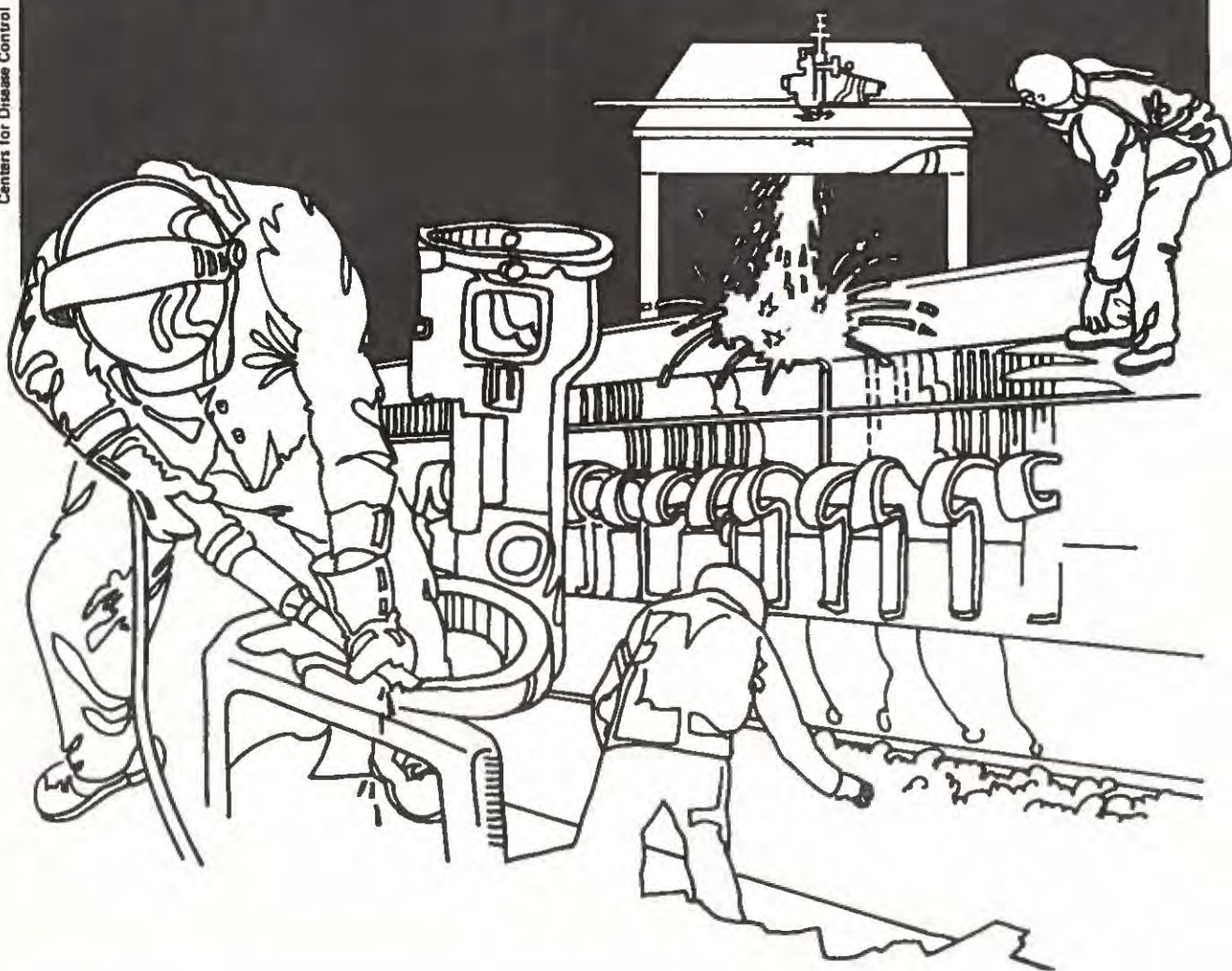


# NIOSH



## Health Hazard Evaluation Report

HHE 80-025-989  
U.S. STEEL, TUBING SPECIALTIES  
GARY, INDIANA

## 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.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.



HHE 80-025-989  
November 1981  
U.S. Steel, Tubing Specialties  
Gary, Indiana

NIOSH INVESTIGATORS:  
William J. Daniels, I.H.  
Peter Orris, M.D.

