

U. S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control
National Institute for Occupational Safety and Health
Health Hazard Evaluation Determination
Report No. 81-000-113
Martin-Marietta Cement
Tulsa, Oklahoma

I. SUMMARY

On June 23, 1981 the National Institute for Occupational Safety and Health (NIOSH) received a request from the United Cement, Lime, Gypsum and Allied Workers Union Local 421 in Tulsa to examine possible health hazards arising from burning "high-sulfur" coal at the Martin-Marietta Cement Plant in Tulsa, Oklahoma. Of specific concern were exposures to sulfur dioxide (SO₂), carbon monoxide (CO), carbon dioxide (CO₂), and hydrogen sulfide (H₂S). Two rounds of a mail questionnaire were sent out prior to a hazard survey October 22-23, 1981. During the survey employees were questioned about medical complaints and area samples were collected for sulfur dioxide, sulfates, sulfites, carbon monoxide, nitrogen dioxide, and hydrogen sulfide.

Sulfur dioxide is being released into the plant environment from kiln exhausts escaping from baghouses. Workers have been intermittently reporting irritant symptoms compatible with sulfur dioxide exposure. Concentrations of SO₂ measured in the kiln baghouses, kiln feed building, and on top of the raw silos were at 1.2, 1.8, and 1.7 ppm respectively. These levels are capable of causing irritation and acute bronchial airway changes. Levels of carbon monoxide and nitrogen dioxide were detected in the mobile equipment maintenance garage, but these measurements were below concentrations known to cause toxic effects. Corrective action should be taken to reduce or eliminate sulfur dioxide exposure in the plant environment.

Key words: SIC 3241 (Portland Cement) Portland Cement, sulfur dioxide, carbon monoxide, nitrogen dioxide, mucosal irritation.

II. BACKGROUND

The Martin-Marietta cement plant is located east of Tulsa, four miles from Tulsa International Airport. The plant was built twenty years ago adjacent to limestone and shale reserves. Limestone and shale are brought from the quarry, crushed, and ground into a fine powder in ball mills. Other raw materials such as sand and iron ore may be added in the milling process. This dry powder is then blended to the desired chemical and physical compositions and pumped into rotary kilns. The kilns heat the mix to about 2700°F. At this temperature the raw mix is fused forming

"clinker minerals". The four chief clinker minerals are tricalcium silicate (3CaO-SiO_2), dicalcium silicate (2CaO-SiO_2), tricalcium aluminate ($3\text{CaO-Al}_2\text{O}_3$), and tetracalcium aluminoferrite ($4\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$). (1,2) Gypsum is added to the clinkers and they are milled in ball mills to increase fineness. The ground powder is Portland Cement. The cement is then either bagged or loaded out as bulk in trucks or rail cars.

Coal is used to fuel the kilns. The coal comes from the Croweburg seam in eastern Oklahoma. This seam is reported to contain as high as 3.1% sulfur by weight with an average of 1.6%. (3) Before 1976 the kilns were fired with natural gas. Workers maintain that irritant symptoms began to occur only after coal became the kiln fuel.

MSHA has evaluated exposures at the plant on several occasions (see Attachment A) and found acutely "hazardous" carbon monoxide and sulfur dioxide levels in the kiln baghouses. Since then workers have been provided a self-contained respirator in the baghouse during servicing and half-mask respirators with acid gas cartridges while working around the baghouse. Workers who were concerned about this exposure to exhaust gases within the plant initiated a request for a NIOSH health hazard determination.

One feature of this plant is that it has no discharge stack for the kiln gases. The kiln gases pass through noncompartmentalized baghouses which are open at the top. Gases escape through the top of the baghouses. The top of the baghouses are 40 feet above ground level and several structures and work stations near the baghouses are above this height.

III. MATERIALS AND METHODS

A. Medical

We originally tried to define prevalence of complaints by a self-administered questionnaire. The questionnaire was sent to hourly and salaried employees between August and October 1981. Because of the low response rate we telephoned several individuals and were told the "real problem" was not SO_2 irritation but syncopal episodes and chest pain. We set up a list of persons who had reportedly been hospitalized or seen in emergency rooms with syncope and chest pain. A walk-through was conducted October 22, 1981. The evening before, a meeting was held with workers, and medical interviews were conducted. Occupational and medical histories focusing on neurological symptoms, strokes, chest pain and mucous membrane irritation were recorded. Where appropriate, physical exams were performed.

For workers with major medical problems a review of recent hospitalizations or personal contact with physicians was attempted.

B. Environmental

All samples were area samples and are indirectly related to worker exposure. The duties of many cement workers vary from day to day and station to station. Also, there is variation in atmospheric conditions such as wind speed and direction, and occurrence and duration of temperature inversions. Because of this, personal samples collected on one day do not accurately represent potential worker exposure to exhaust gases. We elected therefore to document the presence of irritant gases in the kiln exhaust, and measure these levels primarily in work areas near the back end of the kiln. These measurements probably reflect the worst case conditions for this plant on this particular day. Most of the samples were long term samples (greater than five hours) which average the concentrations over the sampling period. We also sampled for toxic gas (CO and NO₂) from engine exhausts in the mobile equipment garage.

