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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
CINCINNATI, OHIO 45202

HEALTH HAZARD EVALUATION DETERMINATION  
REPORT NO. 74-40-167

YOUNGSTOWN SHEET AND TUBE COMPANY  
EAST CHICAGO, INDIANA

JANUARY 1975

I. TOXICITY DETERMINATION

It has been determined that emissions from the treatment of blast furnace iron with Mag Coke<sup>®</sup> (magnesium impregnated coke) conducted in the Charging Aisle of the BOF Building of the Youngstown Sheet and Tube Company (Indiana Harbor Works) are not toxic to groundmen at the Hot Metal Station and to crane operators at the concentrations measured during this evaluation (June 21, 1974). This determination is based on measured concentrations of carbon monoxide, oxides of nitrogen, sulfur dioxide, and airborne particulate; interviews with exposed employees; observation of work practices; and on information regarding the toxic properties of the stated contaminants.

II. DISTRIBUTION AND AVAILABILITY OF THE DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

- a) Youngstown Sheet and Tube Company - East Chicago, Indiana
- b) Authorized Representative of Employees
- c) U.S. Department of Labor - Region V
- d) NIOSH - Region V

For the purposes of informing the approximately 12 "affected employees" the employer will promptly "post" the Determination Report in prominent places where affected employees work for a period of 30 calendar days.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following written request by 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.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees regarding exposure of crane operators and groundmen to emissions from the "Mag Coking" of molten blast furnace iron in the Basic Oxygen Furnace (BOF) building of the Youngstown Sheet and Tube Company (Indiana Harbor Works), East Chicago, Indiana. The request was precipitated by employee concern regarding possible harmful effects from exposure to emissions generated by the Mag Coking operation.

#### IV. HEALTH HAZARD EVALUATION

##### A. Evaluation Progress

The Youngstown Sheet and Tube Company (Indiana Harbor Works) in East Chicago, Indiana was visited on June 21, 1974 by NIOSH investigators, Mr. Robert Vandervort and Mr. Thomas F. Bloom. A preliminary meeting was held with union and management representatives to explain the nature of the Health Hazard Evaluation Request and to obtain background information. Following this meeting, a survey of the Charging Aisle side of the BOF building was made. Both union and management representatives were helpful in explaining processes and highlighting areas of concern.

##### B. Description of Process - Conditions of Use

Molten blast furnace iron is transported to the BOF building in railcars. The railcars are emptied into large, refractory-lined, charging ladles (220 ton capacity) at the Hot Metal Station. The ladles are moved to the front part of the ladle pit at the Hot Metal Station and a sample of the molten iron is obtained for laboratory analysis.

If the molten iron is acceptable with regard to sulfur contamination, the ladle is moved to the slag skimmer where the ladle is tipped forward and the slag skimmed off with a mechanical paddle. The slag falls into a collector which is equipped with local exhaust ventilation. After skimming, the ladle is transported by crane to the BOF where the molten iron is poured into the BOF.

If the molten iron as received from the blast furnace is high in sulfur it must be treated with Mag Coke<sup>®</sup> to lower the sulfur content. Mag Coke<sup>®</sup> (magnesium impregnated coke) is manufactured by the American Cast Iron Pipe Company of Birmingham, Alabama. It had been used as a desulfurizing agent for blast furnace iron for approximately one year prior to this evaluation.

Mag Coke<sup>®</sup> is received in metal drums which are somewhat taller but narrower than 55 gallon oil drums. Two drums of Mag Coke<sup>®</sup> are used for each ladle of iron needing treatment. The drums of Mag Coke<sup>®</sup> are pushed up into a conveying apparatus using a forklift. A diagram of this apparatus is shown in Diagram A.

