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SULPHURIC ACID MIST AND OCCUPATIONAL HEALTH ISSUES

Position Paper

PREPARED BY
AIOH Exposure Standards Committee
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AUTHORISATION
This Position Paper has been prepared by the AIOH Exposure Standards Committee and authorised by AIOH Council.

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AUSTRALIAN INSTITUTE OF OCCUPATIONAL HYGIENISTS INC (AIOH)

The Australian Institute of Occupational Hygienists Inc. (AIOH) is the association that represents professional occupational hygienists in Australia. Occupational hygiene is the science and art of anticipation, recognition, evaluation and control of hazards in the workplace and the environment. Occupational hygienists specialise in the assessment and control of:

- Chemical hazards (including dusts such as silica, carcinogens such as arsenic, fibrous dusts such as asbestos, gases such as chlorine, irritants such as ammonia and organic vapours such as petroleum hydrocarbons);
- Physical hazards (heat and cold, noise, vibration, ionising radiation, lasers, microwave radiation, radiofrequency radiation, ultra-violet light, visible light); and
- Biological hazards (bacteria, endotoxins, fungi, viruses, zoonoses).

Therefore the AIOH has a keen interest in the potential for workplace exposures to sulphuric acid mist, as its members are the professionals most likely to be asked to identify associated hazards and assess any exposure risks.

The Institute was formed in 1979 and incorporated in 1988. An elected governing Council, comprising the President, President Elect, Secretary, Treasurer and three Councillors, manages the affairs of the Institute. The AIOH is a member of the International Occupational Hygiene Association (IOHA).

The overall objective of the Institute is to help ensure that workplace health hazards are eliminated or controlled. It seeks to achieve this by:

- Promoting the profession of occupational hygiene in industry, government and the general community.
- Improving the practice of occupational hygiene and the knowledge, competence and standing of its practitioners.
- Providing a forum for the exchange of occupational hygiene information and ideas.
- Promoting the application of occupational hygiene principles to improve and maintain a safe and healthy working environment for all.
- Representing the profession nationally and internationally.

More information is available at our website – http://www.aioh.org.au.

EXPOSURE STANDARDS COMMITTEE MISSION STATEMENT

The AIOH established the Exposure Standards Committee to provide expert guidance and comment to the exposure standards setting process at a State and National level and internationally where appropriate, through development of AIOH Position Papers, AIOH guidance publications or comment on relevant Standards, Regulations and Codes of Practice. The Committee's remit is to confirm that the exposure standards numbers, and Standards and Codes of Practice, are changed for valid occupational hygiene and scientific reasons.

STATEMENT OF POSITION REGARDING AIOH POSITION PAPERS

The AIOH is not a standards setting body. Through its Position Papers, the AIOH seeks to provide relevant information on substances of interest where there is uncertainty about existing Australian exposure standards. This is done primarily through a review of the existing published, peer-reviewed scientific literature but may include anecdotal evidence based on the practical experience of certified AIOH members. The Position Papers attempt to recommend a health-based exposure value that can be measured; that is, it is technically feasible to assess workplace exposures against the derived OEL. It does not consider economic or engineering feasibility. As far as reasonably possible, the AIOH formulates a recommendation on the level of exposure that the typical worker can experience without adverse health effects.

Any recommended exposure value should not be viewed as a fine line between safe and unsafe exposures. They also do not represent quantitative estimates of risk at different exposure levels or by different routes of exposure. Any recommended exposure value should be used as a guideline by professionals trained in the practice of occupational hygiene to assist in the control of health hazards.

CONSULTATION WITH AIOH MEMBERS

AIOH activities are managed through committees drawn from hygienists nationally. This Position Paper has been prepared by the Exposure Standards Committee, with comments sought from AIOH members generally and active consultation with particular members selected for their known interest and/or expertise in this area. Various AIOH members were contributors in the development of this Position Paper. Key contributors included: Tim White and Ian Firth.

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LIST OF ABBREVIATIONS AND ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIOH	Australian Institute of Occupational Hygienists
AS	Australian Standard
ASTM	American Society for Testing and Materials
BEI	Biological Exposure Index
BGIA	Berufsgenossenschaftliches Institut für Arbeitsschutz (German Institute for OSH)
CIA	Chemical Industries Association (UK)
CI	Confidence Interval
COSHH	Control of Substances Hazardous to Health (UK Regulation)
DME	Department of Minerals and Energy
EC	European Commission
FEV	Forced expiratory volume
FVC	Forced vital capacity
HSE	Health and Safety Executive (United Kingdom)
IARC	International Agency for Research on Cancer
IOM	Institute of Occupational Medicine
ISO	International Standards Organization
LEV	Local Exhaust Ventilation
LoQ	Limit of Quantitation
mg/m^3	milligrams (10^{-3} g) per cubic metre
µ	micro-, (10^{-6}) as in micrometre (µm)
µg	microgram (10^{-6} g)
MMAD	Mass Median Aerodynamic Diameter
NIOSH	National Institute for Occupational Safety and Health
NOAEL	No Observed Adverse Effect Level
NOHSC	National Occupational Health and Safety Commission
NTP	National Toxicology Program of the US Department of Health and Human Services, Public Health Service
NSAA	National Sulphuric Acid Association (UK)
OEL	Occupational Exposure Limit
OHS	Occupational Health & Safety
OSHA	Occupational Safety and Health Administration
PM	Particulate Matter
PPE	Personal protective equipment
PTFE	Polytetrafluoroethylene
RPE	Respiratory protection equipment
SCOEL	Scientific Committee on Occupational Exposure Limits (EC)
SIR	Standardised incidence ratio
SMR	Standardised mortality ratio
STEL	Short Term Exposure Limit
SWA	Safe Work Australia
TLV	Threshold Limit Value
TWA	Time Weighted Average
UK	United Kingdom
WES	Workplace Exposure Standard
WHO	World Health Organization

AIOH POSITION ON SULPHURIC ACID MISTS AND ITS POTENTIAL FOR OCCUPATIONAL HEALTH ISSUES

Key messages

- Sulphuric acid mist at high concentrations causes corrosion of the teeth and is irritating to the respiratory system, but long-term low concentration exposure can also cause cancer of the larynx.
- The AIOH believes that exposure may be adequately controlled by conventional means such as local exhaust ventilation and segregation of workers from areas of high concentration.
- A standard to limit exposure to no more than 0.1 mg of sulphuric acid mist in each cubic metre of air is recommended for the measured inhalable fraction.