Oxides of Sulfur Samples

Samples for sulfate and sulfite particulates and sulfur dioxide gas were collected by drawing a known volume of air through a filter train consisting of two cellulose ester filters in series. Particulate matter, including sulfates and sulfites, is collected on the first filter. Sulfur dioxide passes through the first filter and is collected on the second filter which has been impregnated with potassium hydroxide. The filters were extracted with deionized water and the extracts analyzed by ion-chromotography. (4)

These samples were collected for periods between 5 and 6 hours. The measurements reflect the average concentration over this period. Since oxides of sulfur are produced from the combustion of coal containing elemental sulfur, these samples were placed mainly in areas near the kilns and associated processes.

Nitrogen Dioxide Samples

Nitrogen dioxide sampling was done using passive dosimeters for both area and personal sampling. Full shift time weighted average exposures were determined. Dosimeters were constructed by cutting lengths of acrylic tubing to give a length to area ratio of 0.1. One end of the tube was fitted with a removable cap-plug and the other end was sealed with a cap containing the collection grids. These grids were coated with triethanolamine which quantitatively absorbs NO₂. During exposure, the cap-plug was removed and the contaminant gas diffused to the collection grid according to Fick's Law of Diffusion. After collection a sulfanilamide-phosphoric acid-NEDA solution was added to the dosimeter, where a red color complex with NO₂ was formed. The solution was transferred to a spectrophotometer and the absorbtivity is measured at 540 nm. This was compared against a standard curve to give nanomoles NO₂, from which the concentration was calculated as: (5,36)

$$\text{Conc, ppm} = \frac{(\text{nanomoles NO}_2)}{2.3 \times (\text{Hours of Exposure})}$$

These samples were collected for periods between 5 and 6 hours. The measurements reflect the average concentration over this period. Since nitrogen dioxide is produced from the combustion of organic compounds containing nitrogen, these samples were placed in areas near the kilns and in the mobile equipment garage.

Gas Indicator Tube Samples

NIOSH certified detector tubes were used to take short term samples for carbon monoxide, oxides of nitrogen (NO + NO₂), and sulfur dioxide. They produce results within + 25% of the true concentration at levels between one and five times the TLV and within + 35% at one-half of the TLV. For purposes of this study this precision is adequate since a 25% variation around a given exposure level is not likely to produce significant differences in physiological response. The sampling times are only a few minutes and the tubes may be read immediately.

Direct Reading Instrument

Portable direct reading analyzers were used to detect sulfur dioxide and hydrogen sulfide gas. Air was drawn through an electrochemical voltammetric sensor. As the gas passed over a gas diffusion-type electrode, some of the molecules diffused into, and were absorbed on the electrode, where they were electrochemically oxidized. This electrochemical reaction generated an electric current directly proportional to the gas concentrations. The results were read in parts per million of air (ppm). Measurements were taken in various locations for only a few minutes. The direct reading instruments were not specific for each contaminant, but were influenced by the presence of other gases such as carbon monoxide and sulfur-containing compounds.

All sampling equipment was calibrated the morning of the survey in Tulsa. Temperature and pressure corrections were applied to the volumes of collected gas samples.

IV. REVIEW OF LITERATURE AND EVALUATION CRITERIA

A. Sulfur Dioxide

Sulfur dioxide is a colorless gas, highly soluble in water, which imparts a characteristic taste and odor. (6) All but a small fraction of inhaled sulfur dioxide is absorbed by the liquid lining of the upper airways, particularly during quiet breathing. During activity, especially when mouth breathing becomes necessary, penetration of the gas to the lower airways may occur.

Following absorption, the gas reacts with water forming a weak acid solution that contains sulfite (SO_3), bisulfite (HSO_3), and acid hydrogen (H^+) ions. The relative contribution of these ions to the irritation produced is uncertain. An enzyme, sulfite oxidase, hastens the conversion of bisulfite to sulfate ions. Sulfate ions are nontoxic and are excreted in the urine.

It is well documented that workers engaged in occupations involving exposures to sulfur dioxide greater than 10 ppm demonstrate mucous membrane irritation and reflex bronchoconstriction with increase airways resistance. (6,7,8,9) It is difficult to use past epidemiological studies to assess at what concentration sulfur dioxide causes injury to the respiratory tract, because they are all lacking in exposure data. However, several human experimental studies have been conducted to determine at what concentrations deleterious effects of sulfur dioxide are exhibited.

