U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION
REPORT HE 79-10-576

CITIES SERVICE COMPANY
MIAMI, ARIZONA

March 1979

I. TOXICITY DETERMINATION

A Health Hazard Evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) at the Cities Service Company, Miami, Arizona, on November 7 and 8, 1978. It is the judgement of the investigators that workers may have been exposed to potentially toxic concentrations of sulfuric acid mist (H_2SO_4). This determination is based on environmental measurements of airborne sulfuric acid mist; physical examination with particular attention to irritation of mucous membranes, eyes, skin and respiratory tract; a review of pertinent literature; observations of employees work practices; and engineering controls.

Airborne concentrations of sulfuric acid mist were collected in the workers' breathing zone and general work area on November 7 and 8, 1978. The levels of H_2SO_4 measured approached but did not exceed the 1 mg/M^3 eight-hour time-weighted average NIOSH criteria and OSHA standard; however, the medical histories and physical examinations conducted on the seven exposed employees showed conjunctivitis, skin rash and dental discoloration signs which correlate closely with sulfuric acid mist exposure.

Recommendations designed to aid in providing a safe and healthful working environment are included in Section V in this determination report.

DISTRIBUTION AND AVAILABILITY

Copies of this determination report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH Publications office at the Cincinnati address.

Copies have been sent to:

a) Cities Service Company, Miami, Arizona
b) Authorized Representative of Employees-United Steelworkers of America; Local 4338, Miami, Arizona
c) United Steelworkers of America-Pittsburgh, Pennsylvania
d) U.S. Department of Labor - Region IX
e) NIOSH-Region IX

For the purpose of informing the approximately 20 "affected employees" the employer shall promptly "post" for a period of 30 calendar days the determination report in a prominent place(s) near where exposed employees work.

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 a 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 received such a request from an authorized representative of employees of the United Steelworkers of America, Local 4338 for a Health Hazard Evaluation in the solvent extraction electrowinning plant (SXEW) of the Cities Service Company in Miami, Arizona. The request alleged employee exposure to sulfuric acid mist resulting in transient mucous membrane irritation and splash burns among the workers of the "Tank House".

HEALTH HAZARD EVALUATION

A. Plant Process

Some 30,000 pounds of marketable 99.9 percent pure copper cathode is produced at the Miami operations daily and is sold to fabricators for use in the electrical, construction, and automobile industries. The Metals Division of Cities Service handles both production and sales of the finished cathode.

A solvent extraction/electrowinning plant was built in 1976 making it possible to produce the marketable copper from nonprofitable low content copper ore. A leach solution is circulated through a caved area over the old underground mine, collected on the 1000 foot level of the mine, pumped to the surface and into the SXEW plant where solvent extraction is used to produced a concentrated copper sulfate solution. Electrowinning is accomplished by passing an electric current through this solution to plate the copper on cathodes. The cathodes weigh approximately 180 pounds.

B. Evaluation Design

An initial survey was conducted on November 6, 1978. This survey included obtaining background information and conducting a walk-through survey in the areas where the alleged hazard was present.

On November 7 and 8, 1978, airborne samples were collected for sulfuric acid mist.

A total of seven, first shift employees were interviewed and examined by a NIOSH physician assistant; all seven employees spoke of previous irritation they believed due to their sulfuric acid exposure. Three of these individuals evidenced a greenish-black discoloration of their upper incisors.

An Interim #1 Report to company and union representatives was distributed in November 17, 1978, reporting the findings to date and recommendations for future actions to be taken.

C. Evaluation Methods

1. Environmental

Personal air samples were used to evaluate employee exposures to sulfuric acid. The personal samples were obtained by attaching a battery powered vacuum pump to the worker's belt with the sampling media (e.g., "AA" filter in a closed face cassette) in a holder attached to the shirt lapel of the worker to obtain a representative sample of air in the breathing zone of the worker. Samples were obtained for a sufficient period of time at an air flow rate of 1.5 liters per minute so that for all practical purposes they may be considered as eight-hour time-weighted averages. The samples were analyzed for sulfuric acid via ion chromatography with a Dionex Model 10 ion chromatograph. The limit of detection was 10 µg/filter.