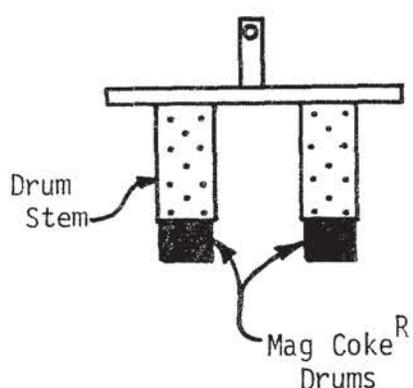


Diagram A

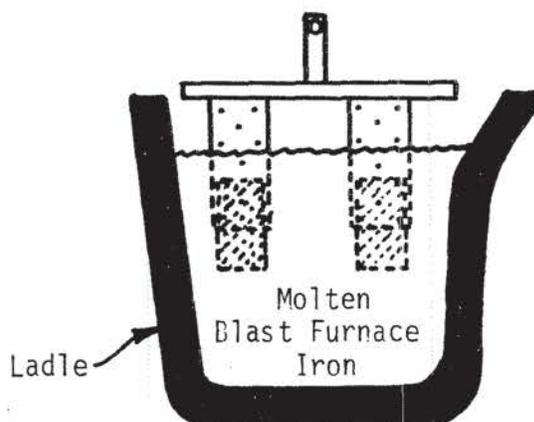


Diagram B

The conveying apparatus is then moved by crane over the ladle at the Hot Metal Station and lowered into the ladle as shown in Diagram B. The molten iron melts the Mag Coke<sup>®</sup> drums in a few seconds and then a vigorous reaction between the Mag Coke<sup>®</sup> and iron takes place with a bright white light (like that of burning magnesium) and billows of white fume are produced. The Mag Coking operation lasts for 12 minutes after which the stem conveying apparatus is removed and the ladle is moved to the skimmer. From this point the iron in the ladle is handled as previously described for untreated blast furnace iron.

During the Mag Coking process, the sulfur in the blast furnace iron combines with the magnesium in the Mag Coke<sup>®</sup> to form a magnesium sulfide slag which floats on the molten iron. Magnesium oxide fume escapes into the working environment while the slag is being formed.

The crane remains hooked to the stem conveying apparatus throughout the Mag Coking process. The crane cab is offset from directly over the ladle as shown in Diagram C. Depending on the wind strength and direction, the crane cab is more or less in the plume of emissions from the Mag Coking operation. The crane cabs are enclosed and air conditioned, however, the air conditioning system is not filtered efficiently.

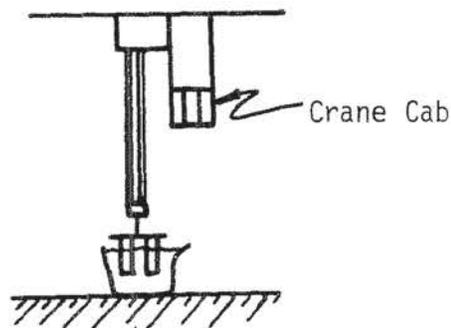


Diagram C

The groundmen assigned to the Hot Metal Station either remain in their operating enclosure or at a safe distance from the ladle during the Mag Coking operation. Most of the emissions are carried to the upper reaches of the BOF building, thus, exposure of personnel at ground level is minimal. Groundmen could possibly be injured by splashes of molten metal during the vigorous reaction of the Mag Coke<sup>®</sup>.

Seven to eight BOF heats are made during each eight hour workshift. Each heat requires one ladle of blast furnace iron and a charge of scrap. The Mag Coking operation is highly variable in frequency, but approximately three heats or ladles per eight hour shift require Mag Coke<sup>®</sup> treatment. On some shifts, no Mag Coke<sup>®</sup> is used and on others every heat requires Mag Coke<sup>®</sup> treatment.

### C. Evaluation Methods

#### 1. Employee Interviews

Employees were privately asked non-directed followed by directed questions regarding their health and employment. Employee responses were recorded and later discussed with NIOSH physicians in Cincinnati.

#### 2. Environmental Sampling

Workroom concentrations of carbon monoxide, oxides of nitrogen, and sulfur dioxide were measured using Draeger gas detector tubes. Airborne particulate concentrations were measured using MSA Model G battery powered pumps and preweighed PVC filters. Filters were gravimetrically analyzed for total particulate and then wet ashed so that magnesium could be determined by Atomic Absorption spectroscopy. Additionally, both total and respirable airborne particulate concentrations were measured using a Model RDM-101 Respirable Dust Monitor manufactured by the Technology Division of GCA Corporation. Particulate concentrations obtained with this instrument are reported by its manufacturer to be within + 25% of the true concentration at the 95% confidence level. Using known concentrations of coal dust, NIOSH has recently confirmed the advertised accuracy of this instrument.<sup>1</sup>

D. Evaluation Criteria

The three primary sources of environmental evaluation criteria considered in this report are: (1) NIOSH Criteria Documents recommending occupational health standards, (2) American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values with supporting documentation, and (3) federal occupational health standards. For brevity, federal standards are used as reference points in the following presentation of evaluation criteria.

