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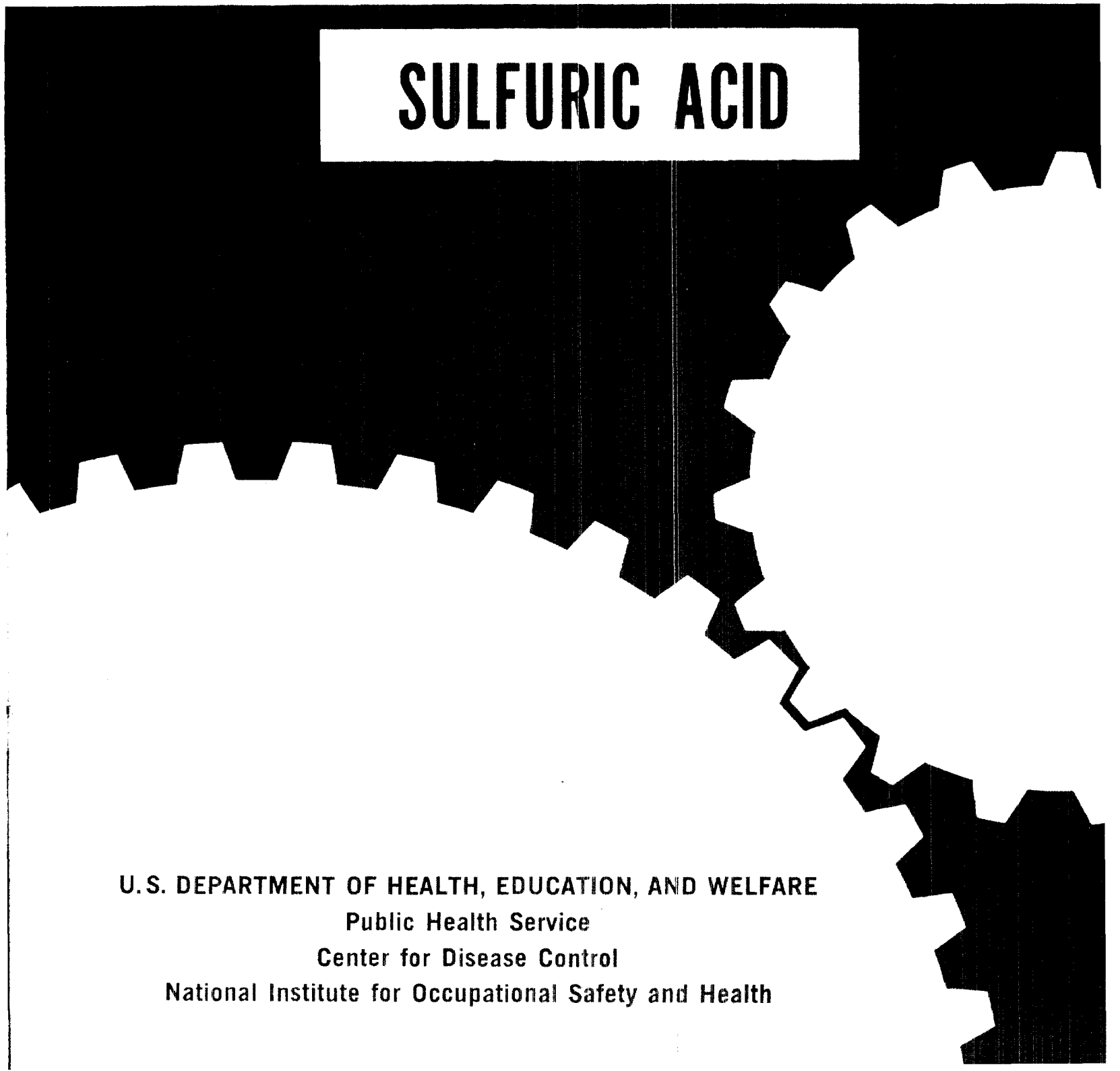
criteria for a recommended standard

OCCUPATIONAL EXPOSURE TO

SULFURIC ACID

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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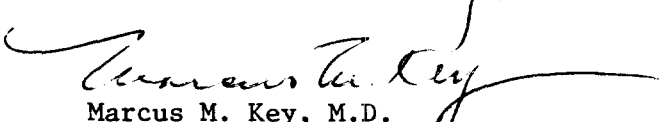
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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. To provide relevant data from which valid criteria and effective standards can be deduced, the National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices.