## I. SUMMARY

In November, 1979, the National Institute for Occupational Safety and Health (NIOSH) received a request from the United Steel Workers of America, Local 2697, for a health hazard evaluation at the United States Steel Corporation, Tubing Specialties, Gary, Indiana. The requestor was concerned with possible adverse health effects resulting from employee exposure to sulfuric acid mist at pickling operations within the plant.

NIOSH investigators conducted an initial survey in January 1980. In February 1980, environmental samples were collected to assess 8-hour time weighted average (TWA) exposures to sulfuric acid. In August 1981, additional environmental samples were collected to assess short-term (15 minute) exposure to sulfuric and phosphoric acid. Follow-up medical surveys were conducted in October 1980 and January 1981. Confidential interviews and pulmonary function tests were administered to all employees working at the pickling operations.

Analysis of the environmental data indicated that levels of sulfuric acid were below the NIOSH recommended standard, and the Occupational Safety and Health Administration (OSHA) standard, of one milligram per cubic meter of air ( $1 \text{ mg/m}^3$ ) for an eight-hour time weighted average (TWA). Personal exposures to sulfuric acid in long-term (TWA) samples ranged from  $0.08$  to  $0.47 \text{ mg/m}^3$ , with a mean value of  $0.17 \text{ mg/m}^3$ . Only one of six short-term samples was above the NIOSH limit of detection, with a concentration of  $0.93 \text{ mg/m}^3$  for a 15 minute sample period. There is currently no ceiling criteria for sulfuric acid. Phosphoric acid was not detected in the long or short term samples.

Analysis of the medical questionnaires revealed significant irritative effects from exposure to the sulfuric acid mist. Of 17 employees, 94% reported mucous membrane irritation, 65% shortness of breath, 71% chronic cough, and 88% chronic sputum production. The results of the pulmonary function tests were within normal limits, indicating no substantial long term pulmonary problems.

Based on data obtained in this investigation, NIOSH determined that a potential for ill effects from exposure to sulfuric acid mist exists at the pickling operations. Measured concentrations of the acid were below the OSHA standard of  $1 \text{ mg/m}^3$ , but were, nonetheless, found to cause respiratory irritation among the employees. Recommendations for work practice and engineering controls, designed to alleviate this exposure hazard, are incorporated in Section VIII.

KEY WORDS: SIC 3317, sulfuric acid, batch pickling, irritative effects, chronic cough, chronic sputum, shortness of breath.



## II. INTRODUCTION

On November 14, 1979, NIOSH received a request from an authorized representative of the United Steel Workers of America, Local 2697, for a health hazard evaluation at the United States Steel Corporation, Tubing Specialties, Gary, Indiana. The requestor was concerned with possible adverse health effects resulting from employee exposure to sulfuric acid mist at pickling operations within the plant.

NIOSH investigators conducted an initial survey on January 15, 1980. An opening conference was held with representatives of management and the local union, followed by a walk-through inspection of the pickling areas. Confidential interviews were conducted with all employees working at the pickling operations. On February 12-13, 1980, and August 6, 1981, environmental samples were collected to assess 8-hour TWA and short term exposures to sulfuric acid and phosphoric acid. On October 28, 1980 an additional questionnaire was administered to the employees involved in the pickling operations, followed by pulmonary function tests on January 27, 1981.

## III. BACKGROUND

### A. General Description of Pickling

Pickling, or acid descaling, is an industrial process in which scale and oxides are chemically removed from a metallic surface by immersion in a dilute inorganic acid bath. Hydrogen bubbles and steam resulting from the process carry acid mist from the surface of the solution into the surrounding environment. The rate of pickling, and hence the rate of hydrogen evolution and mist formation, depends on many factors. Increasing the concentration of the acid from 0% to about 25% by weight will result in a direct increase in the pickling rate. Increasing the temperature of the bath causes an even greater increase in the pickling rate. For example, with 15% sulfuric acid, an increase in temperature between 20° and 100° Celsius (C) doubles the pickling rate for each rise of 8-11°C.<sup>1</sup> Additionally, many higher alloy steels react more rapidly with the acid causing a greater amount of mist than that normally generated. In many instances inhibitors are added to the dilute acid solution to lessen the attack of the acid on the metal, without affecting the pickling action. The inhibitor usually contains a foaming agent which produces a layer of foam on the surface of the bath and reduces the escape of acid mist.