The occupational health standards promulgated by the U.S. Department of Labor (Federal Register, June 27, 1974, Vol. 39, No. 125, Title 29, Chap. XVII, Part 1910, Subpart G, Table G-1) applicable to the individual substances of this evaluation are as follows:

Substance	8-hour Time-Weighted-Average Exposure Standard	
	ppm <sup>a</sup>	mg/M <sup>3</sup> <sup>b</sup>
Magnesium Oxide Fume <sup>c</sup> (MgO)		15
Carbon Monoxide <sup>d</sup> (CO)	50	
Nitrogen Dioxide <sup>e</sup> (NO <sub>2</sub> )	5	
Nitric Oxide (NO)	25	
Sulfur Dioxide (SO <sub>2</sub> ) <sup>f</sup>	5	

<sup>a</sup> Parts of vapor or gas per million parts of contaminated air by volume.

<sup>b</sup> Approximate milligrams of particulate per cubic meter of air.

<sup>c</sup> The ACGIH in its Threshold Limit Values for Chemical Substances in Workroom Air recommend that employee exposure to Magnesium Oxide Fume (MgO) be controlled to 10 mg/M<sup>3</sup> on an 8-hour time-weighted-average basis.

<sup>d</sup> NIOSH in its Criteria for a Recommended Standard - Occupational Exposure to Carbon Monoxide recommends that employee exposure to Carbon Monoxide be controlled to 35 ppm on an 8-hour time-weighted-average basis, and that employees should never be exposed to concentrations of Carbon Monoxide in excess of 200 ppm.

<sup>e</sup> The ACGIH recommends that employee exposure to Nitrogen Dioxide should never exceed the 5 ppm level.

<sup>f</sup> NIOSH in its Criteria for a Recommended Standard - Occupational Exposure to Sulfur Dioxide recommends that employee exposure to Sulfur Dioxide be controlled to 2 ppm on an 8-hour time-weighted-average basis.

Occupational health standards for individual substances are generally established at levels designed to protect workers occupationally exposed on an 8-hour per day, 40-hour per week basis over a working lifetime.

E. Evaluation Results

1. Employee Interviews

Four of a total of six (4 of 6) crane operators and three of a total of six (3 of 6) groundmen at the Hot Metal Station were interviewed.

Three of the four crane operators interviewed related the occurrence of symptoms to the Mag Coking operation. One crane operator stated that the Mag Coking emissions cause a headache which can be prevented by breathing through a handkerchief during the operation. A second crane operator stated that the Mag Coking emissions cause a drying sensation in his sinuses which results in a runny or drippy nose after shift. A third crane operator stated that the Mag Coking emissions cause a mild cough which subsides with cessation of exposure. This crane operator also stated that he smokes approximately four packages of cigarettes per day. A fourth crane operator reported no health complaints.

None of the three groundmen interviewed reported any health complaints in association with the Mag Coking operation.

Many of the men interviewed felt that the Mag Coking operation should be conducted in the Charging Aisle next to the Slag Skimmer and not in the Ladle Pits at the Hot Metal Station. This mode of operation would reduce the danger from spills of molten iron caused by the vigorous Mag Coking reaction. When Mag Coking is conducted in the Ladle Pits at the Hot Metal Station, there is a danger that molten iron will spill over and fall onto accumulations of moisture in the bottom of the pits and produce an explosion-like reaction.

## 2. Environmental Sampling

Gas detector tube measurements for carbon monoxide (CO), oxides of nitrogen (NO + NO<sub>2</sub>), and for sulfur dioxide (SO<sub>2</sub>) were made in the East Crane Cab during both the 1st and 2nd workshifts on June 21, 1974. The results of this sampling follow:

### 1st Shift

#### Carbon Monoxide Measurements

- 1) Crane cab air conditioning on; windows open. Less than 5 ppm of carbon monoxide detected.
- 2) Crane cab air conditioning on; windows closed. Less than 5 ppm of carbon monoxide detected.
- 3) Crane cab air conditioning on; windows closed; Mag Coking in progress. Less than 5 ppm of carbon monoxide detected.