It is intended to present successive reports as research and epidemiologic studies are completed and sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on sulfuric acid by members of my staff, the valuable and constructive comments presented by the Review Consultants on Sulfuric Acid, the ad hoc committees of the Industrial Medical Association and the American Conference of Governmental Industrial Hygienists, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by Professor William A. Burgess, NIOSH consultant on respiratory protection. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on sulfuric acid. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.


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The Office of Research and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for sulfuric acid. Tabershaw-Cooper Associates, Inc., developed the basic information for consideration by NIOSH staff and consultants under contract No. HSM-99-72-116. Douglas L. Smith, Ph.D., served as criteria manager and had NIOSH program responsibility for development of the document.

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CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN
OCCUPATIONAL EXPOSURE STANDARD FOR SULFURIC ACID

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I. RECOMMENDATIONS FOR A SULFURIC ACID STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to sulfuric acid (H₂SO₄) at the workplace be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for up to a 40-hour work week over a working lifetime; compliance with the standard should therefore prevent adverse effects of sulfuric acid on the health and safety of workers. The standard is measurable by techniques that are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and will be revised as necessary.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Occupational exposure to sulfuric acid mist shall be controlled so that workers shall not be exposed to a concentration greater than one milligram per cubic meter of air (1 mg/cu m) determined as a time-weighted average (TWA) exposure for up to a 10-hour work day, 40-hour work week.

(b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis of environmental samples shall be as provided in Appendix I or by any method

shown to be equivalent in accuracy, precision, and sensitivity to the method specified.

(c) Exposure

"Exposure to sulfuric acid" means exposure to a concentration of liquid, mist, or special dry powder of sulfuric acid, or to sulfur trioxide associated with oleum (fuming sulfuric acid) equal to or above one-half the recommended environmental standard. Exposures at lower environmental concentrations will not require adherence to the following sections except for work practices, equipment, and clothing which may be necessary to guard against the occurrence of foreseeable accidents such as from spray or splash. Procedures for identification of exposure areas can be accomplished by time-weighted average (TWA) determinations by the method described in Appendix I or by any method shown to be equivalent in accuracy, precision, and sensitivity.

Section 2 - Medical

(a) Comprehensive preplacement and annual medical examinations shall be provided for all workers subject to "exposure to sulfuric acid." The examination shall be directed toward, but not limited to, the teeth, eyes, skin, and the cardiopulmonary system. Particular attention shall be focused on dental erosion and complaints of mucous membrane irritation and cough. An evaluation of the advisability of a worker's using negative- or positive-pressure respirators shall also be made.

(b) Initial examinations for presently employed workers shall be offered within 6 months of the promulgation of a standard incorporating these recommendations and annually thereafter.

(c) The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, and of the employer shall have access to all medical records. Physicians designated and authorized by any employee or former employee shall have access to his medical records.

(d) Medical records shall be maintained for persons employed one or more years in work involving exposure to sulfuric acid. X-rays for the 5 years preceding termination of employment and all medical records with pertinent supporting documents shall be maintained at least 20 years after the individual's employment is terminated.

Section 3 - Labeling (Posting)

(a) Areas where sulfuric acid is used, handled, or stored shall be posted with a sign reading:

SULFURIC ACID

Danger! Causes Severe Burns

Do not get in eyes, on skin, on clothing.

Avoid breathing mist.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

Use protective clothing and equipment as instructed.

Do not add water to acid.

UNAUTHORIZED PERSONS KEEP OUT

(b) Areas where oleum (fuming sulfuric acid) is used, handled, or stored shall be posted with a sign reading:

OLEUM

Fuming Sulfuric Acid

Danger! Causes Severe Burns

Do not get in eyes, on skin, on clothing.

Avoid breathing mist or gas.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention.

Use protective clothing and equipment as instructed.

Do not add water to acid.

UNAUTHORIZED PERSONS KEEP OUT

(c) Areas where bags of dry sulfuric acid are handled or stored shall be posted with a sign reading:

SULFURIC ACID

Dry Sulfuric Acid

Avoid contamination with foreign matter.

Do not rebag contaminated material.

Place broken and torn bags and contents in slipover bags.

Dispose of bags as instructed.

Sweep up and promptly dispose of all spilled material as instructed.

In case of fire avoid use of water directly on bags.

Use protective clothing and equipment as instructed.