Summary

This paper was compiled to give guidance on the assessment, evaluation and control of occupational exposure to sulphuric acid mist, with an emphasis on recommending a health-based occupational exposure limit (OEL). The current Safe Work Australia (SWA) workplace exposure standard (WES) and current international OELs are discussed and the possible health effects examined.

Sulphuric acid is a dense oily liquid clear to dark brown in colour. It mixes with water in all proportions and is corrosive and non-flammable. Sulphuric acid is used in the manufacture of chemicals, detergents, dyes, explosives and fertilisers. It is the acid in lead acid batteries. Sulphuric acid is also used in metal cleaning and electroplating, and solutions of metal sulphates and sulphuric acid are used in the electrowinning of metals.

The current SWA WES for sulphuric acid mist is a time weighted average (TWA) value of 1 mg/m^3, based on the 1991 American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV®).

Sulphuric acid mists have been long recognised as corrosive to teeth and irritant to the respiratory system. In 1992, the International Agency for Research on Cancer (IARC) classified strong acid mists containing sulphuric acid as known to be carcinogenic to humans (Category 1).

In 2001, the United Kingdom Health and Safety Executive (UK HSE) issued a Chemical Hazard Alert Notice based on research done by the European Sulphuric Acid Association, advising that the occupational exposure standard of 1.0 mg/m^3 may not protect against chronic inflammation of the larynx. It was suggested that exposure to sulphuric acid be reduced to below 0.3 mg/m^3 in order to control against inflammation. In 2004, the ACGIH issued a revised TLV® of 0.2 mg/m^3 measured as thoracic particulate mass, but maintained an A2 *Suspected Human Carcinogen* rating.

In 2007, the European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL) reviewed the available OELs for sulphuric acid mist. From animal studies they noted "*evidence of slight changes in the laryngeal epithelium at the lowest concentration tested, 0.3 mg/m^3. Other experimental studies in a range of animal species suggest respiratory tract effects on repeated exposure to concentrations around 0.3 mg/m^3, with the possibility of effects of some health significance even at concentrations down to about 0.1 mg/m^3*". They concluded that "*long-term exposure should be maintained below 0.1 mg/m^3 in order to provide sufficient reassurance of avoidance of possible adverse consequences for the respiratory tract epithelium. Hence SCOEL recommends an 8h TWA limit of 0.05 mg/m^3 in order to satisfy this requirement*".

In 2012, SCOEL added Annex 2 *Sampling aspects* to their documentation. Based on the aerosol size of acid mists and the target organ including the upper respiratory tract and larynx, SCOEL concluded that sampling should be as the inhalable fraction of airborne aerosol. The AIOH concurs with this. Collection of the acid aerosol on a quartz fibre filter for analysis by ion chromatography is also recommended.

Studies of the carcinogenicity of sulphuric acid mist have frequently been undertaken without exposure measurements and with potential confounding exposures not well accounted for. In a review of 25 epidemiology studies a moderate association was found between exposure to sulphuric acid mist and laryngeal cancer. However, while the data suggest a dose-response relationship, the biological plausibility and the possible carcinogenic mechanism remained uncertain.

Non-malignant respiratory effects exist at 1 to 3 mg/m^3 while short-term reduced lung clearance rates were observed at 0.1 mg/m^3. Worker exposure to about 0.5 mg/m^3 has been reported to cause an average of 5 acute effect symptoms (e.g. sneezing, irritated nose, cough, runny nose and dry nose). Practical experience within the AIOH Exposure Standards Committee members has found exposure to 0.1 mg/m^3 is clearly perceptible, 0.2 mg/m^3 can cause coughing, sneezing and shortness of breath while exposure to 1 mg/m^3 is intolerable to many people.

Chronic effects have been noted in rats exposed at 0.5 and 1.0 mg/m^3 but effects at 0.2 mg/m^3 were minimal. A review of animal studies found effects noted in several species at exposure levels above 1 mg/m^3 while effects were not noted at 0.1 mg/m^3.

The TWA occupational exposure limit for sulphuric acid mist recommended by the AIOH is 0.1 mg/m^3, to be measured as the inhalable aerosol fraction according to AS 3640. This standard is set to minimise the incidence of irritant and respiratory effects and of laryngeal cancer. A recommended STEL of 0.5mg/m^3 is feasible but may not be particularly useful in its purpose of warning of possible acute effects, considering delay in reporting due to the requirements of laboratory analysis of collected samples. There is no doubt that such a level causes acute health effects even after a single short term exposure, to which the usual response in most people is withdrawal from the exposure or use of respiratory protection.

Currently, no feasible biomarker is available to be used for biological monitoring.

1. What is sulphuric acid mist?

Sulphuric acid (H_2SO_4) is a clear, odourless (unless heated) and colourless oily liquid, although impure or spent sulphuric acid is a dark brown to black liquid. Thermal decomposition to sulphur trioxide and water occurs at 340°C. It produces a sharp, penetrating and choking odour when heated. Sulphuric acids are available in the following grades: commercial, electrolyte (high purity), textile (low organic content) and chemically pure or reagent grades.

A mist is defined as a liquid aerosol formed by condensation of a vapour or by the atomisation of a liquid. Strong inorganic acid mists containing sulphuric acid may be generated during a process when factors such as evaporation, solution strength, temperature and pressure combine to effect release of a mist. Liquid sulphuric acid may exist in air as a vapour or a mist. However, it exists most often as mist (an aerosol) because of its low volatility and high affinity for water.[1]

Inorganic acid mists containing sulphuric acid are not only used in industry or in commercial products, but can be generated from either natural or industrial sources. In particular, sulphuric acid mists may be produced during the manufacture or use of sulphuric acid, sulphur trioxide, or oleum.

Strong inorganic acid mists containing sulphuric acid may be produced as a result of the use of mixtures of strong inorganic acids, including sulphuric acid, in industrial processes such as acid treatment of metals, electrowinning of metals, phosphate fertilizer manufacture and lead battery manufacture. The degree of vapour or mist evolution varies with the process and method.

Examples of mist generation relevant to sulphuric acid include:

- Agitation of liquids, resulting in aerosol generation above the liquid surface.
- Bubble break-up at the free surface of a liquid (e.g. mist may escape from acid tanks during the pickling process when hydrogen bubbles and steam rise from the surface of the solution or in electrowinning when oxygen bubbles break the surface).
- Free-fall of the liquid (e.g. from a pipe) on to solid or liquid surfaces.
- Reaction of sulphur trioxide and oleum with water vapour (in the air) (NSAA, 2013).