### B. General Description of Plant Operations and Workforce

Established in 1926, the plant is engaged in the manufacture of seamless steel tubing. Production is estimated at 13,000 tons a month, with approximately one-fifth of the tubing being pickled. The plant workforce consists of 1,350 production and 250 administrative personnel, of which 14 production and 2 administrative employees are involved directly with the pickling operations. Pickling is conducted in the center of the "tube hollow conditioning room" and in the center of the "main plant building"; which are referred to in this report as the "east" and "west" pickling operations, respectively. Both are batch type operations and normally operate two shifts per day.



### C. Specific Processes and Employee Duties

A solution of 10% sulfuric acid is initially added to the pickling tanks in both areas. This solution is replaced when the concentration diminishes below 1% (about once per week). The temperature of the tanks is adjusted between 49° and 82°C, depending on the acid concentration and the type of steel to be treated.

The pickling process in the east area begins when a quantity of steel pipe (the charge) is lowered by crane into one of two sulfuric acid tanks. The charge is next hoisted by the crane and lowered into an adjacent water tank for rinsing. The charge is then placed in a neutralizing tank which prevents further pickling action. Operations on each shift are conducted by three employees. The "craneman", located in the cab of the overhead crane, is responsible for transporting the charges through the various tanks during the pickling process. Each charge is held by two chains which are manually hooked and unhooked from the crane. This enables the craneman to perform other duties during the time which a charge must remain in an acid tank. The "batch pickler" is responsible for directing the overall operation. This includes selecting the charges for pickling, monitoring the acid concentration and temperature, and determining the time that each charge will spend in the acid tank. The "tub cleaner" is responsible for assembling the charges to undergo pickling and cleaning out the various tanks after they are drained. Additionally, the batch pickler and the tub cleaner help direct the charges into the tanks, and subsequently remove the chain hooks from the crane.

The pickling sequence on the west side differs from that of the east side due to the use of two additional tanks in the process. A phosphoric acid tank is used for additional pickling, and a tank containing a lubricant is used to prepare the pipe for further processing. Since it is a more involved process, an additional "pickle helper" is utilized in the west pickling operation. This employee is located in the tank area and is responsible for helping assemble the charges, directing the charges into the tanks, and removing the chains from the charges.

### D. Control of Exposure

Control of the acid temperature and concentration, and the use of a foamer and inhibitor in the bath, slow the rate of pickling and minimize the escape of acid mist. Dilution ventilation is provided through ceiling exhaust fans and openings in the building structure. Personal protective equipment consists of hardhats, safety boots, chemical goggles, and rubber gloves. Emergency showers and eye wash stations are present in each of the pickling areas. Respiratory protection is not worn by the employees.

## IV. METHODS AND MATERIALS

### A. Environmental Survey of February 1980

Based on the significant potential for exposure in each of the various jobs, all 14 production employees in the pickling operations were selected for personal sampling. Sample collection was conducted near the employees breathing zone to assess exposure to sulfuric acid mist. Samples were collected using battery powered pumps operating at 1.5 liters per minute (lpm) attached via tygon tubing to 37 mm diameter mixed cellulose ester membrane



filters (AA) held in closed-faced cassettes. The duration of each sample is given in Table 1. Upon completion of sampling, the filters were transferred to screw cap bottles and subsequently analyzed via ion chromatography for sulfuric acid.

In order to assess the magnitude of short-term exposures to sulfuric acid, samples were collected during tasks requiring the workers to be in close proximity to the pickling tanks. The samples were collected using battery powered pumps operating at 1.0 lpm attached via tygon tubing to the collecting media. Pre-washed silica gel tubes were selected as the collection media for short-term samples due to their inherently lower background levels of the specific acid anions, when compared to the membrane filters. One long term sample was collected from each area to determine the TWA exposure. The samples were analyzed for sulphuric acid via ion chromatography. In addition, the samples collected on the west side pickling operation were also analyzed for phosphoric acid, due to its limited use in that area. Information pertinent to sample collection is given in Table 1. The analytical methods are detailed in Appendix 1.

#### B. Medical

During the course of the evaluation, NIOSH investigators conducted medical interviews with a total of seventeen employees; those employees currently working at the pickling operations, as well as 3 former employees. These interviews consisted of the administration of a questionnaire designed to gather information on the employees work and medical histories, and the presence of work related health problems. Additionally, a supplemental questionnaire was administered which pertained specifically to respiratory problems (Appendix 2). Pulmonary Function Testing (spirometry) was conducted by a Certified Pulmonary Function Technician using a Spirotech 2008. Exposed teeth were examined for mottling and discoloration on 16 of the employees by a NIOSH investigator.