Frank (10) found that 1 ppm produced increased temporary flow-resistance in only 1 of 11 human subjects. A concentration of 5 ppm produced an average temporary increase of 39% above control, the value for 13 ppm was 72% above control. The responses were related to concentration and not to total dose, because extending the exposure time from 10 to 30 minutes did not increase the response. Tomono (11) found 1.6 ppm to be the lowest concentrations which produced bronchoconstriction in 46 healthy subjects. Lawther (12) found a response to 1.0-3.0 ppm when subjects breathed deeply through the mouth. The response to a given concentration has been found to be greater when breathed through the mouth than when breathed through the nose. (16) Weir (13) exposed 12 healthy young adult males continuously for 120 hours to sulfur dioxide. No changes were observed in subjective complaints or pulmonary function at concentrations of 0.3 or 1 ppm. A concentration of 3 ppm caused slight increase in small airway resistance, and a decrease in compliance. Controlled exposures at concentrations of 9 ppm for 60 minutes have produced increases in airway resistance accompanied by rhinorrhea and lacrimation. (14) Melville (15) found changes in the airway conductance in 49 healthy volunteers at concentrations of 2.5 ppm.

Generally, it has been found that acute responses to higher levels diminish shortly after removal from exposure, and at times even as exposure continues. Of more frequent occurrence than high-level acute exposure is prolonged exposure to relatively low levels. There is some evidence that this may irritate or exacerbate chronic obstructive pulmonary disease. (6)

It is debatable whether synergism between sulfur dioxide and airborne particulates has been demonstrated in human subjects. Animal toxicology suggests that synergism may be expected between sulfur dioxide and some aerosols especially particulates which can absorb the gas. (16,17)

The current federal standard for sulfur dioxide in occupational settings is 5 ppm based on an eight-hour time-weighted average (TWA) working time. According to the documentation used in proposing this standard (18) 5ppm should prevent respiratory tract irritation in most workers. However, workers who are not able to become acclimatized or are sensitive to sulfur dioxide may develop respiratory tract irritation at concentrations below 5ppm. Although 5 ppm sulfur dioxide may not produce subjective irritation in acclimatized workers, it may cause bronchoconstriction and thereby temporarily compromise pulmonary function.

The American Conference of Governmental Industrial Hygienists state that available data indicate a reduction in the TLV from 5 ppm is desirable. They recommend a TLV-TWA of 2 ppm and a 15 minute excursion limit (STEL) of 5 ppm. (25, 26)

NIOSH recommended in 1974 a limit of 2 ppm as a TWA. (23) In 1977 this limit was lowered to 0.5 ppm based on conclusions from four recent studies. These were studies of chronic disease among populations exposed to sulfur dioxide over a long period of time. The NIOSH study of Archer and Gillam (19) found statistically significant reductions in FVC and FEV₁ and an increase in symptoms of respiratory disease among copper smelter workers with TWA mean exposures of 2 ppm. Smith (20) found a statistically significant increase in the annual FEV₁ and FVC mean decrements among copper smelter workers whose SO₂ TWA exposures were between 1 and 4 ppm when compared to those whose mean exposure was less than 1 ppm. The Ministry of Health in Canada (21) reported statistically significant increases in respiratory disease and decreases in FVC and FEV₁ among copper smelter workers exposed for ten years or more. Average exposure was reported as 2.5 ppm. Lowe (22) found no definite effects in 10,000 steel industry workers exposed to a mean of 0.35 ppm sulfur dioxide.

Nitrogen Dioxide

Nitrogen dioxide is a reddish-brown gas which is a common contaminant in the exhaust of internal combustion engines. It is an irritant to the mucous membranes and its inhalation may cause coughing, sometimes severe, which may be accompanied by mild or transient headache. (24)

Based on animal studies ACGIH recommends a ceiling limit (the concentrations, not to be exceeded even instantaneously) of 5 ppm. (25) This level was considered sufficiently low to insure against immediate injury or adverse physiologic effects from prolonged daily exposures. The present federal standard (MSHA and OSHA) for nitrogen dioxide is 5 ppm as an 8-hour time weighted average (TWA). (27) This was based upon the ACGIH TLV except that the ceiling designation was omitted. (24) A number of human experiments and animal studies suggest that humans with normal respiratory function may be affected by exposure at or below this level and that the conditions of workers with diseases such as bronchitis may be aggravated by such exposures. (28, 29, 30, 31) NIOSH recommends a ceiling of 1 ppm to protect workers with preexisting chronic bronchitis. ACGIH maintains a STEL of 5 ppm and a TWA of 3 ppm.