2. Medical

The seven people who participated in this study did so because of their occupational exposure to sulfuric acid. These seven people comprised the entire day shift, (6 people in all) as well as the single evening operator. Each individual was questioned regarding any pertinent past medical history, or as regards specific symptoms known to be associated with excessive sulfuric acid exposure. A physical examination with particular attention to mucus membranes, eyes, skin and respiratory tract was given to each study participant. Permission was obtained from each worker to review their personal medical records.

D. Evaluation Criteria

1. Environmental

To assess the potential toxicity for the concentrations of sulfuric acid mist in the place of employment, three primary sources of criteria are generally consulted: (1) NIOSH Criteria for Recommended Standards for Occupational Exposure to Substances (Criteria Documents); (2) Recommended and Proposed Threshold Limit Values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH) 1978; and (3) Occupational Health Standard as promulgated by the U.S. Department of Labor (29 CFR Part 1910.1000).

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

In this instance all three sources show an identical recommended criteria or standard for sulfuric acid mist; that is 1.0 mg/M^3 based on a eight-hour time-weighted average exposure.

TLV's or Occupational Health Standards for substances are usually established at levels designed to protect workers occupationally exposed for an 8-hours per day, 40-hours per week basis over a working lifetime. Because of a wide variation in individual susceptibility, some workers may experience ill effects at or below the designated levels. Thus, an evaluation of the workplace can not be based entirely upon comparisons made against such TLV's or standards, as various TLV's and standards do not represent absolute protection of all workers. Setting of legal standards and enforcement is a responsibility of the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA)

2. Physiological Effects

Sulfuric acid mist is severely irritating to the respiratory tract, eyes, and skin. Delayed onset of pulmonary edema may occur. If the liquid is splashed in the eye, transient loss of vision may result. It may cause increased symptoms in asthmatics and increased incidence of lower respiratory tract disease. Prolonged exposure to low concentration of sulfuric acid can cause erosion and staining of the teeth. Chronic exposures to sulfuric which are generally tolerated by workers has not been associated with irreversible health effects. However, exposure to sulfuric acid has been claimed to result in conjunctivitis, frequent respiratory infection, emphysema, and digestive disturbances.

E. Evaluation Results and Discussion

1. Environmental

Results of environmental samples showed the levels of sulfuric acid measured approached but did not exceed the 1 mg/M^3 eight-hour time-weighted average NIOSH criteria and OSHA standard. For a detailed description of sample results, please refer to Table I.

2. Medical

A total of seven workers (3 female and 4 male) were interviewed and examined. Their age range was 24 to 41 years with a mean of 31.5 years. Their average employment span in SXEW Plant was 2 years. Symptomatology elucidated from the respondents yeilded a number of common complaints during the course of the study while performing physical examinations. Burning eyes were reported by all seven employees.

Transient throat irritation and sinus inflamation was reported by all study participants. Rash and skin irritation was evident about the face and arms of 5 of the individuals. A greenish-black discoloration of the front teeth was discerned in 3 individuals. The medical records review revealed two individuals with pulmonary disease. One individual had been "diagnosed" and treated for asthma. The other person had an X-ray interpretation stating, "mild pulmonary fibrosis". Both individuals had a long history of allergic manifestations.

3. Conclusions

It has been determined on the basis of environmental evaluation by NIOSH on November 7 and 8, 1978, that workers' were exposed to concentrations of sulfuric acid mist which approached the NIOSH and OSHA recommended standard.

Based on the medical histories and physical examinations, the conjunctivitis, skin rash and dental discoloration, all correlate closely with sulfuric acid exposure. A review of two workers' medical records revealed documented pre-employment pulmonary disease in both cases. Clearly, their work exposure to sulfuric acid may serve to aggravate and further compromise their respiratory function.