### V. EVALUATION CRITERIA

#### A. Adverse Health Effects

Sulfuric acid mist exposure can cause irritation of the mucous membranes. The mist also causes etching of the dental enamel followed by erosion of the enamel and dentine with loss of tooth substance. Central and lateral incisors are mainly affected. Breathing high concentrations of sulfuric acid causes tickling in the nose and throat, sneezing, and coughing. At lower levels of exposure sulfuric acid causes a reflex increase in respiratory rate and diminution of depth, with reflex bronchoconstriction resulting in increased pulmonary air flow resistance. Repeated excessive exposure over long periods have resulted in bronchitic symptoms, rhinorrhea, lacrimation, and epistaxis. Long term exposures may also result in conjunctivitis, frequent respiratory infections, emphysema, and digestive disturbances.<sup>2</sup>

Leikauf, et. al. 1981, reported that exposures to 0.11 mg/m<sup>3</sup> sulfuric acid mist stimulated, and 0.98 mg/m<sup>3</sup> retarded mucociliary transport in healthy non-smoking volunteers.<sup>3</sup> Lippman, et. al. 1980, further reported that donkeys exposed to 0.1 mg/m<sup>3</sup> of sulfuric acid mist for one hour daily for six months developed mucociliary clearance abnormalities that persisted for at least three months following cessation of exposure.<sup>4</sup> Another study of



mucociliary clearance by Newhouse et. al. 1978, demonstrated increased clearance at the  $1 \text{ mg/m}^3$  level in health non-smoking adults.<sup>5</sup> The difference in findings has been postulated to be attributable to the blockage of the nasal passages in the Newhouse study and the possible accumulation of neutralizing ammonia secondary to that blockage.

With respect to pulmonary function testing, no changes in FEV<sub>1</sub> or FVC have been noted in the literature at these low levels of exposure. Newhouse et. al. found a slight decrease in FEF<sub>25-75</sub> following exposure to  $1 \text{ mg/m}^3$  of sulphuric acid aerosol for a two hour period.<sup>5</sup> Morrow, et. al. 1979, reported a small decrease in specific airway conductance at the  $1 \text{ mg/m}^3$  exposure level.<sup>6</sup>

## B. Environmental Criteria

The NIOSH recommended standard, and the current Occupational Safety and Health Administration (OSHA) standard, for exposure to sulfuric acid mist is one milligram per cubic meter of air ( $1 \text{ mg/m}^3$ ) determined as an 8-hour time weighted average (TWA).<sup>7</sup> It is believed that concentrations below this limit represent conditions under which nearly all workers may be repeatedly exposed 8-10 hours per day, 40 hours per week, without suffering adverse health effects. Due to variations in individual susceptibility, a small percentage of workers may experience effects at levels at or below this environmental limit; a smaller percentage may be more seriously affected by aggravation of a pre-existing condition or by a hypersensitivity reaction.<sup>8</sup>

## C. Medical Criteria

### 1. Chronic Cough

The literature was reviewed to establish historical controls for this cohort. The prevalence of chronic cough in 1,274 male factory workers without overt evidence of pulmonary or heart disease was found to be 2.0% in nonsmokers and 51.0% in smokers, by Phillips et. al. in 1956.<sup>9</sup> In another study of 4,218 male and female postal employees it was noted that 7.0% of nonsmokers, 12.4% of pipe or cigar smokers, and 27.0 % of cigarette smokers had a chronic cough.<sup>10</sup> The Health and Nutrition Examination Survey done between 1971 and 1975 questioned 1,000 white male blue collar workers throughout the country, and found that 210 (21%) of the 996 workers responding reported a morning cough in summer or winter (adjusted for age, sex, race, and smoking habits of the examined population).<sup>11, 11a</sup>

### 2. Chronic Sputum Production

The prevalence of chronic sputum production, found in a study of 1,451 male light industry workers in California was 11.0% for nonsmokers and 30.4% for smokers.<sup>12</sup> An English study in 1955 found the prevalence of habitual cough and sputum production to be 15.8% in 474 nonsmoking and 18.4% in 1,940 smoking male clerical workers.<sup>13</sup> The Health and Nutrition Examination Survey indicated that 201 (20%) of the 990 employees responding produced morning phlegm in winter or summer (adjusted for age, sex, race, and smoking habits of the examined population).<sup>11, 11a</sup>