UNAUTHORIZED PERSONS KEEP OUT

These signs shall be printed both in English and in the predominant primary language of non-English-speaking workers, if any.

Section 4 - Protective Clothing and Personal Protective Equipment

Engineering controls shall be used to maintain sulfuric acid concentrations below the prescribed limit. Administrative controls may also be used to reduce exposure. Requirements for personal protective equipment shall be as approved under provisions of 29 CFR 1910 (37 FR 22102, Subpart I, October 18, 1972).

(a) Skin Protection

(1) 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 shall be provided by the employer

and used by the employee as appropriate to the severity and likelihood of body contact with liquid acid.

(2) Sulfuric acid-wetted clothing, unless impervious, shall be removed promptly.

(3) Protective clothing should be changed at least twice a week or more frequently if required.

(b) Eye Protection

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

(1) Selection, use, and maintenance of eye protective equipment shall be in accordance with provisions of the American National Standard Practice for Occupational and Educational Eye and Face Protection, ANSI Z87.1-1968.

(2) Chemical safety goggles-- cup-type, cover-cup-type, or rubber-framed goggles, equipped with approved impact-resistant glass or plastic lenses, shall be worn whenever there is danger of sulfuric acid eye contact.

(3) Face shields-- 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.

(c) Respiratory Protection

This subsection shall apply whenever a variance from the standard recommended in Section 1 (a) is granted under provisions of the

Occupational Safety and Health Act, or in the interim period during the application for a variance. When the limits of exposure to sulfuric acid prescribed in subsection (a) of Section 1 cannot be met by controlling the concentration of sulfuric acid in the work environment, an employer must utilize, as provided in this subsection, a program of respiratory protection to effect the required protection of every worker exposed. Respirators shall also be provided and used for nonroutine operations (occasional brief exposures above the TWA of 1 mg/cu m and for emergencies); however, for these instances, a variance is not required, but the requirements set forth below continue to apply. Appropriate respirators as described in Table I-1 shall only be used pursuant to the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure the atmospheric concentration of sulfuric acid in the workplace when the initial application for variance is made and thereafter whenever process, worksite, or climate changes occur which are likely to increase the sulfuric acid concentration. This requirement shall not apply when only atmosphere-supplying positive pressure respirators are used. The employer shall ensure through proper respirator selection, fit, use, and maintenance that no worker is being exposed to sulfuric acid in excess of the standard.

(2) The respirator and cartridge or canister used shall be of the appropriate class, as determined on the basis of exposure to sulfuric acid.

TABLE I-1

REQUIREMENTS FOR RESPIRATOR USAGE

<u>Maximum Use Concentration (Multiples of TWA limit)</u>	<u>Respirator Type (for both sulfuric acid mist and sulfur trioxide unless specified)</u>
Less than or equal to 10x	<p>(1) Type C supplied air respirator, demand type (negative pressure), with quarter, half, or full facepiece; if eye irritation noted, full facepiece must be worn.</p> <p>Sulfur trioxide only--Chemical cartridge respirator for sulfur dioxide with quarter, half, or full facepiece; if eye irritation noted, full facepiece must be worn. Use mist filter when sulfuric acid mist is present.</p> <p>Sulfuric acid mist only--Air purifying mist respirator with cartridge and half mask facepiece; if eye irritation noted, full facepiece must be worn.</p>
Less than or equal to 100x	<p>(1) Gas mask with chin style canister for acid gases and acid mists.</p> <p>(2) Gas mask with front or back mounted chest type canister for acid gases and acid mists.</p> <p>(3) Type C supplied air respirator, demand (negative pressure); pressure-demand; or continuous flow type with full facepiece.</p> <p>(4) Self-contained breathing apparatus in demand mode (negative pressure) with full facepiece.</p>
Greater than 100x	<p>(1) Self-contained breathing apparatus in pressure-demand mode (positive pressure) with full facepiece.</p> <p>(2) Combination supplied air respirator, pressure-demand type, with auxiliary self-contained air supply with full facepiece.</p>

TABLE I-1
(continued)

REQUIREMENTS FOR RESPIRATOR USAGE

<u>Maximum Use Concentration (Multiples of TWA limit)</u>	<u>Respirator Type (for both sulfuric acid mist and sulfur trioxide unless specified)</u>
Emergency (No concentration limit)	(1) Self-contained breathing apparatus in pressure-demand mode (positive pressure) with full facepiece. (2) Combination supplied air respirator, pressure-demand type, with auxiliary self-contained air supply with full facepiece.
Evacuation or escape (No concentration limit)	(1) Self-contained breathing apparatus in demand or pressure-demand mode (negative or positive pressure). (2) Gas mask with acid gas chest canister, and mouthpiece respirator for acid gases and acid mists.