2. How do we measure it?

Documented methods for sampling and analysis of sulphuric acid mist include:

- NIOSH method[2] 7903, which employs adsorption on a silica gel sorbent (collecting the total particulate fraction) and analysis by ion chromatography.
- NIOSH method[2] 7908, which employs adsorption on a quartz fibre filter or a polytetrafluoroethylene (PTFE) filter (collecting the inhalable fraction when using an inhalable sampler) and analysis by ion chromatography. Practical experience is that use of the PTFE filter exerts a high back pressure on the sampling pump and may make it difficult to maintain a 2 L/minute flow rate over extended sampling periods.
- OSHA method[3] ID-113, which requires sample collection on a 0.8 µm mixed cellulose ester filter in a 'total' dust cassette (e.g. Millipore) using a flow rate of 2 litres per minute (collecting the total particulate fraction), with the filters desorbed and the sample analysed by ion chromatography.
- OSHA method[3] ID-165SG, which requires sample collection into a silica gel tube with particulates collected on a glass fibre plug (collecting the total particulate fraction), then are desorbed and the sample analysed by ion chromatography.
- BGIA (Berufsgenossenschaftliches Institut für Arbeitsschutz) method,[4] which collects inhalable fraction acid aerosol on a quartz fibre filter for analysis by ion chromatography with conductivity detection.
- ISO21438-1 (2007),[5] which specifies a method for the determination of the TWA inhalable fraction mass concentration of sulphuric acid and phosphoric acid in workplace air by ion chromatography.
- ASTM D4856-11,[6] which specifies sample collection on a mixed cellulose ester filter (although other filter types are also suitable) for determining sulphuric acid mist in workplace atmospheres using ion chromatography.

Murdoch *et al* (1995) reviewed methods for the collection and analysis of sulphuric acid mist. They found good correlation between the various methods although for the silica gel method most of the collected acid was found on the glass wool plug at the front of the tube. This emphasises the importance of analysing the glass wool along with the sorbent. They found it was also necessary to use specially cleaned silica gel tubes as unwashed tubes showed background levels of sulphate present. The use of mixed cellulose ester filters was also problematic as they were found to decompose when exposed to the acid.

Hsu *et al* (2007) found that measurements by NIOSH method 7903 were 1.5 to 229 times higher than those by the cascade impactor. Moreover, using the NIOSH method, the sulphuric acid concentrations measured at the lower flow rate (0.30 L/min) were higher than those at the higher

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[1] The hygroscopic nature of sulphuric acid (affinity for water) exists down to concentrations of 10% by volume.

[2] Available from http://www.cdc.gov/niosh/docs/2003-154/

[3] Available from https://www.osha.gov/dts/sltc/methods/index.html

[4] Available from http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-Analysenverfahren-f%c3%bcr-chemische-Stoffe/index.jsp

[5] Available from http://www.iso.org/iso/catalogue_detail.htm?csnumber=40239

[6] Available from http://www.astm.org/Standards/D4856.htm and http://www.skcinc.com/guides.asp

flow rate (0.45 L/min). One possible reason for the significant differences between the results from the cascade impactor and the NIOSH method is the potential artefact resulting from the interaction of SO_2 with silica gel and glass fibre used in this NIOSH method.

NIOSH method 7908 specifies the use of a quartz fibre filter or PTFE filter and is now their recommended analytical method (Breuer & Ashley 2014).

Bråtveit *et al* (2004) showed that when using stationary sampling, the Millipore sampler (OSHA method ID-113) and the inhalable fraction of a RespiCon® impactor underestimated the sulphuric acid concentration by factors of 1.5 and 2.1 compared with the IOM sampler, which samples the inhalable fraction.

An important conclusion here is that the measured exposure concentration can vary significantly depending on the sampling method chosen.

The European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL, 2012) provides an annex on '*Analytical aspects to determine sulphuric acid at the values recommended by SCOEL*'. It focuses on the limit of quantitation (LOQ) for each of the methods: NIOSH 7903, OSHA ID-113, OSHA ID-165SG, BGIA and BASF, expressed in the same units established for the SCOEL sulphuric acid mist OEL. To conform to European standard EN 482 (1994) the LOQ has to be less than 20% of the OEL, however a minimum of 10% is recommended. SCOEL determined that the two OSHA methods and the BGIA method can be used to determine a TWA-OEL down to 0.05 mg/m^3 however, exposure peaks cannot be determined to assess a short term exposure limit (STEL) at levels less than 0.1 mg/m^3.

In some industries there will be exposure at the same time to other forms of sulphate such as manganese sulphate in the electrolysis plant of an electro manganese dioxide plant. In this situation manganese can also be measured and the sulphate associated with manganese determined by stoichiometry can be subtracted from total sulphate in order to quantify that present in sulphuric acid.

NSAA (2013) suggest that the ISO method is probably the best approach currently available. The revised ACGIH TLV suggests analysis of the thoracic fraction of particulate matter.

Size analysis in an electrolytic zinc refining plant showed 10% particles < 6 µm, 13% from 6 to 10 µm and 77% greater than 10 µm. The geometric mean sulphuric acid concentrations (± geometric standard deviation) of PM_{23} (aerodynamic cut size smaller than 23 µm), PM_{10} and $PM_{2.5}$ from the cascade impactor were 41.7 (± 5.5), 37.9 (± 5.8) and 22.1 (± 4.5) µg/m^3, respectively (Hsu *et al*, 2007).

It should be noted though that the measured particle diameters of a given sulphuric acid mist will increase in size as the particles adsorb water on entering the respiratory tract. For a dry climate of 5% relative humidity, sulphuric acid mist particles will triple in size in the respiratory tract. At 60% relative humidity, particles will double in size, while particles in humid regions will increase very little. In the respiratory tract, the particles will deposit according to their size at 98% relative humidity (Cavender *et al*, 1977).

Breuer *et al* (2012) performed a comparison of the inhalable to thoracic fractions and found little difference at concentrations below 0.1 mg/m^3. At higher concentrations larger droplets have a marked effect on the measured values and the thoracic fraction accounts for only 32.1 ± 12.5% of the inhalable fraction.

When deciding upon an appropriate sulphuric acid exposure monitoring method, a competent person must select a methodology that takes account of both limitations and interferences. SCOEL (2012) recommends sampling the inhalable fraction on the grounds that:

- While collection of the thoracic fraction would collect aerosol that could affect the central airways (i.e. clearance and pulmonary function changes), as well as lead to laryngeal cancer;
- Collection of the inhalable fraction would also protect from acute or longer term inflammation along the respiratory tract epithelium, and ultimately the possibility of tumour formation in the respiratory tract.