### 3. Dyspnea

The prevalence of shortness of breath on walking up a slight hill was found to be 25.6% in reviewing the responses to the Health and Nutrition Examination Survey. This was calculated on the basis of 254 positive answers from a total group of 991 (adjusted for age, sex, race, and smoking habits of the examined population).<sup>11, 11a</sup>



#### 4. Pulmonary Function Tests

Normal values for Pulmonary Function Tests were developed by Ronald J. Knudson et. al. in 1976. They established predictive normal pulmonary function tables for the U.S. population, corrected for age and height. A value of 80% or greater for the subject's Forced Vital Capacity (FVC) and One Second Forced Expiratory Volume (FEV<sub>1</sub>) when compared with the predicted is considered normal. A ratio of FEV<sub>1</sub>/FVC of 75% or greater is considered normal as well.<sup>14</sup>

## VI. RESULTS

### A. Environmental

In the environmental survey of February 1980, the TWA concentrations for the long term personal air samples for sulfuric acid ranged from 0.08 to 0.47 mg/m<sup>3</sup>, with a mean value of 0.17 mg/m<sup>3</sup>. When dividing the results between the two operations, exposures on the east side ranged from 0.16 to 0.47 mg/m<sup>3</sup>, with a mean value of 0.26 mg/m<sup>3</sup>, while exposures for the west side ranged from 0.08 to 0.14 mg/m<sup>3</sup>, with a mean value of 0.11 mg/m<sup>3</sup>.

In the environmental survey of August 1981, of the six samples collected to assess short-term exposure to sulfuric acid, only one sample was above the limit of analytical detection (0.67 mg/M<sup>3</sup> for a 15 minute sample at 1.0 lpm) with a concentration of 0.97 mg/m<sup>3</sup>. All samples collected for phosphoric acid were below the limit of analytical detection (0.67 mg/M<sup>3</sup> for a 15 minute sample at 1.0 lpm). A detailed listing of the environmental results is given in Table 1.

### B. Medical

The environmental data indicated a small increase in sulfuric acid exposure on the part of the workers in the east area as opposed to those in the west. Therefore, the medical data was divided along these lines to assess whether this increase was significant with respect to symptomatology or physical findings.

Of the 16 men and 1 woman working in the two areas, there appeared to be no significant difference in symptoms reported. In the overall group of 17 employees, 94% reported some mucous membrane irritation, 65% indicated shortness of breath, 71% chronic cough, and 88% chronic sputum production. A detailed listing of the symptomatology is given in Table 2.

The proportion of smokers and ex-smokers were equal for both groups, with current and ex-smokers accounting for 70% of the surveyed employees. This information, is detailed in Tables 4 and 5.

Due to the large number of employees with substantial dental disease throughout their mouths, and others with prostheses, examination of the teeth of the employees by the NIOSH investigators did not demonstrate identifiable reactions to sulfuric acid mist (e.g. mottling). Results indicated 4 of 7 (67%) employees on the east side and 1 of 10 (10%) employees on the west side with discoloration of exposed teeth.



The pulmonary function tests were within normal limits, with the exception of those individuals that reported upper respiratory infections within the last month. Despite a median age of 48.3 years for the workers on the west side and 39.7 years for those on the east, the west side workers had consistently better FVC and FEV<sub>1</sub> values than the east side workers. However, these differences were not statistically significant even when corrected for age. Results of the pulmonary function tests are summarized in Tables 5 and 6.

## VII. DISCUSSION AND CONCLUSIONS

### A. Environmental

Analysis of the environmental samples indicated that all exposures were below the environmental criteria for sulfuric acid; however, in light of the results of the medical survey, further discussion of these results is appropriate.

Based on observation of employee work practices, it appeared that a large portion of the employee exposure occurred when the employee was in close proximity to the sulphuric acid tank (e.g., when directing charges into the tank and removing the chain hooks). This was especially true immediately after the charge was lowered into the acid tank and the rate of mist formation would be greatest. A short term sample indicated that an employee was exposed to 0.96 mg/M<sup>3</sup> during the performance of this task, however, the actual time spent at the pickling tank by the employee was only a small percentage of the 15 minute sampling period, and the peak exposure was probably much higher.