#### Measurements for Oxides of Nitrogen (NO+ NO<sub>2</sub>)

- 1) Crane cab air conditioning on; windows closed; Mag Coking in progress. No oxides of nitrogen were detected. (Method sensitive to approximately 0.5 ppm)

#### Sulfur Dioxide Measurements

- 1) Crane cab air conditioning on; windows closed; Mag Coking in progress. No sulfur dioxide was detected. (Method sensitive to approximately 1.0 ppm)

2nd Shift

## Carbon Monoxide Measurements

- 1) Crane cab air conditioning off; windows open. Less than 5 ppm of carbon monoxide detected.
- 2) Crane cab air conditioning off; windows open; ladle maneuvering in progress. Less than 5 ppm of carbon monoxide detected.
- 3) Crane cab air conditioning off; windows closed; Mag Coking in progress. Less than 5 ppm of carbon monoxide detected.

Measurements for Oxides of Nitrogen (NO + NO<sub>2</sub>)

- 1) Crane cab air conditioning off; windows closed; Mag Coking in progress. No oxides of nitrogen were detected.

## Sulfur Dioxide Measurements

- 1) Crane cab air conditioning off; windows closed; Mag Coking in progress. No sulfur dioxide was detected.

Although carbon monoxide, oxides of nitrogen, and sulfur dioxide were suspected to be possible emissions from the Mag Coking operation, the above data show that they present no apparent health hazard to crane operators.

Measurement of employee exposure to airborne particulate and, in particular, to magnesium oxide fume was accomplished using both personal breathing zone and area sampling techniques. Employees assigned to the Hot Metal Station were asked to wear total mass, personal sampling equipment for a portion of their workshift. In each case, one ladle of blast furnace iron was treated with Mag Coke<sup>®</sup> during the period sampled. The results of this sampling are shown below:

<u>Shift</u>	<u>Job</u>	<u>Sampling Interval</u>	<u>Magnesium Oxide Fume</u>	<u>Total Airborne Particulate</u>
1	Hot Metal Car Operator	12:12 to 2:45 PM	0.03 mg/M <sup>3</sup>	2.3 mg/M <sup>3</sup>
1	Hot Metal Tender	12:12 to 2:45 PM	0.06 mg/M <sup>3</sup>	4.0 mg/M <sup>3</sup>
2	Hot Metal Car Operator	3:21 to 4:31 PM	N.D.*	N.D.*

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\* N.D. = None Detected. The monitored employee remained inside the operator's station during much of the sampling period.

As can be seen from these data, the groundmen at the Hot Metal Station experience minimal exposure to magnesium oxide fume. They spend a large portion of their workshift inside the operator's station and most of the emissions from the Mag Coking operation are carried to the upper reaches of the BOF building. Although not specifically analyzed for compounds other than magnesium oxide, the material reported as "total airborne particulate" can be assumed to contain carbon particulate and iron oxide which are both byproducts of the BOF steel making and Mag Coking processes.

Measurement of crane operator exposures to emissions from the Mag Coking operation was complicated by the short duration of the procedure (approximately 12 minutes). To insure that sufficient material would be collected to permit meaningful laboratory analysis, a filter sample was obtained from a location just outside the crane cab during both the first and second Mag Coking operations. The results of this sampling follow:

<u>Shift</u>	<u>Sampling Interval</u>	<u>Magnesium Oxide Fume</u>	<u>Total Airborne Particulate</u>
1	12:30 to 12:52 PM	11 mg/M <sup>3</sup>	22 mg/M <sup>3</sup>
2	3:56 to 4:15 PM	1.9 mg/M <sup>3</sup>	6.8 mg/M <sup>3</sup>

These data show that magnesium oxide fume concentrations outside the crane cab are dependent on air movement inside the BOF building. During collection of the first shift sample, the plume of Mag Coking emissions was rising almost directly to the crane cab from the charging ladle. In contrast, at the time the second shift sample was collected a breeze was blowing a significant portion of the emissions away from the crane cab.