Carbon Monoxide

Carbon monoxide is a colorless, almost odorless gas, which is encountered as a product of incomplete combustion of almost any carbonaceous material. Carbon monoxide is a chemical asphyxiant, which rapidly diffuses across the alveolar membrane and reversibly binds with hemoglobin resulting in a reduction in the oxygen-carrying capacity of the blood. The body compensates for this stress by increasing the cardiac output and blood flow to specific organs, such as the brain and heart. When this ability to compensate is overcome tissue injury results. (25)

The signs and symptoms of acute exposure to high concentrations of CO are well known and easily recognized. These may include headache, nausea, vomiting, dizziness, drowsiness, and collapse. There are conflicting reports of effects to exposures at and below 100 ppm. (32, 33) ACGIH recommends a TLV of 50 ppm since prolonged exposure to this concentration should not result in blood CO levels above 10 percent, a level above which the development of clinical symptoms such as headache, fatigue, and dizziness occur. (34) The federal standard for carbon monoxide is also 50 ppm for an 8 hour exposure time.

The effect of carbon monoxide is increased by factors such as an increase in physical activity, high environmental temperatures, high altitudes, and simultaneous exposure to narcotic solvents. Also, individual variability in cardiovascular disease status, ability to take up CO, and habit of smoking may augment the effects of CO. NIOSH recommends 35 ppm as a TWA and 200 as an excursion limit to provide a margin of safety for the employee with chronic heart disease. (35)

<u>Substance</u>	<u>MSHA-PEL-ppm</u>	<u>ACGIH-TLV ppm</u>	<u>NIOSH-ppm</u>
Sulfur Dioxide (SO ₂)	5 ppm	2 ppm	0.5 ppm
Nitrogen dioxide (NO ₂)	5	3 STEL - 5	Ceiling - 1
Carbon monoxide (CO)	50	50 STEL - 400	35 STEL - 200

V. RESULTS

A. Preliminary Inquiries

The mail questionnaires generated response rates of 24% (in hourly) and 0% (in salaried) employees. We compiled a list of 19 persons with syncopal attacks (episodes of loss of consciousness) and "strokes"(n=14) or atypical chest pain (n=5). 17.5% of the workers were interviewed before the walk-through. It is clear that both questionnaire-respondents and interviewees are self-selected populations.

B. Medical

1. Mucous membrane irritation:

62%(18/29) of the questionnaire respondents and 95%(20/21) of the workers interviewed complained of mucous membrane irritation. All admitted it was a sporadic occurrence. No conjunctivitis was observed in any workers during the walk-through.

2. Chest pain:

Of the five persons with chest pain (under V. A.), one had clinical symptoms of esophagitis, one had an upper gastro-intestinal series reporting reflux and coarsened gastric folds ("Menetriere's") without clinical complaints, one had chest wall pain, one could not be contacted, and the fifth had atherosclerotic heart disease and will be referred to later. One additional worker with intermittent symptoms of esophagitis was asymptomatic at the time of the survey.

3. Syncope and "strokes":

Of the fourteen persons who reportedly had had syncope or strokes (see A.), eleven (78%) could be located. Only one had an episode of true loss of consciousness without other obvious explanation. The other attacks of dizziness were not associated with a single plant location or time pattern. The records of the one worker who had true syncope and was taken to an emergency room were not available.

4. Of the six workers we found in the plant with medically defined disease, one belonged to management, one worked in the plant at large, and four worked in the maintenance garage. Three of the four diseases could be associated with diesel exhaust fumes.

We found complaints of mucous membrane irritation in a self-selected population, but no evidence for "clustering" of disease of the same kind.

C. Industrial Hygiene

Sulfate, sulfite, and sulfur dioxide concentrations are presented in Table 1. The AREA column tells where the samples were collected. The sulfates and sulfites are reported as micrograms per cubic meter (Ug/m^3), and the sulfur dioxide as parts per million (ppm).

The highest levels of sulfate and sulfite particulates and sulfur dioxide gas were detected in the kiln baghouses and work areas above the baghouses. Sulfur dioxide levels in these areas were in the range 1.2-1.8 ppm for a 6 hour time weighted average. Because clinker production is a continuous process and the kiln must be maintained within narrow ranges of conditions, the average concentration in these areas was probably the same throughout this day. SO_2 was measured at 0.2 ppm downwind from the baghouses.

The nitrogen dioxide concentrations as measured by the Palmes passive dosimeters are presented in Table 2. The concentrations are in ppm. The highest levels for a 6-hour time weighted average were found inside the kiln baghouse and the mobile garage. Engines in the maintenance garage are generally only run for short time periods. We cannot determine what the peak concentrations may have been from time weighted average data, but a gas indicator tube gave an instantaneous reading of 2 ppm for nitrogen dioxide and nitric oxide.

Table 3 lists concentrations of carbon monoxide (CO), oxides of nitrogen (nitrous oxide and nitrogen dioxide), and sulfur dioxide (SO₂) as measured by direct reading indicator tubes. Table 4 lists the concentrations of sulfur dioxide measured by the Interscan direct reading instrument. Hydrogen sulfide was also measured by this method in kiln feed, finish, and raw mill areas. None was detected.

D. Environmental

Tulsa is known to have an air pollution problem on days with weather inversions. Information from the airport meteorological service in Oklahoma City indicate that inversions occur on the average of fifteen times a year. We cannot determine if weather inversions correlate with complaints at this cement plant since we had no access to health records.