Crane operators were exposed to the acid in a different manner than that of employees working at the pickling tanks. Although the crane cab is not positioned directly above the acid tanks, the operator could receive a significant exposure due to movement of the rising acid mist by the air currents within the building. The highest TWA exposure to sulfuric acid exposure was recorded for the east craneman (0.47 mg/m<sup>3</sup>), while exposure for the west craneman was comparatively low (0.08 and 0.10 mg/m<sup>3</sup>). The difference in these exposures most likely results from the absence of an air-conditioned crane cab on the east side.

### B. Medical

Two design problems hinder the ability to draw conclusions from this study. The small size of the cohort does not allow for a precise analysis of minimal to moderate effects of the acid fumes. Secondly, the pulmonary function tests, as performed, could be expected to show only substantial reductions in lung functioning, not early changes in function.

In light of these study design problems, and reflecting on the acute and possibly chronic pulmonary function changes noted in the literature in laboratory settings with sophisticated and far more sensitive equipment than used in this study, the finding of essentially normal pulmonary function tests must be considered with some caution.

No significance could be attached to the dental examination, due to the existence of numerous prostheses and generalized tooth decay, which did not allow for a true estimate of the effects of the low level acid mist exposure.



With respect to symptomatology, almost all employees in the pickling areas reported mucous membrane irritation. Further, there would appear to be a substantial increase in all assessed symptoms above what would be expected in the U.S. population. Specifically, the incidence of shortness of breath and chronic cough and sputum production in this group of workers is far higher than what one would expect. This is not accounted for by the number of smokers in the cohort. Due to the small size of this study population, most of the results were not statistically significant when compared with the historical controls. However, when the Health and Nutrition Examination Survey findings were compared with the responses in this study, the results were different. The data, adjusted for age and smoking, indicated significant increases in the amount of dyspnea, cough, and phlegm reported in the exposed workers. The relative risk for an employee in this study to have dyspnea was 3.73 (p less than 0.02), cough was 4.78 (p less than 0.01), and Phlegm was 8.64 (p less than 0.001). The significance was calculated utilizing the Fisher's exact test due to the small cohort (Table 7). These symptomatologic findings are consistent with the recent human laboratory evidence of changes in the mucociliary clearance time at these exposure levels.

Therefore, it would appear that the level of employee exposure to sulfuric acid mist during the performance of work duties, which is below the NIOSH recommended standard, produces substantial irritative effects; however, these effects could not be quantitated objectively by the methods used in this study.

#### VIII. RECOMMENDATIONS

The following recommendations are made in order to alleviate the possibility of further irritative effects of the sulfuric acid mist.

1. The acid strength and temperature should be closely regulated to maintain effective pickling action and minimal generation of acid mist, particularly during the treatment of the more reactive steel alloys. Small changes in these process variables can greatly influence the rate of mist production.
2. The inhibitor/foaming agent(s) presently used should be evaluated for proper use. The effectiveness of these substances should be periodically evaluated as elevated bath temperatures over long periods of time may thermally degrade these protective substances. The feasibility of the use of chips, additional foaming agent, or other surface active agents should be examined.
3. If process controls fail to substantially reduce exposures to the acid mist, the possible addition of exhaust ventilation at the pickling tanks should be examined. A detailed discussion of ventilation design specifications can be found in Industrial Ventilation, by the American Conference of Governmental Industrial Hygienists.<sup>15</sup>
4. The employees should remain at a reasonable distance from the sulfuric acid tanks during the initial placement of the charge into the acid bath when the greatest potential for mist production would be present.
5. It would be prudent to install an air filtration system in the east side crane cab to reduce the possibility of exposure to the acid mist adversely affecting job performance and possibly endangering the safety of employees working at the pickling tanks.