The AIOH concurs with SCOEL and recommends the collection of the inhalable fraction using AS 3640 (2009), which is a widely used method in Australia. Thoracic samplers are relatively expensive and the use of the inhalable sampler errs on the side of caution in that it will slightly over estimate exposure compared to a thoracic sampler. Collection of the acid aerosol on a quartz fibre filter for analysis by ion chromatography is also recommended.

An initial survey can be undertaken by using colorimetric tubes (note that all mineral acids will interfere). The human nose can also be a good indicator of the presence of hazardous levels of sulphuric acid mist. Murdoch *et al* (1995) found that the threshold of perception for an individual unaccustomed to sulphuric acid mist exposure is about 0.02 to 0.05 mg/m^3; 0.1 mg/m^3 is clearly perceptible and 0.2 mg/m^3 can cause coughing or sneezing.

No specific biomarker for biological monitoring of exposure to sulphuric acid is currently available.

3. Hazards associated with sulphuric acid and its mist

Sulphuric acid is a strong acid and will oxidise, dehydrate or sulphonate most organic compounds. Dehydration occurs because sulphuric acid has a strong affinity for water. It forms various hydrates when in contact with organic matter or water vapour. Although it is miscible with water, contact with water generates heat and may produce a violent reaction. The reaction with water releases toxic and corrosive fumes and mists. Sulphuric acid is non-combustible, but it can release flammable hydrogen gas when in contact with metals.

Sulphuric acid mists have long been recognised as having the potential to cause the following health effects (NSAA, 2013):

- Short-term irritation of eyes and skin.
- Irritant dermatitis (red, itchy, dry skin) and itching due to repeated exposure to low concentrations of mists or aerosols.
- Etching of teeth after a few weeks exposure, progressing to erosion after a few months exposure. Dental etching and erosion occurred about four times as frequently in a high exposure group (> 0.3 mg/m^3) compared to a low exposure group (< 0.07 mg/m^3).

- Irritation of the lungs (chemical pneumonitis) and upper respiratory tract after brief exposure to high concentrations of sulphuric acid mist and in severe cases may cause pulmonary oedema. Symptoms include coughing and shortness of breath and can be delayed until hours or days after the exposure.
- Nasal problems, throat irritation bronchial hyper reactivity and/or damage to the lining of the throat in the region of the larynx after repeated exposure to lower concentrations of the mist.

In 1992 IARC classified strong acid mists containing sulphuric acid as a group 1 carcinogen (known human carcinogen). IARC (2012) reaffirmed this classification for "mists from strong inorganic acids", noting that such mists cause cancer of the larynx. IARC (2012) also note that a positive association has been observed between exposure to mists from strong inorganic acids and cancer of the lung.

The National Toxicology Program (NTP, 2014) first listed "*Strong Inorganic Acid Mists Containing Sulfuric Acid*" as being '*Known to be human carcinogens*' in 2000. They state that occupational exposure to strong inorganic acid mists containing sulphuric acid is specifically associated with laryngeal and lung cancer.

ACGIH (2011) maintain that sulphuric acid is a suspected human carcinogen that decreases lung function in individuals with pre-existing respiratory disease.

SCOEL (2012) found no evidence that sulphuric acid caused any signs of systemic toxicity upon penetration of the skin (penetration is via corrosion of the skin) hence there is no requirement for a 'Sk' notation.

It should be noted that the carcinogen classification is for inorganic acid mists containing sulphuric acid only and does not apply to sulphuric acid or sulphuric acid solutions where no mist or vapour is generated.

4. Major uses / potential for exposure (in Australia)

Sulphuric acid is used in the following industries: fertiliser, explosives, petroleum refining, mining and metallurgy, ore processing, alumina refining (for descaling), inorganic chemicals and pigments, organic chemicals, synthetic rubber and plastics, pulp and paper, soap and detergents, water treatment, cellulose fibres and films, and inorganic pigments and paints. Sulphuric acid use is declining in some industries. There is a trend in the steel industry to use hydrochloric acid instead of sulphuric acid in pickling, and hydrofluoric acid has replaced sulphuric acid for some uses in the petroleum industry. The primary consumer product that contains sulphuric acid is the lead-acid battery; however, this accounts for a small fraction of the overall use.

Sulphuric acid is one of the most widely used industrial chemicals; however, most of it is used as a reagent rather than an ingredient. Therefore, most of the sulphuric acid used ends up as a spent acid or a sulphate waste. Exacting purity grades are required for use in storage batteries and for the rayon, dye, and pharmaceutical industries. Sulphuric acids used in the steel, chemical, and fertiliser industries have less exacting purity requirements.

Major industries with exposure to strong inorganic acid mists include those that manufacture phosphate fertiliser, isopropanol (isopropyl alcohol), synthetic ethanol (ethyl alcohol), sulphuric acid, nitric acid, and lead-acid batteries. Exposure also occurs during copper smelting, and pickling and other acid treatment of metals such as in metal cleaning and electroplating, and solutions of metal sulphates and sulphuric acid are used in the electrowinning of metals. The National Pollutant Inventory[7] notes that primary sources of sulphuric acid emissions in Australia are the industries that manufacture it or use it in production. Some of the industries that use it in production are the metal smelters, phosphate fertiliser producers, oil refiners, the chemical industry, battery manufacturers, manufacturers or fabricated metal products, manufacturers of electronic components, and manufacturers of measuring and controlling devices.

Foster *et al* (1996) conducted a study of exposures, control methods and the occurrence of respiratory symptoms associated with sulphuric acid mist in a selection of Australian industries. Ninety-four personal and 134 static air samples were collected in 13 workplaces representing lead-acid battery manufacture, metal refining, fertiliser manufacture, electroplating and wool carbonising. The highest airborne concentrations were found in lead-acid battery manufacture, with mean personal exposures ranging from 0.03 to 1.5 mg/m^3 for different jobs. Exposures in metal refining were moderate, ranging from 0.04 to 0.5 mg/m^3 for various tasks, while concentrations up to 0.5 mg/m^3 were recorded in electroplating workplaces. Fertiliser production and sulphuric acid manufacture exposures were low (<0.15 mg/m^3).