Attachment C lists the percent frequency of wind originating from 16 compass point directions. By comparing Attachments C and D, the frequency which kiln exhausts might be carried through portions of the plant can be determined. On the day of the survey:

Barometric pressure	= 744 mm Hg
Temperature	= 46°F
Relative Humidity	= 57%
Wind	= 1200 fpm (13.6 mph) - out of the north-northeast

Weather reports including SO₂ and CO concentrations and air quality indices were obtained for the days MSHA was at the plant. There were no weather inversions during the MSHA survey (see attachment B; data kindly provided by Rene Koestler, Tulsa City/County Health Department).

VI. DISCUSSION AND CONCLUSIONS

Two groups of self-selected workers complained of mucous membrane irritation compatible with SO₂ exposure. These complaints are intermittent. Sulfur dioxide is being released into the plant environment from kiln exhausts escaping from the baghouses.

Two groups of self-selected workers complained of mucous membrane irritation compatible with sulfur dioxide exposure. Sulfur dioxide is being released into the plant environment from kiln exhausts escaping from the baghouses. These complaints occur on an intermittent basis, possibly because of the relative infrequency of work assignments in areas in and around the baghouses and fluctuations in sulfur dioxide concentrations with changes in atmospheric conditions. Our measurements document the sulfur dioxide concentrations only for one particular day. Under different atmospheric or process conditions, these concentrations may be lower or may be higher. Concentrations in the kiln baghouses, the kiln feed building, and on top of the raw silos were at levels which have been documented to cause irritation and acute bronchial airway changes. SO₂ at a concentration of .2 ppm was also detected in the plant environment downwind from the kiln exhausts. Peaks in SO₂ concentration in other areas of the plant may reach levels capable of causing irritation. Sporadic complaints of mucosal irritation may or may not continue to occur in the future.

Research has indicated that prolonged daily exposure to SO₂ at levels between 1 and 2.5 ppm may cause chronic loss of lung function. (19, 20, 21) Sulfur dioxide may also absorb on particulates. Because of the alkalinity of limestone, SO₂ is known to readily absorb onto limestone particulates. (37, 38) When these particulates are inhaled, they may carry the absorbed SO₂ deeper into the lung. The association of these particulates and SO₂ may act to increase the effect on lung function, but this has not been documented by any study.

Table 5 presents the highest concentrations of sulfur dioxide measured at 13 Portland cement plants participating in the NIOSH Cement Workers Morbidity Study (these data are preliminary and as yet unpublished). SO₂ was assessed by the cellulose ester filter method (NIOSH P&CAM 268). These samples were area samples collected around baghouses, stacks, and work areas near the back end of kilns. The 13 plants are identified by type of production process. Only the highest concentrations found during a week long survey are listed. All plants used coal as their kiln fuel except one which was fueled by natural gas. When compared with these SO₂ levels, those at Martin-Marietta are higher.

Levels of carbon monoxide and nitrogen dioxide were detected in the mobile equipment maintenance garage. These measurements were below concentrations known to cause toxic effects. However, concentrations of CO and NO₂ may be higher during other work periods. The day of our survey, engines were only run for very short periods, the overhead doors were frequently open, and there was a moderate wind velocity (13 mph). In the event of increased production of CO and NO₂, the garage may not be adequately equipped to remove engine exhausts quickly enough to avoid build up of toxic gases. Air changes are accomplished by passive dilution through the overhead doors and air vents near the ceiling of the garage.

Nitric oxide (NO) is a common contaminant found in conjunction with NO₂. Nitric oxide causes the formation of methemoglobin, altering the oxygen carrying capacity of the blood and effecting the central nervous system. (25) Although we do not have concentration data on NO, there may be additive effects from CO, NO₂ and NO.

The maintenance garage was a source of concern. Three persons had disease that might be associated with diesel exhaust. Because of the small and changing number of workers and the high prevalence of smokers in that area a carboxyhemoglobin survey would not be of much use. Another approach would be a medical history review of all workers associated with the garage with an appropriate comparison group. At the time of this survey, Martin-Marietta already had plans to install a supplied-air ventilation system into the shop; this was done in the Spring of 1982 with the installation of three 5000 cfm fans in the roof. Nineteen workers were reported to have syncope, "strokes" and chest pain. There is no evidence that these symptoms are occupationally related.

VII. RECOMMENDATIONS

1. The most salient characteristic of this cement plant is the open nature of the kiln baghouses which are the emission sources of the sulfur dioxide. These baghouses should be constructed so that exhaust gases cannot escape, until they are shunted up a discharge stack. The stack should be 20-30 feet above the highest nearby buildings. Placement of the stack away from other buildings would reduce the turbulent air flow about the stack.

2. The source of SO_2 is from the combustion of sulfur in the coal. Use a fuel which contains a lower amount of sulfur, such as low-sulfur coal or natural gas will yield less SO_2 upon combustion.