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#### X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared By: William J. Daniels, Industrial Hygienist  
Peter Orris, M.D., Medical Officer  
NIOSH - Region V  
Chicago, Illinois

Environmental Evaluation: Thomas F. Bloom, C.I.H.  
Industrial Hygienist  
Division of Surveillance Hazard  
Evaluations & Field Studies  
Cincinnati, Ohio

Originating Office: Division of Surveillance Hazard  
Evaluations & Field Studies  
Hazard Evaluation and  
Technical Assistance Branch  
Cincinnati, Ohio

Analytical Laboratory Services: Utah Biomedical Test Laboratory  
Salt Lake City, Utah

#### XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Services (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH publications office at the Cincinnati address. Copies of this report have been sent to the following:

- A. United Steel Workers of America, Local No. 2697
- B. United States Steel Corporation, Tubing Specialties, Gary, Indiana
- C. U. S. Department of Labor, OSHA - Region V
- D. NIOSH Regional Offices/Divisions

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



Table 1

RESULTS OF PERSONAL SAMPLING FOR SULFURIC ACID  
(Concentrations Expressed as TWA for the Sample Duration)

<u>Job Location/Title</u>	<u>Sample Date</u>	<u>Sample Volume (Liters)</u>	<u>Sample Duration (minutes)</u>	<u>Concentration (mg/m<sup>3</sup>)</u>
West Pickler	2/12/80	644	428	0.09
West Tub Cleaner	2/12/80	633	422	0.10
West Pickle Helper	2/12/80	633	422	0.13
West Crane Operator	2/12/80	622	415	0.08
East Pickler	2/12/80	590	393	0.16
East Tub Cleaner	2/12/80	590	393	0.20
East Crane Operator*	2/12/80			
West Pickle Helper	2/13/80	638	425	0.14
West Crane Operator	2/13/80	662	441	0.10
West Pickler	2/13/80	627	418	0.11
West Tub Cleaner	2/13/80	628	419	0.13
East Tub Cleaner	2/13/80	627	418	0.24
East Pickler	2/13/80	435	290	0.25
East Crane Operator	2/13/80	615	410	0.47
West Tub Cleaner*	8/6/81	81	406	
West Pickle Helper	8/6/81	15	15	0.97
	8/6/81	15	15	ND
	8/6/81	16	16	ND
East Pickle Helper	8/6/81	75	375	ND
East Pickler	8/6/81	15	15	ND
	8/6/81	26	26	ND
	8/6/81	15	15	ND

\* Samples void

ND = none detected (Samples were below the level of analytical detection of 10 micrograms per sample.)

Note: Samples for West Tub Cleaner and Pickle Helper were also analyzed for phosphoric acid. All samples were below the limit of analytical detection of 10 micrograms per sample.



TABLE 2

REPORTED SYMPTOMS FROM EXPOSURE TO SULFURIC ACID MIST  
(Expressed in the Number (n) and Percentage (%) of Employees)

Symptom	East (n=7)		West (n=10)		Combined (n=17)	
	n	%	n	%	n	%
Chronic Cough	5	71%	7	70%	12	71%
Chronic Sputum Production	7	100%	8	80%	15	88%
Shortness of Breath With Exercise	4	57%	7	70%	11	65%
Chronic Sinus Congestion	6	86%	6	60%	12	71%
Chronic Rhinitis	5	71%	7	70%	12	71%
Epistaxis	2	29%	3	30%	5	29%
Dry Throat	5	71%	7	70%	12	71%
Eye Irritation	4	57%	8	80%	12	71%
Headaches	2	29%	5	50%	7	41%
Skin Rash	5	71%	5	50%	10	59%
All Mucous Membrane Irritation	7	100%	9	90%	16	94%

Table 3

CLASSIFICATION OF PICKLING EMPLOYEES BY SMOKING HISTORY  
(Expressed in the Number (n) and Percentage (%) of Employees)

Classifications	East (n=7)		West (n=10)		Combined (n=17)	
	n	%	n	%	n	%
Current Smokers	4	57%	6	60%	10	59%
Past Smokers	1	14%	1	10%	2	12%
Non Smokers	2	29%	3	30%	5	29%



Table 4

DIVISION OF MAJOR SYMPTOMATOLOGY WITH RESPECT TO SMOKING HABITS  
(Expressed in the Number (n) and Percentage (%) of Employees)

Symptom	Smokers (n = 12)		Non Smokers (n = 5)	
	n	%	n	%
Chronic Cough	9	75%	3	60%
Chronic Sputum Production	11	92%	5	80%
Shortness of Breath With Exercise	8	66%	3	60%

Table 5

OVERALL RESULTS OF PULMONARY FUNCTION TESTS  
(Mean and Standard Deviation Values Given)