Bråtveit *et al* (2004) characterised workers' exposure to sulphuric acid mist in two cell houses of a zinc production plant using personal sampling with a 37 mm Millipore cassette. The geometric means of the exposure levels for the workers in the two cell houses were 0.07 mg/m^3 (range 0.01–0.48 mg/m^3) and 0.04 mg/m^3 (range 0.01–0.15 mg/m^3). They also estimated previous exposures to sulphuric acid by simulating the process conditions from before 1975, by removing the foam layer from the electrolyte surface. Under these conditions, the concentration of sulphuric acid mist increased from 0.11 to 6.04 mg/m^3 in stationary measurement using the Millipore sampler. Thus, today's exposure levels appear to be lower than those reported to be associated with an increased prevalence of laryngeal cancer in other industries, but the levels prior to 1975 seem to have been much higher. By mass, most of the inhalable aerosol was in the size fractions considered to be highly relevant for the effects of sulphuric acid on the respiratory system.

Hsu *et al* (2007) used NIOSH method 7903 and a cascade impactor for measuring the total sulphuric acid mist concentration and size-resolved sulphuric acid mist concentration, respectively, at eight phosphate fertilizer plants and two background sites in Florida. The highest sulphuric acid concentrations by the cascade impactor were obtained at the sulphuric acid pump tank area. When 'high' aerosol mass concentrations (0.1 mg/m^3) were observed at this area, the sulphuric acid mists were in the coarse mode. The geometric mean (±geometric standard deviation) for

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[7] Available from http://www.npi.gov.au/resource/sulfuric-acid

total sulphuric acid concentration from the NIOSH method samples was 0.14 (±0.005) mg/m^3. Sulphuric acid mist concentrations varied significantly among the plants and even at the same location.

5. Risk of health effects

Review of health outcomes, both malignant and non-malignant respiratory disease, with the level of exposure of workers exposed to sulphuric acid mist is required. Much of the work reported to date is dated with very little or no assessment of exposure. The review by Sathiakulmar *et al* (1997) highlights these short comings. In the revision of the documentation for the TLV® for sulphuric acid mist in 2004, the ACGIH (2011) cites 85 papers. Of these only 5 were published in the past decade, and of these 2 were reviews which presented no new data and 2 were extensions of previous studies. Similarly for the SCOEL (2012) review, which cites 28 papers; there are only 4 papers quoted post 2000.

SCOEL (2012) notes "*Concern about the toxicity of sulphuric acid in the workplace atmosphere is focussed on its potential, as an inhaled aerosol, to exert local effects on the respiratory tract, as a consequence of low pH. Such effects can be manifested as sensory irritation of nerve endings, acute or longer term inflammation at various sites along the length of the respiratory tract epithelium, and ultimately the possibility of tumour formation in the respiratory tract, believed to be a consequence of sustained tissue inflammation and repair processes.*" A threshold would apply to this presumed carcinogenic mechanism, that being the dose at which the buffering capacity of the epithelial cells is overwhelmed and a significant fall in cellular pH occurs.

Animal studies

Kilgour *et al* (2002) exposed Wistar rats to 50% sulphuric acid aerosols at 0.2, 1.0 and 5.0 mg/m^3 sulphuric acid over 5 and 28 day periods. There were no macroscopic changes observed in any group. There were dose-related changes and significant cell proliferation to laryngeal cells at the higher doses after 5 and 28 days and minimal changes at the lower dose after 28 days. Recovery was partial after 8 days and only limited additional recovery was observed after 4 weeks. No changes were observed in the lung or nasal passages.

A review of chronic toxicity and carcinogenicity in animals was conducted by Swenberg and Beauchamp (1997). Groups of cynomolgus monkeys exposed to sulphuric acid mist for 78 weeks showed reduced lung function and changes in the lung and bronchioles at 2.4 or 4.8 mg/m^3. Guinea pigs exposed at 0.08 to 0.9 mg/m^3 for up to 52 weeks had no exposure related toxicity, however 3 of 4 groups of monkeys exposed at 0.88 to 0.99 mg/m^3 for 78 weeks showed lesions in their lungs. No effects were demonstrable at 0.1 mg/m^3. Although pulmonary function was impaired, no histopathological changes were evident in eight dogs exposed at 0.9 mg/m^3 sulphuric acid for 21 hours per day for 620 days. In another study Syrian hamsters were exposed to either benzo(a)pyrene and or sulphuric acid mist. Swenberg and Beauchamp (1997) concluded that the study did not show any evidence of carcinogenic activity and was considered equivocal for co-carcinogenic or promoting activity.

Human studies – cancer studies

Lynch *et al* (1979) investigated the mortality and morbidity of respiratory cancer, in particular cancer of the larynx, in workers at alcohol manufacturing plants. The plants used sulphuric acid at either 99% or 60% to 70% (strong acid or weak acid process). Other exposures were to tar and diethyl or diisopropyl sulphate. No measures of exposure were available for any of the workplace contaminants and the authors used man months of employment in either the strong acid or the weak acid plant. The Standardised Mortality Ratios (SMR) for laryngeal cancer was 5 with 4 cases versus 0.8 expected. Additionally 3 of the 4 cases spent more than 70% of their time in the ethanol (strong acid) plant compared to less than 20% for the cohort as a whole. The authors concluded that exposure to one of the agents in the strong acid plant resulted in a higher incidence of laryngeal cancer and thought dimethyl sulphate was most likely. The possibility the agent was sulphuric acid mist cannot be ruled out.

The mortality of workers in an isopropyl alcohol plant (262 men) and two methyl ethyl ketone (MEK) dewaxing plants (446 men) was investigated (Alderson & Rattan, 1980). The former involved exposure to sulphuric acid but not the latter. Other chemicals used at the plants included benzene and cresylic acid. There are no estimates or any measure of exposure presented. In the isopropyl alcohol plant there was only one death from laryngeal cancer and two in the MEK plant. The observed rate of lung cancer was low at both plants, 1 observed verses 6 expected at the MEK plant possibly due to the lower rate of smoking. While this paper is quoted by the ACGIH, the very low number of laryngeal cancer cases (1 of 262 with some exposure to sulphuric acid and 2 of 446 with no exposure), the lack of any exposure data and the potential for other exposures, limits any conclusions in respect of sulphuric acid exposure and laryngeal cancer.

Cancer mortality was studied in two lead-acid battery manufacturing plants and in two steel works involving a cohort of 4401 men (Coggon *et al*, 1996). In one lead-acid battery plant, fixed position sulphuric acid monitoring was carried out sporadically from the 1970s. This showed concentrations in the range 0.1 to 0.7 mg/m^3, while at the other plant fixed position monitoring during 1970-1990 showed concentrations mostly in the range 0.4 to 2.0 mg/m^3. Exposures to crocidolite, chrysotile, lead, stibine and pitch were also noted. No indication is given of the number of exposure measurements or how they were taken or analysed. For the steel plants, no workplace monitoring data is available, although the authors note that some people were not able to tolerate the levels in certain areas. No excess of lung or laryngeal cancer was observed and no differences in rates were observed between workers definitely exposed to acid mist and those definitely not exposed. A nested control analysis found nothing significant. Numbers of cases were small and when confidence intervals (CIs) were considered no association approached significance.