3. Flue-gas desulfurization processes may remove 80-95% of the sulfur dioxide from the exhaust gases. There are currently six types of flue-gas desulfurization systems or scrubbers used in the United States. Many of the scrubbers use lime or limestone slurry. In these systems the sulfur dioxide reacts with calcium carbonate to form calcium sulfite. (38)

Before corrective actions are taken and when workers must enter the baghouses to make repairs, they may need to be protected with personal respiratory devices. For employees working in areas around the baghouse, half mask respirators with acid-gas cartridges may be adequate. These cartridges will only filter out gas and not particulates. If dust is a problem, the respirators may need a combination dust and gas cartridge. Because of the high levels of CO which have been shown to occur in the baghouses, (see Attachment A - MSHA data) a supplied air or self contained respirator is recommended for work inside the baghouses. These respirators should be full facepiece to protect the eyes from irritation.

Respirators should be individually fitted to workers, to insure against leaks about the facepiece. Respirators should not be considered the solution to toxic gas exposures. Controls should be implemented to reduce or eliminate the emission of toxic gas exposures into the plant environment.

VIII. REFERENCES

1. Shreve R, Brink J; Chemical Process Industries, McGraw-Hill, New York, New York 1977; 156-162.
2. Skalny J, Daugherty K, Everything you always wanted to know about Portland Cement, Chemtech, Jan 1972, Vol 41.
3. Keystone Coal Industry Manual - 1980; McGraw-Hill, New York, New York; 560-565.
4. NIOSH Manual of Analytical Methods. "Sulfates, Sulfites, and Sulfur dioxide" Vol 5, P&CAM 1979; 268
5. Palmes E; et al, Personal Sampler for Nitrogen Dioxide, Am Ind Hygiene Assoc J Oct 1976; Vol 37; 570-577
6. NIOSH, Occupational Exposure to Sulfur Dioxide. Criteria of a recommended standard. National Institute for Occupational Safety and Health, 1974.
7. Kehoe R, et al, On the Effects of Prolonged Exposure to Sulfur Dioxide, Journal of Ind Hyg. 14:159-73, 1932.
8. Skalpe I, Long-term effects of sulfur dioxide exposure in pulp mills, British Journal Ind Med. 21:69-73, 1964.
9. Ferris B, et al, Prevalence of chronic respiratory disease in a pulp mill and a paper mill in the United States, Br J Ind Med, 24:26-37, 1967.
10. Frank N, et al, Effects of acute controlled exposure to SO₂ on respiratory mechanics in healthy male adults, J Appl Physiol, 17: 252-58, 1962.
11. Tomono Y, Japan J Ind. Health, 3:77, 1961.
12. Lawther P, "Pulmonary Function and Sulfur Dioxide" Environmental Research 10:355-367, 1975.
13. Weir F, et al, Pulmonary function studies of men exposed for 120 hours to sulfur dioxide, Abstracts of the Society of Toxicology, March 1972, 87.
14. Sim V, Effects of possible smog irritants on human subjects, JAMA 165:1908-13, 1957.
15. Melville G, Changes in specific airway conductance in healthy volunteers following nasal and oral inhalation of SO₂, West Indian Medical J., 19:231-35, 1970.

16. Amdur M, The effects of various aerosols on the responses of guinea pigs to sulfur dioxide, Archives Environ Health, 16:460-468, 1968.
17. McJilton C, et al, Role of relative humidity in the synergistic effect of a sulfur dioxide - aerosol mixture on the lung, Science, 182:503-504, 1973.
18. Sulfur dioxide, in Documentation of the Threshold Limit Values for Substances in Workroom Air, ed 3, Cincinnati, ACGIH, 1971, pp 238-239.
19. Archer V, Gillam J, Chronic sulfur dioxide-exposure in a smelter, I: indices of chest disease, Journal of Occup Med 1977.
20. Smith J, et al, Pulmonary impairment from chronic exposure to SO₂, American Review of Respiratory Diseases, 1977.
21. Ministry of Health: Chronic obstructive lung disease among persons employed for ten years and more in the converter plant of the International Nickel Co. of Canada, Copper Cliff, Ontario, Canada, March 1976.
22. Lowe, C, et al, Bronchitis in two integrated steel works. III. Respiratory symptoms and ventilatory capacity related to atmospheric pollution, Brit J Industr Med, 27:121, 1970.
23. NIOSH: Testimony at OSHA hearings on sulfur dioxide (May 12, 1977)
24. NIOSH: Occupational Exposure to Oxides of Nitrogen, Criteria for a recommended standard. National Institute for Occupational Safety and Health, 1976.
25. ACGIH, Documentation of the Threshold Limit Values, 4th ed, Cincinnati, OH, 1980.
26. ACGIH, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment, Cincinnati, Ohio, 1981.
27. 29 CFR 1910.1000, published in the Federal Register, 39:23642, June 27, 1974.
28. Von Nieding G, et al, Protective action of atropine meclastine and orciprenaline on provocation tests with NO₂ in health subjects and patients with chronic non-specific bronchitis, In Arch Arbeitsmed, 29:55-63, 1971.
29. Von Nieding, et al, Studies of the acute effects of NO₂ on lung function, influence on diffusion, perfusion, and ventilation in the lungs, Int Arch Arbeitsmed, 31:61-72, 1973.