Test	East (n=6)		West (n=10)		Combined (n=16)	
	Mean	S.D.*	Mean	S.D.	Mean	S.D.
Forced Vital Capacity (FVC)						
Liters of air	3.57	0.79	3.90	1.97	3.78	0.69
% of Normal Value	90.00	11.26	103.10	16.98	98.19	16.07
1 Second Forced Expiratory Volume (FEV <sub>1</sub> )						
Liters of air	2.93	0.67	3.10	0.52	3.03	0.57
% of Normal Value	91.67	14.38	102.20	15.05	98.25	15.25
FEV <sub>1</sub> /FVC Ratio	0.82	0.04	0.79	0.06	0.80	0.05

\* S.D. = Standard Deviation from the mean value



Table 6

ABNORMAL RESULTS OF PULMONARY FUNCTION TESTS\*  
(Number and Percentage of Workers)

Test	East (n=7)		West (n=10)		Combined (n=17)	
	n	%	n	%	n	%
Forced Vital Capacity (FVC) [normal - above 80%]	1	16.7%	1	10.0%	2	12.5%
1 Second Forced Expiratory Volume (FEV <sub>1</sub> ) [normal - above 80%]	1	16.67%	1	10.0%	2	12.5%
FEV <sub>1</sub> /FVC. [normal - above 0.75]	0	00.0%	2	20.0%	2	12.5%

\*Note: All had upper respiratory infection in last 4 weeks.

Table 7

COMPARISON OF SYMPTOMATOLOGY NOTED IN THIS STUDY  
with  
THAT RECORDED BY THE HEALTH AND NUTRITION EXAMINATION SURVEY

Symptom:	U.S. Steel Pickling	Health and Nutr. Exam. Survey.	Rel. Risk	X <sup>2</sup>	P value (less than)
Dyspnea	9/16	254/991	3.73	6.15	0.02
Cough	9/16	210/996	4.78	9.39	0.01
Phlegm	11/16	201/990	8.64	19.4	0.001



## APPENDIX 1

### ANALYTICAL METHOD FOR SULPHURIC ACID

#### Membrane Filters

The samples were analyzed for sulfuric acid via ion chromatography with a Dionex Model 10 ion chromatograph.

Sulfuric acid was extracted from the AA-filters with 10 ml of deionized water added to each scintillation vial with subsequent sonification for 5 minutes. Blanks were run concurrently with the samples; the average calculated amount of  $H_2SO_4$  in the blanks is subtracted from the reported results of samples.

A series of working sulfate standards covering the range 0.5-50 ppm was prepared to construct a calibration curve. Peak heights were measured to quantitate samples, standards, and blanks. Results for sulfate were gravimetrically converted to sulfuric acid for reporting purposes.

Ion chromatograph conditions were as follows: 3mm x 500mm anion separator column preceded by a pre-column; 6mm x 250mm anion suppressor column; 3.0mM  $NaHCO_3$  / 2.4mM  $Na_2CO_3$  eluent, 24% eluent flow rate, and variable conducting detector settings. Under these conditions, a retention time of 12.4 minutes was observed.

Samples are reported in the units of micrograms  $H_2SO_4$ /filter; a limit of detection of 5 ug/filter is noted.

#### Silica Gel Tubes

Adsorbent and back-up sections of each silica gel tube were placed in separate centrifuge tubes, 6 mL of eluent solution added to each, and the solutions heated for 10 minutes in boiling water. Upon cooling, each solution was adjusted to a volume of 10 mL, mixed vigorously, filtered through a 0.45 micron pore-size membrane filter and injected into a Dionex Model 10 ion chromatograph. Blank samples were prepared analogously to samples and run. Results from these blanks were subtracted from sample values for reporting purposes. Treated silica gel obtained from SKC, Inc. (Cat. No. 226-10-03, Lot 130) was utilized for preparing blanks.

Ion chromatograph conditions were as follows; Eluent - 0.003 M.  $NaHCO_3$ /0.0024 M.  $Na_2CO_3$  at 138 mL/hr. Flow rate; columns - 4 x 50 mm anion precolumn/concentrator, 4 x 250 mm anion separator, and 9 x 100 mm anion suppressor; 100 uL injection Log; 0.5 cm/min. chart speed; and 3 uMHO/cm detector sensitivity setting. Observable retention times for the phosphate and sulfate ion were 8 minutes and twenty-two minutes respectively under these conditions.



DEPARTMENT OF HEALTH AND HUMAN SERVICES  
PUBLIC HEALTH SERVICE  
CENTERS FOR DISEASE CONTROL  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
ROBERT A. TAFT LABORATORIES  
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