside Kiln #4
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Location/Operation	ID Fan	Date	Time	Total Dust Concentration mg/m^3	Inhalable Dust Concentration mg/m^3	Respirable Dust Concentration mg/m^3
27 ft inside front of kiln; workers removing coating and old bricks from first 25 ft of front of kiln	On	12/3/96	11:46 a.m. – 12:42 p.m. 4:54 p.m. – 9:01 p.m.	0.84	0.88	0.10
5 ft uphill from chains in back end of kiln; workers removing coating and old bricks from first 25 ft of front end of kiln	On	12/3/96	5:42 p.m. – 9:26 p.m.	0.54	1.13	0.10
5 ft uphill from chains in back end of kiln; workers rebricking first 25 ft of front end of kiln	On	12/4/96	8:26 a.m. – 5:13 p.m.	2.67	0.93	0.21
30 ft uphill from tire door near middle of kiln; no workers inside kiln	Off	12/5/96	3:43 a.m. – 8:25 a.m.	0.67	0.70	0.15
5 ft uphill from chains in back end of kiln; no workers inside kiln	Off	12/5/96	3:52 a.m. – 8:15 a.m.	0.96	1.49	0.20

Table 4
Concentrations of Selected Metals from Personal and Area Total Air Filter Samples and Bulk Dust Samples
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Personal and Area Air Filter Samples	Date	Time	Metals Concentrations in Air Filter Samples (µg/m^3)					
			Cd	Cr	Cu	Mg	Ni	Zn
Personal: Worker removing coating and old bricks from first 25 ft of kiln #4	12/3/96	11:04 a.m. – 6:36 p.m.	<LOD	1.0	0.49	175	<LOD	3.6
Personal: Worker rebricking first 25 ft of kiln #4	12/4/96	7:32 a.m. – 3:45 p.m.	<LOD	0.82	0.62	143	<LOD	2.1
Area: 27 ft inside front of kiln	12/3/96	11:46 a.m. – 12:42 p.m. 4:54 p.m. – 9:01 p.m.	<LOD	<LOD	0.36	35	<LOD	3.0
Area: 5 ft uphill from chains in back end of kiln	12/3/96	5:42 p.m. – 9:26 p.m.	<LOD	<LOD	0.45	13	<LOD	2.7
Area: 5 ft uphill from chains in back end of kiln	12/4/96	8:26 a.m. – 5:13 p.m.	0.09	6.3	0.58	122	2.4	2.3
Area: 30 ft uphill from tire door near middle of kiln	12/5/96	3:43 a.m. – 8:25 a.m.	<LOD	<LOD	<LOD	17	<LOD	3.4
Area: 5 ft uphill from chains in back end of kiln	12/5/96	3:52 a.m. – 8:15 a.m.	<LOD	<LOD	<LOD	13	<LOD	2.8
Bulk Dust Samples Collected from Locations Inside Kiln			**Metals Concentrations in Bulk Dust Samples (µg/gm)**					
Bulk: Front end of kiln			3.4	39	16	14,000	14	120
Bulk: Middle of kiln near tire insert door			8.6	270	19	15,000	21	120
Bulk: Back end of kiln near start of chains			17.0	740	38	13,000	350	94

Table 5
Summary of Ozone Measurements
Lehigh Portland Cement Company
Union Bridge, Maryland
HETA 96–0226

Location & Operation	Date	Sampling Instrument	ID Fan	Electrostatic Precipitator	Ozone Concentration (ppm)
Plant Yard – Background	Dec. 3–4	color indicator tube	NA	NA	ND
		Metrosonic meter			0.02 – 0.03
Inside Front End of Kiln – Workers Replacing Kiln Bricks	Dec. 3–4	color indicator tube	ON	OFF	ND
		Metrosonic meter			0.03
Inside Back End of Kiln – Workers Replacing Kiln Bricks	Dec. 3–4	color indicator tube	ON	OFF	ND
		Metrosonic meter			0.03
Just Outside Front End of Kiln – No Workers Inside Kiln	Dec. 5	color indicator tube	OFF	ON	0.6 – 0.7
		Metrosonic meter			0.09 – 0.11
Through Portal in Back End of Kiln – No Workers Inside Kiln	Dec. 5	color indicator tube	OFF	ON	>0.7
		Metrosonic meter			4.5

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