(3) A respiratory protective program meeting the general requirements outlined in Section 3.5 of American National Standard Practices for Respiratory Protection Z88.2-1969 shall be established and enforced by the employer. In addition, Sections 3.6 (Program Administration), 3.7 (Medical Limitations), and 3.8 (Approval) shall be adopted and enforced.

(4) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided.

(5) Respiratory protective devices described in Table I-1 shall be those approved under provisions of 30 CFR 11 (37 FR 6244, March 25, 1972) as amended.

(6) Respirators specified for use in higher concentrations of sulfuric acid are permitted in atmospheres of lower concentrations.

(7) Employees shall be given instruction on the use of respirators assigned to them, day-to-day maintenance and cleaning of the respirators, and how to test for leakage.

(8) Emergency and escape-type respirators shall be made immediately available at the work stations for each worker.

Section 5 - Appraisal of Employees of Hazards from Sulfuric Acid

At the beginning of employment in a sulfuric acid area, employees exposed to sulfuric acid shall be informed of all hazards, relevant symptoms of overexposure, appropriate emergency procedures, and proper conditions and precautions for safe use or exposure. The information shall be posted in the work area and kept on file and readily accessible to the worker at all places of employment where sulfuric acid is involved in unit processes and operations or is released as a product, byproduct, or contaminant.

A continuing educational program shall be instituted to ensure that all workers have current knowledge of job hazards, proper maintenance procedures and cleanup methods, and that they know how to correctly use respiratory protective equipment and protective clothing.

Information as required shall be recorded on US Department of Labor Form OSHA-20 "Material Safety Data Sheet" or a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

Emphasis shall be placed upon handling, cleanup, inspection and repair of equipment and leaks, storage, and proper disposal of materials.

(a) Handling

(1) Transfer of sulfuric acid from one container to another, or into any process, shall be performed in such a manner as to prevent spillage or leakage. The safe handling practices for sulfuric acid described in Sulfuric Acid, Use and Handling by Fasullo, 1965, are recommended.

(2) Carboys and drums of sulfuric acid should be emptied by gravity or by siphon--never by pressure. Employees opening such containers should wear approved impervious clothing, goggles, face shields, and rubber gloves.

(3) If it is necessary to enter an uncleaned, enclosed tank which has contained sulfuric acid, workers shall be equipped with hood-type face shields or goggles, impervious clothes, rubber safety toe-cap shoes, rubber gloves, brimmed felt or treated fiber hats, and self-contained or supplied air respiratory protective equipment.

(4) If acid is to be diluted with water, the acid shall be added to the water except that in special cases when water must be added to acid, suitable precautions shall be taken.

(b) Emergency, Cleanup, and Inspection

(1) Procedures for emergencies shall be established to meet foreseeable events. The irritant and corrosive properties of sulfuric acid demand that corrective measures be instituted as soon as possible.

(2) In the event of spills or leaks, sulfuric acid shall be neutralized with soda ash (sodium carbonate), washing soda, or suitable material and washed down with copious amounts of water. The contaminated area shall be immediately zoned off and ventilated thoroughly.

(3) Where there is the possibility of sulfuric acid contact on the eyes or skin, safety showers, eye-wash fountains, and cleansing facilities shall be installed and maintained to provide prompt, immediate access by the workers. The safety showers should have quick-acting valves and deluge-type heads. Inspections and tests shall be conducted at least every 30 days to ensure proper operation.

(4) Appropriate respirators shall be immediately available for wear during evacuation.

(5) Each shipment of sulfuric acid shall be inspected for leakage upon arrival or upon transfer or filling operations. Pipelines, equipment, and containers shall be examined periodically for leaks at least every 3 months.

(c) Exhaust Systems and Enclosure

(1) Exhaust ventilation and enclosure processes shall be used wherever practicable to control workplace concentrations. Systems

shall be designed and maintained to prevent the accumulation or recirculation of sulfuric acid into the workplace.