A study of Italian soap makers (Forastiere *et al*, 1987) found the incidence of, but not mortality from, squamous laryngeal cancers to be significantly elevated; 5 observed versus from 0.72 to 1.44 expected, depending on the reference population. All were smokers. They had from 4 to 24 years of exposure to sulphuric acid mist. Concentration was estimated at from 0.64 to 1.12 mg/m^3 but no details are provided on the number of exposure measures or how they were taken or analysed.

Steenland *et al* (1988) studied the incidence of laryngeal cancer in a cohort of 1156 men who worked in the pickling operations of three mid-western (USA) steel mills. Exposure data presented consists of 15 personal samples at one plant (7 samples for pickle hookers, 4 for assistant pickle hookers and 4 for crane men) and 39 area samples across two of the plants. From these data, exposures were estimated at about 0.2 mg/m^3, but there is no information on the sampling or analysis methods. After correcting for alcohol consumption and smoking a standard incidence ratio of about 2.3 was observed compared to USA data. The incidence was not related to duration of exposure or time since first employment.

A follow up study of lung cancer mortality in the above cohort (Steenland & Beaumont, 1989) found a lung cancer SMR of 1.55 (95% CI 1.12 to 2.11). There was no significant trend with increasing duration of exposure. A nested case control study confirmed the lack of trend with duration and the odds ratio for 10 years exposure versus 6 months exposure was 0.95.

These workers were followed for a further 10 years to 1994 (Steenland, 1997). Two workers had died of laryngeal cancer (1.9 expected) while a further six cases had been diagnosed. The overall Standardised Incident Ratio (SIR) remained at 2.2 (95% CI 1.2 to 3.7). There was no evidence of a positive trend with duration of exposure (SIR = 2.3 for < 5 years exposure, SIR = 2.1 for >5 years exposure) or latency.

Soskolne *et al* (1992) conducted a case referent, population based interview study of confirmed laryngeal cancer cases in Southern Ontario. The study matched 204 people who had laryngeal cancer with referent for age, gender and neighbourhood of residence. The work history of each of the 408 people was ascertained by interview and exposure to sulphuric acid mist estimated by knowledge of the exposures associated with each job. Exposure was estimated blind to the status of case or referent. No measures of exposure were taken for this study. They found that laryngeal cancer was significantly more likely in people who had worked with sulphuric acid with the risk apparently related to higher concentrations and longer periods of exposure.

The effect of the different summary work life exposure measures was investigated by Suarez-Almazore *et al* (1992), who reviewed the Baton Rouge (Lynch *et al*, 1979) and Southern Ontario (Soskolne *et al*, 1992) studies. Five different summary exposure measures were used: cumulative exposure, mean grade (cumulative exposure/time exposed), highest grade ever (highest exposure for 7 days), TWA grade (cumulative exposure/time employed) and total time exposed. Odds ratios were calculated using each of the five summary exposure measures. For the Baton Rouge cohort odds ratios for upper respiratory tract cancer and exposure to sulphuric acid mist varied from 0.48 to 4.69 for moderately exposed and from 0.7 to 5.2 for high exposed. Only mean grade for moderately exposed and highest ever exposure for high exposure achieved significance. In the case of the Southern Ontario study the odds ratios for the different measures for low exposure varied from 1.94 to 2.43 while the odds ratio for high exposure varied from 3.60 to 4.61 and all were statistically significant. The authors suggested that where no exposure data are available, the summary exposure metric selected could have a profound effect on study outcome.

Sathiakulmar *et al* (1997) undertook a review of 25 epidemiological studies of the carcinogenicity of sulphuric acid mist. Based on studies in the production of sulphuric acid, isopropanol, soap and detergent, synthetic ethanol, phosphate fertilisers, nitric acid and lead batteries and in copper and zinc refining and metal pickling they concluded that:

- There is no persuasive evidence that a causal relationship exists between sulphuric acid mist and lung cancer.
- There is evidence of a moderate association between exposure to sulphuric acid mist and larynx cancer.

In the case of lung cancer they observed that the magnitude of positive associations were weak and inconsistent, could be readily explained by known confounding exposures and lacked clear dose response trends. In the case of larynx cancer the associations were stronger and on aggregation of the studies the association was stronger in industries which have higher potential exposure levels. Quantitative dose response could not be deduced.

It should be noted that other risk factors for laryngeal cancer are heavy alcohol and tobacco use, and low intake of fruit and vegetables or Beta-carotene (Parent *et al*, 2000).

Human studies – non cancer studies

Grasel *et al* (2003) reported on clinical and histopathological findings in 52 process workers from 5 anodising plants in Sao Paulo in Brazil. Workers included in the study were only exposed to sulphuric acid. Metallic agents were not involved. Exposure was estimated by collecting mist on 0.8 µm cellulose ester filters, washing the filter three times with water and analysing by ion chromatography. Results ranged from 0.005 to 0.03 mg/m^3 at one plant and from 0.24 to 0.86 mg/m^3 at a second. Following statistical analysis of the results the geometric mean was presented, which is of limited use for interpretation. Histopathological evaluation showed workers exposed to sulphuric acid mist had significantly more abnormalities than unexposed workers. There was no association with age, smoking habits or exposure duration with the parameters measured, however a strong association was found with exposure level.

The response of 12 healthy volunteers to inhalation of sulphuric acid mist and sodium chloride (NaCl) at 1 mg/m^3 was investigated by Frampton *et al* (1992). The volunteers were exposed for 2 hours to either of these substances and then two weeks later to the alternate exposure (as a blind test). Lung function was assessed prior to, immediately following and 18 hours after exposure. No significant differences were noted in forced expiratory volume (FEV), forced vital capacity (FVC) or specific airways resistance following either exposure. No significant difference was found in any investigated parameter following bronchoalveolar lavage or with alveolar macrophage function. The mass median aerodynamic diameter (MMAD) of the particles was 0.9 µm.

The response of young, non-smoking asthmatics to fogs containing sulphuric acid was investigated by Aris *et al* (1991). Three studies were undertaken:

- To assess the influence of particle size and osmolarity on H_2SO_4 aerosol exposure;
- To evaluate the effect of relative humidity; and
- To determine if inhalation of large particle H_2SO_4 aerosol during intermittent exercise would increase airway resistance.