V. RECOMMENDATIONS

1. The following medical procedures should be made available to each employee who is exposed sulfuric acid.

   a. A complete history and physical examination. The purpose is to detect pre-existing condition that might place the exposed employee at increased risk and to establish a baseline for future health monitoring. Examination of the respiratory system, eyes, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

   b. 14" x 17" chest roentgenogram. Sulfuric acid may cause acute lung damage. Surveillance of the lungs is indicated.

c. FVC and FEV (1 sec.). Sulfuric acid is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

d. The above medical examinations are to be repeated on an annual basis except that an X-ray is required only when indicated by pulmonary function testing.

2. Skin contact with sulfuric acid will produce burns at the site of contact. Impervious protective clothing, such as rubber gloves, aprons, suits, hoods, and boots should be provided by the employer and used by the employee as appropriate to the severity and likelihood of body contact with liquid acid.

3. Sulfuric acid-wetted clothing, unless impervious, should be removed promptly.

4. Protective clothing should be changed at least twice a week or more frequently.

5. Eye protection equipment should be provided by the employer and used by the employee where eye contact with liquid sulfuric acid is likely.

6. Full length, 8-inch minimum plastic shields with forehead protection may be worn in place of, or in addition to, goggles. If there is danger of material striking the eyes from underneath, or around the sides of the face shield, chemical safety goggles should be worn as added protection.

7. Respirators used should be those certified under the NIOSH respirators standard, 30 CRF, Part 11.

8. An educational program should be instituted so that employees are made aware of the hazard associated with sulfuric acid. Good work practices and first aid procedures should be included in this program.

REFERENCES

1. Patty, Frank A.: Industrial Hygiene and Toxicology, Vol. II-Toxicology (2nd ed. revised), Interscience Publishing Company, New York, 1963, pp 895-896.

2. Amdur, M.O., et al: "Inhalation of Sulfuric Acid Mist by Human Subjects", AMA Archives of Industrial Hygiene and Occupational Medicine 6:305-313, 1952.

3. Baum, Gerald, et al 1974. Textbook of Pulmonary Diseases. Little Brown and Company.

4. National Institute of Occupational Safety and Health (NIOSH) 1974. Criteria for a Recommended Standard . . .Occupational Exposure to Sulfuric Acid. HEW Publication No. (NIOSH) 74-128.

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Table 1

Results of Environmental Sampling in the Solvent Extraction Electrowinning Plant

Cities Service Company
Miami, Arizona

November 7-8, 1978

Job and/or Location	Date	Sampling Period	Sample Volume(liters)	Type	Sulfuric Acid (mg/M^3*)
Tank House Helper	11/7/78	0806-1431	577	BZ**	0.12
Tank House Helper	11/7/78	0810-1429	568	BZ	0.19
E & W Operator	11/7/78	0811-1452	601	BZ	0.70
Tank House Helper	11/7/78	0814-1450	594	BZ	0.79
Tank House Helper	11/7/78	0815-1450	592	BZ	0.20
Tank House Helper	11/7/78	0818-1450	588	BZ	0.09
Copper Stripping Area	11/7/78	0822-1440	567	GA***	0.12
Wash Down Area	11/7/78	0830-1454	576	GA	0.35
Tank House Helper	11/8/78	0805-1345	510	BZ	0.08
Tank House Helper	11/8/78	0810-1345	502	BZ	0.02
Copper Stripper	11/8/78	0811-1345	501	BZ	0.06
Tank House Helper	11/8/78	0813-1345	498	BZ	0.52
E & W Operator	11/8/78	0812-1345	499	BZ	0.40
Tank House Helper	11/8/78	0815-1345	495	BZ	0.04
Copper Stripping Area	11/8/78	0817-1350	500	GA	0.08
Wash Down Area	11/8/78	0818-1350	498	GA	0.28

The NIOSH 1974 Criteria Document, the 1978 ACGIH TLV and current OSHA Standard 1.0

*mg/M^3 - Milligrams of substance per cubic meter of air
**BZ - Personal breathing zone
***GA - General area

Sulfuric Acid Limit of Detection was 10 µg/filter.