Total and respirable airborne particulate measurements were made inside the crane cab before, during, and after the Mag Coking operation using a GCA Corporation, Model RDM-101 Respirable Dust Monitor. Although these measurements were not specific for magnesium oxide fume, iron oxide, or carbon particulate, it can be concluded that no one of these materials was present in concentrations in excess of the concentrations indicated by the instrument. The results of this sampling follow:

#### 1st Shift

- Measurement No. 1: Crane cab air conditioning off; windows closed; prior to Mag Coking operation.  
Total particulate = 0.04 mg/M<sup>3</sup> (12:00 noon)
- Measurement No. 2: Crane cab air conditioning on; windows closed; prior to Mag Coking operation.  
Total particulate = 0.02 mg/M<sup>3</sup> (12:04 P.M.)

- Measurement No. 3: Crane cab air conditioning on; windows closed; ladle of iron being poured into BOF. Total particulate = 0.06 mg/M<sup>3</sup> (12:15 P.M.)
- Measurement No. 4: Crane cab air conditioning on; windows closed; Mag Coking in progress at Hot Metal Station. Total particulate = 2.2 mg/M<sup>3</sup> (12:35 P.M.)
- Measurement No. 5: Crane cab air conditioning on; windows closed; Mag Coking in progress at Hot Metal Station. Total particulate = 1.1 mg/M<sup>3</sup> (12:40 P.M.)
- Measurement No. 6: Crane cab air conditioning on; windows closed; Mag Coking in progress at Hot Metal Station. Total particulate = 3.0 mg/M<sup>3</sup> (12:45 P.M.)

### 2nd Shift

- Measurement No. 1: Crane cab air conditioning on; windows open; prior to Mag Coking operation. Total particulate = 0.5 mg/M<sup>3</sup> (3:35 P.M.)
- Measurement No. 2: Crane cab air conditioning on; windows open; prior to Mag Coking operation. Respirable particulate = 0.26 mg/M<sup>3</sup> (3:40 P.M.)
- Measurement No. 3: Crane cab air conditioning off (simulating wintertime operation); windows closed; Mag Coking in progress in Charging Aisle at Slag Skimmer. Respirable particulate = 2.8 mg/M<sup>3</sup> (3:56 P.M.)
- Measurement No. 4: Crane cab air conditioning off (simulating wintertime operation); windows closed; Mag Coking in progress in Charging Aisle at Slag Skimmer. Total particulate = 3.2 mg/M<sup>3</sup> (4:02 P.M.)
- Measurement No. 5: Crane cab air conditioning off (simulating wintertime operation); windows closed; Mag Coking in progress in Charging Aisle at Slag Skimmer. Respirable particulate = 2.0 mg/M<sup>3</sup> (4:06 P.M.)
- Measurement No. 6: Crane cab air conditioning off (simulating wintertime operation); windows closed; during retraction of coking apparatus from ladle. Total particulate = 1.5 mg/M<sup>3</sup> (4:11 P.M.)

From the above data it is evident that airborne particulate concentrations (magnesium oxide fume, etc.) are not excessive inside the crane cab during the Mag Coking operation. Furthermore, the duration of exposure is small (Maximum of eight heats per shift using Mag Coke<sup>®</sup> with approximately twenty minutes of exposure per heat which translates into a maximum of less than three hours of total exposure).

#### F. Conclusions and Recommendations

Exposure of groundmen and crane operators to emissions from the Mag Coking operation has been evaluated. Airborne concentrations of carbon monoxide, oxides of nitrogen, sulfur dioxide, and particulate (especially magnesium oxide fume) to which the seven employees (4 crane operators and 3 groundmen) monitored were exposed, were all found to be well below currently accepted levels for occupational exposure. Two crane operator employees reported minor symptomatology consistent with low level exposure to freshly generated metal fume (drying sensation in sinuses resulting in drippy nose; stimulation of mild cough in heavy smoker). The occurrence of mild headache in one crane operator employee can not be explained by exposure to magnesium oxide fume or to carbon monoxide, but may be related to the stress and exacting nature of the crane operator work.

It is recommended that Mag Coking be performed in the Charging Aisle next to the Slag Skimmer and not in the pits at the Hot Metal Station. This work practice should help to minimize the safety hazard associated with splashes of molten metal.

#### V. REFERENCES

1. Solomon, M., B.P. Almich, and G.A. Carson, Ph.D., A Theoretical and Laboratory Evaluation of a Portable Direct Reading Particulate Mass Concentration Instrument. Paper presented at the May, 1974 American Industrial Hygiene Conference, Miami, Florida.

#### VI. AUTHORSHIP AND ACKNOWLEDGMENT

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