In each case a NaCl aerosol was used as a control. There was no significant difference between the response to H_2SO_4 or NaCl, although in almost all cases airways resistance was reduced following exposure to the aerosols or fogs. The mean score for throat irritation was different for the low relative humidity aerosols and airways resistance increased, however the response to both H_2SO_4 and NaCl was similar. The concentration of H_2SO_4 was approximately 3 mg/m^3 for the first two studies mentioned above and 1 mg/m^3 for the third.

Spektor *et al* (1989) looked at the respiratory clearance rates of two different sized gamma labelled ferric oxide aerosols by 12 healthy volunteers following inhalation of either 0.1 or 1 mg/m^3 of H_2SO_4 aerosol for either 1 or 2 hours. Deposition of the ferric oxide aerosol was unchanged; however clearance rates were significantly longer after inhalation of H_2SO_4. Increasing the period of exposure from one hour to two hours had a similar effect as increasing the concentration from 0.1 to 1.0 mg/m^3.

A self-administered questionnaire on respiratory symptoms and their severity was completed by 82 exposed workers and 75 controls (Foster *et al*, 1996). Significant correlations were found between reporting of respiratory symptoms and exposure. The most commonly reported symptoms were sneezing, irritated nose and cough. Those with low exposure (< 0.15 mg/m^3), typically reported one symptom (especially sneezing), whereas those with exposure of about 0.5 mg/m^3 reported an average of 5 symptoms (especially sneezing, irritated nose, cough, runny nose and dry nose).

SCOEL (2012) noted that a number of volunteer studies are available in which asthmatic and non-asthmatic subjects have been exposed for brief durations to H_2SO_4 mists. They concluded that the available information does not indicate that asthmatics are more sensitive to the effects of sulphuric acid mist. In general, most studies indicated that there were no observable adverse respiratory tract effects in lung function or bronchial reactivity testing on single exposure to around 0.5 mg/m^3.

6. Available controls

Concentrations to which workers may be exposed depend on proximity to the source of the acid mist and controls of ventilation and containment. The National Sulphuric Acid Association (NSAA, 2013) has published guidance for industrial users of sulphuric acid who need to protect the health of their workforce from sulphuric acid mist. It is based on the approach required under the Control of Substances Hazardous to Health Regulations (COSHH) in the UK. Controls may be needed for the following events / processes / tasks:

- Spills, loss of containment etc.
- Delivery operations.
- Handling the material in the process, particularly from electrowinning and aeration / sparging processes.
- Sampling contents of vessels or tanks.
- Maintenance activities (including breaking into equipment containing sulphuric acid).
- Cleaning operations.

Exposure prevention can include the following:

- Eliminating the use or production of sulphuric acid in a process.
- Changing the method of work so that the operation giving rise to the exposure is eliminated.
- Changing the process so that sulphuric acid mist is not generated.
- Substituting sulphuric acid for another material.

Some practical ideas for controlling exposure to sulphuric acid mist include:

- Provide lids on tanks and drains where mist could be released.
- Reduce the aeration rate on open tanks containing sulphuric acid solution (for example where material must be kept in suspension in the acid solution.
- Local exhaust ventilation. This would be most practical on small to medium-sized sources of mist, although well designed systems can work effectively on large sources such as vats and open tanks.
- General mechanical ventilation is less effective than well-designed local ventilation but it can help lower background levels where there might be fugitive emissions of mist (note: general ventilation will not control the emission at its source).
- Minimise the number of workers being exposed along with the duration and intensity of exposure (e.g. automate part or all of the process).
- Introduce restricted areas and cordons/barriers to keep personnel away from activities that will generate acid mist. For example during tank filling/tanker unloading, work areas involving lead-acid battery charging, metal pre-treatment/pickling baths, anodising/plating.
- Clearly mark work stations where workers may be exposed with warning signs. Specific hygiene measures should be considered, including bans on smoking, eating and drinking in areas contaminated with chemicals, the proximity of washing and toilet facilities and the use, storage and maintenance of protective clothing.
- The use of scrubbing units or mist suppression systems for acid storage tank vents/overflows that are not externalized.
- Isolate the process from the workforce by installing purpose built containment such as rooms, encasements, lids, hoods, etc.

Personal protective equipment used alone is the least effective option for controlling exposure.[8] It should always be used in combination with other methods of exposure control.

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[8] More detail on PPE and other controls can be found in the NSAA 2013 publication at http://www.sulphuric-acid.org/_materiel/nsaa-sa-mist-guidance_final-2013.pdf. AS/NZS 1715 provides guidance on the selection, use and maintenance of respiratory protection devices.

Foster *et al* (1996) in their study of control methods for sulphuric acid mist in a selection of Australian industries determined that control of worker exposure to levels below 0.1 mg/m^3 in lead-acid battery manufacture was achievable by enclosure and ventilation of some processes, and segregation of processes within the workplace. Exposures in metal refining could be reduced somewhat by mist suppression agents, but control by enclosure and ventilation, while effective, would not be feasible in most workplaces, and hence the use of respiratory protection may be required to control worker exposure in metal refining. Mist appeared to be adequately controlled by local exhaust ventilation and surface foams in electroplating processes. Exposures in fertiliser production, wool carbonising, soap and margarine manufacture, tanning, catalytic alkylation of hydrocarbons, and sulphuric acid manufacture were low, due to enclosure of the processes.

Practical experience indicates that control of worker exposure to levels below 0.1 mg/m^3 is possible in electrowinning tank houses by a combination of covering the liquid surface with plastic balls, addition of a surfactant, covering the cells with ceramic cloth or ventilation hoods, and good general ventilation of the tank house.

7. Current applicable legislation and standards

The current Safe Work Australia (SWA) workplace exposure standard (WES) for sulphuric acid mist (Table 1) was derived from the ACGIH 1991 version of the *Documentation of Threshold Limit Values and Biological Exposure Indices* (6th Edition). It is classified as being a corrosive substance that causes severe burns (H314).

The current ACGIH (2011) TLV-TWA of 0.2 mg/m^3 (thoracic fraction), last updated in 2004, was set to minimise the potential for loss of lung function in individuals with pre-existing respiratory disease and to also minimise the mucociliary clearance alterations that have been demonstrated to occur in both animals and humans after exposure to sulphuric acid aerosols. Regarding carcinogenicity, the ACGIH (2011) concluded that there was considerable controversy around the quality of the data provided in support of an association of respiratory cancers with exposure to sulphuric acid aerosols. They noted that there was: a frequent lack of specific monitoring of sulphuric acid; and difficulty in interpreting the results due to confounding factors such as alcohol consumption, tobacco use and co-exposure to other potential carcinogenic agents. They however stated that "*the data suggested an association between occupational exposure to sulfuric acid and certain respiratory tract tumors*." Based on lead-acid battery plant studies, the particle size of sulphuric acid aerosols is generally less than 10 µm, hence the thoracic fraction best characterises exposure. ACGIH also noted that there was no data to recommend a STEL.