30. Kosmider S, et al, Zentralbl. Arbeitsmed. 22:362, 1972.
31. Vigdortschik N, et al, J Ind Hyg and Tox, 19:469, 1937.
32. Carbon Monoxide - A bibliograph with abstracts. Compiled by A.G. Cooper, U.S.P.H.S., Pub. No. 1503, 1966.
33. Halperin M, et al, The time-course of effects of carbon monoxide on visual thresholds, J of Physio, Vol 146:583-593, 1959.
34. Ebersole J, New England J of Med, Vol 262:599, 1960.
35. NIOSH, Occupational Exposure to Carbon Monoxide. Criteria of a recommended standard. National Institute for Occupational Safety and Health, 1972.
36. Hearl F, Industrial hygiene studies of diesel emissions in coal mines, NIOSH, 1981.
37. Strauss W, Industrial Gas Cleaning, Pergamon Press, Oxford, 1966.
38. Lippman M, Sclesinger R: Chemical contaminants in the human environment. Oxford Univ Press, New York; 1977

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Attachment C

Wind Direction Data from Tulsa, Oklahoma

Provided by

The National Oceanic and Atmospheric Administration-Department of Commerce

<u>Wind Direction</u>	<u>Percent Frequency</u>	<u>Average Speed</u>
N	11.6%	9.6 mph
NNE	4.8%	10.2 mph
NE	3.3%	8.5 mph
ENE	2.1%	7.2 mph
E	2.7%	6.8 mph
ESE	2.1%	7.2 mph
SE	3.8%	8.9 mph
SSE	8.5%	9.8 mph
S	28.8%	10.6 mph
SSW	6.1%	12.8 mph
SW	3.1%	10.6 mph
WSW	1.8%	8.8 mph
W	2.5%	8.4 mph
WNW	2.6%	8.5 mph
NW	4.0%	8.7 mph
NNW	4.9%	8.4 mph
CALM	7.6%	

TABLE 1

Oxides of Sulfur Analysis
Sampling

<u>Station #</u>	<u>Area</u>	<u>Sulfate</u> <u>ug/m³</u>	<u>Sulfite</u> <u>ug/m³</u>	<u>SO₂</u> <u>ppm</u>
1	On Pole at Southwest corner of West Baghouse	8.13	LLD	0.4
2	On pole, 10 yd further south than station #1	26.50	LLD	0.8
3	Inside #1 Baghouse	129.17	12.50	1.2
4	Kiln Feed Bldg on Mezzanine. Higher than Baghouses	23.21	8.44	1.8
5	Kiln Feed Bldg 20 ft. west of Sample Station #4	32.36	LLD	1.8
6	Downwind of the kiln area. On a pole near office Bldg.	10.75	LLD	0.2
7	Between the two kilns 1/4 way from the feed end	LLD	LLD	0.2
8	Top of blending silos	28.99	13.38	1.7

Cellulose Ester Filter Followed by BaseTreated Cellulose Ester Filter

LLD = below analytical detection level.

TABLE 2

Nitrogen Dioxide Analysis
Passive Dosimeters -

<u>Station #</u>	<u>Area</u>	<u>Concentrations in ppm</u>
1	Southwest corner of baghouses	.04
2	Southwest corner of baghouses - 10 yd further south	.08
3	Inside East baghouse	.22
4	Kiln feed mezzanine above east baghouse	.10
5	Kiln feed mezzanine above west baghouse	.15
6	Downwind of baghouses	.05
8	Top of blending silos	.05
9	On east loft in Maintenance Garage	.24
10	Personal sample diesel mechanic	.12
11	Work bench in center of the shop	.18

NO₂ measurements at stations 1-6 and 8 correspond to SO₂ measurements at stations 1-6 and 8.