(2) Ventilation, enclosure, surface active agents, chips, etc, shall be used where operations or processes result in the evolution of sulfuric acid so as to protect employees from airborne concentrations in excess of the requirements of Section 1 (a) of the Standard. It is also necessary to remove hazardous concentrations of toxic gases such as arsine or hydrogen selenide which may result from the interaction of hydrogen with impurities present either in sulfuric acid or in metals with which the acid comes in contact.

(d) Storage

(1) Sulfuric acid shall be isolated from organic materials, nitrates, carbides, chlorates, chromates, cyanides, metallic sulfides, and metal powders or other noncompatible materials because contact with these materials may cause evolution of toxic gases and/or ignition. Storage shall be on separate, well ventilated, cool, dry premises.

(2) Smoking, open lights, flames, and spark-producing tools shall not be permitted near sulfuric acid carboys, drums, tank cars, or metal storage tanks because of the possible production of explosive mixtures of hydrogen during storage.

(e) Disposal

(1) All local, state, and federal regulations concerning waste disposal into landfills, streams, municipal treatment plants, or impounding basins shall be followed.

Section 7 - Monitoring and Reporting Requirements

Workroom areas where it has been determined, on the basis of an industrial hygiene survey or the judgment of a compliance officer, that environmental levels do not exceed half the environmental standard shall not be considered to have sulfuric acid exposure. Records of these surveys, including the basis for concluding that air levels are not above half the environmental standard, shall be maintained until a new survey is conducted. Surveys shall be repeated when any process change indicates a need for reevaluation or at the discretion of the compliance officer. Requirements set forth below apply to areas in which there is sulfuric acid exposure.

Employers shall maintain records of accidental sulfuric acid release requiring evacuation. In addition, records of environmental exposures to sulfuric acid shall be maintained based upon the following sampling and recording schedules except as otherwise indicated by a professional industrial hygiene survey. In all monitoring, samples representative of the exposure in the breathing zone of employees shall be collected. An adequate number of samples shall be collected to permit construction of a time-weighted average (TWA) exposure for every operation or process. The minimum number of representative TWA determinations for an operation or process shall be based on the number of workers exposed as provided in Table I-2.

(a) Initial and Recurrent Sampling Procedures

(1) The first environmental sampling shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(2) Samples shall be collected at least semiannually in accordance with Appendix I for the evaluation of the work environment with respect to the recommended standard.

(b) Special Sampling Procedures

(1) Environmental monitoring of an operation or process shall be repeated at 15-day intervals when the sulfuric acid concentrations have been found to exceed the recommended environmental standard. In such cases, suitable controls shall be initiated, and monitoring shall continue at 15-day intervals until two consecutive surveys indicate the adequacy of the controls.

(2) Environmental samples shall be taken within 30 days after installation of a new process or process change.

(c) Recordkeeping Procedures

(1) Records of all sampling and medical examinations shall be maintained for at least 20 years after the individual's employment is terminated. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Records shall be maintained so that they can be classified by employee. Each employee shall be able to obtain information on his own environmental exposure.

TABLE I-2
SAMPLING SCHEDULE

<u>Number of Employees Exposed</u>	<u>Number of TWA Determinations</u>
1-20	50% of the total number of workers
21-100	10 plus 25% of the excess over 20 workers
over 100	30 plus 5% of the excess over 100 workers

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to sulfuric acid. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe... exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultations with others, has formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. It should be pointed out that any recommended criteria for a standard should enable management and labor to develop better engineering controls resulting in more healthful work practices and should not be used as a final goal.

These criteria for a standard for sulfuric acid are part of a continuing series of criteria developed by NIOSH. The proposed standard applies to the processing, manufacture, and use of sulfuric acid, or its release as an intermediate, byproduct, or impurity as applicable under the Occupational Safety and Health Act of 1970.

These criteria were developed to ensure that the standard based thereon would (1) protect against development of acute and chronic sulfuric acid poisoning, (2) be measurable by techniques that are valid, reproducible, and available to industry and governmental agencies, and (3) be attainable with existing technology.

From the health hazard standpoint, sulfuric acid must be handled with utmost care because of its highly corrosive action on the skin, eyes, and respiratory tract. The importance of good work practices is emphasized herein, along with the necessary documentation from which the proposed environmental standard is recommended. In addition, it is recognized that a great potential hazard exists, particularly by inhalation, from the use of oleum (fuming sulfuric acid).

These criteria were not designed for the population-at-large and any extrapolation beyond general occupational exposures is not warranted.