Table 1: Various country OELs

Country	Organisation	Occupational Exposure Limit[9]	Carcinogen Rating
European Union	European Commission (EC)	TWA = 0.05 mg/m^3 (as thoracic fraction)	None
Italy, Ireland, Netherlands & UK	Government (HSE in UK)	TWA = 0.05 mg/m^3 (as thoracic fraction)	None
France	Government	TWA = 0.05 mg/m^3 & STEL = 3.0 mg/m^3 (as thoracic fraction)	
Austria & Sweden	Government	TWA = 0.1 mg/m^3 & STEL = 0.2 mg/m^3 (as inhalable fraction)	
Germany & Switzerland	Government	TWA = 0.1 mg/m^3 & STEL = 0.1 mg/m^3 (as inhalable fraction)	
USA	ACGIH	TWA = 0.2 mg/m^3 (as thoracic fraction)	A2 suspected human carcinogen
USA	NIOSH	TWA = 1.0 mg/m^3	Possible human carcinogen
USA	OSHA	TWA = 1.0 mg/m^3 (as total particulate)	None
South Africa	DME	TWA = 1.0 mg/m^3 STEL = 3.0 mg/m^3	None
Australia	NOHSC / SWA	TWA = 1.0 mg/m^3 STEL = 3.0 mg/m^3	None

The recommendation from SCOEL (2012) of a TWA OEL of 0.05 mg/m^3 was based on avoiding possible adverse consequences for the respiratory tract epithelium. They state that the identification of a clear NOAEL for the range of potential respiratory tract effects is difficult from the available data. However, they cite the Kilgour *et al* (2002) 28-day inhalation study in rats as providing evidence of slight changes in the laryngeal epithelium at the lowest concentration tested (0.3 mg/m^3). Other experimental studies in a range of animal species suggest respiratory tract effects on repeated exposure to concentrations around 0.3 mg/m^3, with the possibility of effects of some health significance even at concentrations down to about 0.1 mg/m^3. SCOEL thus conclude: "*long-term exposure should be maintained below 0.1 mg/m^3*".

SCOEL (2012) also considered that it would be desirable to recommend a STEL of 0.1 mg/m^3 to avoid short-term irritant effects. However, at present there is no available measurement method which can accommodate a short-term limit at this value. In addition, they note that due to the relatively poor quality of the exposure data presented in past epidemiological studies of human carcinogenicity potential and the recently recognised difficulties with the analytical techniques used to monitor sulphuric acid mist exposures in the past, it is not possible to associate the increase in cancer incidence with particular exposure levels. And, overall, the experimental animal data provide little useful or reliable information on the carcinogenic potential of sulphuric acid.

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[9] Available from http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-Internationale-Grenzwerte-für-chemische-Substanzen-limit-values-for-chemical-agents/index-2.jsp

8. AIOH RECOMMENDATION

Studies of the carcinogenicity of sulphuric acid mist have frequently been undertaken without exposure measurements and with potential confounding exposures not well accounted for. While Steenland (1997) found an excess of cancer of the larynx there was no trend with duration of exposure or time since first employment. Lynch *et al* (1979) and Forastiere *et al* (1987) also found excess laryngeal cancer, while Coggon *et al* (1996) did not. Soskoline *et al* (1992) found that laryngeal cancer was more common in people who worked with sulphuric acid mist.

IARC and NTP both consider sulphuric acid mist as a known human carcinogen. The review by Sathiakulmar *et al* (1997) reaches the same conclusion for laryngeal cancer. The studies do not provide a persuasive indication of a dose response for carcinogenicity.

Non-malignant respiratory effects exist at 1 to 3 mg/m^3 (Aris *et al*, 1991; Frampton *et al*, 1992) while short-term reduced lung clearance rates were observed at 0.1 mg/m^3 (Spektor *et al*, 1989).

The threshold of perception for individuals unaccustomed to sulphuric acid mist exposure is about 0.02 to 0.05 mg/m^3, while 0.1 mg/m^3 is clearly perceptible and 0.2 mg/m^3 can cause coughing or sneezing (Murdoch *et al*, 1995). Worker exposure to about 0.5 mg/m^3 has been reported to cause an average of 5 acute effect symptoms (e.g. sneezing, irritated nose, cough, runny nose and dry nose) (Foster *et al*, 1996). Practical experience within the AIOH Exposure Standards Committee members has found exposure to 0.1 mg/m^3 is clearly perceptible, 0.2 mg/m^3 can cause coughing, sneezing and shortness of breath while exposure to 1 mg/m^3 is intolerable to many people. These effects may guide short term exposure response.

Chronic effects were noted in rats exposed at 0.5 and 1.0 mg/m^3 but effects at 0.2 mg/m^3 were minimal (Kilgour *et al*, 2002). The review of animal studies (Swenberg & Beauchamp, 1997) found effects in several species at exposure levels above 1 mg/m^3 while effects were not noted in monkeys exposed at 0.1 mg/m^3.

The review by the ACGIH (2011) in 2004 concluded a TLV of 0.2 mg/m^3 (thoracic fraction) was appropriate while SCOEL (2012) recommended a TWA-OEL of 0.05 mg/m^3 (inhalable fraction), which was subsequently and inexplicably adopted as the thoracic fraction by the European Commission.

The AIOH considers that there are still information gaps for health aspects of sulphuric acid mist, although there is sufficient documentation to derive a protective TWA OEL. The AIOH recommends a TWA OEL of 0.1 mg/m^3, measured as the inhalable fraction according to AS 3640, collected on a quartz fibre filter for analysis by ion chromatography. As with all substances suspected to have carcinogenic potential the ALARP principle should be applied to all exposures.

A STEL of 0.5mg/m^3 is feasible but may not be particularly useful in its purpose of warning of possible acute effects, considering delay in reporting due to the requirements of laboratory analysis of collected samples. There is no doubt that such a level causes acute health effects even after a single short term exposure, to which the usual response in most people is withdrawal from the exposure or use of respiratory protection.

It should be noted that the measured exposure concentration can vary significantly depending on the sampling method chosen, hence the sampling method must be for inhalable particulate using AS 3640.

Currently, no feasible biomarker is available to be used for biological monitoring.

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