TABLE 3

Gas Indicator Tube
Short-Term Samples

<u>Location</u>	<u>Gas</u>	<u>Concentrations in ppm</u>
Maintenance Garage		
Center of shop	CO	7
Center of shop	NO _x	2
West loft of shop	CO	5
Center of east baghouse	SO ₂	7
Doorway of east baghouse	CO	ND
Doorway of east baghouse	NO _x	ND
Doorway of east baghouse	SO ₂	ND

ND = not detected

TABLE 4

Interscan Direct Reading Instrument
SO₂ Samples

<u>Location</u>	<u>Reading in ppm</u>
Ground at southwest corner of baghouses	.5
Kiln feed building	2 1-2 range
Maintenance garage	ND
Center of east baghouse (inside)	10 7-20 range
Doorway of east baghouse	2.0
Inside of east baghouse near window	2.5
Between baghouses	.5
Center of west baghouse	6

Reading reported in parts per million; when readings fluctuate a range is listed

TABLE 5

Highest Sulfur Dioxide Concentrations from 13 Portland Cement Plants
participating in the NIOSH Cement Workers Morbidity Study
(unpublished data)

<u>Process</u>	<u>#Samples</u>	<u>High SO2 Measurement in ppm</u>
Wet	1	.01
Dry	6	.30
Dry	9	.02
Wet	6	LLD
Wet	12	.13
Wet	11	.01 Natural Gas fired
Dry	8	.02
Wet/Dry	9	.97
Dry	4	.01
Wet	6	.09
Dry	8	.10
Dry	6	.14
Dry	3	LLD

ATTACHMENT A: MSHA data collected on site visits

Substance	Date	Location	Concentration	Method
Carbon monoxide	8/28/79	Kiln Feed Level	0.00	Bistable
"	"	Baghouse #1	0.00	"
"	"	Kiln Feed Level	0.00	"
"	"	Baghouse #2	0.00	"
"	"	Baghouse #2	0.00	"
"	9/19/79	Baghouse #2	0.00	"
"	"	Baghouse #1	0.00	"
"	"	Baghouse #2	0.00	"
"	10/10/79	Baghouse #2	0.00	Detector tube
"	"	Baghouse #2	575.00	"
"	"	Baghouse #1	8.00	"
"	10/11/79	Baghouse #2	0.00	Vacuum Bottle
"	"	Baghouse #1	0.00	Detector tube
"	"	Baghouse #2	10.00	"
"	"	Baghouse #1	0.00	Vacuum Bottle
"	3/19/80	Baghouse #1	90.00	Bistable
"	"	Baghouse #2	190.00	"
"	8/22/80	Baghouse #1	5.00	Detector tube
"	"	Baghouse #2	10.00	"
Sulfur dioxide	8/28/79	Baghouse #1	0.00	Bistable
"	9/19/79	Baghouse #2	0.00	"
"	"	Baghouse #2	0.00	"
"	"	Baghouse #1	0.00	"
"	10/10/79	Baghouse #2	25.00	Detector tube
"	"	Baghouse #2	25.00	"
"	"	Baghouse #1	18.00	"
"	10/11/79	Baghouse #1	25.00	"
"	"	Baghouse #2	25.00	"
"	3/19/80	Baghouse #1	0.00	Bistable
"	"	Baghouse #2	0.00	"
Hydrogen sulfide	10/10/79	Baghouse #1	0.00	Detector tube
Nitrogen dioxide	10/10/79	Baghouse #1	0.00	"
Sulfuric acid mist	7/29/76	Bloch #4	0.00	Vacuum bottle
Chlorine	4/26/79	Draw hole	0.00	Bistable
Carbon dioxide	8/28/79	Baghouse #1	0.00	"
"	"	Baghouse #2	0.00	"
"	"	Kiln feed level	0.00	"
"	9/19/79	Baghouse #2	0.00	"
"	"	Baghouse #2	0.00	"
"	"	Baghouse #1	0.00	"
"	10/10/79	Baghouse #1	0.90	Detector tube
"	"	Baghouse #2	1.00	"
"	10/11/79	Baghouse #1	0.00	Vacuum bottle
"	"	Baghouse #2	0.00	"

Attachment B: Meteorologic and Environmental data from Tulsa, Oklahoma on days of MSHA and NIOSH site-visits

Dates	SO ₂	CO	Pollution Index		Wind Direction	Wind Speed	Ceiling heights	
	24 hr. avg. ug/m ³	24 hr. avg. mg/m ³	(PI)		by compass	average over 24 hrs- mph	in feet- station level	
			AM	PM				
08/28/79	1.58	0.99	34 (03)	46 (03)	175	15.0	AM 6000	PM 25000
09/19/79	12.0	1.28	47 (CO)	51 (03)	333	9.8	clear for 24 hours	
10/10/70	NA	2.12	72 (CO)	63 (CO)	225	16.3	25000	
10/11/70	1.80	1.80	59 (CO)	51 (CO)	234	14.3	24000	
03/19/80	NA	1.97	10 (CO)	48 (03)	207	20.5	AM 8000	PM 26000
08/22/80	4.20	1.70	42 (03)	59 (03)	81	7.1	10000	
10/23/81	4.16	2.1	19 (03)	21 (03)	126	8.4	clear for 24 hours	

NA: "not available"

PI: "Pollutant Standards Index", according to "The Guideline for Public Reporting of Daily Air Quality- Pollutant Standard Index, EPA-450/2-76-013. 0-50:good; 50-100: moderate; 100-200 unhealthful; 200-300: very unhealthful; 300-500: hazardous.

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